QMCPACK Manual

QMCPACK Developers

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QMCPACK

CHAPTER

ONE

INTRODUCTION

QMCPACK is an open-source, high-performance electronic structure code that implements numerous Quantum Monte Carlo (QMC) algorithms. Its main applications are electronic structure calculations of molecular, periodic 2D, and periodic 3D solid-state systems. Real-space variational Monte Carlo (VMC), diffusion Monte Carlo (DMC), and a number of other advanced QMC algorithms are implemented. A full set of orbital-space auxiliary-field QMC (AFQMC) methods is also implemented. By directly solving the Schrodinger equation, QMC methods offer greater accuracy than methods such as density functional theory but at a trade-off of much greater computational expense. Distinct from many other correlated many-body methods, QMC methods are readily applicable to both isolated molecular systems and to bulk (periodic) systems including metals and insulators. The few systematic errors in these methods are increasingly testable allowing for greater confidence in predictions and convergence to e.g. chemically accurate results in some cases.

QMCPACK is written in C++ and is designed with the modularity afforded by object-oriented programming. High parallel and computational efficiencies are achievable on the largest supercomputers. Because of the modular architecture, the addition of new wavefunctions, algorithms, and observables is relatively straightforward. For parallelization, QMCPACK uses a fully hybrid (OpenMP,CUDA)/MPI approach to optimize memory usage and to take advantage of the growing number of cores per SMP node or graphical processing units (GPUs) and accelerators. Finally, QMCPACK uses standard file formats for input and output in XML and HDF5 to facilitate data exchange.

This manual currently serves as an introduction to the essential features of QMCPACK and as a guide to installing and running it. Over time this manual will be expanded to include a fuller introduction to QMC methods in general and to include more of the specialized features in QMCPACK.

Besides studying this manual we recommend reading a recent review of QMCPACK developments [[KAB+20]] as well as the QMCPACK citation paper [[KBB+18]].

1.1 Quickstart and a first QMCPACK calculation

In case you are keen to get started, this section describes how to quickly build and run a first QMCPACK calculation on a standard UNIX or Linux-like system. The build system usually works without much fuss on these systems. If C++, MPI, BLAS/LAPACK, FFTW, HDF5, and CMake are already installed, QMCPACK can be built and run within five minutes. For supercomputers, cross-compilation systems, and some computer clusters, the build system might require hints on the locations of libraries and which versions to use, typical of any code; see *Obtaining, installing, and validating QMCPACK*. *Installation instructions for common workstations and supercomputers* includes complete examples of installations for common workstations and supercomputers that you can reuse.

To build QMCPACK:

1. Download the latest QMCPACK distribution from http://www.qmcpack.org.
2. Untar the archive (e.g., `tar xvf qmcpack_v1.3.tar.gz`).
3. Check the instructions in the README file.

4. Run CMake in a suitable build directory to configure QMCPACK for your system: `cd qmcpack/build; cmake ..`
5. If CMake is unable to find all needed libraries, see *Obtaining, installing, and validating QMCPACK* for instructions and specific build instructions for common systems.
6. Build QMCPACK: `make` or `make -j 16`; use the latter for a faster parallel build on a system using, for example, 16 processes.
7. The QMCPACK executable is usually `bin/qmcpack`. If you build the complex version it is `bin/qmcpack_complex`.

QMCPACK is distributed with examples illustrating different capabilities. Most of the examples are designed to run quickly with modest resources. We'll run a short diffusion Monte Carlo calculation of a water molecule:

1. Go to the appropriate example directory: `cd ../examples/molecules/H2O`.
2. (Optional) Put the QMCPACK binary on your path: `export PATH=\$PATH:location-of-qmcpack/build/bin`
3. Run QMCPACK: `../../../build/bin/qmcpack simple-H2O.xml` or `qmcpack simple-H2O.xml` if you followed the step above.
4. The run will output to the screen and generate a number of files:

```
$ls H2O*
H2O.HF.wfs.xml      H2O.s001.scalar.dat H2O.s002.cont.xml
H2O.s002.qmc.xml    H2O.s002.stat.h5    H2O.s001.qmc.xml
H2O.s001.stat.h5    H2O.s002.dmc.dat    H2O.s002.scalar.dat
```

5. Partially summarized results are in the standard text files with the suffixes scalar.dat and dmc.dat. They are viewable with any standard editor.

If you have Python and matplotlib installed, you can use the analysis utility to produce statistics and plots of the data. See *Analyzing QMCPACK data* for information on analyzing QMCPACK data.

```
export PATH=$PATH:location-of-qmcpack/nexus/bin
export PYTHONPATH=$PYTHONPATH:location-of-qmcpack/nexus/library
qmca H2O.s002.scalar.dat         # For statistical analysis of the DMC data
qmca -t -q e H2O.s002.scalar.dat # Graphical plot of DMC energy
```

The last command will produce a graph as per Fig. 1.1. This shows the average energy of the DMC walkers at each timestep. In a real simulation we would have to check equilibration, convergence with walker population, time step, etc.

Congratulations, you have completed a DMC calculation with QMCPACK!

1.2 Authors and History

Development of QMCPACK was started in the late 2000s by Jeongnim Kim while in the group of Professor David Ceperley at the University of Illinois at Urbana-Champaign, with later contributions being made at Oak Ridge National Laboratory (ORNL). Over the years, many others have contributed, including students and researchers in the groups of Professor David Ceperley and Professor Richard M. Martin, and increasingly staff and postdocs at Lawrence Livermore National Laboratory, Sandia National Laboratories, Argonne National Laboratory, and ORNL.

Additional developers, contributors, and advisors include Anouar Benali, Mark A. Berrill, David M. Ceperley, Simone Chiesa, Raymond C. III Clay, Bryan Clark, Kris T. Delaney, Kenneth P. Esler, Paul R. C. Kent, Jaron T. Krogel, Ying Wai Li, Ye Luo, Jeremy McMinis, Miguel A. Morales, William D. Parker, Nichols A. Romero, Luke Shulenburger, Norman M. Tubman, and Jordan E. Vincent. See the authors of [[KAB+20]] and [[KBB+18]].

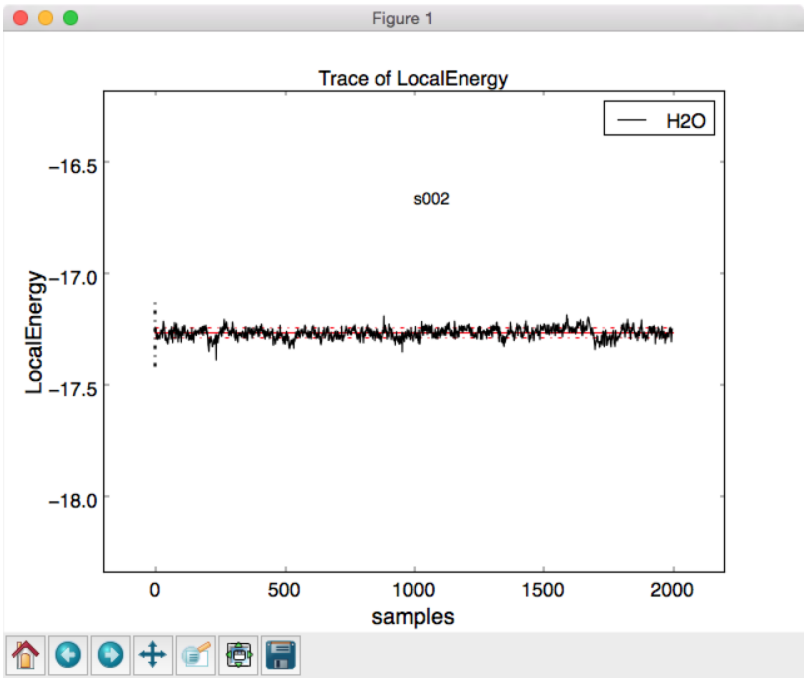

Fig. 1.1: Trace of walker energies produced by the qmca tool for a simple water molecule example.

If you should be added to these lists, please let us know.

Development of QMCPACK has been supported financially by several grants, including the following:

- "Center for Predictive Simulation of Functional Materials", supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, as part of the Computational Materials Sciences Program.
- The Exascale Computing Project (17-SC-20-SC), a joint project of the U.S. Department of Energy's Office of Science and National Nuclear Security Administration, responsible for delivering a capable exascale ecosystem, including software, applications, and hardware technology, to support the nation's exascale computing imperative.
- "Network for ab initio many-body methods: development, education and training" supported through the Predictive Theory and Modeling for Materials and Chemical Science program by the U.S. Department of Energy Office of Science, Basic Energy Sciences.
- "QMC Endstation," supported by Accelerating Delivery of Petascale Computing Environment at the DOE Leadership Computing Facility at ORNL.
- PetaApps, supported by the US National Science Foundation.
- Materials Computation Center (MCC), supported by the US National Science Foundation.

1.3 Support and Contacting the Developers

Questions about installing, applying, or extending QMCPACK can be posted on the QMCPACK Google group at https://groups.google.com/forum/#!forum/qmcpack. You may also email any of the developers, but we recommend checking the group first. Particular attention is given to any problem reports. Technical questions can also be posted on the QMCPACK GitHub repository https://github.com/QMCPACK/qmcpack/issues.

1.4 Performance

QMCPACK implements modern Monte Carlo (MC) algorithms, is highly parallel, and is written using very efficient code for high per-CPU or on-node performance. In particular, the code is highly vectorizable, giving high performance on modern central processing units (CPUs) and GPUs. We believe QMCPACK delivers performance either comparable to or better than other QMC codes when similar calculations are run, particularly for the most common QMC methods and for large systems. If you find a calculation where this is not the case, or you simply find performance slower than expected, please post on the Google group or contact one of the developers. These reports are valuable. If your calculation is sufficiently mainstream we will optimize QMCPACK to improve the performance.

1.5 Open Source License

QMCPACK is distributed under the University of Illinois at Urbana-Champaign/National Center for Supercomputing Applications (UIUC/NCSA) Open Source License.

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```
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OTHER DEALINGS WITH THE SOFTWARE.
```

Copyright is generally believed to remain with the authors of the individual sections of code. See the various notations in the source code as well as the code history.

1.6 Contributing to QMCPACK

QMCPACK is fully open source, and we welcome contributions. If you are planning a development, early discussions are encouraged. Please post on the QMCPACK Google group, on the QMCPACK GitHub repository, or contact one of the developers. We can tell you whether anyone else is working on a similar feature or whether any related work has been done in the past. Credit for your contribution can be obtained, for example, through citation of a paper or by becoming one of the authors on the next version of the standard QMCPACK reference citation.

See *Development Guide* for details about developing for QMCPACK, including instructions on how to work with GitHub, the style guide, and examples about the code architecture.

Contributions are made under the same license as QMCPACK, the UIUC/NCSA open source license. If this is problematic, please discuss with a developer.

Please note the following guidelines for contributions:

- Additions should be fully synchronized with the latest release version and the latest develop branch on GitHub. Merging of code developed on older versions is error prone.
- Code should be cleanly formatted, commented, portable, and accessible to other programmers. That is, if you need to use any clever tricks, add a comment to note this, why the trick is needed, how it works, etc. Although we appreciate high performance, ease of maintenance and accessibility are also considerations.
- Comment your code. You are not only writing it for the compiler for also for other humans! (We know this is a repeat of the previous point, but it is important enough to repeat.)
- Write a brief description of the method, algorithms, and inputs and outputs suitable for inclusion in this manual.
- Develop tests that exercise the functionality that can be used for validation and for examples. Where is it practical to write them, we prefer unit tests and fully deterministic tests ahead of stochastic tests. Stochastic tests naturally fail on occasion, which is a property that does not scale to hundreds of tests. We can help with this and tests integration into the test system.

1.7 QMCPACK Roadmap

A general outline of the QMCPACK roadmap is given in the following sections. Suggestions for improvements from current and potential users are very welcome, particularly those that would facilitate new uses or new users. For example, if an interface to a particular quantum chemical or density functional code, or an improved tutorial would be helpful, these would be given strong consideration.

1.7.1 Code

We will continue to improve the accessibility and usability of QMCPACK through combinations of more convenient input parameters, improved workflow, integration with more quantum chemical and density functional codes, and a wider range of examples. Suggestions are very welcome, both from new users of QMC and from those experienced with other QMC codes.

A main development focus is the creation of a single performance portable version of the code. All features will consequently be available on all platforms, including accelerators (GPUs) from NVIDIA, AMD, and Intel. These new implementations are currently referred to as the *batched code*. As the initial batched implementation is matured, observables and other functionality will be prioritized based on feedback received.

1.7.2 Documentation and examples

This manual describes the core features of QMCPACK that are required for routine research calculations and standard QMC workflows, i.e., the VMC and DMC methods, auxiliary field QMC, how to obtain and optimize trial wavefunctions, and simple observables. This covers at least 95% of use cases, and nearly all production research calculations.

Because of its history as an academically developed research code, QMCPACK also contains a variety of additional QMC methods, trial wavefunction forms, potentials, etc., that, although far from critical, might be very useful for specialized calculations or particular material or chemical systems. If you are interested in these please ask - generally the features are immature, but we might have historical inputs available. New descriptions will be added over time but can also be prioritized and added on request (e.g., if a specialized Jastrow factor would help or a historical Jastrow form is needed for benchmarking).

CHAPTER

TWO

FEATURES OF QMCPACK

Note that besides direct use, most features are also available via Nexus, an advanced workflow tool to automate all aspects of QMC calculation from initial DFT calculations through to final analysis. Use of Nexus is highly recommended for research calculations due to the greater ease of use and increased reproducibility.

2.1 Real-space Monte Carlo

The following list contains the main production-level features of QMCPACK for real-space Monte Carlo. If you do not see a specific feature that you are interested in, check the remainder of this manual or ask if that specific feature can be made available.

- Variational Monte Carlo (VMC).
- Diffusion Monte Carlo (DMC).
- Reptation Monte Carlo.
- Single and multideterminant Slater Jastrow wavefunctions.
- Wavefunction updates using optimized multideterminant algorithm of Clark et al.
- Backflow wavefunctions.
- One, two, and three-body Jastrow factors.
- Excited state calculations via flexible occupancy assignment of Slater determinants.
- All electron and nonlocal pseudopotential calculations.
- Casula T-moves for variational evaluation of nonlocal pseudopotentials (non-size-consistent and size-consistent variants).
- Spin-orbit coupling from relativistic pseudopotentials following the approach of Melton, Bennett, and Mitas.
- Support for twist boundary conditions and calculations on metals.
- Wavefunction optimization using the “linear method” of Umrigar and coworkers, with an arbitrary mix of variance and energy in the objective function.
- Blocked, low memory adaptive shift optimizer of Zhao and Neuscamman.
- Gaussian, Slater, plane-wave, and real-space spline basis sets for orbitals.
- Interface and conversion utilities for plane-wave wavefunctions from Quantum ESPRESSO (Plane-Wave Self-Consistent Field package [PWSCF]).
- Interface and conversion utilities for Gaussian-basis wavefunctions from GAMESS, PySCF, and QP2. Many more are supported via the molden format and molden2qmc.

- Easy extension and interfacing to other electronic structure codes via standardized XML and HDF5 inputs.
- MPI parallelism, with scaling to millions of cores.
- Fully threaded using OpenMP.
- Highly efficient vectorized CPU code tailored for modern architectures. [[MLC+17]]
- OpenMP-offload-based performance portable GPU implementation, see *Supported GPU features for real space QMC*.
- Legacy GPU (NVIDIA CUDA) implementation (limited functionality - see *Supported GPU features for real space QMC*).
- Analysis tools for minimal environments (Perl only) through to Python-based environments with graphs produced via matplotlib (included with Nexus).

2.2 Auxiliary-Field Quantum Monte Carlo

The orbital-space Auxiliary-Field Quantum Monte Carlo (AFQMC) method is now also available in QMCPACK. The main input data are the matrix elements of the Hamiltonian in a given single particle basis set, which must be produced from mean-field calculations such as Hartree-Fock or density functional theory. A partial list of the current capabilities of the code follows. For a detailed description of the available features, see *Auxiliary-Field Quantum Monte Carlo*.

- Phaseless AFQMC algorithm of Zhang et al. [[ZK03]].
- Very efficient GPU implementation for most features.
- "Hybrid" and "local energy" propagation schemes.
- Hamiltonian matrix elements from (1) Molpro's FCIDUMP format (which can be produced by Molpro, PySCF, and VASP) and (2) internal HDF5 format produced by PySCF (see AFQMC section below).
- AFQMC calculations with RHF (closed-shell doubly occupied), ROHF (open-shell doubly occupied), and UHF (spin polarized broken symmetry) symmetry.
- Single and multideterminant trial wavefunctions. Multideterminant expansions with either orthogonal or nonorthogonal determinants.
- Fast update scheme for orthogonal multideterminant expansions.
- Distributed propagation algorithms for large systems. Enables calculations where data structures do not fit on a single node.
- Complex implementation for PBC calculations with complex integrals.
- Sparse representation of large matrices for reduced memory usage.
- Mixed and back-propagated estimators.
- Specialized implementation for solids with k-point symmetry (e.g. primitive unit cells with k-points).

2.3 Supported GPU features for real space QMC

There are two GPU implementations in the code base.

- **Performance portable implementation** (recommended). Implements real space QMC methods using OpenMP offload programming model and accelerated linear algebra libraries. Runs with good performance on NVIDIA and AMD GPUs, and the Intel GPU support is under development. Unlike the "legacy" implementation, it is feature complete and users may mix and match CPU-only and GPU-accelerated features.
- **Legacy implementation**. Fully based on NVIDIA CUDA. Achieves very good speedup on NVIDIA GPUs. However, only a very limited subset of features is available.

QMCPACK supports running on multi-GPU node architectures via MPI.

Supported GPU features:

Feature	Performance portable	Legacy CUDA
QMC methods	VMC, WFOpt, DMC	VMC, WFOpt, DMC
boundary conditions	periodic, mixed, open	periodic, open
Complex-valued wavefunction	supported	supported
Single-Slater determinants	accelerated	accelerated
Multi-Slater determinants	on host now, being ported	not supported
3D B-spline orbitals	accelerated	accelerated
LCAO orbitals	on host now, being ported	not supported
One-body Jastrow factors	on host	accelerated
Two-body Jastrow factors	accelerated	accelerated
Other Jastrow factors	on host	not supported
Nonlocal pseudopotentials	accelerated	accelerated
Coulomb interaction PBC e-i	on host	accelerated
Coulomb interaction PBC e-e	accelerated	accelerated
Coulomb interaction OpenBC	on host	accelerated
Model periodic Coulomb (MPC)	on host	accelerated

Additional information:

- Performance portable implementation requires using batched QMC drivers.
- Legacy CUDA implementation only supports T-move v0 or no T-move.
- In most features, the algorithmic and implementation details differ a lot between these two GPU implementations.

2.3.1 Sharing of spline data across multiple GPUs

Sharing of GPU spline data enables distribution of the data across multiple GPUs on a given computational node. For example, on a two-GPU-per-node system, each GPU would have half of the orbitals. This allows use of larger overall spline tables than would fit in the memory of individual GPUs and potentially up to the total GPU memory on a node. To obtain high performance, large electron counts or a high-performing CPU-GPU interconnect is required. This feature is only supported in the legacy implementation.

To use this feature, the following needs to be done:

- The CUDA Multi-Process Service (MPS) needs to be used (e.g., on OLCF Summit/SummitDev use "-alloc_flags gpumps" for bsub). If MPI is not detected, sharing will be disabled.

- CUDA_VISIBLE_DEVICES needs to be properly set to control each rank's visible CUDA devices (e.g., on OLCF Summit/SummitDev create a resource set containing all GPUs with the respective number of ranks with "jsrun –task-per-rs Ngpus -g Ngpus").
- In the determinant set definition of the <wavefunction> section, the "gpusharing" parameter needs to be set (i.e., <determinantset gpusharing="yes">). See *3D B-splines orbitals*.

CHAPTER

THREE

OBTAINING, INSTALLING, AND VALIDATING QMCPACK

This section describes how to obtain, build, and validate QMCPACK. This process is designed to be as simple as possible and should be no harder than building a modern plane-wave density functional theory code such as Quantum ESPRESSO, QBox, or VASP. Parallel builds enable a complete compilation in under 2 minutes on a fast multicore system. If you are unfamiliar with building codes we suggest working with your system administrator to install QMCPACK.

3.1 Installation steps

To install QMCPACK, follow the steps below. Full details of each step are given in the referenced sections.

1. Download the source code from *Obtaining the latest release version* or *Obtaining the latest development version*.
2. Verify that you have the required compilers, libraries, and tools installed (*Prerequisites*).
3. If you will use Quantum ESPRESSO, download and patch it. The patch adds the pw2qmcpack utility (*Installing and patching Quantum ESPRESSO*).
4. Run the cmake configure step and build with make (*Building with CMake* and *Quick build instructions (try first)*). Examples for common systems are given in *Installation instructions for common workstations and supercomputers*. To activate workflow tests for Quantum ESPRESSO, RMG, or PYSCF, be sure to specify QE_BIN, RMG_BIN, or ensure that the python modules are available when cmake is run.
5. Run the tests to verify QMCPACK (*Testing and validation of QMCPACK*).

Hints for high performance are in *How to build the fastest executable version of QMCPACK*. Troubleshooting suggestions are in *Troubleshooting the installation*.

Note that there are two different QMCPACK executables that can be produced: the general one, which is the default, and the "complex" version, which supports periodic calculations at arbitrary twist angles and k-points. This second version is enabled via a cmake configuration parameter (see *Configuration Options*). The general version supports only wavefunctions that can be made real. If you run a calculation that needs the complex version, QMCPACK will stop and inform you.

3.2 Obtaining the latest release version

Major releases of QMCPACK are distributed from http://www.qmcpack.org. Because these versions undergo the most testing, we encourage using them for all production calculations unless there are specific reasons not to do so.

Releases are usually compressed tar files that indicate the version number, date, and often the source code revision control number corresponding to the release. To obtain the latest release:

- Download the latest QMCPACK distribution from http://www.qmcpack.org.
- Untar the archive (e.g., `tar xvf qmcpack_v1.3.tar.gz`).

Releases can also be obtained from the 'master' branch of the QMCPACK git repository, similar to obtaining the development version (*Obtaining the latest development version*).

3.3 Obtaining the latest development version

The most recent development version of QMCPACK can be obtained anonymously via

```
git clone https://github.com/QMCPACK/qmcpack.git
```

Once checked out, updates can be made via the standard `git pull`.

The 'develop' branch of the git repository contains the day-to-day development source with the latest updates, bug fixes, etc. This version might be useful for updates to the build system to support new machines, for support of the latest versions of Quantum ESPRESSO, or for updates to the documentation. Note that the development version might not be fully consistent with the online documentation. We attempt to keep the development version fully working. However, please be sure to run tests and compare with previous release versions before using for any serious calculations. We try to keep bugs out, but occasionally they crawl in! Reports of any breakages are appreciated.

3.4 Prerequisites

The following items are required to build QMCPACK. For workstations, these are available via the standard package manager. On shared supercomputers this software is usually installed by default and is often accessed via a modules environment—check your system documentation.

Use of the latest versions of all compilers and libraries is strongly encouraged but not absolutely essential. Generally, newer versions are faster; see *How to build the fastest executable version of QMCPACK* for performance suggestions. Versions of compilers over two years old are unsupported and untested by the developers although they may still work.

- C/C++ compilers such as GNU, Clang, Intel, and IBM XL. C++ compilers are required to support the C++ 17 standard. Use of recent ("current year version") compilers is strongly encouraged.
- An MPI library such as OpenMPI (http://open-mpi.org) or a vendor-optimized MPI.
- BLAS/LAPACK, numerical, and linear algebra libraries. Use platform-optimized libraries where available, such as Intel MKL. ATLAS or other optimized open source libraries can also be used (http://math-atlas.sourceforge.net).
- CMake, build utility (http://www.cmake.org).
- Libxml2, XML parser (http://xmlsoft.org).
- HDF5, portable I/O library (http://www.hdfgroup.org/HDF5/). Good performance at large scale requires parallel version $>=$ 1.10.

- BOOST, peer-reviewed portable C++ source libraries (http://www.boost.org). Minimum version is 1.61.0.
- FFTW, FFT library (http://www.fftw.org/).

To build the GPU accelerated version of QMCPACK, an installation of NVIDIA CUDA development tools is required. Ensure that this is compatible with the C and C++ compiler versions you plan to use. Supported versions are included in the NVIDIA release notes.

Many of the utilities provided with QMCPACK require Python (v3). The numpy and matplotlib libraries are required for full functionality.

3.5 C++ 17 standard library

The C++ standard consists of language features—which are implemented in the compiler—and library features—which are implemented in the standard library. GCC includes its own standard library and headers, but many compilers do not and instead reuse those from an existing GCC install. Depending on setup and installation, some of these compilers might not default to using a GCC with C++ 17 headers (e.g., GCC 4.8 is common as a base system compiler, but its standard library only supports C++ 11).

The symptom of having header files that do not support the C++ 17 standard is usually compile errors involving standard include header files. Look for the GCC library version, which should be present in the path to the include file in the error message, and ensure that it is 8.1 or greater. To avoid these errors occurring at compile time, QMCPACK tests for a C++ 17 standard library during configuration and will halt with an error if one is not found.

At sites that use modules, it is often sufficient to simply load a newer GCC.

3.5.1 Intel compiler

The Intel compiler version must be 19 or newer due to use of C++17 and bugs and limitations in earlier versions.

If a newer GCC is needed, the `-cxxlib` option can be used to point to a different GCC installation. (Alternately, the `-gcc-name` or `-gxx-name` options can be used.) Be sure to pass this flag to the C compiler in addition to the C++ compiler. This is necessary because CMake extracts some library paths from the C compiler, and those paths usually also contain to the C++ library. The symptom of this problem is C++ 17 standard library functions not found at link time.

3.6 Building with CMake

The build system for QMCPACK is based on CMake. It will autoconfigure based on the detected compilers and libraries. The most recent version of CMake has the best detection for the greatest variety of systems. The minimum required version of CMake is 3.15.0. Most computer installations have a sufficiently recent CMake, though it might not be the default.

If no appropriate version CMake is available, building it from source is straightforward. Download a version from https://cmake.org/download/ and unpack the files. Run `./bootstrap` from the CMake directory, and then run `make` when that finishes. The resulting CMake executable will be in the directory. The executable can be run directly from that location.

Previously, QMCPACK made extensive use of toolchains, but the build system has since been updated to eliminate the use of toolchain files for most cases. The build system is verified to work with GNU, Intel, and IBM XLC compilers. Specific compile options can be specified either through specific environment or CMake variables. When the libraries are installed in standard locations (e.g., /usr, /usr/local), there is no need to set environment or CMake variables for the packages.

3.6.1 Quick build instructions (try first)

If you are feeling lucky and are on a standard UNIX-like system such as a Linux workstation, the following might quickly give a working QMCPACK:

The safest quick build option is to specify the C and C++ compilers through their MPI wrappers. Here we use Intel MPI and Intel compilers. Move to the build directory, run CMake, and make

```
cd build
cmake -DCMAKE_C_COMPILER=mpiicc -DCMAKE_CXX_COMPILER=mpiicpc ..
make -j 8
```

You can increase the "8" to the number of cores on your system for faster builds. Substitute mpicc and mpicxx or other wrapped compiler names to suit your system. For example, with OpenMPI use

```
cd build
cmake -DCMAKE_C_COMPILER=mpicc -DCMAKE_CXX_COMPILER=mpicxx ..
make -j 8
```

If you are feeling particularly lucky, you can skip the compiler specification:

```
cd build
cmake ..
make -j 8
```

The complexities of modern computer hardware and software systems are such that you should check that the autoconfiguration system has made good choices and picked optimized libraries and compiler settings before doing significant production. That is, check the following details. We give examples for a number of common systems in *Installation instructions for common workstations and supercomputers*.

3.6.2 Environment variables

A number of environment variables affect the build. In particular they can control the default paths for libraries, the default compilers, etc. The list of environment variables is given below:

```
CXX              C++ compiler
CC               C Compiler
MKL_ROOT         Path for MKL
HDF5_ROOT        Path for HDF5
BOOST_ROOT       Path for Boost
FFTW_HOME        Path for FFTW
```

3.6.3 Configuration Options

In addition to reading the environment variables, CMake provides a number of optional variables that can be set to control the build and configure steps. When passed to CMake, these variables will take precedent over the environment and default variables. To set them, add -D FLAG=VALUE to the configure line between the CMake command and the path to the source directory.

- Key QMCPACK build options

```
QMC_CUDA              Enable legacy CUDA code path for NVIDIA GPU acceleration␣
↪(1:yes, 0:no)
QMC_COMPLEX           Build the complex (general twist/k-point) version (1:yes,␣
↪0:no)
```

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```
QMC_MIXED_PRECISION   Build the mixed precision (mixing double/float) version
                      (1:yes (QMC_CUDA=1 default), 0:no (QMC_CUDA=0 default)).
                      Mixed precision calculations can be signifiantly faster but␣
↪should be
                      carefully checked validated against full double precision␣
↪runs,
                      particularly for large electron counts.
ENABLE_CUDA           ON/OFF(default). Enable CUDA code path for NVIDIA GPU␣
↪acceleration.
                      Production quality for AFQMC. Pre-production quality for␣
↪real-space.
                      Use CMAKE_CUDA_ARCHITECTURES, default 70, to set the actual␣
↪GPU architecture.
ENABLE_OFFLOAD        ON/OFF(default). Enable OpenMP target offload for GPU␣
↪acceleration.
ENABLE_TIMERS         ON(default)/OFF. Enable fine-grained timers. Timers are on␣
↪by default but at level coarse
                      to avoid potential slowdown in tiny systems.
                      For systems beyond tiny sizes (100+ electrons) there is no␣
↪risk.
```

- General build options

```
CMAKE_BUILD_TYPE     A variable which controls the type of build
                     (defaults to Release). Possible values are:
                     None (Do not set debug/optmize flags, use
                     CMAKE_C_FLAGS or CMAKE_CXX_FLAGS)
                     Debug (create a debug build)
                     Release (create a release/optimized build)
                     RelWithDebInfo (create a release/optimized build with debug␣
↪info)
                     MinSizeRel (create an executable optimized for size)
CMAKE_SYSTEM_NAME    Set value to CrayLinuxEnvironment when cross-compiling in␣
↪Cray Programming Environment.
CMAKE_C_COMPILER     Set the C compiler
CMAKE_CXX_COMPILER   Set the C++ compiler
CMAKE_C_FLAGS        Set the C flags.  Note: to prevent default
                     debug/release flags from being used, set the CMAKE_BUILD_
↪TYPE=None
                     Also supported: CMAKE_C_FLAGS_DEBUG,
                     CMAKE_C_FLAGS_RELEASE, and CMAKE_C_FLAGS_RELWITHDEBINFO
CMAKE_CXX_FLAGS      Set the C++ flags.  Note: to prevent default
                     debug/release flags from being used, set the CMAKE_BUILD_
↪TYPE=None
                     Also supported: CMAKE_CXX_FLAGS_DEBUG,
                     CMAKE_CXX_FLAGS_RELEASE, and CMAKE_CXX_FLAGS_RELWITHDEBINFO
CMAKE_INSTALL_PREFIX Set the install location (if using the optional install step)
INSTALL_NEXUS        Install Nexus alongside QMCPACK (if using the optional␣
↪install step)
```

- Additional QMCPACK build options

```
QE_BIN                Location of Quantum ESPRESSO binaries including pw2qmcpack.
↪x
RMG_BIN               Location of RMG binary (rmg-cpu)
QMC_DATA              Specify data directory for QMCPACK performance and␣
↪integration tests
```

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```
QMC_INCLUDE            Add extra include paths
QMC_EXTRA_LIBS         Add extra link libraries
QMC_BUILD_STATIC       ON/OFF(default). Add -static flags to build
QMC_SYMLINK_TEST_FILES Set to zero to require test files to be copied. Avoids␣
↪space
                       saving default use of symbolic links for test files. Useful
                       if the build is on a separate filesystem from the source,␣
↪as
                       required on some HPC systems.
```

- BLAS/LAPACK related

```
BLA_VENDOR          If set, checks only the specified vendor, if not set checks␣
↪all the possibilities.
                    See full list at https://cmake.org/cmake/help/latest/module/
↪FindLAPACK.html
MKL_ROOT            Path to MKL libraries. Only necessary when auto-detection␣
↪fails or overriding is desired.
```

- Scalar and vector math functions

```
QMC_MATH_VENDOR     Select a vendor optimized library for scalar and vector math␣
↪functions.
                    Providers are GENERIC INTEL_VML IBM_MASS AMD_LIBM
```

- libxml2 related

```
LIBXML2_INCLUDE_DIR   Include directory for libxml2

LIBXML2_LIBRARY       Libxml2 library
```

- HDF5 related

```
HDF5_PREFER_PARALLEL TRUE(default for MPI build)/FALSE, enables/disable parallel␣
↪HDF5 library searching.
ENABLE_PHDF5         ON(default for parallel HDF5 library)/OFF, enables/disable␣
↪parallel collective I/O.
```

- FFTW related

```
FFTW_INCLUDE_DIRS   Specify include directories for FFTW
FFTW_LIBRARY_DIRS   Specify library directories for FFTW
```

- CTest related

```
MPIEXEC_EXECUTABLE     Specify the mpi wrapper, e.g. srun, aprun, mpirun, etc.
MPIEXEC_NUMPROC_FLAG   Specify the number of mpi processes flag,
                       e.g. "-n", "-np", etc.
MPIEXEC_PREFLAGS       Flags to pass to MPIEXEC_EXECUTABLE directly before the␣
↪executable to run.
```

- Sanitizers Developer Options

```
ENABLE_SANITIZER  link with the GNU or Clang sanitizer library for asan, ubsan,␣
↪tsan or msan (default=none)
```

Clang address sanitizer library asan

Clang address sanitizer library ubsan

Clang thread sanitizer library tsan

Clang thread sanitizer library msan

See *Sanitizer Libraries* for more information.

3.6.4 Notes for OpenMP target offload to accelerators (experimental)

QMCPACK is currently being updated to support OpenMP target offload and obtain performance portability across GPUs from different vendors. This is currently an experimental feature and is not suitable for production. Additional implementation in QMCPACK as well as improvements in open-source and vendor compilers is required for production status to be reached. The following compilers have been verified:

- LLVM Clang 11. Support NVIDIA GPUs.

```
-D ENABLE_OFFLOAD=ON -D USE_OBJECT_TARGET=ON
```

  Clang and its downstream compilers support two extra options

```
OFFLOAD_TARGET for the offload target. default nvptx64-nvidia-cuda.
OFFLOAD_ARCH for the target architecture (sm_80, gfx906, ...) if not using the␣
↪compiler default.
```

- AMD AOMP Clang 11.8. Support AMD GPUs.

```
-D ENABLE_OFFLOAD=ON -D OFFLOAD_TARGET=amdgcn-amd-amdhsa -D OFFLOAD_ARCH=gfx906
```

- Intel oneAPI beta08. Support Intel GPUs.

```
-D ENABLE_OFFLOAD=ON -D OFFLOAD_TARGET=spir64
```

- HPE Cray 11. It is derived from Clang and supports NVIDIA and AMD GPUs.

```
-D ENABLE_OFFLOAD=ON -D OFFLOAD_TARGET=nvptx64-nvidia-cuda -D OFFLOAD_ARCH=sm_80
```

OpenMP offload features can be used together with vendor specific code paths to maximize QMCPACK performance. Some new CUDA functionality has been implemented to improve efficiency on NVIDIA GPUs in conjunction with the Offload code paths: For example, using Clang 11 on Summit.

```
-D ENABLE_OFFLOAD=ON -D USE_OBJECT_TARGET=ON -D ENABLE_CUDA=ON -D CMAKE_CUDA_
↪ARCHITECTURES=70 -D CMAKE_CUDA_HOST_COMPILER=`which gcc`
```

3.6.5 Installation from CMake

Installation is optional. The QMCPACK executable can be run from the `bin` directory in the build location. If the install step is desired, run the `make install` command to install the QMCPACK executable, the converter, and some additional executables. Also installed is the `qmcpack.settings` file that records options used to compile QMCPACK. Specify the `CMAKE_INSTALL_PREFIX` CMake variable during configuration to set the install location.

3.6.6 Role of QMC_DATA

QMCPACK includes a variety of optional performance and integration tests that use research quality wavefunctions to obtain meaningful performance and to more thoroughly test the code. The necessarily large input files are stored in the location pointed to by QMC_DATA (e.g., scratch or long-lived project space on a supercomputer). These multi-gigabyte files are not included in the source code distribution to minimize size. The tests are activated if CMake detects the files when configured. See tests/performance/NiO/README, tests/solids/NiO_afqmc/README, tests/performance/C-graphite/README, and tests/performance/C-molecule/README for details of the current tests and input files and to download them.

Currently the files must be downloaded via https://anl.box.com/s/yxz1ic4kxtdtgpva5hcmlom9ixfl3v3c.

The layout of current complete set of files is given below. If a file is missing, the appropriate performance test is skipped.

```
QMC_DATA/C-graphite/lda.pwscf.h5
QMC_DATA/C-molecule/C12-e48-pp.h5
QMC_DATA/C-molecule/C12-e72-ae.h5
QMC_DATA/C-molecule/C18-e108-ae.h5
QMC_DATA/C-molecule/C18-e72-pp.h5
QMC_DATA/C-molecule/C24-e144-ae.h5
QMC_DATA/C-molecule/C24-e96-pp.h5
QMC_DATA/C-molecule/C30-e120-pp.h5
QMC_DATA/C-molecule/C30-e180-ae.h5
QMC_DATA/C-molecule/C60-e240-pp.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S1.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S2.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S4.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S8.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S16.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S32.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S64.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S128.h5
QMC_DATA/NiO/NiO-fcc-supertwist111-supershift000-S256.h5
QMC_DATA/NiO/NiO_afm_fcidump.h5
QMC_DATA/NiO/NiO_afm_wfn.dat
QMC_DATA/NiO/NiO_nm_choldump.h5
```

3.6.7 Configure and build using CMake and make

To configure and build QMCPACK, move to build directory, run CMake, and make

```
cd build
cmake ..
make -j 8
```

As you will have gathered, CMake encourages “out of source” builds, where all the files for a specific build configuration reside in their own directory separate from the source files. This allows multiple builds to be created from the same source files, which is very useful when the file system is shared between different systems. You can also build versions with different settings (e.g., QMC_COMPLEX) and different compiler settings. The build directory does not have to be called build—use something descriptive such as build_machinename or build_complex. The “..” in the CMake line refers to the directory containing CMakeLists.txt. Update the “..” for other build directory locations.

3.6.8 Example configure and build

- Set the environments (the examples below assume bash, Intel compilers, and MKL library)

```
export CXX=icpc
export CC=icc
export MKL_ROOT=/usr/local/intel/mkl/10.0.3.020
export HDF5_ROOT=/usr/local
export BOOST_ROOT=/usr/local/boost
export FFTW_HOME=/usr/local/fftw
```

- Move to build directory, run CMake, and make

```
cd build
cmake -D CMAKE_BUILD_TYPE=Release ..
make -j 8
```

3.6.9 Build scripts

We recommended creating a helper script that contains the configure line for CMake. This is particularly useful when avoiding environment variables, packages are installed in custom locations, or the configure line is long or complex. In this case it is also recommended to add "rm -rf CMake*" before the configure line to remove existing CMake configure files to ensure a fresh configure each time the script is called. Deleting all the files in the build directory is also acceptable. If you do so we recommend adding some sanity checks in case the script is run from the wrong directory (e.g., checking for the existence of some QMCPACK files).

Some build script examples for different systems are given in the config directory. For example, on Cray systems these scripts might load the appropriate modules to set the appropriate programming environment, specific library versions, etc.

An example script build.sh is given below. It is much more complex than usually needed for comprehensiveness:

```
export CXX=mpic++
export CC=mpicc
export HDF5_ROOT=/opt/hdf5
export BOOST_ROOT=/opt/boost

rm -rf CMake*

cmake                                                 \
  -D CMAKE_BUILD_TYPE=Debug                           \
  -D LIBXML2_INCLUDE_DIR=/usr/include/libxml2        \
  -D LIBXML2_LIBRARY=/usr/lib/x86_64-linux-gnu/libxml2.so \
  -D FFTW_INCLUDE_DIRS=/usr/include                   \
  -D FFTW_LIBRARY_DIRS=/usr/lib/x86_64-linux-gnu      \
  -D QMC_DATA=/projects/QMCPACK/qmc-data              \
  ..
```

3.6.10 Using vendor-optimized numerical libraries (e.g., Intel MKL)

Although QMC does not make extensive use of linear algebra, use of vendor-optimized libraries is strongly recommended for highest performance. BLAS routines are used in the Slater determinant update, the VMC wavefunction optimizer, and to apply orbital coefficients in local basis calculations. Vectorized math functions are also beneficial (e.g., for the phase factor computation in solid-state calculations). CMake is generally successful in finding these libraries, but specific combinations can require additional hints, as described in the following:

Using Intel MKL with non-Intel compilers

To use Intel MKL with, e.g. an MPICH wrapped gcc:

```
cmake \
  -DCMAKE_C_COMPILER=mpicc -DCMAKE_CXX_COMPILER=mpicxx \
  -DMKL_ROOT=YOUR_INTEL_MKL_ROOT_DIRECTORY \
  ..
```

MKL_ROOT is only necessary when MKL is not auto-detected successfully or a particular MKL installation is desired. YOUR_INTEL_MKL_ROOT_DIRECTORY is the directory containing the MKL bin, examples, and lib directories (etc.) and is often /opt/intel/mkl.

Serial or multithreaded library

Vendors might provide both serial and multithreaded versions of their libraries. Using the right version is critical to QMCPACK performance. QMCPACK makes calls from both inside and outside threaded regions. When being called from outside an OpenMP parallel region, the multithreaded version is preferred for the possibility of using all the available cores. When being called from every thread inside an OpenMP parallel region, the serial version is preferred for not oversubscribing the cores. Fortunately, nowadays the multithreaded versions of many vendor libraries (MKL, ESSL) are OpenMP aware. They use only one thread when being called inside an OpenMP parallel region. This behavior meets exactly both QMCPACK needs and thus is preferred. If the multithreaded version does not provide this feature of dynamically adjusting the number of threads, the serial version is preferred. In addition, thread safety is required no matter which version is used.

3.6.11 Cross compiling

Cross compiling is often difficult but is required on supercomputers with distinct host and compute processor generations or architectures. QMCPACK tried to do its best with CMake to facilitate cross compiling.

- On a machine using a Cray programming environment, we rely on compiler wrappers provided by Cray to correctly set architecture-specific flags. Please also add `-DCMAKE_SYSTEM_NAME=CrayLinuxEnvironment` to cmake. The CMake configure log should indicate that a Cray machine was detected.
- If not on a Cray machine, by default we assume building for the host architecture (e.g., -xHost is added for the Intel compiler and -march=native is added for GNU/Clang compilers).
- If -x/-ax or -march is specified by the user in CMAKE_C_FLAGS and CMAKE_CXX_FLAGS, we respect the user's intention and do not add any architecture-specific flags.

The general strategy for cross compiling should therefore be to manually set CMAKE_C_FLAGS and CMAKE_CXX_FLAGS for the target architecture. Using `make VERBOSE=1` is a useful way to check the final compilation options. If on a Cray machine, selection of the appropriate programming environment should be sufficient.

3.7 Installation instructions for common workstations and supercomputers

This section describes how to build QMCPACK on various common systems including multiple Linux distributions, Apple OS X, and various supercomputers. The examples should serve as good starting points for building QMCPACK on similar machines. For example, the software environment on modern Crays is very consistent. Note that updates to operating systems and system software might require small modifications to these recipes. See *How to build the fastest executable version of QMCPACK* for key points to check to obtain highest performance and *Troubleshooting the installation* for troubleshooting hints.

3.7.1 Installing on Ubuntu Linux or other apt-get–based distributions

The following is designed to obtain a working QMCPACK build on, for example, a student laptop, starting from a basic Linux installation with none of the developer tools installed. Fortunately, all the required packages are available in the default repositories making for a quick installation. Note that for convenience we use a generic BLAS. For production, a platform-optimized BLAS should be used.

```
sudo apt-get install cmake g++ openmpi-bin libopenmpi-dev libboost-dev
sudo apt-get install libatlas-base-dev liblapack-dev libhdf5-dev libxml2-dev fftw3-dev
export CXX=mpiCC
cd build
cmake ..
make -j 8
ls -l bin/qmcpack
```

For qmca and other tools to function, we install some Python libraries:

```
sudo apt-get install python-numpy python-matplotlib
```

3.7.2 Installing on CentOS Linux or other yum-based distributions

The following is designed to obtain a working QMCPACK build on, for example, a student laptop, starting from a basic Linux installation with none of the developer tools installed. CentOS 7 (Red Hat compatible) is using gcc 4.8.2. The installation is complicated only by the need to install another repository to obtain HDF5 packages that are not available by default. Note that for convenience we use a generic BLAS. For production, a platform-optimized BLAS should be used.

```
sudo yum install make cmake gcc gcc-c++ openmpi openmpi-devel fftw fftw-devel \
                 boost boost-devel libxml2 libxml2-devel
sudo yum install blas-devel lapack-devel atlas-devel
module load mpi
```

To set up repoforge as a source for the HDF5 package, go to http://repoforge.org/use. Install the appropriate up-to-date release package for your operating system. By default, CentOS Firefox will offer to run the installer. The CentOS 6.5 settings were still usable for HDF5 on CentOS 7 in 2016, but use CentOS 7 versions when they become available.

```
sudo yum install hdf5 hdf5-devel
```

To build QMCPACK:

```
module load mpi/openmpi-x86_64
which mpirun
```

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```
# Sanity check; should print something like   /usr/lib64/openmpi/bin/mpirun
export CXX=mpiCC
cd build
cmake ..
make -j 8
ls -l bin/qmcpack
```

3.7.3 Installing on Mac OS X using Macports

These instructions assume a fresh installation of macports and use the gcc 10.2 compiler.

Follow the Macports install instructions at https://www.macports.org/.

- Install Xcode and the Xcode Command Line Tools.
- Agree to Xcode license in Terminal: sudo xcodebuild -license.
- Install MacPorts for your version of OS X.

We recommend to make sure macports is updated:

```
sudo port -v selfupdate # Required for macports first run, recommended in general
sudo port upgrade outdated # Recommended
```

Install the required tools. For thoroughness we include the current full set of python dependencies. Some of the tests will be skipped if not all are available.

```
sudo port install gcc11
sudo port select gcc mp-gcc11
sudo port install openmpi-gcc11
sudo port select --set mpi openmpi-gcc11-fortran

sudo port install fftw-3 +gcc11
sudo port install libxml2
sudo port install cmake
sudo port install boost +gcc11
sudo port install hdf5 +gcc11

sudo port install python310
sudo port select --set python python310
sudo port select --set python3 python310
sudo port install py310-numpy +gcc11
sudo port select --set cython cython310
sudo port install py310-scipy +gcc11
sudo port install py310-h5py +gcc11
sudo port install py310-pandas
sudo port install py310-lxml
sudo port install py310-matplotlib  #For graphical plots with qmca
```

QMCPACK build:

```
cd build
cmake -DCMAKE_C_COMPILER=mpicc -DCMAKE_CXX_COMPILER=mpiCXX ..
make -j 4 # Adjust for available core count
ls -l bin/qmcpack
```

Run the deterministic tests:

```
ctest -R deterministic
```

This recipe was verified on February 28, 2022, on a Mac running OS X 11.6.4 “Big Sur”.

3.7.4 Installing on Mac OS X using Homebrew (brew)

Homebrew is a package manager for OS X that provides a convenient route to install all the QMCPACK dependencies. The following recipe will install the latest available versions of each package. This was successfully tested under OS X 10.15.7 “Catalina” on October 26, 2020.

1. Install Homebrew from http://brew.sh/:

```
/usr/bin/ruby -e "$(curl -fsSL
  https://raw.githubusercontent.com/Homebrew/install/master/install)"
```

2. Install the prerequisites:

```
brew install gcc # 10.2.0 when tested
brew install openmpi
brew install cmake
brew install fftw
brew install boost
brew install hdf5
export OMPI_CC=gcc-10
export OMPI_CXX=g++-10
```

3. Configure and build QMCPACK:

```
cmake -DCMAKE_C_COMPILER=/usr/local/bin/mpicc \
      -DCMAKE_CXX_COMPILER=/usr/local/bin/mpicxx ..
make -j 6 # Adjust for available core count
ls -l bin/qmcpack
```

4. Run the deterministic tests

```
ctest -R deterministic
```

3.7.5 Installing on ALCF Theta, Cray XC40

Theta is a 9.65 petaflops system manufactured by Cray with 3,624 compute nodes. Each node features a second-generation Intel Xeon Phi 7230 processor and 192 GB DDR4 RAM.

```
export CRAYPE_LINK_TYPE=dynamic
module load cmake/3.16.2
module unload cray-libsci
module load cray-hdf5-parallel
module load gcc   # Make C++ 14 standard library available to the Intel compiler
export BOOST_ROOT=/soft/libraries/boost/1.64.0/intel
cmake -DCMAKE_SYSTEM_NAME=CrayLinuxEnvironment ..
make -j 24
ls -l bin/qmcpack
```

3.7.6 Installing on ORNL OLCF Summit

Summit is an IBM system at the ORNL OLCF built with IBM Power System AC922 nodes. They have two IBM Power 9 processors and six NVIDIA Volta V100 accelerators.

Building QMCPACK

Note that these build instructions are preliminary as the software environment is subject to change. As of December 2018, the IBM XL compiler does not support C++14, so we currently use the gnu compiler.

For ease of reproducibility we provide build scripts for Summit.

```
cd qmcpack
./config/build_olcf_summit.sh
ls bin
```

Building Quantum ESPRESSO

We provide a build script for the v6.4.1 release of Quantum ESPRESSO (QE). The following can be used to build a CPU version of QE on Summit, placing the script in the external_codes/quantum_espresso directory.

```
cd external_codes/quantum_espresso
./build_qe_olcf_summit.sh
```

Note that performance is not yet optimized although vendor libraries are used. Alternatively, the wavefunction files can be generated on another system and the converted HDF5 files copied over.

3.7.7 Installing on NERSC Cori, Haswell Partition, Cray XC40

Cori is a Cray XC40 that includes 16-core Intel "Haswell" nodes installed at NERSC. In the following example, the source code is cloned in $HOME/qmc/git_QMCPACK and QMCPACK is built in the scratch space.

```
mkdir $HOME/qmc
mkdir $HOME/qmc/git_QMCPACK
cd $HOME/qmc_git_QMCPACK
git clone https://github.com/QMCPACK/qmcpack.git
cd qmcpack
git checkout v3.7.0 # Edit for desired version
export CRAYPE_LINK_TYPE=dynamic
module unload cray-libsci
module load boost/1.70.0
module load cray-hdf5-parallel
module load cmake/3.14.4
module load gcc/8.3.0 # Make C++ 14 standard library available to the Intel compiler
cd $SCRATCH
mkdir build_cori_hsw
cd build_cori_hsw
cmake -DQMC_SYMLINK_TEST_FILES=0 -DCMAKE_SYSTEM_NAME=CrayLinuxEnvironment $HOME/qmc/
↪git_QMCPACK/qmcpack/
nice make -j 8
ls -l bin/qmcpack
```

When the preceding was tested on June 15, 2020, the following module and software versions were present:

```
build_cori_hsw> module list
Currently Loaded Modulefiles:
1) modules/3.2.11.4                                    13) xpmem/2.2.20-7.0.1.1_4.8__
↪g0475745.ari
2) nsg/1.2.0                                           14) job/2.2.4-7.0.1.1_3.34__
↪g36b56f4.ari
3) altd/2.0                                            15) dvs/2.12_2.2.156-7.0.1.1_8.6__
↪g5aab709e
4) darshan/3.1.7                                       16) alps/6.6.57-7.0.1.1_5.10__
↪g1b735148.ari
5) intel/19.0.3.199                                    17) rca/2.2.20-7.0.1.1_4.42__
↪g8e3fb5b.ari
6) craype-network-aries                                18) atp/2.1.3
7) craype/2.6.2                                        19) PrgEnv-intel/6.0.5
8) udreg/2.3.2-7.0.1.1_3.29__g8175d3d.ari              20) craype-haswell
9) ugni/6.0.14.0-7.0.1.1_7.32__ge78e5b0.ari            21) cray-mpich/7.7.10
10) pmi/5.0.14                                         22) craype-hugepages2M
11) dmapp/7.1.1-7.0.1.1_4.43__g38cf134.ari             23) gcc/8.3.0
12) gni-headers/5.0.12.0-7.0.1.1_6.27__g3b1768f.ari    24) cmake/3.14.4
```

The following slurm job file can be used to run the tests:

```
#!/bin/bash
#SBATCH --qos=debug
#SBATCH --time=00:10:00
#SBATCH --nodes=1
#SBATCH --tasks-per-node=32
#SBATCH --constraint=haswell
echo --- Start `date`
echo --- Working directory: `pwd`
ctest -VV -R deterministic
echo --- End `date`
```

3.7.8 Installing on NERSC Cori, Xeon Phi KNL partition, Cray XC40

Cori is a Cray XC40 that includes Intel Xeon Phi Knight's Landing (KNL) nodes. The following build recipe ensures that the code generation is appropriate for the KNL nodes. The source is assumed to be in $HOME/qmc/git_QMCPACK/qmcpack as per the Haswell example.

```
export CRAYPE_LINK_TYPE=dynamic
module swap craype-haswell craype-mic-knl # Only difference between Haswell and KNL␣
↪recipes
module unload cray-libsci
module load boost/1.70.0
module load cray-hdf5-parallel
module load cmake/3.14.4
module load gcc/8.3.0 # Make C++ 14 standard library available to the Intel compiler
cd $SCRATCH
mkdir build_cori_knl
cd build_cori_knl
cmake -DQMC_SYMLINK_TEST_FILES=0 -DCMAKE_SYSTEM_NAME=CrayLinuxEnvironment $HOME/qmc/
↪git_QMCPACK/qmcpack/
nice make -j 8
ls -l bin/qmcpack
```

When the preceding was tested on June 15, 2020, the following module and software versions were present:

```
build_cori_knl> module list
  Currently Loaded Modulefiles:
  1) modules/3.2.11.4                                    13) xpmem/2.2.20-7.0.1.1_4.8__
↪g0475745.ari
  2) nsg/1.2.0                                           14) job/2.2.4-7.0.1.1_3.34__
↪g36b56f4.ari
  3) altd/2.0                                            15) dvs/2.12_2.2.156-7.0.1.1_8.
↪6__g5aab709e
  4) darshan/3.1.7                                       16) alps/6.6.57-7.0.1.1_5.10__
↪g1b735148.ari
  5) intel/19.0.3.199                                    17) rca/2.2.20-7.0.1.1_4.42__
↪g8e3fb5b.ari
  6) craype-network-aries                                18) atp/2.1.3
  7) craype/2.6.2                                        19) PrgEnv-intel/6.0.5
  8) udreg/2.3.2-7.0.1.1_3.29__g8175d3d.ari              20) craype-mic-knl
  9) ugni/6.0.14.0-7.0.1.1_7.32__ge78e5b0.ari            21) cray-mpich/7.7.10
 10) pmi/5.0.14                                          22) craype-hugepages2M
 11) dmapp/7.1.1-7.0.1.1_4.43__g38cf134.ari              23) gcc/8.3.0
 12) gni-headers/5.0.12.0-7.0.1.1_6.27__g3b1768f.ari     24) cmake/3.14.4
```

3.7.9 Installing on systems with ARMv8-based processors

The following build recipe was verified using the 'Arm Compiler for HPC' on the ANL JLSE Comanche system with Cavium ThunderX2 processors on November 6, 2018.

```
# load armclang compiler
module load Generic-AArch64/RHEL/7/arm-hpc-compiler/18.4
# load Arm performance libraries
module load ThunderX2CN99/RHEL/7/arm-hpc-compiler-18.4/armpl/18.4.0
# define path to pre-installed packages
export HDF5_ROOT=</path/to/hdf5/install/>
export BOOST_ROOT=</path/to/boost/install> # header-only, no need to build
```

Then using the following command:

```
mkdir build_armclang
cd build_armclang
cmake -DCMAKE_C_COMPILER=armclang -DCMAKE_CXX_COMPILER=armclang++ -DQMC_MPI=0 \
    -DLAPACK_LIBRARIES="-L$ARMPL_DIR/lib -larmpl_mp" \
    -DFFTW_INCLUDE_DIR="$ARMPL_DIR/include" \
    -DFFTW_LIBRARIES="$ARMPL_DIR/lib/libarmpl_mp.a" \
    ..
make -j 56
```

Note that armclang is recognized as an 'unknown' compiler by CMake v3.13* and below. In this case, we need to force it as clang to apply necessary flags. To do so, pass the following additionals option to CMake:

```
-DCMAKE_C_COMPILER_ID=Clang -DCMAKE_CXX_COMPILER_ID=Clang \
-DCMAKE_CXX_COMPILER_VERSION=5.0 -DCMAKE_CXX_STANDARD_COMPUTED_DEFAULT=98 \
```

3.7.10 Installing on Windows

Install the Windows Subsystem for Linux and Bash on Windows. Open a bash shell and follow the install directions for Ubuntu in *Installing on Ubuntu Linux or other apt-get–based distributions*.

3.8 Installing via Spack

Spack is a package manager for scientific software. One of the primary goals of Spack is to reduce the barrier for users to install scientific software. Spack is intended to work on everything from laptop computers to high-end supercomputers. More information about Spack can be found at https://spack.readthedocs.io/en/latest. The major advantage of installation with Spack is that all dependencies are automatically built, potentially including all the compilers and libraries, and different versions of QMCPACK can easily coexist with each other. The QMCPACK Spack package also knows how to automatically build and patch QE. In principle, QMCPACK can be installed with a single Spack command.

3.8.1 Known limitations

The QMCPACK Spack package inherits the limitations of the underlying Spack infrastructure and its dependencies. The main limitation is that installation can fail when building a dependency such as HDF5, MPICH, etc. For `spack install qmcpack` to succeed, it is very important to leverage preinstalled packages on your computer or supercomputer. The other frequently encountered challenge is that the compiler configuration is nonintuitive. This is especially the case with the Intel compiler. If you encounter any difficulties, we recommend testing the Spack compiler configuration on a simpler package, e.g. HDF5.

Here are some additional limitations that new users should be aware of:

- CUDA support in Spack still has some limitations. It will not catch the most recent compiler-CUDA conflicts.
- The Intel compiler must find a recent and compatible GCC compiler in its path or one must be explicitly set with the `-gcc-name` and `-gxx-name` flags in your `compilers.yaml`.
- Cross-compilation is non-intuitive. If the host OS and target OS are the same, but only the processors differ, you will just need to add the `target=<target CPU>`. However, if the host OS is different from the target OS and you will need to add `os=<target OS>`. If both the OS and CPU differ between host and target, you will need to set the `arch=<platform string>`. For more information, see: https://spack.readthedocs.io/en/latest/basic_usage.html?highlight=cross%20compilation#architecture-specifiers

3.8.2 Setting up the Spack environment

Begin by cloning Spack from GitHub and configuring your shell as described at https://spack.readthedocs.io/en/latest/getting_started.html.

The goal of the next several steps is to set up the Spack environment for building. First, we highly recommend limiting the number of build jobs to a reasonable value for your machine. This can be accomplished by modifying your `~/.spack/config.yaml` file as follows:

```
config:
  build_jobs: 16
```

Make sure any existing compilers are properly detected. For many architectures, compilers are properly detected with no additional effort.

```
your-laptop> spack compilers
==> Available compilers
-- gcc sierra-x86_64 ---------------------------------------------
gcc@7.2.0  gcc@6.4.0  gcc@5.5.0  gcc@4.9.4  gcc@4.8.5  gcc@4.7.4  gcc@4.6.4
```

However, if your compiler is not automatically detected, it is straightforward to add one:

```
your-laptop> spack compiler add <path-to-compiler>
```

The Intel ("classic") compiler and other commercial compilers may require extra environment variables to work properly. If you have an module environment set-up by your system administrators, it is recommended that you set the module name in `~/.spack/linux/compilers.yaml`. Here is an example for the Intel compiler:

```
- compiler:
  environment:{}
  extra_rpaths:  []
  flags: {}
  modules:
  - intel/18.0.3
  operating_system: ubuntu14.04
  paths:
    cc: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/icc
    cxx: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/icpc
    f77: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/ifort
    fc: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/ifort
  spec: intel@18.0.3
  target: x86_64
```

If a module is not available, you will have to set-up the environment variables manually:

```
- compiler:
  environment:
    set:
      INTEL_LICENSE_FILE: server@national-lab.doe.gov
  extra_rpaths:
  ['/soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/compiler/
↪lib/intel64',
  '/soft/apps/packages/gcc/gcc-6.2.0/lib64']
  flags:
    cflags: -gcc-name=/soft/apps/packages/gcc/gcc-6.2.0/bin/gcc
    fflags: -gcc-name=/soft/apps/packages/gcc/gcc-6.2.0/bin/gcc
    cxxflags: -gxx-name=/soft/apps/packages/gcc/gcc-6.2.0/bin/g++
  modules: []
  operating_system: ubuntu14.04
  paths:
    cc: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/icc
    cxx: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/icpc
    f77: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/ifort
    fc: /soft/com/packages/intel/18/u3/compilers_and_libraries_2018.3.222/linux/bin/
↪intel64/ifort
```

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```
  spec: intel@18.0.3
  target: x86_64
```

This last step is the most troublesome. Pre-installed packages are not automatically detected. If vendor optimized libraries are already installed, you will need to manually add them to your `~/.spack/packages.yaml`. For example, this works on Mac OS X for the Intel MKL package.

```
your-laptop> cat \~/.spack/packages.yaml
packages:
  intel-mkl:
      paths:
          intel-mkl@2018.0.128: /opt/intel/compilers_and_libraries_2018.0.104/mac/mkl
      buildable: False
```

Some trial-and-error might be involved to set the directories correctly. If you do not include enough of the tree path, Spack will not be able to register the package in its database. More information about system packages can be found at http://spack.readthedocs.io/en/latest/getting_started.html#system-packages.

Beginning with QMCPACK v3.9.0, Python 3.x is required. However, installing Python with a compiler besides GCC is tricky. We recommend leveraging your local Python installation by adding an entry in `~/.spack/packages.yaml`:

```
packages:
  python:
     modules:
       python@3.7.4: anaconda3/2019.10
```

Or if a module is not available

```
packages:
  python:
     paths:
        python@3.7.4: /nfs/gce/software/custom/linux-ubuntu18.04-x86_64/anaconda3/
↪2019.10/bin/python
   buildable: False
```

3.8.3 Building QMCPACK

The QMCPACK Spack package has a number of variants to support different compile time options and different versions of the application. A full list can be displayed by typing:

```
your laptop> spack info qmcpack
CMakePackage:   qmcpack

Description:
  QMCPACK, is a modern high-performance open-source Quantum Monte Carlo
  (QMC) simulation code.

Homepage: http://www.qmcpack.org/

Tags:
  ecp  ecp-apps

Preferred version:
```

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```
  3.11.0     [git] https://github.com/QMCPACK/qmcpack.git at tag v3.11.0

Safe versions:
  develop    [git] https://github.com/QMCPACK/qmcpack.git
  3.11.0     [git] https://github.com/QMCPACK/qmcpack.git at tag v3.11.0
  3.10.0     [git] https://github.com/QMCPACK/qmcpack.git at tag v3.10.0
  3.9.2      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.9.2
  3.9.1      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.9.1
  3.9.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.9.0
  3.8.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.8.0
  3.7.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.7.0
  3.6.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.6.0
  3.5.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.5.0
  3.4.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.4.0
  3.3.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.3.0
  3.2.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.2.0
  3.1.1      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.1.1
  3.1.0      [git] https://github.com/QMCPACK/qmcpack.git at tag v3.1.0

Variants:
  Name [Default]          Allowed values          Description
  ====================    ====================    ============================

  afqmc [off]             on, off                 Install with AFQMC support.
                                                  NOTE that if used in
                                                  combination with CUDA, only
                                                  AFQMC will have CUDA.
  build_type [Release]    Debug, Release,         The build type to build
                          RelWithDebInfo
  complex [off]           on, off                 Build the complex (general
                                                  twist/k-point) version
  cuda [off]              on, off                 Build with CUDA
  cuda_arch [none]        none, 53, 20, 62,       CUDA architecture
                          60, 61, 50, 75, 70,
                          72, 32, 52, 30, 35
  da [off]                on, off                 Install with support for basic
                                                  data analysis tools
  gui [off]               on, off                 Install with Matplotlib (long
                                                  installation time)
  mixed [off]             on, off                 Build the mixed precision
                                                  (mixture of single and double
                                                  precision) version for gpu and
                                                  cpu
  mpi [on]                on, off                 Build with MPI support
  phdf5 [on]              on, off                 Build with parallel collective
                                                  I/O
  ppconvert [off]         on, off                 Install with pseudopotential
                                                  converter.
  qe [on]                 on, off                 Install with patched Quantum
                                                  Espresso 6.4.0
  timers [off]            on, off                 Build with support for timers

Installation Phases:
  cmake    build    install

Build Dependencies:
  blas  boost  cmake  cuda  fftw-api  hdf5  lapack  libxml2  mpi  python
```

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```
Link Dependencies:
  blas  boost  cuda  fftw-api  hdf5  lapack  libxml2  mpi  python

Run Dependencies:
  py-matplotlib  py-numpy  quantum-espresso

Virtual Packages:
  None
```

For example, to install the complex-valued version of QMCPACK in mixed-precision use:

```
your-laptop> spack install qmcpack+mixed+complex%gcc@7.2.0 ^intel-mkl
```

where

```
%gcc@7.2.0
```

specifies the compiler version to be used and

```
^intel-mkl
```

specifies that the Intel MKL should be used as the BLAS and LAPACK provider. The ^ symbol indicates the the package to the right of the symbol should be used to fulfill the dependency needed by the installation.

It is also possible to run the QMCPACK regression tests as part of the installation process, for example:

```
your-laptop> spack install --test=root qmcpack+mixed+complex%gcc@7.2.0 ^intel-mkl
```

will run the unit and deterministic tests. The current behavior of the QMCPACK Spack package is to complete the install as long as all the unit tests pass. If the deterministic tests fail, a warning is issued at the command prompt.

For CUDA, you will need to specify and extra `cuda_arch` parameter otherwise, it will default to `cuda_arch=61`.

```
your-laptop> spack install qmcpack+cuda%intel@18.0.3 cuda_arch=61 ^intel-mkl
```

Due to limitations in the Spack CUDA package, if your compiler and CUDA combination conflict, you will need to set a specific version of CUDA that is compatible with your compiler on the command line. For example,

```
your-laptop> spack install qmcpack+cuda%intel@18.0.3 cuda_arch=61 ^cuda@10.0.130 ^
↪intel-mkl
```

3.8.4 Loading QMCPACK into your environment

If you already have modules set-up in your environment, the Spack modules will be detected automatically. Otherwise, Spack will not automatically find the additional packages. A few additional steps are needed. Please see the main Spack documentation for additional details: https://spack.readthedocs.io/en/latest/module_file_support.html.

3.8.5 Dependencies that need to be compiled with GCC

Failing to compile a QMCPACK dependency is the most common reason that a Spack build fails. We recommend that you compile the following dependencies with GCC:

For MPI, using MPICH as the provider, try:

```
your-laptop> spack install qmcpack%intel@18.0.3 ^boost%gcc ^pkgconf%gcc ^perl%gcc ^
↪libpciaccess%gcc ^cmake%gcc ^findutils%gcc ^m4%gcc
```

For serial,

```
your-laptop> spack install qmcpack~mpi%intel@18.0.3 ^boost%gcc ^pkgconf%gcc ^perl%gcc␣
↪^cmake%gcc
```

3.8.6 Installing QMCPACK with Spack on Linux

Spack works robustly on the standard flavors of Linux (Ubuntu, CentOS, Ubuntu, etc.) using GCC, Clang, NVHPC, and Intel compilers.

3.8.7 Installing QMCPACK with Spack on Mac OS X

Spack works on Mac OS X but requires installation of a few packages using Homebrew. You will need to install at minimum the GCC compilers, CMake, and pkg-config. The Intel compiler for Mac on OS X is not well supported by Spack packages and will most likely lead to a compile time failure in one of QMCPACK's dependencies.

3.8.8 Installing QMCPACK with Spack on Cray Supercomputers

Spack now works with the Cray environment. To leverage the installed Cray environment, both a `compilers.yaml` and `packages.yaml` file should be provided by the supercomputing facility. Additionally, Spack packages compiled by the facility can be reused by chaining Spack installations https://spack.readthedocs.io/en/latest/chain.html.

3.8.9 Installing Quantum-ESPRESSO with Spack

More information about the QE Spack package can be obtained directly from Spack

```
spack info quantum-espresso
```

There are many variants available for QE, most, but not all, are compatible with QMCPACK patch. Here is a minimalistic example of the Spack installation command that needs to be invoked:

```
your-laptop> spack install quantum-espresso+qmcpack~patch@6.7%gcc hdf5=parallel
```

The ~ decorator means deactivate the `patch` variant. This refers not to the QMCPACK patch, but to the upstream patching that is present for some versions of QE. These upstream QE patches fix specific critical autoconf/configure fixes. Unfortunately, some of these QE upstream patches are incompatible with the QMCPACK patch. Note that the Spack package will prevent you from installing incompatible variants and will emit an error message explaining the nature of the incompatibility.

A serial (no MPI) installation is also available, but the Spack installation command is non-intuitive for Spack newcomers:

```
your-laptop> spack install quantum-espresso+qmcpack~patch~mpi~scalapack@6.7%gcc␣
↪hdf5=serial
```

QE Spack package is well tested with GCC and Intel compilers, but will not work with the NVHPC compiler or in a cross-compile environment.

3.8.10 Reporting Bugs

Bugs with the QMCPACK Spack package should be filed at the main GitHub Spack repo https://github.com/spack/spack/issues.

In the GitHub issue, include `@naromero77` to get the attention of our developer.

3.9 Testing and validation of QMCPACK

We **strongly encourage** running the included tests each time QMCPACK is built. A range of unit and integration tests ensure that the code behaves as expected and that results are consistent with known-good mean-field, quantum chemical, and historical QMC results.

The tests include the following:

- Unit tests: to check fundamental behavior. These should always pass.
- Stochastic integration tests: to check computed results from the Monte Carlo methods. These might fail statistically, but rarely because of the use of three sigma level statistics. These tests are further split into "short" tests, which have just sufficient length to have valid statistics, and "long" tests, to check behavior to higher statistical accuracy.
- Converter tests: to check conversion of trial wavefunctions from codes such as QE and GAMESS to QMCPACK's formats. These should always pass.
- Workflow tests: in the case of QE, we test the entire cycle of DFT calculation, trial wavefunction conversion, and a subsequent VMC run.
- Performance: to help performance monitoring. Only the timing of these runs is relevant.

The test types are differentiated by prefixes in their names, for example, `short-LiH_dimer_ae_vmc_hf_noj_16-1` indicates a short VMC test for the LiH dime.

QMCPACK also includes tests for developmental features and features that are unsupported on certain platforms. To indicate these, tests that are unstable are labeled with the CTest label "unstable." For example, they are unreliable, unsupported, or known to fail from partial implementation or bugs.

When installing QMCPACK you should run at least the unit tests:

```
ctest -R unit
```

These tests take only a few seconds to run. All should pass. A failure here could indicate a major problem with the installation.

A wider range of deterministic integration tests are being developed. The goal is to test much more of QMCPACK than the unit tests do and to do so in a manner that is reproducible across platforms. All of these should eventually pass 100% reliably and quickly. At present, some fail on some platforms and for certain build types.

```
ctest -R deterministic -LE unstable
```

If time allows, the "short" stochastic tests should also be run. The short tests take a few minutes each on a 16-core machine—about 1 hour total depending on the platform. You can run these tests using the following command in the build directory:

```
ctest -R short -LE unstable  # Run the tests with "short" in their name.
                             # Exclude any known unstable tests.
```

The output should be similar to the following:

```
Test project build_gcc
    Start  1: short-LiH_dimer_ae-vmc_hf_noj-16-1
1/44 Test  #1: short-LiH_dimer_ae-vmc_hf_noj-16-1 ..............  Passed   11.20 sec
    Start  2: short-LiH_dimer_ae-vmc_hf_noj-16-1-kinetic
2/44 Test  #2: short-LiH_dimer_ae-vmc_hf_noj-16-1-kinetic ......  Passed    0.13 sec
..
42/44 Test #42: short-monoO_1x1x1_pp-vmc_sdj-1-16 ...............  Passed   10.02 sec
    Start 43: short-monoO_1x1x1_pp-vmc_sdj-1-16-totenergy
43/44 Test #43: short-monoO_1x1x1_pp-vmc_sdj-1-16-totenergy .....  Passed    0.08 sec
    Start 44: short-monoO_1x1x1_pp-vmc_sdj-1-16-samples
44/44 Test #44: short-monoO_1x1x1_pp-vmc_sdj-1-16-samples .......  Passed    0.08 sec

100% tests passed, 0 tests failed out of 44

Total Test time (real) = 167.14 sec
```

Note that the number of tests run varies between the standard, complex, and GPU compilations. These tests should pass with three sigma reliability. That is, they should nearly always pass, and when rerunning a failed test it should usually pass. Overly frequent failures suggest a problem that should be addressed before any scientific production.

The full set of tests consist of significantly longer versions of the short tests, as well as tests of the conversion utilities. The runs require several hours each for improved statistics and a much more stringent test of the code. To run all the tests, simply run CTest in the build directory:

```
ctest -LE unstable           # Run all the stable tests. This will take several hours.
```

You can also run verbose tests, which direct the QMCPACK output to the standard output:

```
ctest -V -R short   # Verbose short tests
```

The test system includes specific tests for the complex version of the code.

The input data files for the tests are located in the `tests` directory. The system-level test directories are grouped into `heg`, `molecules`, and `solids`, with particular physical systems under each (for example `molecules/H4_ae`[1]). Under each physical system directory there might be tests for multiple QMC methods or parameter variations. The numerical comparisons and test definitions are in the `CMakeLists.txt` file in each physical system directory.

If *all* the QMC tests fail it is likely that the appropriate mpiexec (or mpirun, aprun, srun, jsrun) is not being called or found. If the QMC runs appear to work but all the other tests fail, it is possible that Python is not working on your system. We suggest checking some of the test console output in `build/Testing/Temporary/LastTest.log` or the output files under `build/tests/`.

Note that because most of the tests are very small, consisting of only a few electrons, the performance is not representative of larger calculations. For example, although the calculations might fit in cache, there will be essentially no vectorization because of the small electron counts. **These tests should therefore not be used for any benchmarking or performance analysis**. Example runs that can be used for testing performance are described in *Performance tests*.

[1] The suffix "ae" is short for "all-electron," and "pp" is short for "pseudopotential."

3.9.1 Deterministic and unit tests

QMCPACK has a set of deterministic tests, predominantly unit tests. All of these tests can be run with the following command (in the build directory):

```
ctest -R deterministic -LE unstable
```

These tests should always pass. Failure could indicate a major problem with the compiler, compiler settings, or a linked library that would give incorrect results.

The output should look similar to the following:

```
Test project qmcpack/build
    Start  1: unit_test_numerics
1/11 Test  #1: unit_test_numerics ..............   Passed    0.06 sec
    Start  2: unit_test_utilities
2/11 Test  #2: unit_test_utilities ..............   Passed    0.02 sec
    Start  3: unit_test_einspline
...
10/11 Test #10: unit_test_hamiltonian .............   Passed    1.88 sec
    Start 11: unit_test_drivers
11/11 Test #11: unit_test_drivers .................   Passed    0.01 sec

100% tests passed, 0 tests failed out of 11

Label Time Summary:
unit    =   2.20 sec

Total Test time (real) =   2.31 sec
```

Individual unit test executables can be found in `build/tests/bin`. The source for the unit tests is located in the `tests` directory under each directory in `src` (e.g. `src/QMCWavefunctions/tests`).

See *Unit Testing* for more details about unit tests.

3.9.2 Integration tests with Quantum ESPRESSO

As described in *Installing and patching Quantum ESPRESSO*, it is possible to test entire workflows of trial wavefunction generation, conversion, and eventual QMC calculation. A patched QE must be installed so that the pw2qmcpack converter is available.

By adding `-D QE_BIN=your_QE_binary_path` in the CMake command line when building your QMCPACK, tests named with the "qe-" prefix will be included in the test set of your build. If CMake finds pw2qmcpack.x and pw.x in the same location on the PATH, these tests will also be activated. You can test the whole `pw > pw2qmcpack > qmcpack` workflow by

```
ctest -R qe
```

This provides a very solid test of the entire QMC toolchain for plane wave–generated wavefunctions.

3.9.3 Performance tests

Performance tests representative of real research runs are included in the tests/performance directory. They can be used for benchmarking, comparing machine performance, or assessing optimizations. This is in contrast to the majority of the conventional integration tests in which the particle counts are too small to be representative. Care is still needed to remove initialization, I/O, and compute a representative performance measure.

The CTest integration is sufficient to run the benchmarks and measure relative performance from version to version of QMCPACK and to assess proposed code changes. Performance tests are prefixed with "performance." To obtain the highest performance on a particular platform, you must run the benchmarks in a standalone manner and tune thread counts, placement, walker count (etc.). This is essential to fairly compare different machines. Check with the developers if you are unsure of what is a fair change.

For the largest problem sizes, the initialization of spline orbitals might take a large portion of overall runtime. When QMCPACK is run at scale, the initialization is fast because it is fully parallelized. However, the performance tests usually run on a single node. Consider running QMCPACK once with `save_coefs="yes"` XML input tag added to the line of 'determinantset' to save the converted spline coefficients to the disk and load them for later runs in the same folder. See *3D B-splines orbitals* for more information.

The delayed update algorithm in *Single determinant wavefunctions* significantly changes the performance characteristics of QMCPACK. A parameter scan of the maximal number of delays specific to every architecture and problem size is required to achieve the best performance.

NiO performance tests

Follow the instructions in tests/performance/NiO/README to enable and run the NiO tests.

The NiO tests are for bulk supercells of varying size. The QMC runs consist of short blocks of (1) VMC without drift (2) VMC with drift term included, and (3) DMC with constant population. The tests use spline wavefunctions that must be downloaded as described in the README file because of their large size. You will need to set `-DQMC_DATA=YOUR_DATA_FOLDER` when running CMake as described in the README file.

Two sets of wavefunction are tested: spline orbitals with one- and two-body Jastrow functions and a more complex form with an additional three-body Jastrow function. The Jastrows are the same for each run and are not reoptimized, as might be done for research purposes. Runs in the hundreds of electrons up to low thousands of electrons are representative of research runs performed in 2017. The largest runs target future machines and require very large memory.

Table 3.1: System sizes and names for NiO performance tests. GPU performance tests are named similarly but have different walker counts.

Performance test name	Historical name	Atoms	Electrons	Electrons/spin
performance-NiO-cpu-a32-e384	S8	32	384	192
performance-NiO-cpu-a64-e768	S16	64	768	384
performance-NiO-cpu-a128-e1536	S32	128	1536	768
performance-NiO-cpu-a256-e3072	S64	256	3072	1536
performance-NiO-cpu-a512-e6144	S128	512	6144	3072
performance-NiO-cpu-a1024-e12288	S256	1024	12288	6144

3.9.4 Troubleshooting tests

CTest reports briefly pass or fail of tests in printout and also collects all the standard outputs to help investigating how tests fail. If the CTest execution is completed, look at `Testing/Temporary/LastTest.log`. If you manually stop the testing (ctrl+c), look at `Testing/Temporary/LastTest.log.tmp`. You can locate the failing tests by searching for the key word "Fail."

3.9.5 Slow testing with OpenMPI

OpenMPI has a default binding policy that makes all the threads run on a single core during testing when there are two or fewer MPI ranks. This significantly increases testing time. If you are authorized to change the default setting, you can just add "hwloc_base_binding_policy=none" in /etc/openmpi/openmpi-mca-params.conf.

3.10 Automated testing of QMCPACK

The QMCPACK developers run automatic tests of QMCPACK on several different computer systems, many on a continuous basis. See the reports at https://cdash.qmcpack.org/CDash/index.php?project=QMCPACK. The combinations that are currently tested can be seen on CDash and are also listed in https://github.com/QMCPACK/qmcpack/blob/develop/README.md. They include GCC, Clang, Intel, and PGI compilers in combinations with various library versions and different MPI implementations. NVIDIA GPUs are also tested.

3.11 Building ppconvert, a pseudopotential format converter

QMCPACK includes a utility—ppconvert—to convert between different pseudopotential formats. Examples include effective core potential formats (in Gaussians), the UPF format used by QE, and the XML format used by QMCPACK itself. The utility also enables the atomic orbitals to be recomputed via a numerical density functional calculation if they need to be reconstructed for use in an electronic structure calculation. Use of ppconvert is an expert feature and discouraged for casual use: a poor choice of orbitals for the creation of projectors in UPF can introduce severe errors and inaccuracies.

3.12 Installing and patching Quantum ESPRESSO

For trial wavefunctions obtained in a plane-wave basis, we mainly support QE. Note that ABINIT and QBox were supported historically and could be reactivated.

QE stores wavefunctions in a nonstandard internal "save" format. To convert these to a conventional HDF5 format file we have developed a converter—pw2qmcpack—which is an add-on to the QE distribution.

To simplify the process of patching QE we have developed a script that will automatically download and patch the source code. The patches are specific to each version. For example, to download and patch QE v6.3:

```
cd external_codes/quantum_espresso
./download_and_patch_qe6.3.sh
```

After running the patch, you must configure QE with the HDF5 capability enabled in either way:

- If your system already has HDF5 installed with Fortran, use the -{}-with-hdf5 configuration option.

```
cd qe-6.3
./configure --with-hdf5=/opt/local   # Specify HDF5 base directory
```

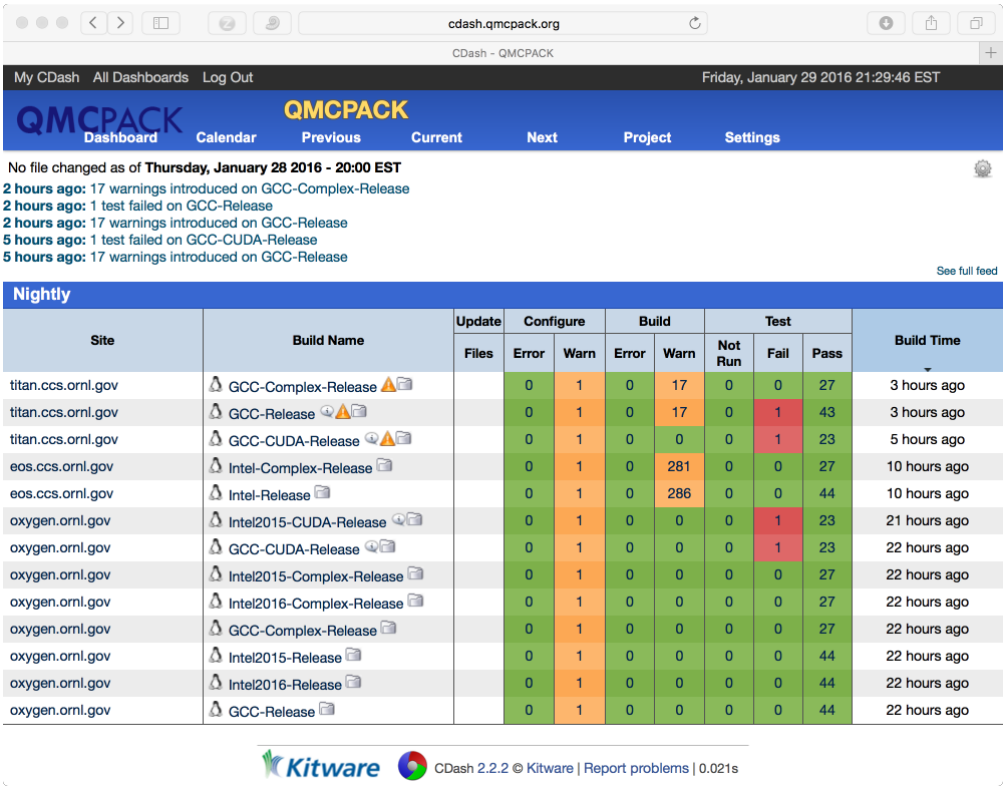

Fig. 3.1: Example test results for QMCPACK showing data for a workstation (Intel, GCC, both CPU and GPU builds) and for two ORNL supercomputers. In this example, four errors were found. This dashboard is accessible at https://cdash.qmcpack.org

Check the end of the configure output if HDF5 libraries are found properly. If not, either install a complete library or use the other scheme. If using a parallel HDF5 library, be sure to use the same MPI with QE as used to build the parallel HDF5 library.

Currently, HDF5 support in QE itself is preliminary. To enable use of pw2qmcpack but use the old non-HDF5 I/O within QE, replace `-D__HDF5` with `{-D__HDF5_C}` in make.inc.

- If your system has HDF5 with C only, manually edit make.inc by adding `-D__HDF5_C` and `-DH5_USE_16_API` in `DFLAGS` and provide include and library path in `IFLAGS` and `HDF5_LIB`.

The complete process is described in external_codes/quantum_espresso/README.

The tests involving pw.x and pw2qmcpack.x have been integrated into the test suite of QMCPACK. By adding `-D QE_BIN=your_QE_binary_path` in the CMake command line when building your QMCPACK, tests named with the "qe-" prefix will be included in the test set of your build. You can test the whole `pw > pw2qmcpack > qmcpack workflow` by

```
ctest -R qe
```

See *Integration tests with Quantum ESPRESSO* and the testing section for more details.

3.13 How to build the fastest executable version of QMCPACK

To build the fastest version of QMCPACK we recommend the following:

- Use the latest C++ compilers available for your system. Substantial gains have been made optimizing C++ in recent years.
- Use a vendor-optimized BLAS library such as Intel MKL and AMD AOCL. Although QMC does not make extensive use of linear algebra, it is used in the VMC wavefunction optimizer to apply the orbital coefficients in local basis calculations and in the Slater determinant update.
- Use a vector math library such as Intel VML. For periodic calculations, the calculation of the structure factor and Ewald potential benefit from vectorized evaluation of sin and cos. Currently we only autodetect Intel VML, as provided with MKL, but support for MASSV and AMD LibM is included via #defines. See, for example, src/Numerics/e2iphi.h. For large supercells, this optimization can gain 10% in performance.

Note that greater speedups of QMC calculations can usually be obtained by carefully choosing the required statistics for each investigation. That is, do not compute smaller error bars than necessary.

3.14 Troubleshooting the installation

Some tips to help troubleshoot installations of QMCPACK:

- First, build QMCPACK on a workstation you control or on any system with a simple and up-to-date set of development tools. You can compare the results of CMake and QMCPACK on this system with any more difficult systems you encounter.
- Use up-to-date development software, particularly a recent CMake.
- Verify that the compilers and libraries you expect are being configured. It is common to have multiple versions installed. The configure system will stop at the first version it finds, which might not be the most recent. If this occurs, directly specify the appropriate directories and files (*Configuration Options*). For example,

```
cmake -DCMAKE_C_COMPILER=/full/path/to/mpicc -DCMAKE_CXX_COMPILER=/full/path/to/
↪mpicxx ..
```

- To monitor the compiler and linker settings, use a verbose build, `make VERBOSE=1`. If an individual source file fails to compile you can experiment by hand using the output of the verbose build to reconstruct the full compilation line.

If you still have problems please post to the QMCPACK Google group with full details, or contact a developer.

CHAPTER

FOUR

RUNNING QMCPACK

QMCPACK requires at least one xml input file, and is invoked via:

```
qmcpack [command line options] <XML input file(s)>
```

4.1 Command line options

QMCPACK offers several command line options that affect how calculations are performed. If the flag is absent, then the corresponding option is disabled:

- `--dryrun` Validate the input file without performing the simulation. This is a good way to ensure that QMCPACK will do what you think it will.
- `--enable-timers=none|coarse|medium|fine` Control the timer granularity when the build option `ENABLE_TIMERS` is enabled.
- `help` Print version information as well as a list of optional command-line arguments.
- `noprint` Do not print extra information on Jastrow or pseudopotential. If this flag is not present, QMCPACK will create several `.dat` files that contain information about pseudopotentials (one file per PP) and Jastrow factors (one per Jastrow factor). These file might be useful for visual inspection of the Jastrow, for example.
- `--verbosity=low|high|debug` Control the output verbosity. The default low verbosity is concise and, for example, does not include all electron or atomic positions for large systems to reduce output size. Use "high" to see this information and more details of initialization, allocations, QMC method settings, etc.
- `version` Print version information and optional arguments. Same as `help`.

4.2 Input files

The input is one or more XML file(s), documented in *Input file overview*.

4.3 Output files

QMCPACK generates multiple files documented in *Output Overview*.

4.4 Stopping a running simulation

As detailed in *Input file overview*, QMCPACK will cleanly stop execution at the end of the current block if it finds a file named `project_id.STOP`, where `project_id` is the name of the project given in the input XML. You can also set the `max_seconds` parameter to establish an overall time limit.

4.5 Running in parallel with MPI

QMCPACK is fully parallelized with MPI. When performing an ensemble job, all the MPI ranks are first equally divided into groups that perform individual QMC calculations. Within one calculation, all the walkers are fully distributed across all the MPI ranks in the group. Since MPI requires distributed memory, there must be at least one MPI per node. To maximize the efficiency, more facts should be taken into account. When using MPI+threads on compute nodes with more than one NUMA domain (e.g., AMD Interlagos CPU on Titan or a node with multiple CPU sockets), it is recommended to place as many MPI ranks as the number of NUMA domains if the memory is sufficient (e.g., one MPI task per socket). On clusters with more than one GPU per node (NVIDIA Tesla K80), it is necessary to use the same number of MPI ranks as the number of GPUs per node to let each MPI rank take one GPU.

4.6 Using OpenMP threads

Modern processors integrate multiple identical cores even with hardware threads on a single die to increase the total performance and maintain a reasonable power draw. QMCPACK takes advantage of this compute capability by using threads and the OpenMP programming model as well as threaded linear algebra libraries. By default, QMCPACK is always built with OpenMP enabled. When launching calculations, users should instruct QMCPACK to create the right number of threads per MPI rank by specifying environment variable OMP_NUM_THREADS. Assuming one MPI rank per socket, the number of threads should typically be the number of cores on that socket. Even in the GPU-accelerated version, using threads significantly reduces the time spent on the calculations performed by the CPU.

4.6.1 Nested OpenMP threads

Nested threading is an advanced feature requiring experienced users to finely tune runtime parameters to reach the best performance.

For small-to-medium problem sizes, using one thread per walker or for multiple walkers is most efficient. This is the default in QMCPACK and achieves the shortest time to solution.

For large problems of at least 1,000 electrons, use of nested OpenMP threading can be enabled to reduce the time to solution further, although at some loss of efficiency. In this scheme multiple threads are used in the computations of each walker. This capability is implemented for some of the key computational kernels: the 3D spline orbital evaluation, certain portions of the distance tables, and implicitly the BLAS calls in the determinant update. Use of the batched nonlocal pseudopotential evaluation is also recommended.

Nested threading is enabled by setting `OMP_NUM_THREADS=AA,BB`, `OMP_MAX_ACTIVE_LEVELS=2` and `OMP_NESTED=TRUE` where the additional `BB` is the number of second-level threads. Choosing the thread affinity is critical to the performance. QMCPACK provides a tool qmc-check-affinity (source file src/QMCTools/check-

affinity.cpp for details), which might help users investigate the affinity. Knowledge of how the operating system logical CPU cores (/prco/cpuinfo) are bound to the hardware is also needed.

For example, on Blue Gene/Q with a Clang compiler, the best way to fully use the 16 cores each with 4 hardware threads is

```
OMP_NESTED=TRUE
OMP_NUM_THREADS=16,4
MAX_ACTIVE_LEVELS=2
OMP_PLACES=threads
OMP_PROC_BIND=spread,close
```

On Intel Xeon Phi KNL with an Intel compiler, to use 64 cores without using hardware threads:

```
OMP_NESTED=TRUE
OMP_WAIT_POLICY=ACTIVE
OMP_NUM_THREADS=16,4
MAX_ACTIVE_LEVELS=2
OMP_PLACES=cores
OMP_PROC_BIND=spread,close
KMP_HOT_TEAMS_MODE=1
KMP_HOT_TEAMS_MAX_LEVEL=2
```

Most multithreaded BLAS/LAPACK libraries do not spawn threads by default when being called from an OpenMP parallel region. See the explanation in *Serial or multithreaded library*. This results in the use of only a single thread in each second-level thread team for BLAS/LAPACK operations. Some vendor libraries like MKL support using multiple threads when being called from an OpenMP parallel region. One way to enable this feature is using environment variables to override the default behavior. However, this forces all the calls to the library to use the same number of threads. As a result, small function calls are penalized with heavy overhead and heavy function calls are slow for not being able to use more threads. Instead, QMCPACK uses the library APIs to turn on nested threading only at selected performance critical calls. In the case of using a serial library, QMCPACK implements nested threading to distribute the workload wherever necessary. Users do not need to control the threading behavior of the library.

4.6.2 Performance considerations

As walkers are the basic units of workload in QMC algorithms, they are loosely coupled and distributed across all the threads. For this reason, the best strategy to run QMCPACK efficiently is to feed enough walkers to the available threads.

In a VMC calculation, the code automatically raises the actual number of walkers per MPI rank to the number of available threads if the user-specified number of walkers is smaller, see "walkers/mpi=XXX" in the VMC output.

In DMC, for typical small to mid-sized calculations choose the total number of walkers to be a significant multiple of the total number of threads (MPI tasks * threads per task). This will ensure a good load balance. e.g., for a calculation on a few nodes with a total 512 threads, using 5120 walkers may keep the load imbalance around 10%. For the very largest calculations, the target number of walkers should be chosen to be slightly smaller than a multiple of the total number of available threads across all the MPI ranks. This will reduce occurrences worse-case load imbalance e.g. where one thread has two walkers while all the others have one.

To achieve better performance, a mixed-precision version (experimental) has been developed in the CPU code. The mixed-precision CPU code uses a mixed of single precision (SP) and double precision (DP) operations, while the default code use DP exclusively. This mixed precision version is more aggressive than the GPU CUDA version in using single precision (SP) operations. The Current implementation uses SP on most calculations, except for matrix inversions and reductions where double precision is required to retain high accuracy. All the constant spline data in wavefunction, pseudopotentials, and Coulomb potentials are initialized in double precision and later stored in single precision. The mixed-precision code is as accurate as the double-precision code up to a certain system size, and

may have double the throughput. Cross checking and verification of accuracy is always required but is particularly important above approximately 1,500 electrons.

4.6.3 Memory considerations

When using threads, some memory objects are shared by all the threads. Usually these memory objects are read only when the walkers are evolving, for instance the ionic distance table and wavefunction coefficients. If a wavefunction is represented by B-splines, the whole table is shared by all the threads. It usually takes a large chunk of memory when a large primitive cell was used in the simulation. Its actual size is reported as "MEMORY increase XXX MB BsplineSetReader" in the output file. See details about how to reduce it in *3D B-splines orbitals*.

The other memory objects that are distinct for each walker during random walks need to be associated with individual walkers and cannot be shared. This part of memory grows linearly as the number of walkers per MPI rank. Those objects include wavefunction values (Slater determinants) at given electronic configurations and electron-related distance tables (electron-electron distance table). Those matrices dominate the N^2 scaling of the memory usage per walker.

4.7 Running on GPU machines

The GPU version is fully incorporated into the main source code.

QMCPACK supports running on multi-GPU node architectures via MPI. Each MPI rank gets assigned a primary GPU based on the list of GPUs visible to it and its rank id in the smallest MPI communicator, usually the node local communicator, enclosing that list of GPUs. When there are more GPUs than the MPI ranks, excessive GPUs will be left idle. Please avoid this scenario in production runs. When there are more MPI ranks than GPUs, the primary GPU will be assigned in the following way. Performance portable implementation assigns GPUs to equal amount of blocks of MPI ranks. MPI ranks within a block are assigned the same GPU as their primary GPU. Legacy implementation assigns GPUs to MPI ranks in a round-robin order. It is guaranteed that MPI ranks are distributed among GPUs as evenly as possbile. Currently, for medium to large runs, 1 MPI task should be used per GPU per node. For very smaller system sizes, use of multiple MPI tasks per GPU might yield improved performance.

4.7.1 Performance portable implementation

Works on any GPUs with OpenMP offload support including NVIDIA, AMD and Intel GPUs. Using batched drivers is required.

4.7.2 Legacy implementation

Works on NVIDIA and AMD GPUs. Commonly used functionalities for solid-state and molecular systems using B-spline single-particle orbitals are supported. Use of Gaussian basis sets, three-body Jastrow functions, and many observables are not yet supported. A detailed description of the GPU implementation can be found in [[EKCS12]].

Vectorization is achieved over walkers, that is, all walkers are propagated in parallel. In each GPU kernel, loops over electrons, atomic cores, or orbitals are further vectorized to exploit an additional level of parallelism and to allow coalesced memory access.

4.7.3 Performance considerations

To run with high performance on GPUs it is crucial to perform some benchmarking runs: the optimum configuration is system size, walker count, and GPU model dependent. The GPU implementation vectorizes operations over multiple walkers, so generally the more walkers that are placed on a GPU, the higher the performance that will be obtained. Performance also increases with electron count, up until the memory on the GPU is exhausted. A good strategy is to perform a short series of VMC runs with walker count increasing in multiples of two. For systems with 100s of electrons, typically 128–256 walkers per GPU use a sufficient number of GPU threads to operate the GPU efficiently and to hide memory-access latency. For smaller systems, thousands of walkers might be required. For QMC algorithms where the number of walkers is fixed such as VMC, choosing a walker count the is a multiple of the number of streaming multiprocessors can be most efficient. For variable population DMC runs, this exact match is not possible.

To achieve better performance, the current GPU implementation uses single-precision operations for most of the calculations. Double precision is used in matrix inversions and the Coulomb interaction to retain high accuracy. The mixed-precision GPU code is as accurate as the double-precision CPU code up to a certain system size. Cross checking and verification of accuracy are encouraged for systems with more than approximately 1,500 electrons. For typical calculations on smaller electron counts, the statistical error bars are much larger then the error introduced by mixed precision.

4.7.4 Memory considerations

In the GPU implementation, each walker has a buffer in the GPU's global memory to store temporary data associated with the wavefunctions. Therefore, the amount of memory available on a GPU limits the number of walkers and eventually the system size that it can process. Additionally, for calculations using B-splines, this data is stored on the GPU in a shared read-only buffer. Often the size of the B-spline data limits the calculations that can be run on the GPU.

If the GPU memory is exhausted, first try reducing the number of walkers per GPU. Coarsening the grids of the B-splines representation (by decreasing the value of the mesh factor in the input file) can also lower the memory usage, at the expense (risk) of obtaining inaccurate results. Proceed with caution if this option has to be considered. It is also possible to distribute the B-spline coefficients table between the host and GPU memory, see option Spline_Size_Limit_MB in *3D B-splines orbitals*.

CHAPTER

FIVE

UNITS USED IN QMCPACK

Internally, QMCPACK uses atomic units throughout. Unless stated, all inputs and outputs are also in atomic units. For convenience the analysis tools offer conversions to eV, Ry, Angstrom, Bohr, etc.

CHAPTER

SIX

INPUT FILE OVERVIEW

This chapter introduces XML as it is used in the QMCPACK input file. The focus is on the XML file format itself and the general structure of the input file rather than an exhaustive discussion of all keywords and structure elements.

QMCPACK uses XML to represent structured data in its input file. Instead of text blocks like

```
begin project
  id     = vmc
  series = 0
end project

begin vmc
  move     = pbyp
  blocks   = 200
  steps    =  10
  timestep = 0.4
end vmc
```

QMCPACK input looks like

```
<project id="vmc" series="0">
</project>

<qmc method="vmc" move="pbyp">
   <parameter name="blocks"  >  200 </parameter>
   <parameter name="steps"   >   10 </parameter>
   <parameter name="timestep">  0.4 </parameter>
</qmc>
```

XML elements start with `<element_name>`, end with `</element_name>}`, and can be nested within each other to denote substructure (the trial wavefunction is composed of a Slater determinant and a Jastrow factor, which are each further composed of ...). `id` and `series` are attributes of the `<project/>` element. XML attributes are generally used to represent simple values, like names, integers, or real values. Similar functionality is also commonly provided by `<parameter/>` elements like those previously shown.

The overall structure of the input file reflects different aspects of the QMC simulation: the simulation cell, particles, trial wavefunction, Hamiltonian, and QMC run parameters. A condensed version of the actual input file is shown as follows:

```
<?xml version="1.0"?>
<simulation>

<project id="vmc" series="0">
  ...
</project>
```

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```
<qmcsystem>

  <simulationcell>
    ...
  </simulationcell>

  <particleset name="e">
    ...
  </particleset>

  <particleset name="ion0">
    ...
  </particleset>

  <wavefunction name="psi0" ... >
    ...
    <determinantset>
      <slaterdeterminant>
        ..
      </slaterdeterminant>
    </determinantset>
    <jastrow type="One-Body" ... >
       ...
    </jastrow>
    <jastrow type="Two-Body" ... >
      ...
    </jastrow>
  </wavefunction>

  <hamiltonian name="h0" ... >
    <pairpot type="coulomb" name="ElecElec" ... />
    <pairpot type="coulomb" name="IonIon"   ... />
    <pairpot type="pseudo" name="PseudoPot" ... >
      ...
    </pairpot>
  </hamiltonian>

 </qmcsystem>

 <qmc method="vmc" move="pbyp">
   <parameter name="warmupSteps">   20 </parameter>
   <parameter name="blocks"     >  200 </parameter>
   <parameter name="steps"      >   10 </parameter>
   <parameter name="timestep"   >  0.4 </parameter>
 </qmc>

</simulation>
```

The omitted portions `...` are more fine-grained inputs such as the axes of the simulation cell, the number of up and down electrons, positions of atomic species, external orbital files, starting Jastrow parameters, and external pseudopotential files.

6.1 Project

The <project> tag uses the id and series attributes. The value of id is the first part of the prefix for output file names.

Output file names also contain the series number, starting at the value given by the series tag. After every <qmc> section, the series value will increment, giving each section a unique prefix.

For the input file shown previously, the output files will start with vmc.s000, for example, vmc.s000.scalar.dat. If there were another <qmc> section in the input file, the corresponding output files would use the prefix vmc.s001.

<project> tag accepts additional control parameters <parameters/>. Batched drivers check against max_seconds and make efforts to stop the execution cleanly at the end of a block before reaching the maximum time. Classic drivers can also take the now-deprecated maxcpusecs parameter for the same effect in the per driver XML section.

In addition, a file named id plus .STOP, in this case vmc.STOP, stops QMCPACK execution on the fly cleanly once being found in the working directory.

6.2 Random number initialization

The random number generator state is initialized from the random element using the seed attribute:

```
<random seed="1000"/>
```

If the random element is not present, or the seed value is negative, the seed will be generated from the current time.

To initialize the many independent random number generators (one per thread and MPI process), the seed value is used (modulo 1024) as a starting index into a list of prime numbers. Entries in this offset list of prime numbers are then used as the seed for the random generator on each thread and process.

If checkpointing is enabled, the random number state is written to an HDF file at the end of each block (suffix: .random.h5). This file will be read if the mcwalkerset tag is present to perform a restart. For more information, see the checkpoint element in the QMC methods *Quantum Monte Carlo Methods* and *Checkpoint and restart files* on checkpoint and restart files.

CHAPTER

SEVEN

SPECIFYING THE SYSTEM TO BE SIMULATED

7.1 Specifying the Simulation Cell

The `simulationcell` block specifies the geometry of the cell, how the boundary conditions should be handled, and how ewald summation should be broken up.

`simulationcell` Element:

Parent elements:	`qmcsystem`
Child elements:	None

Attribute:

parameter name	datatype	values	default	description
`lattice`	9 floats	any float	Must be specified	Specification of lattice vectors.
`bconds`	string	"p" or "n"	"n n n "	Boundary conditions for each axis.
`vacuum`	float	≥ 1.0	1.0	Vacuum scale.
`LR_dim_cutoff`	float	float	15	Ewald breakup distance.
`LR_tol`	float	float	3e-4	Tolerance in Ha for Ewald ion-ion energy per atom.

An example of a block is given below:

```
<simulationcell>
    <parameter name="lattice">
      3.8       0.0       0.0
      0.0       3.8       0.0
      0.0       0.0       3.8
    </parameter>
    <parameter name="bconds">
       p p p
    </parameter>
    <parameter name="LR_dim_cutoff"> 20 </parameter>
  </simulationcell>
```

Here, a cubic cell 3.8 bohr on a side will be used. This simulation will use periodic boundary conditions, and the maximum k vector will be $20/r_{wigner-seitz}$ of the cell.

7.1.1 Lattice

The cell is specified using 3 lattice vectors.

7.1.2 Boundary conditions

QMCPACK offers the capability to use a mixture of open and periodic boundary conditions. The parameter expects a single string of three characters separated by spaces, *e.g.* "p p p" for purely periodic boundary conditions. These characters control the behavior of the x, y, and z, axes, respectively. Non periodic directions must be placed after the periodic ones. Examples of valid include:

"p p p" Periodic boundary conditions. Corresponds to a 3D crystal.

"p p n" Slab geometry. Corresponds to a 2D crystal.

"p n n" Wire geometry. Corresponds to a 1D crystal.

"n n n" Open boundary conditions. Corresponds to an isolated molecule in a vacuum.

7.1.3 Vacuum

The vacuum option allows adding a vacuum region in slab or wire boundary conditions (`bconds= p p n` or `bconds= p n n`, respectively). The main use is to save memory with spline or plane-wave basis trial wavefunctions, because no basis functions are required inside the vacuum region. For example, a large vacuum region can be added above and below a graphene sheet without having to generate the trial wavefunction in such a large box or to have as many splines as would otherwise be required. Note that the trial wavefunction must still be generated in a large enough box to sufficiently reduce periodic interactions in the underlying electronic structure calculation.

With the vacuum option, the box used for Ewald summation increases along the axis labeled by a factor of `vacuum`. Note that all the particles remain in the original box without altering their positions. i.e. Bond lengths are not changed by this option. The default value is 1, no change to the specified axes.

An example of a `simulationcell` block using is given below. The size of the box along the z-axis increases from 12 to 18 by the vacuum scale of 1.5.

```
<simulationcell>
    <parameter name="lattice">
      3.8       0.0       0.0
      0.0       3.8       0.0
      0.0       0.0      12.0
    </parameter>
    <parameter name="bconds">
       p p n
    </parameter>
    <parameter name="vacuum"> 1.5 </parameter>
    <parameter name="LR_dim_cutoff"> 20 </parameter>
  </simulationcell>
```

7.1.4 LR_dim_cutoff

When using periodic boundary conditions direct calculation of the Coulomb energy is not well behaved. As a result, QMCPACK uses an optimized Ewald summation technique to compute the Coulomb interaction. [[NC95]]

In the Ewald summation, the energy is broken into short- and long-ranged terms. The short-ranged term is computed directly in real space, while the long-ranged term is computed in reciprocal space. controls where the short-ranged term ends and the long-ranged term begins. The real-space cutoff, reciprocal-space cutoff, and are related via:

$$\text{LR\_dim\_cutoff} = r_c \times k_c$$

where r_c is the Wigner-Seitz radius, and k_c is the length of the maximum k-vector used in the long-ranged term. Larger values of increase the accuracy of the evaluation. A value of 15 tends to be conservative.

7.2 Specifying the particle set

The `particleset` blocks specify the particles in the QMC simulations: their types, attributes (mass, charge, valence), and positions.

7.2.1 Input specification

`particleset` element:

Parent elements	`simulation`
Child elements	`group`, `attrib`

Attribute:

Name	Datatype	Values	Default	Description
`name/id`	Text	*Any*	e	Name of particle set
`size`^{o}	Integer	*Any*	0	Number of particles in set
`random`^{o}	Text	Yes/no	No	Randomize starting positions
`randomsrc/randomsrc`^{o}	Text	`particleset.name`	*None*	Particle set to randomize
`spinor`^{o}	Text	Yes/no	No	particleset treated as spinor

7.2.2 Detailed attribute description

Required particleset attributes

- `name/id`
  Unique name for the particle set. Default is “e” for electrons. “i” or “ion0” is typically used for ions. For special cases where an empty particle set is needed, the special name “empty” can be used to bypass the zero-size error check.

Optional particleset attributes

- `size`
  Number of particles in set.

`Group` element:

Parent elements	`particleset`
Child elements	`parameter`, `attrib`

Attribute:

Name	Datatype	Values	Default	Description
`name`	Text	*Any*	e	Name of particle set
`size`^{o}	Integer	*Any*	0	Number of particles in set
`mass`^{o}	Real	*Any*	1	Mass of particles in set
`unit`^{o}	Text	au/amu	au	Units for mass of particles

Parameters:

Name	Datatype	Values	Default	Description
`charge`	Real	*Any*	0	Charge of particles in set
`valence`	Real	*Any*	0	Valence charge of particles in set
`atomicnumber`	Integer	*Any*	0	Atomic number of particles in set

`attrib` element:

Parent elements	`particleset`, `group`

Attribute:

Name	**Datatype**	**Values**	**Default**	**Description**
`name`	String	*Any*	*None*	Name of attrib
`datatype`	String	IntArray, realArray, posArray, stringArray	*None*	Type of data in attrib
`size`^{o}	String	*Any*	*None*	Size of data in attrib

- `random`
  Randomize starting positions of particles. Each component of each particle's position is randomized independently in the range of the simulation cell in that component's direction.
- `randomsrc`/`random_source`
  Specify source particle set around which to randomize the initial positions of this particle set.
- `spinor`
  Sets an internal flag that the particleset (usually for electrons) is a spinor object. This is used in the wavefunction builders and QMC drivers to determiane if spin sampling will be used

Required name attributes

- `name/id`
  Unique name for the particle set group. Typically, element symbols are used for ions and "u" or "d" for spin-up and spin-down electron groups, respectively.

Optional group attributes

- `mass`
  Mass of particles in set.
- `unit`
  Units for mass of particles in set (au[m_e = 1] or amu[$\frac{1}{12}m_{^{12}\mathrm{C}}$ = 1]).

7.2.3 Example use cases

Particleset elements for ions and electrons randomizing electron start positions.

```
<particleset name="i" size="2">
  <group name="Li">
    <parameter name="charge">3.000000</parameter>
    <parameter name="valence">3.000000</parameter>
    <parameter name="atomicnumber">3.000000</parameter>
  </group>
  <group name="H">
    <parameter name="charge">1.000000</parameter>
    <parameter name="valence">1.000000</parameter>
    <parameter name="atomicnumber">1.000000</parameter>
  </group>
  <attrib name="position" datatype="posArray" condition="1">
  0.0   0.0   0.0
  0.5   0.5   0.5
  </attrib>
  <attrib name="ionid" datatype="stringArray">
     Li H
  </attrib>
</particleset>
<particleset name="e" random="yes" randomsrc="i">
  <group name="u" size="2">
    <parameter name="charge">-1</parameter>
  </group>
  <group name="d" size="2">
    <parameter name="charge">-1</parameter>
  </group>
</particleset>
```

Particleset elements for ions and electrons specifying electron start positions.

```
<particleset name="e">
  <group name="u" size="4">
    <parameter name="charge">-1</parameter>
    <attrib name="position" datatype="posArray">
  2.9151687332e-01 -6.5123272502e-01 -1.2188463918e-01
  5.8423636048e-01  4.2730406357e-01 -4.5964306231e-03
  3.5228575807e-01 -3.5027014639e-01  5.2644808295e-01
```

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```
     -5.1686250912e-01 -1.6648002292e+00  6.5837023441e-01
    </attrib>
  </group>
  <group name="d" size="4">
    <parameter name="charge">-1</parameter>
    <attrib name="position" datatype="posArray">
  3.1443445436e-01  6.5068682609e-01 -4.0983449009e-02
     -3.8686061749e-01 -9.3744432997e-02 -6.0456005388e-01
  2.4978241724e-02 -3.2862514649e-02 -7.2266047173e-01
     -4.0352404772e-01  1.1927734805e+00  5.5610824921e-01
    </attrib>
  </group>
</particleset>
<particleset name="ion0" size="3">
  <group name="O">
    <parameter name="charge">6</parameter>
    <parameter name="valence">4</parameter>
    <parameter name="atomicnumber">8</parameter>
  </group>
  <group name="H">
    <parameter name="charge">1</parameter>
    <parameter name="valence">1</parameter>
    <parameter name="atomicnumber">1</parameter>
  </group>
  <attrib name="position" datatype="posArray">
    0.0000000000e+00  0.0000000000e+00  0.0000000000e+00
    0.0000000000e+00 -1.4308249289e+00  1.1078707576e+00
    0.0000000000e+00  1.4308249289e+00  1.1078707576e+00
  </attrib>
  <attrib name="ionid" datatype="stringArray">
    O H H
  </attrib>
</particleset>
```

Particleset elements for ions specifying positions by ion type.

```
<particleset name="ion0">
  <group name="O" size="1">
    <parameter name="charge">6</parameter>
    <parameter name="valence">4</parameter>
    <parameter name="atomicnumber">8</parameter>
    <attrib name="position" datatype="posArray">
      0.0000000000e+00  0.0000000000e+00  0.0000000000e+00
    </attrib>
  </group>
  <group name="H" size="2">
    <parameter name="charge">1</parameter>
    <parameter name="valence">1</parameter>
    <parameter name="atomicnumber">1</parameter>
    <attrib name="position" datatype="posArray">
      0.0000000000e+00 -1.4308249289e+00  1.1078707576e+00
      0.0000000000e+00  1.4308249289e+00  1.1078707576e+00
    </attrib>
  </group>
</particleset>
```

CHAPTER

EIGHT

TRIAL WAVEFUNCTION SPECIFICATION

8.1 Introduction

This section describes the input blocks associated with the specification of the trial wavefunction in a QMCPACK calculation. These sections are contained within the `<wavefunction>` ... `</wavefunction>` xml blocks. **Users are expected to rely on converters to generate the input blocks described in this section.** The converters and the workflows are designed such that input blocks require minimum modifications from users. Unless the workflow requires modification of wavefunction blocks (e.g., setting the cutoff in a multideterminant calculation), only expert users should directly alter them.

The trial wavefunction in QMCPACK has a general product form:

$$\Psi_T(\vec{r}) = \prod_k \Theta_k(\vec{r}), \tag{8.1}$$

where each $\Theta_k(\vec{r})$ is a function of the electron coordinates (and possibly ionic coordinates and variational parameters). For problems involving electrons, the overall trial wavefunction must be antisymmetric with respect to electron exchange, so at least one of the functions in the product must be antisymmetric. Notice that, although QMCPACK allows for the construction of arbitrary trial wavefunctions based on the functions implemented in the code (e.g., slater determinants, jastrow functions), the user must make sure that a correct wavefunction is used for the problem at hand. From here on, we assume a standard trial wavefunction for an electronic structure problem

$$Psi_T(\vec{r}) = A(\vec{r}) \prod_k J_k(\vec{r}), \tag{8.2}$$

where $A(\vec{r})$ is one of the antisymmetric functions: (1) slater determinant, (2) multislater determinant, or (3) pfaffian and J_k is any of the Jastrow functions (described in *Jastrow Factors*). The antisymmetric functions are built from a set of single particle orbitals (SPO) `(sposet)`. QMCPACK implements four different types of `sposet`, described in the following section. Each `sposet` is designed for a different type of calculation, so their definition and generation varies accordingly.

Listing 8.1: wavefunction XML element skeleton.

```
<wavefunction>
  <sposet_collection ...>
    <sposet ...>
      ...
    </sposet>
  </sposet_collection>
  <determinantset>
    <slaterdeterminant ...>
      ...
    </slaterdeterminant>
```

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```
    <backflow>
      ...
    </backflow>
  </determinantset>
  <jastrow ...>
  </jastrow>
</wavefunction>
```

8.2 Single-particle orbitals

A single particle orbital set (SPOSet) is a set of orbitals evaluated at a single electron real-space position. A typical Slater determinant is calculated from a N-by-N matrix constructed from N orbitals at the positions of N electrons. QMCPACK supports a range of SPOSet types:

- *3D B-splines orbitals*
- *Linear combination of atomic orbitals (LCAO) with Gaussian and/or Slater-type basis sets*
- *Hybrid orbital representation*
- *Plane-wave basis sets*

8.2.1 sposet_collection input style

Listing 8.2: SPO XML element framework.

```
<!-- build a sposet collection of type bspline. /-->
<sposet_collection type="bspline" ...>
  <sposet name="spo-up" ... /sposet>
  ...
</sposet_collection>
```

The `sposet_collection` element forms the container for `sposet` and a few other tags. The contents and attributes in a `sposet_collection` node and `sposet` node depend on the `type` being used. The `name` of each `sposet` must be unique. It is used for look-up by *Single determinant wavefunctions* and *Multideterminant wavefunctions*.

`sposet_collection` element:

Parent elements	`wavefunction`
Child elements	`sposet`

attribute:

Name	Datatype	Values	Default	Description
`type`	Text	See below	'' ''	Type of `sposet`

`type` Type of `sposet`. Accepted values are 'spline' ('bspline' or 'einspline'), 'MolecularOrbital', 'pw', 'heg', 'composite'.

If QMCPACK printout contains *!!!!!!! Deprecated input style: creating SPO set inside determinantset. Support for this usage will soon be removed. SPO sets should be built outside.*, users need to update the input XML by moving

all the SPOSet construction related details out of `determinantset`. This revised specification keeps the basis set details separate from information about the determinants.

Listing 8.3: Deprecated input style.

```
<determinantset type="einspline" href="pwscf.pwscf.h5" tilematrix="2 0 0 0 1 0 0 0 1"␣
↪source="ion0" meshfactor="1.0" precision="double">
   <slaterdeterminant>
      <determinant id="updet" size="8">
         <occupation mode="ground" spindataset="0"/>
      </determinant>
      <determinant id="downdet" size="8">
         <occupation mode="ground" spindataset="0"/>
      </determinant>
   </slaterdeterminant>
</determinantset>
```

After updating the input style.

Listing 8.4: Updated input style.

```
<!-- all the attributes are moved from determinantset.-->
<sposet_collection type="einspline" href="pwscf.pwscf.h5" tilematrix="2 0 0 0 1 0 0 0␣
↪1" source="ion0" meshfactor="1.0" precision="double">
  <!-- all the attributes and contents are moved from determinant.  Change 'id' tag␣
↪to 'name' tag.
       Need only one sposet for unpolarized calculation.-->
  <sposet name="spo-ud" size="8">
     <occupation mode="ground" spindataset="0"/>
  </sposet>
</sposet_collection>
<determinantset>
   <slaterdeterminant>
      <!-- build two determinants from the same sposet named 'spo-ud'. One for each␣
↪spin.-->
      <determinant sposet="spo-ud"/>
      <determinant sposet="spo-ud"/>
   </slaterdeterminant>
</determinantset>
```

In the case of multi-determinants, all the attributes of `determinantset` need to be moved to `sposet_collection` and existing `sposet` xml nodes need to be moved under `sposet_collection`. If there is a `basisset` node, it needs to be moved under `sposet_collection` as well.

8.2.2 3D B-splines orbitals

In this section we describe the use of spline basis sets to expand the `sposet`. Spline basis sets are designed to work seamlessly with plane wave DFT codes (e.g.,Quantum ESPRESSO as a trial wavefunction generator). Codes that utilize regular real space grids as a basis can also be seamlessly interfaced.

In QMC algorithms, all the SPOs $\{\phi(\vec{r})\}$ need to be updated every time a single electron moves. Evaluating SPOs takes a very large portion of computation time. In principle, PW basis set can be used to express SPOs directly in QMC, as in DFT. But it introduces an unfavorable scaling because the basis set size increases linearly as the system size. For this reason, it is efficient to use a localized basis with compact support and a good transferability from the plane wave basis.

In particular, 3D tricubic B-splines provide a basis in which only 64 elements are nonzero at any given point in

[[AlfeG04]]. The 1D cubic B-spline is given by

$$f(x) = \sum_{i'=i-1}^{i+2} b^{i',3}(x)\ p_{i'}, \tag{8.3}$$

where $b^i(x)$ is the piecewise cubic polynomial basis functions and $i = \text{floor}(\Delta^{-1}x)$ is the index of the first grid point $\leq x$. Constructing a tensor product in each Cartesian direction, we can represent a 3D orbital as

$$\phi_n(x,y,z) = \sum_{i'=i-1}^{i+2} b_x^{i',3}(x) \sum_{j'=j-1}^{j+2} b_y^{j',3}(y) \sum_{k'=k-1}^{k+2} b_z^{k',3}(z)\ p_{i',j',k',n}. \tag{8.4}$$

This allows the rapid evaluation of each orbital in constant time unlike with a plane wave basis set where the cost increases with system size. Furthermore, this basis is systematically improvable with a single spacing parameter so that accuracy is not compromised compared with the plane wave basis.

The use of 3D tricubic B-splines greatly improves computational efficiency. The gain in computation time compared to an equivalent plane wave basis set becomes increasingly large as the system size grows. On the downside, this computational efficiency comes at the expense of increased memory use, which is easily overcome, however, by the large aggregate memory available per node through OpenMP/MPI hybrid QMC.

The input xml block for the spline SPOs is given in *Spline SPO XML element*. A list of options is given in Table 8.2.2.

Listing 8.5: Spline SPO XML element

```
<sposet_collection type="bspline" source="i" href="pwscf.h5"
                tilematrix="1 1 3 1 2 -1 -2 1 0" gpu="yes" meshfactor="0.8"
                twist="0  0  0" precision="double">
  <sposet name="spo-up" size="208">
    <occupation mode="ground" spindataset="0"/>
  </sposet>
  <!-- spin polarized case needs two sposets /-->
  <sposet name="spo-dn" size="208">
    <occupation mode="ground" spindataset="1"/>
  </sposet>
</sposet_collection>
```

`sposet_collection` element:

Parent elements	`wavefunction`
Child elements	`sposet`

attribute:

Name	Datatype	Values	Default	Description
type	Text	Bspline		Type of sposet
href	Text			Path to hdf5 file from pw2qmcpack.x.
tilematrix	9 integers			Tiling matrix used to expand supercell.
twistnum	Integer			Index of the super twist.
twist	3 floats			Super twist.
meshfactor	Float	≤ 1.0		Grid spacing ratio.
precision	Text	Single/double		Precision of spline coefficients
gpu	Text	Yes/no		GPU switch.
gpusharing	Text	Yes/no	No	Share B-spline table across GPUs.
Spline_Size_Limit_MB	Integer			Limit B-spline table size on GPU.
check_orb_norm	Text	Yes/no	Yes	Check norms of orbitals from h5 file.
save_coefs	Text	Yes/no	No	Save the spline coefficients to h5 file.
source	Text	Any	Ion0	Particle set with atomic positions.
skip_checks	Text	Yes/no	No	skips checks for ion information in h5

Table 3 Options for the sposet_collection xml-block associated with B-spline single particle orbital sets.

Additional information:

- **precision** Only effective on CPU versions without mixed precision, "single" is always imposed with mixed precision. Using single precision not only saves memory use but also speeds up the B-spline evaluation. We recommend using single precision since we saw little chance of really compromising the accuracy of calculation.
- **meshfactor** The ratio of actual grid spacing of B-splines used in QMC calculation with respect to the original one calculated from h5. A smaller meshfactor saves memory use but reduces accuracy. The effects are similar to reducing plane wave cutoff in DFT calculations. Use with caution!
- **twistnum** We recommend not using it in the input because the ordering of orbitals depends on how they are being stored in the h5 file. twistnum gets ignored if twist exists in the input. If positive, it is the index. If negative, the super twist is referred by twist. This input parameter is kept only for keeping old input files working.
- **twist** The twist angle. If neither twist nor twistnum is provided, Take Gamma point, (0, 0, 0).
- **save_coefs** If yes, dump the real-space B-spline coefficient table into an h5 file on the disk. When the orbital transformation from k space to B-spline requires more than the available amount of scratch memory on the compute nodes, users can perform this step on fat nodes and transfer back the h5 file for QMC calculations.
- **gpusharing** If enabled, spline data is shared across multiple GPUs on a given computational node. For example, on a two-GPU-per-node system, each GPU would have half of the orbitals. This enables larger overall spline tables than would normally fit in the memory of individual GPUs to be used, potentially up to the total GPU memory on a node. To obtain high performance, large electron counts or a high-performing CPU-GPU interconnect is required. To use this feature, the following needs to be done:
  - The CUDA Multi-Process Service (MPS) needs to be used (e.g., on Summit use "-alloc_flags gpumps" for bsub). If MPS is not detected, sharing will be disabled.
  - CUDA_VISIBLE_DEVICES needs to be properly set to control each rank's visible CUDA devices (e.g., on OLCF Summit one needs to create a resource set containing all GPUs with the respective number of ranks with "jsrun –task-per-rs Ngpus -g Ngpus").
- **Spline_Size_Limit_MB** Allows distribution of the B-spline coefficient table between the host and GPU memory. The compute kernels access host memory via zero-copy. Although the performance penalty introduced by it is significant, it allows large calculations to go through.

- **skip_checks** When converting the wave function from convertpw4qmc instead of pw2qmcpack, there is missing ionic information. This flag bypasses the requirement that the ionic information in the eshdf.h5 file match the input xml.

8.2.3 Linear combination of atomic orbitals (LCAO) with Gaussian and/or Slater-type basis sets

In this section we describe the use of localized basis sets to expand the `sposet`. The general form of a single particle orbital in this case is given by:

$$\phi_i(\vec{r}) = \sum_k C_{i,k}\, \eta_k(\vec{r}), \tag{8.5}$$

where $\{\eta_k(\vec{r})\}$ is a set of M atom-centered basis functions and $C_{i,k}$ is a coefficient matrix. This should be used in calculations of finite systems employing an atom-centered basis set and is typically generated by the *convert4qmc* converter. Examples include calculations of molecules using Gaussian basis sets or Slater-type basis functions. Initial support for periodic systems is described in *Periodic LCAO for Solids*. Even though this section is called "Gaussian basis sets" (by far the most common atom-centered basis set), QMCPACK works with any atom-centered basis set based on either spherical harmonic angular functions or Cartesian angular expansions. The radial functions in the basis set can be expanded in either Gaussian functions, Slater-type functions, or numerical radial functions.

In this section we describe the input sections of `sposet_collection` for the atom-centered basis set. Here is an *example* of single determinant with LCAO. The input sections for multideterminant trial wavefunctions are described in *Multideterminant wavefunctions*.

Listing 8.6: `slaterdeterminant` with an LCAO `sposet_collection` example

```
<sposet_collection type="MolecularOrbital" source="ion0" cuspCorrection="no">
  <basisset name="LCAOBSet">
    <atomicBasisSet name="Gaussian-G2" angular="cartesian" elementType="H" normalized=
↪"no">
      <grid type="log" ri="1.e-6" rf="1.e2" npts="1001"/>
      <basisGroup rid="H00" n="0" l="0" type="Gaussian">
        <radfunc exponent="5.134400000000e-02" contraction="1.399098787100e-02"/>
      </basisGroup>
    </atomicBasisSet>
  </basisset>
  <sposet name="spo" basisset="LCAOBSet" size="1">
    <occupation mode="ground"/>
    <coefficient size="1" id="updetC">
      1.00000000000000e+00
    </coefficient>
  </sposet>
</sposet_collection>
<determinantset>
   <slaterdeterminant>
      <determinant sposet="spo" />
   </slaterdeterminant>
</determinantset>
```

Here is the *basic structure* for LCAO `sposet_collection` input block. A list of options for `sposet_collection` is given in Table 8.2.3.

Listing 8.7: Basic input block for `sposet_collection` for LCAO.

```
<sposet_collection type="MolecularOrbital" ...>
  <basisset name="LCAOBSet" ...>
    ...
  </basisset>
  <sposet name="spo" basisset="LCAOBSet" size="1">
    <occupation mode="ground"/>
    <coefficient size="1" id="updetC">
      1.00000000000000e+00
    </coefficient>
  </sposet>
</sposet_collection>
```

The definition of the set of atom-centered basis functions is given by the `basisset` block and the `sposet` defined within `sposet_collection`. The `basisset` input block is composed from a collection of `atomicBasisSet` input blocks, one for each atomic species in the simulation where basis functions are centered. The general structure for `basisset` and `atomicBasisSet` are given in *Listing 4*, and the corresponding lists of options are given in Table 8.2.3 and Table 8.2.3.

`sposet_collection` element:

Parent elements	`wavefunction`
Child elements	`basisset` , `sposet`

Attribute:

Name	Datatype	Values	Default	Description
`name/id`	Text	*Any*	" "	Name of determinant set
`type`	Text	See below	" "	Type of `sposet`
`keyword`	Text	NMO, GTO, STO	NMO	Type of orbital set generated
`transform`	Text	Yes/no	Yes	Transform to numerical radial functions?
`source`	Text	*Any*	Ion0	Particle set with the position of atom centers
`cuspCorrection`	Text	Yes/no	No	Apply cusp correction scheme to `sposet`?

Table 4 Options for the `sposet_collection` xml-block associated with atom-centered single particle orbital sets.

- **type** Type of `sposet`. For atom-centered based `sposets`, use type="MolecularOrbital" or type="MO".
- **keyword/key** Type of basis set generated, which does not necessarily match the type of basis set on the input block. The three possible options are: NMO (numerical molecular orbitals), GTO (Gaussian-type orbitals), and STO (Slater-type orbitals). The default option is NMO. By default, QMCPACK will generate numerical orbitals from both GTO and STO types and use cubic or quintic spline interpolation to evaluate the radial functions. This is typically more efficient than evaluating the radial functions in the native basis (Gaussians or exponents) and allows for arbitrarily large contractions without any additional cost. To force use of the native expansion (not recommended), use GTO or STO for each type of input basis set.
- **transform** Request (or avoid) a transformation of the radial functions to NMO type. The default and recommended behavior is to transform to numerical radial functions. If `transform` is set to *yes*, the option `keyword` is ignored.
- **cuspCorrection** Enable (disable) use of the cusp correction algorithm (CASINO REFERENCE) for a `basisset` built with GTO functions. The algorithm is implemented as described in (CASINO REFERENCE) and works only with transform="yes" and an input GTO basis set. No further input is needed.

Listing 8.8: Basic input block for `basisset`.

```
<basisset name="LCAOBSet">
  <atomicBasisSet name="Gaussian-G2" angular="cartesian" elementType="C" normalized=
↪"no">
    <grid type="log" ri="1.e-6" rf="1.e2" npts="1001"/>
    <basisGroup rid="C00" n="0" l="0" type="Gaussian">
      <radfunc exponent="5.134400000000e-02" contraction="1.399098787100e-02"/>
      ...
    </basisGroup>
    ...
  </atomicBasisSet>
  <atomicBasisSet name="Gaussian-G2" angular="cartesian" type="Gaussian" elementType=
↪"C" normalized="no">
    ...
  </atomicBasisSet>
  ...
</basisset>
```

`basisset` element:

Parent elements	`sposet_collection`
Child elements	`atomicBasisSet`

Attribute:

Name	Datatype	Values	Default	Description
`name` / `id`	Text	*Any*	” “	Name of atom-centered basis set

Table 5 Options for the `basisset` xml-block associated with atom-centered single particle orbital sets.

`AtomicBasisSet` element:

Parent elements	`basisset`
Child elements	`grid`, `basisGroup`

Attribute:

Name	Datatype	Values	Default	Description
`name` / `id`	Text	*Any*	” “	Name of atomic basis set
`angular`	Text	See below	Default	Type of angular functions
`expandYlm`	Text	See below	Yes	Expand Ylm shells?
`expM`	Text	See below	Yes	Add sign for $(-1)^m$?
`elementType`/ `species`	Text	*Any*	e	Atomic species where functions are centered
`normalized`	Text	Yes/no	Yes	Are single particle functions normalized?

Table 6 Options for the `atomicBasisSet` xml-block.

- **name/id** Name of the basis set. Names should be unique.
- **angular** Type of angular functions used in the expansion. In general, two angular basis functions are allowed: “spherical” (for spherical Ylm functions) and “Cartesian” (for functions of the type $x^n y^m z^l$).

- **expandYlm** Determines whether each basis group is expanded across the corresponding shell of m values (for spherical type) or consistent powers (for Cartesian functions). Options:
  - "No": Do not expand angular functions across corresponding angular shell.
  - "Gaussian": Expand according to Gaussian03 format. This function is compatible only with angular="spherical." For a given input (l,m), the resulting order of the angular functions becomes (1,-1,0) for l=1 and (0,1,-1,2,-2,...,l,-l) for general l.
  - "Natural": Expand angular functions according to (-l,-l+1,...,l-1,l).
  - "Gamess": Expand according to Gamess' format for Cartesian functions. Notice that this option is compatible only with angular="Cartesian." If angular="Cartesian" is used, this option is not necessary.
- **expM** Determines whether the sign of the spherical Ylm function associated with m (-1^m) is included in the coefficient matrix or not.
- **elementType/species** Name of the species where basis functions are centered. Only one `atomicBasisSet` block is allowed per species. Additional blocks are ignored. The corresponding species must exist in the `particleset` given as the `source` option to `determinantset`. Basis functions for all the atoms of the corresponding species are included in the basis set, based on the order of atoms in the `particleset`.

`basicGroup` element:

Parent elements	`AtomicBasisSet`
Child elements	`radfunc`

Attribute:

Name	Datatype	Values	Default	Description
`rid/id`	Text	*Any*	'' ''	Name of the basisGroup
`type`	Text	*Any*	'' ''	Type of basisGroup
`n/l/m/s`	Integer	*Any*	0	Quantum numbers of basisGroup

Table 8.2.3 Options for the `basisGroup` xml-block.

- **type** Type of input basis radial function. Note that this refers to the type of radial function in the input xml-block, which might not match the radial function generated internally and used in the calculation (if `transform` is set to "yes"). Also note that different `basisGroup` blocks within a given `atomicBasisSet` can have different `types`.
- **n/l/m/s** Quantum numbers of the basis function. Note that if `expandYlm` is set to *"yes"* in `atomicBasisSet`, a full shell of basis functions with the appropriate values of *"m"* will be defined for the corresponding value of *"l."* Otherwise a single basis function will be given for the specific combination of *"(l,m)."*

`radfunc` element: attributes for `type` = *"Gaussian"*:

`TBDoc`

8.2.4 Hybrid orbital representation

The hybrid representation of the single particle orbitals combines a localized atomic basis set around atomic cores and B-splines in the interstitial regions to reduce memory use while retaining high evaluation speed and either retaining or increasing overall accuracy. Full details are provided in [[LEKS18]], and **users of this feature are kindly requested to cite this paper**. In practice, we have seen that using a meshfactor=0.5 is often possible and achieves huge memory savings. Fig. 8.1 illustrates how the regions are assigned.

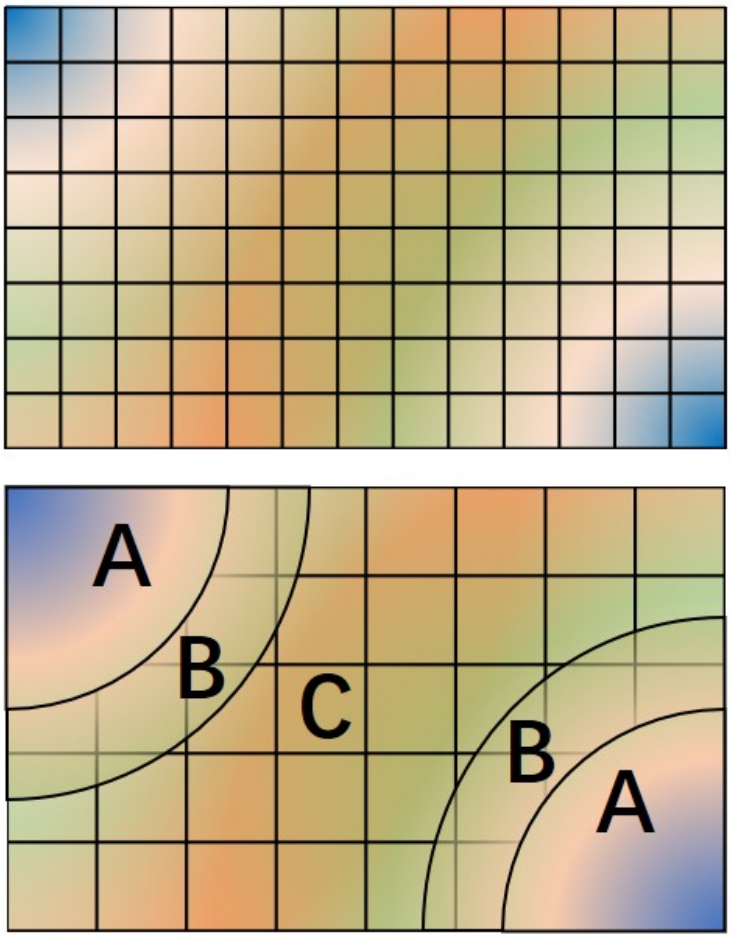

Fig. 8.1: Regular and hybrid orbital representation. Regular B-spline representation (left panel) contains only one region and a sufficiently fine mesh to resolve orbitals near the nucleus. The hybrid orbital representation (right panel) contains near nucleus regions (A) where spherical harmonics and radial functions are used, buffers or interpolation regions (B), and an interstitial region (C) where a coarse B-spline mesh is used.

Orbitals within region A are computed as

$$\phi_n^A(\mathbf{r}) = R_{n,l,m}(r)Y_{l,m}(\hat{r})$$

Orbitals in region C are computed as the regular B-spline basis described in *3D B-splines orbitals* above. The region B interpolates between A and C as

$$\phi_n^B(\mathbf{r}) = S(r)\phi_n^A(\mathbf{r}) + (1 - S(r))\phi_n^C(\mathbf{r}) \tag{8.6}$$

$$(S(r) = \frac{1}{2} - \frac{1}{2}tanh\left[\alpha\left(\frac{r - r_{\mathrm{A/B}}}{r_{\mathrm{B/C}} - r_{\mathrm{A/B}}} - \frac{1}{2}\right)\right] \tag{8.7}$$

To enable hybrid orbital representation, the input XML needs to see the tag `hybridrep="yes"` shown in *Listing 6*.

Listing 8.9: Hybrid orbital representation input example.

```
<sposet_collection type="bspline" source="i" href="pwscf.h5"
              tilematrix="1 1 3 1 2 -1 -2 1 0" gpu="yes" meshfactor="0.8"
              twist="0  0  0" precision="single" hybridrep="yes">
  ...
</sposet_collection>
```

Second, the information describing the atomic regions is required in the particle set, shown in *Listing 7*.

Listing 8.10: particleset elements for ions with information needed by hybrid orbital representation.

```
<group name="Ni">
  <parameter name="charge">          18 </parameter>
  <parameter name="valence">         18 </parameter>
  <parameter name="atomicnumber" >   28 </parameter>
  <parameter name="cutoff_radius" > 1.6 </parameter>
  <parameter name="inner_cutoff" >  1.3 </parameter>
  <parameter name="lmax" >            5 </parameter>
  <parameter name="spline_radius" > 1.8 </parameter>
  <parameter name="spline_npoints">  91 </parameter>
</group>
```

The parameters specific to hybrid representation are listed as

`attrib` element

Attribute:

Name	Datatype	Values	Default	Description
`cutoff_radius`	Real	>=0.0	*None*	Cutoff radius for B/C boundary
`lmax`	Integer	>=0	*None*	Largest angular channel
`inner_cutoff`	Real	>=0.0	Dep.	Cutoff radius for A/B boundary
`spline_radius`	Real	>0.0	Dep.	Radial function radius used in spine
`spline_npoints`	Integer	>0	Dep.	Number of spline knots

- `cutoff_radius` is required for every species. If a species is intended to not be covered by atomic regions, setting the value 0.0 will put default values for all the reset parameters. A good value is usually a bit larger than the core radius listed in the pseudopotential file. After a parametric scan, pick the one from the flat energy region with the smallest variance.
- `lmax` is required if `cutoff_radius` > 0.0. This value usually needs to be at least the highest angular momentum plus 2.
- `inner_cutoff` is optional and set as `cutoff_radius` -0.3 by default, which is fine in most cases.
- `spline_radius` and `spline_npoints` are optional. By default, they are calculated based on `cutoff_radius` and a grid displacement 0.02 bohr. If users prefer inputing them, it is required that `cutoff_radius` <= `spline_radius` $-$ 2 $\times$ `spline_radius`/(`spline_npoints` $-$ 1).

In addition, the hybrid orbital representation allows extra optimization to speed up the nonlocal pseudopotential evaluation using the batched algorithm listed in *Pseudopotentials*.

8.2.5 Plane-wave basis sets

8.2.6 Homogeneous electron gas

The interacting Fermi liquid has its own special `determinantset` for filling up a Fermi surface. The shell number can be specified separately for both spin-up and spin-down. This determines how many electrons to include of each time; only closed shells are currently implemented. The shells are filled according to the rules of a square box; if other lattice vectors are used, the electrons might not fill up a complete shell.

This following example can also be used for Helium simulations by specifying the proper pair interaction in the Hamiltonian section.

Listing 8.11: 2D Fermi liquid example: particle specification

```
<simulationcell name="global">
  <parameter name="rs" pol="0" condition="74">6.5</parameter>
  <parameter name="bconds">p p p</parameter>
  <parameter name="LR_dim_cutoff">15</parameter>
</simulationcell>
<particleset name="e" random="yes">
  <group name="u" size="37">
    <parameter name="charge">-1</parameter>
    <parameter name="mass">1</parameter>
  </group>
  <group name="d" size="37">
    <parameter name="charge">-1</parameter>
    <parameter name="mass">1</parameter>
  </group>
</particleset>
```

Listing 8.12: 2D Fermi liquid example (Slater Jastrow wavefunction)

```
<wavefunction name="psi0" target="e">
  <determinantset type="electron-gas" shell="7" shell2="7" randomize="true">
</determinantset>
<jastrow name="J2" type="Two-Body" function="Bspline" print="no">
  <correlation speciesA="u" speciesB="u" size="8" cusp="0">
    <coefficients id="uu" type="Array" optimize="yes">
  </correlation>
  <correlation speciesA="u" speciesB="d" size="8" cusp="0">
    <coefficients id="ud" type="Array" optimize="yes">
  </correlation>
</jastrow>
</wavefunction>
```

8.3 Single determinant wavefunctions

Placing a single determinant for each spin is the most used ansatz for the antisymmetric part of a trial wavefunction. The input xml block for `slaterdeterminant` is given in *Listing 1*. A list of options is given in Table 8.3.

`slaterdeterminant` element:

Parent elements	`determinantset`
Child elements	`determinant`

Attribute:

Name	Datatype	Values	Default	Description
delay_rank	Integer	>=0	1	Number of delayed updates.
optimize	Text	yes/no	yes	Enable orbital optimization.
gpu	Text	yes/no	yes	Use the GPU acceleration implementation.
batch	Text	yes/no	dep.	Select the batched walker implementation.
matrix_inverter	Text	gpu/host	gpu	Slater matrix inversion scheme.

Table 2 Options for the slaterdeterminant xml-block.

Listing 8.13: Slaterdeterminant set XML element.

```
<sposet_collection ...>
  <sposet name="spo" size="8">
    ...
  </sposet>
</sposet_collection>
<determinantset>
  <slaterdeterminant delay_rank="32">
    <determinant sposet="spo"/>
    <determinant sposet="spo"/>
  </slaterdeterminant>
</determinantset>
```

Additional information:

- delay_rank This option enables delayed updates of the Slater matrix inverse when particle-by-particle move is used. By default or if delay_rank=0 given in the input file, QMCPACK sets 1 for Slater matrices with a leading dimension < 192 and 32 otherwise. delay_rank=1 uses the Fahy's variant [[FWL90]] of the Sherman-Morrison rank-1 update, which is mostly using memory bandwidth-bound BLAS-2 calls. With delay_rank>1, the delayed update algorithm [[LK18], [MDAzevedoL+17]] turns most of the computation to compute bound BLAS-3 calls. Tuning this parameter is highly recommended to gain the best performance on medium-to-large problem sizes (> 200 electrons). We have seen up to an order of magnitude speedup on large problem sizes. When studying the performance of QMCPACK, a scan of this parameter is required and we recommend starting from 32. The best delay_rank giving the maximal speedup depends on the problem size. Usually the larger delay_rank corresponds to a larger problem size. On CPUs, delay_rank must be chosen as a multiple of SIMD vector length for good performance of BLAS libraries. The best delay_rank depends on the processor microarchitecture. GPU support is under development.
- gpu This option is only effective when GPU features are built. Use the implementation with GPU acceleration if yes.
- batch The default value is yes if gpu=yes and no otherwise.
- matrix_inverter If the value is gpu, the inversion happens on the GPU and additional GPU memory is needed. If the value is host, the inversion happens on the CPU and doesn't need GPU memory.

8.4 Multideterminant wavefunctions

`multideterminant` element:

Parent elements	`determinantset`
Child elements	`detlist`

Attribute:

Name	Datatype	Values	Default	Description
`optimize`	Text	yes/no	yes	Enable optimization.
`spo_up`	Text			The name of SPO for spin up electrons
`spo_down`	Text			The name of SPO for spin down electrons
`algorithm`	Text		precomputed_table_method	Slater matrix inversion scheme.

Table 3 Options for the `multideterminant` xml-block.

Additional information:

- `algorithm` algorithms used in multi-Slater determinant implementation. `table_method` table method of Clark et al. [[CMM+11]] . `precomputed_table_method` adds partial sum precomputation on top of `table_method`.

Listing 8.14: multideterminant set XML element.

```
<sposet_collection ...>
  <sposet name="spo" size="85">
    ...
  </sposet>
</sposet_collection>
<determinantset>
  <multideterminant optimize="yes" spo_up="spo" spo_dn="spo">
    <detlist size="1487" type="DETS" nca="0" ncb="0" nea="2" neb="2" nstates="85"␣
↪cutoff="1e-20" href="LiH.orbs.h5">
  </multideterminant>
</determinantset>
```

Multiple schemes to generate a multideterminant wavefunction are possible, from CASSF to full CI or selected CI. The QMCPACK converter can convert MCSCF multideterminant wavefunctions from GAMESS [[SBB+93]] and CIPSI [[EG13]] wavefunctions from Quantum Package [[Sce17]] (QP). Full details of how to run a CIPSI calculation and convert the wavefunction for QMCPACK are given in *CIPSI wavefunction interface*.

The script `utils/determinants_tools.py` can be used to generate useful information about the multideterminant wavefunction. This script takes, as a required argument, the path of an h5 file corresponding to the wavefunction. Used without optional arguments, it prints the number of determinants, the number of CSFs, and a histogram of the excitation degree.

```
> determinants_tools.py ./tests/molecules/C2_pp/C2.h5
Summary:
excitation degree 0 count: 1
excitation degree 1 count: 6
excitation degree 2 count: 148
excitation degree 3 count: 27
excitation degree 4 count: 20
```

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```
n_det 202
n_csf 104
```

If the `--verbose` argument is used, the script will print each determinant, the associated CSF, and the excitation degree relative to the first determinant.

```
> determinants_tools.py -v ./tests/molecules/C2_pp/C2.h5 | head
1
alpha  11110000000000000000000000000000000000000000000000000000
beta   11110000000000000000000000000000000000000000000000000000
scf    22220000000000000000000000000000000000000000000000000000
excitation degree  0

2
alpha  10111000000000000000000000000000000000000000000000000000
beta   10111000000000000000000000000000000000000000000000000000
scf    20222000000000000000000000000000000000000000000000000000
excitation degree  2
```

8.5 Backflow Wavefunctions

One can perturb the nodal surface of a single-Slater/multi-Slater wavefunction through use of a backflow transformation. Specifically, if we have an antisymmetric function $D(\mathbf{x}_{0\uparrow}, \cdots, \mathbf{x}_{N\uparrow}, \mathbf{x}_{0\downarrow}, \cdots, \mathbf{x}_{N\downarrow})$, and if i_α is the i-th particle of species type α, then the backflow transformation works by making the coordinate transformation $\mathbf{x}_{i_\alpha} \rightarrow \mathbf{x}'_{i_\alpha}$ and evaluating D at these new "quasiparticle" coordinates. QMCPACK currently supports quasiparticle transformations given by

$$\mathbf{x}'_{i_\alpha} = \mathbf{x}_{i_\alpha} + \sum_{\alpha \leq \beta} \sum_{i_\alpha \neq j_\beta} \eta^{\alpha\beta}(|\mathbf{x}_{i_\alpha} - \mathbf{x}_{j_\beta}|)(\mathbf{x}_{i_\alpha} - \mathbf{x}_{j_\beta}) \,. \tag{8.8}$$

Here, $\eta^{\alpha\beta}(|\mathbf{x}_{i_\alpha} - \mathbf{x}_{j_\beta}|)$ is a radially symmetric backflow transformation between species α and β. In QMCPACK, particle i_α is known as the "target" particle and j_β is known as the "source." The main types of transformations are so-called one-body terms, which are between an electron and an ion $\eta^{eI}(|\mathbf{x}_{i_e} - \mathbf{x}_{j_I}|)$ and two-body terms. Two-body terms are distinguished as those between like and opposite spin electrons: $\eta^{e(\uparrow)e(\uparrow)}(|\mathbf{x}_{i_e(\uparrow)} - \mathbf{x}_{j_e(\uparrow)}|)$ and $\eta^{e(\uparrow)e(\downarrow)}(|\mathbf{x}_{i_e(\uparrow)} - \mathbf{x}_{j_e(\downarrow)}|)$. Henceforth, we will assume that $\eta^{e(\uparrow)e(\uparrow)} = \eta^{e(\downarrow)e(\downarrow)}$.

In the following, we explain how to describe general terms such as (8.8) in a QMCPACK XML file. For specificity, we will consider a particle set consisting of H and He (in that order). This ordering will be important when we build the XML file, so you can find this out either through your specific declaration of <particleset>, by looking at the hdf5 file in the case of plane waves, or by looking at the QMCPACK output file in the section labeled "Summary of QMC systems."

8.5.1 Input specifications

All backflow declarations occur within a single `<backflow> ... </backflow>` block. Backflow transformations occur in `<transformation>` blocks and have the following input parameters:

Transformation element:

Name	Datatype	Values	Default	Description
name	Text		(Required)	Unique name for this Jastrow function.
type	Text	"e-I"	(Required)	Define a one-body backflow transformation.
	Text	"e-e"		Define a two-body backflow transformation.
function	Text	B-spline	(Required)	B-spline type transformation (no other types supported).
source	Text			"e" if two body, ion particle set if one body.

Just like one- and two-body jastrows, parameterization of the backflow transformations are specified within the `<transformation>` blocks by `<correlation>` blocks. Please refer to *Spline form* for more information.

8.5.2 Example Use Case

Having specified the general form, we present a general example of one-body and two-body backflow transformations in a hydrogen-helium mixture. The hydrogen and helium ions have independent backflow transformations, as do the like and unlike-spin two-body terms. One caveat is in order: ionic backflow transformations must be listed in the order they appear in the particle set. If in our example, helium is listed first and hydrogen is listed second, the following example would be correct. However, switching backflow declaration to hydrogen first then helium, will result in an error. Outside of this, declaration of one-body blocks and two-body blocks are not sensitive to ordering.

```
<backflow>
<!--The One-Body term with independent e-He and e-H terms. IN THAT ORDER -->
<transformation name="eIonB" type="e-I" function="Bspline" source="ion0">
    <correlation cusp="0.0" size="8" type="shortrange" init="no" elementType="He"␣
↪rcut="3.0">
        <coefficients id="eHeC" type="Array" optimize="yes">
            0 0 0 0 0 0 0 0
        </coefficients>
    </correlation>
    <correlation cusp="0.0" size="8" type="shortrange" init="no" elementType="H" rcut=
↪"3.0">
        <coefficients id="eHC" type="Array" optimize="yes">
            0 0 0 0 0 0 0 0
        </coefficients>
    </correlation>
</transformation>

<!--The Two-Body Term with Like and Unlike Spins -->
<transformation name="eeB" type="e-e" function="Bspline" >
    <correlation cusp="0.0" size="7" type="shortrange" init="no" speciesA="u"␣
↪speciesB="u" rcut="1.2">
        <coefficients id="uuB1" type="Array" optimize="yes">
            0 0 0 0 0 0 0
        </coefficients>
    </correlation>
    <correlation cusp="0.0" size="7" type="shortrange" init="no" speciesA="d"␣
↪speciesB="u" rcut="1.2">
        <coefficients id="udB1" type="Array" optimize="yes">
            0 0 0 0 0 0 0
        </coefficients>
    </correlation>
```

(continues on next page)

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```
</transformation>
</backflow>
```

Currently, backflow works only with single-Slater determinant wavefunctions. When a backflow transformation has been declared, it should be placed within the <determinantset> block, but outside of the <slaterdeterminant> blocks, like so:

```
<determinantset ... >
    <!--basis set declarations go here, if there are any -->

    <backflow>
        <transformation ...>
          <!--Here is where one and two-body terms are defined -->
         </transformation>
     </backflow>

     <slaterdeterminant>
         <!--Usual determinant definitions -->
     </slaterdeterminant>
 </determinantset>
```

8.5.3 Optimization Tips

Backflow is notoriously difficult to optimize—it is extremely nonlinear in the variational parameters and moves the nodal surface around. As such, it is likely that a full Jastrow+Backflow optimization with all parameters initialized to zero might not converge in a reasonable time. If you are experiencing this problem, the following pointers are suggested (in no particular order).

Get a good starting guess for Ψ_T:

1. Try optimizing the Jastrow first without backflow.
2. Freeze the Jastrow parameters, introduce only the e-e terms in the backflow transformation, and optimize these parameters.
3. Freeze the e-e backflow parameters, and then optimize the e-I terms.
    - If difficulty is encountered here, try optimizing each species independently.
4. Unfreeze all Jastrow, e-e backflow, and e-I backflow parameters, and reoptimize.

Optimizing Backflow Terms

It is possible that the previous prescription might grind to a halt in steps 2 or 3 with the inability to optimize the e-e or e-I backflow transformation independently, especially if it is initialized to zero. One way to get around this is to build a good starting guess for the e-e or e-I backflow terms iteratively as follows:

1. Start off with a small number of knots initialized to zero. Set r_{cut} to be small (much smaller than an interatomic distance).
2. Optimize the backflow function.
3. If this works, slowly increase r_{cut} and/or the number of knots.
4. Repeat steps 2 and 3 until there is no noticeable change in energy or variance of Ψ_T.

Tweaking the Optimization Run

The following modifications are worth a try in the optimization block:

- Try setting "useDrift" to "no." This eliminates the use of wavefunction gradients and force biasing in the VMC algorithm. This could be an issue for poorly optimized wavefunctions with pathological gradients.
- Try increasing "exp0" in the optimization block. Larger values of exp0 cause the search directions to more closely follow those predicted by steepest-descent than those by the linear method.

Note that the new adaptive shift optimizer has not yet been tried with backflow wavefunctions. It should perform better than the older optimizers, but a considered optimization process is still recommended.

8.6 Jastrow Factors

Jastrow factors are among the simplest and most effective ways of including dynamical correlation in the trial many body wavefunction. The resulting many body wavefunction is expressed as the product of an antisymmetric (in the case of Fermions) or symmetric (for Bosons) part and a correlating Jastrow factor like so:

$$\Psi(\vec{R}) = \mathcal{A}(\vec{R}) \exp\left[J(\vec{R})\right] \tag{8.9}$$

In this section we will detail the types and forms of Jastrow factor used in QMCPACK. Note that each type of Jastrow factor needs to be specified using its own individual `jastrow` XML element. For this reason, we have repeated the specification of the `jastrow` tag in each section, with specialization for the options available for that given type of Jastrow.

8.6.1 One-body Jastrow functions

The one-body Jastrow factor is a form that allows for the direct inclusion of correlations between particles that are included in the wavefunction with particles that are not explicitly part of it. The most common example of this are correlations between electrons and ions.

The Jastrow function is specified within a `wavefunction` element and must contain one or more `correlation` elements specifying additional parameters as well as the actual coefficients. *Example use cases* gives examples of the typical nesting of `jastrow`, `correlation`, and `coefficient` elements.

Input Specification

Jastrow element:

name	datatype	values	defaults	description
name	text		(required)	Unique name for this Jastrow function
type	text	One-body	(required)	Define a one-body function
function	text	Bspline	(required)	BSpline Jastrow
	text	pade2		Pade form
	text	...		...
source	text	name	(required)	Name of attribute of classical particle set
print	text	yes / no	yes	Jastrow factor printed in external file?

elements				
	Correlation			
Contents				
	(None)			

To be more concrete, the one-body Jastrow factors used to describe correlations between electrons and ions take the form below:

$$J1 = \sum_{I}^{ion0} \sum_{i}^{e} u_{ab}(|r_i - R_I|) \tag{8.10}$$

where I runs over all of the ions in the calculation, i runs over the electrons and u_{ab} describes the functional form of the correlation between them. Many different forms of u_{ab} are implemented in QMCPACK. We will detail two of the most common ones below.

Spline form

The one-body spline Jastrow function is the most commonly used one-body Jastrow for solids. This form was first described and used in [[EKCS12]]. Here u_{ab} is an interpolating 1D B-spline (tricublc spline on a linear grid) between zero distance and r_{cut}. In 3D periodic systems the default cutoff distance is the Wigner Seitz cell radius. For other periodicities, including isolated molecules, the r_{cut} must be specified. The cusp can be set. r_i and R_I are most commonly the electron and ion positions, but any particlesets that can provide the needed centers can be used.

Correlation element:

Name	Datatype	Values	Defaults	Description
ElementType	Text	Name	See below	Classical particle target
SpeciesA	Text	Name	See below	Classical particle target
SpeciesB	Text	Name	See below	Quantum species target
Size	Integer	> 0	(Required)	Number of coefficients
Rcut	Real	> 0	See below	Distance at which the correlation goes to 0
Cusp	Real	≥ 0	0	Value for use in Kato cusp condition
Spin	Text	Yes or no	No	Spin dependent Jastrow factor

Elements				
	Coefficients			
Contents				
	(None)			

Additional information:

- **`elementType, speciesA, speciesB, spin`** For a spin-independent Jastrow factor (spin = "no"), elementType should be the name of the group of ions in the classical particleset to which the quantum particles should be correlated. For a spin-dependent Jastrow factor (spin = "yes"), set speciesA to the group name in the classical particleset and speciesB to the group name in the quantum particleset.
- **`rcut`** The cutoff distance for the function in atomic units (bohr). For 3D fully periodic systems, this parameter is optional, and a default of the Wigner Seitz cell radius is used. Otherwise this parameter is required.
- **`cusp`** The one-body Jastrow factor can be used to make the wavefunction satisfy the electron-ion cusp condition :cite:`kato`. In this case, the derivative of the Jastrow factor as the electron approaches the nucleus will be given by

$$\left(\frac{\partial J}{\partial r_{iI}}\right)_{r_{iI}=0} = -Z. \tag{8.11}$$

Note that if the antisymmetric part of the wavefunction satisfies the electron-ion cusp condition (for instance by using single-particle orbitals that respect the cusp condition) or if a nondivergent pseudopotential is used, the Jastrow should be cuspless at the nucleus and this value should be kept at its default of 0.

Coefficients element:

Name	Datatype	Values	Defaults	Description
Id	Text		(Required)	Unique identifier
Type	Text	Array	(Required)	
Optimize	Text	Yes or no	Yes	if no, values are fixed in optimizations
Elements				
(None)				
Contents				
(No name)	Real array		Zeros	Jastrow coefficients

Example use cases

Specify a spin-independent function with four parameters. Because rcut is not specified, the default cutoff of the Wigner Seitz cell radius is used; this Jastrow must be used with a 3D periodic system such as a bulk solid. The name of the particleset holding the ionic positions is "i."

```
<jastrow name="J1" type="One-Body" function="Bspline" print="yes" source="i">
 <correlation elementType="C" cusp="0.0" size="4">
   <coefficients id="C" type="Array"> 0  0  0  0  </coefficients>
 </correlation>
</jastrow>
```

Specify a spin-dependent function with seven up-spin and seven down-spin parameters. The cutoff distance is set to 6 atomic units. Note here that the particleset holding the ions is labeled as ion0 rather than "i," as in the other example. Also in this case, the ion is lithium with a coulomb potential, so the cusp condition is satisfied by setting cusp="d."

```
<jastrow name="J1" type="One-Body" function="Bspline" source="ion0" spin="yes">
  <correlation speciesA="Li" speciesB="u" size="7" rcut="6">
    <coefficients id="eLiu" cusp="3.0" type="Array">
    0.0 0.0 0.0 0.0 0.0 0.0 0.0
    </coefficients>
  </correlation>
  <correlation speciesA="C" speciesB="d" size="7" rcut="6">
    <coefficients id="eLid" cusp="3.0" type="Array">
    0.0 0.0 0.0 0.0 0.0 0.0 0.0
    </coefficients>
  </correlation>
</jastrow>
```

Pade form

Although the spline Jastrow factor is the most flexible and most commonly used form implemented in QMCPACK, there are times where its flexibility can make it difficult to optimize. As an example, a spline Jastrow with a very large cutoff can be difficult to optimize for isolated systems such as molecules because of the small number of samples present in the tail of the function. In such cases, a simpler functional form might be advantageous. The second-order Pade Jastrow factor, given in (8.12), is a good choice in such cases.

$$u_{ab}(r) = \frac{a * r + c * r^2}{1 + b * r} \tag{8.12}$$

Unlike the spline Jastrow factor, which includes a cutoff, this form has an infinite range and will be applied to every particle pair (subject to the minimum image convention). It also is a cuspless Jastrow factor, so it should be used either in combination with a single particle basis set that contains the proper cusp or with a smooth pseudopotential.

Correlation element:

Name	Datatype	Values	Defaults	Description
ElementType	Text	Name	See below	Classical particle target
Elements				
	Coefficients			
Contents				
	(None)			

Parameter element:

Name	Datatype	Values	Defaults	Description
Id	String	Name	(Required)	Name for variable
Name	String	A or B or C	(Required)	See (8.12)
Optimize	Text	Yes or no	Yes	If no, values are fixed in optimizations

Elements				
(None)				
Contents				
(No name)	Real	Parameter value	(Required)	Jastrow coefficients

Example use case

Specify a spin-independent function with independent Jastrow factors for two different species (Li and H). The name of the particleset holding the ionic positions is "i."

```
<jastrow name="J1" function="pade2" type="One-Body" print="yes" source="i">
  <correlation elementType="Li">
    <var id="LiA" name="A">  0.34 </var>
    <var id="LiB" name="B"> 12.78 </var>
    <var id="LiC" name="C">  1.62 </var>
  </correlation>
  <correlation elementType="H"">
    <var id="HA" name="A">  0.14 </var>
    <var id="HB" name="B"> 6.88 </var>
    <var id="HC" name="C"> 0.237 </var>
  </correlation>
</jastrow>
```

Short Range Cusp Form

The idea behind this functor is to encode nuclear cusps and other details at very short range around a nucleus in the region that the Gaussian orbitals of quantum chemistry are not capable of describing correctly. The functor is kept short ranged, because outside this small region, quantum chemistry orbital expansions are already capable of taking on the correct shapes. Unlike a pre-computed cusp correction, this optimizable functor can respond to changes in the wave function during VMC optimization. The functor's form is

$$u(r) = -\exp\left(-r/R_0\right)\left(AR_0 + \sum_{k=0}^{N-1} B_k \frac{(r/R_0)^{k+2}}{1+(r/R_0)^{k+2}}\right) \tag{8.13}$$

in which R_0 acts as a soft cutoff radius ($u(r)$ decays to zero quickly beyond roughly this distance) and A determines the cusp condition.

$$\lim_{r\to 0} \frac{\partial u}{\partial r} = A \tag{8.14}$$

The simple exponential decay is modified by the N coefficients B_k that define an expansion in sigmoidal functions, thus adding detailed structure in a short-ranged region around a nucleus while maintaining the correct cusp condition at the nucleus. Note that sigmoidal functions are used instead of, say, a bare polynomial expansion, as they trend to unity past the soft cutoff radius and so interfere less with the exponential decay that keeps the functor short ranged. Although A, R_0, and the B_k coefficients can all be optimized as variational parameters, A will typically be fixed as the desired cusp condition is known.

To specify this one-body Jastrow factor, use an input section like the following.

```
<jastrow name="J1Cusps" type="One-Body" function="shortrangecusp" source="ion0" print=
↪"yes">
  <correlation rcut="6" cusp="3" elementType="Li">
    <var id="LiCuspR0" name="R0" optimize="yes"> 0.06 </var>
    <coefficients id="LiCuspB" type="Array" optimize="yes">
      0 0 0 0 0 0 0 0 0
    </coefficients>
  </correlation>
  <correlation rcut="6" cusp="1" elementType="H">
    <var id="HCuspR0" name="R0" optimize="yes"> 0.2 </var>
    <coefficients id="HCuspB" type="Array" optimize="yes">
      0 0 0 0 0 0 0 0 0
    </coefficients>
  </correlation>
</jastrow>
```

Here "rcut" is specified as the range beyond which the functor is assumed to be zero. The value of A can either be specified via the "cusp" option as shown above, in which case its optimization is disabled, or through its own "var" line as for R_0, in which case it can be specified as either optimizable ("yes") or not ("no"). The coefficients B_k are specified via the "coefficients" section, with the length N of the expansion determined automatically based on the length of the array.

Note that this one-body Jastrow form can (and probably should) be used in conjunction with a longer ranged one-body Jastrow, such as a spline form. Be sure to set the longer-ranged Jastrow to be cusp-free!

8.6.2 Two-body Jastrow functions

The two-body Jastrow factor is a form that allows for the explicit inclusion of dynamic correlation between two particles included in the wavefunction. It is almost always given in a spin dependent form so as to satisfy the Kato cusp condition between electrons of different spins [[Kat51]].

The two body Jastrow function is specified within a `wavefunction` element and must contain one or more correlation elements specifying additional parameters as well as the actual coefficients. *Example use cases* gives examples of the typical nesting of `jastrow`, `correlation` and `coefficient` elements.

Input Specification

Jastrow element:

name	datatype	values	defaults	description
name	text		(required)	Unique name for this Jastrow function
type	text	Two-body	(required)	Define a one-body function
function	text	Bspline	(required)	BSpline Jastrow
print	text	yes / no	yes	Jastrow factor printed in external file?
elements				
	Correlation			
Contents				
	(None)			

The two-body Jastrow factors used to describe correlations between electrons take the form

$$J2 = \sum_{i}^{e} \sum_{j>i}^{e} u_{ab}(|r_i - r_j|) \tag{8.15}$$

The most commonly used form of two body Jastrow factor supported by the code is a splined Jastrow factor, with many similarities to the one body spline Jastrow.

Spline form

The two-body spline Jastrow function is the most commonly used two-body Jastrow for solids. This form was first described and used in [[EKCS12]]. Here u_{ab} is an interpolating 1D B-spline (tricublc spline on a linear grid) between zero distance and r_{cut}. In 3D periodic systems, the default cutoff distance is the Wigner Seitz cell radius. For other periodicities, including isolated molecules, the r_{cut} must be specified. r_i and r_j are typically electron positions. The cusp condition as r_i approaches r_j is set by the relative spin of the electrons.

Correlation element:

Name	Datatype	Values	Defaults	Description
SpeciesA	Text	U or d	(Required)	Quantum species target
SpeciesB	Text	U or d	(Required)	Quantum species target
Size	Integer	> 0	(Required)	Number of coefficients
Rcut	Real	> 0	See below	Distance at which the correlation goes to 0
Spin	Text	Yes or no	No	Spin-dependent Jastrow factor
Elements				
	Coefficients			
Contents				
	(None)			

Additional information:

- `speciesA, speciesB` The scale function u(r) is defined for species pairs uu and ud. There is no need to define ud or dd since uu=dd and ud=du. The cusp condition is computed internally based on the charge of the quantum particles.

Coefficients element:

Name	Datatype	Values	Defaults	Description
Id	Text		(Required)	Unique identifier
Type	Text	Array	(Required)	
Optimize	Text	Yes or no	Yes	If no, values are fixed in optimizations
Elements				
(None)				
Contents				
(No name)	Real array		Zeros	Jastrow coefficients

Example use cases

Specify a spin-dependent function with four parameters for each channel. In this case, the cusp is set at a radius of 4.0 bohr (rather than to the default of the Wigner Seitz cell radius). Also, in this example, the coefficients are set to not be optimized during an optimization step.

```
<jastrow name="J2" type="Two-Body" function="Bspline" print="yes">
  <correlation speciesA="u" speciesB="u" size="8" rcut="4.0">
    <coefficients id="uu" type="Array" optimize="no"> 0.2309049836 0.1312646071 0.
↪05464141356 0.01306231516</coefficients>
  </correlation>
  <correlation speciesA="u" speciesB="d" size="8" rcut="4.0">
    <coefficients id="ud" type="Array" optimize="no"> 0.4351561096 0.2377951747 0.
↪1129144262 0.0356789236</coefficients>
  </correlation>
</jastrow>
```

8.6.3 User defined functional form

To aid in implementing different forms for $u_{ab}(r)$, there is a script that uses a symbolic expression to generate the appropriate code (with spatial and parameter derivatives). The script is located in `src/QMCWaveFunctions/Jastrow/codegen/user_jastrow.py`. The script requires Sympy (www.sympy.org) for symbolic mathematics and code generation.

To use the script, modify it to specify the functional form and a list of variational parameters. Optionally, there may be fixed parameters - ones that are specified in the input file, but are not part of the variational optimization. Also one symbol may be specified that accepts a cusp value in order to satisfy the cusp condition. There are several example forms in the script. The default form is the simple Padé.

Once the functional form and parameters are specified in the script, run the script from the `codegen` directory and recompile QMCPACK. The main output of the script is the file `src/QMCWaveFunctions/Jastrow/UserFunctor.h`. The script also prints information to the screen, and one section is a sample XML input block containing all the parameters.

There is a unit test in `src/QMCWaveFunctions/test/test_user_jastrow.cpp` to perform some minimal testing of the Jastrow factor. The unit test will need updating to properly test new functional forms. Most of the changes relate to the number and name of variational parameters.

Jastrow element:

name	datatype	values	defaults	description
name	text		(required)	Unique name for this Jastrow function
type	text	One-body	(required)	Define a one-body function
		Two-body	(required)	Define a two-body function
function	text	user	(required)	User-defined functor

See other parameters as appropriate for one or two-body functions

elements				
	Correlation			
Contents				
	(None)			

8.6.4 Long-ranged Jastrow factors

While short-ranged Jastrow factors capture the majority of the benefit for minimizing the total energy and the energy variance, long-ranged Jastrow factors are important to accurately reproduce the short-ranged (long wavelength) behavior of quantities such as the static structure factor, and are therefore essential for modern accurate finite size corrections in periodic systems.

Below two types of long-ranged Jastrow factors are described. The first (the k-space Jastrow) is simply an expansion of the one and/or two body correlation functions in plane waves, with the coefficients comprising the optimizable parameters. The second type have few variational parameters and use the optimized breakup method of Natoli and Ceperley [[NC95]] (the Yukawa and Gaskell RPA Jastrows).

Long-ranged Jastrow: k-space Jastrow

The k-space Jastrow introduces explicit long-ranged dependence commensurate with the periodic supercell. This Jastrow is to be used in periodic boundary conditions only.

The input for the k-space Jastrow fuses both one and two-body forms into a single element and so they are discussed together here. The one- and two-body terms in the k-Space Jastrow have the form:

$$J_1 = \sum_{G \neq 0} b_G \rho_G^I \rho_{-G} \tag{8.16}$$

$$J_2 = \sum_{G \neq 0} a_G \rho_G \rho_{-G} \tag{8.17}$$

Here ρ_G is the Fourier transform of the instantaneous electron density:

$$\rho_G = \sum_{n \in electrons} e^{iG \cdot r_n} \tag{8.18}$$

and ρ_G^I has the same form, but for the fixed ions. In both cases the coefficients are restricted to be real, though in general the coefficients for the one-body term need not be. See *Feature: Reciprocal-space Jastrow factors* for more detail.

Input for the k-space Jastrow follows the familar nesting of `jastrow-correlation-coefficients` elements, with attributes unique to the k-space Jastrow at the `correlation` input level.

`jastrow type=kSpace` element:

parent elements:	`wavefunction`
child elements:	`correlation`

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**kSpace**		must be kSpace
`name`^{r}	text	*anything*	0	Unique name for Jastrow
`source`^{r}	text	`particleset.name`		Ion particleset name

`correlation` element:

parent elements:	`jastrow type=kSpace`
child elements:	`coefficients`

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**One-body, Two-Body**		Must be One-body/Two-body
`kc`^{r}	real	kc ≥ 0	0.0	k-space cutoff in a.u.
`symmetry`^{o}	text	crystal,isotropic,none	crystal	symmetry of coefficients
`spinDependent`^{o}	boolean	yes,no	no	*No current function*

`coefficients` element:

parent elements:	`correlation`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`id`^{r}	text	*anything*	cG1/cG2	Label for coeffs
`type`^{r}	text	`Array`	0	Must be Array

body text: The body text is a list of real values for the parameters.

Additional information:

- It is normal to provide no coefficients as an initial guess. The number of coefficients will be automatically calculated according to the k-space cutoff + symmetry and set to zero.
- Providing an incorrect number of parameters also results in all parameters being set to zero.
- There is currently no way to turn optimization on/off for the k-space Jastrow. The coefficients are always optimized.
- Spin dependence is currently not implemented for this Jastrow.
- `kc`: Parameters with G vectors magnitudes less than `kc` are included in the Jastrow. If `kc` is zero, it is the same as excluding the k-space term.
- `symmetry=crystal`: Impose crystal symmetry on coefficients according to the structure factor.
- `symmetry=isotropic`: Impose spherical symmetry on coefficients according to G-vector magnitude.
- `symmetry=none`: Impose no symmetry on the coefficients.

Listing 8.15: k-space Jastrow with one- and two-body terms.

```
<jastrow type="kSpace" name="Jk" source="ion0">
  <correlation kc="4.0" type="One-Body" symmetry="cystal">
    <coefficients id="cG1" type="Array">
    </coefficients>
  </correlation>
  <correlation kc="4.0" type="Two-Body" symmetry="crystal">
    <coefficients id="cG2" type="Array">
    </coefficients>
 </correlation>
</jastrow>
```

Listing 8.16: k-space Jastrow with one-body term only.

```
<jastrow type="kSpace" name="Jk" source="ion0">
   <correlation kc="4.0" type="One-Body" symmetry="crystal">
      <coefficients id="cG1" type="Array">
      </coefficients>
   </correlation>
</jastrow>
```

Listing 8.17: k-space Jastrow with two-body term only.

```
<jastrow type="kSpace" name="Jk" source="ion0">
   <correlation kc="4.0" type="Two-Body" symmetry="crystal">
```

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```
      <coefficients id="cG2" type="Array">
      </coefficients>
   </correlation>
</jastrow>
```

Long-ranged Jastrows: Gaskell RPA and Yukawa forms

NOTE: The Yukawa and RPA Jastrows do not work at present and are currently being revived. Please contact the developers if you are interested in using them.

The exact Jastrow correlation functions contain terms which have a form similar to the Coulomb pair potential. In periodic systems the Coulomb potential is replaced by an Ewald summation of the bare potential over all periodic image cells. This sum is often handled by the optimized breakup method [[NC95]] and this same approach is applied to the long-ranged Jastrow factors in QMCPACK.

There are two main long-ranged Jastrow factors of this type implemented in QMCPACK: the Gaskell RPA [[Gas61], [Gas62]] form and the [[Cep78]] form. Both of these forms were used by Ceperley in early studies of the electron gas [[Cep78]], but they are also appropriate starting points for general solids.

The Yukawa form is defined in real space. It's long-range form is formally defined as

$$u_Y^{PBC}(r) = \sum_{L\neq 0}\sum_{i<j} u_Y(|r_i - r_j + L|) \tag{8.19}$$

with $u_Y(r)$ given by

$$u_Y(r) = \frac{a}{r}\left(1 - e^{-r/b}\right) \tag{8.20}$$

In QMCPACK a slightly more restricted form is used:

$$u_Y(r) = \frac{r_s}{r}\left(1 - e^{-r/\sqrt{r_s}}\right) \tag{8.21}$$

here "r_s" is understood to be a variational parameter.

The Gaskell RPA form—which contains correct short/long range limits and minimizes the total energy of the electron gas within the RPA—is defined directly in k-space:

$$u_{RPA}(k) = -\frac{1}{2S_0(k)} + \frac{1}{2}\left(\frac{1}{S_0(k)^2} + \frac{4m_e v_k}{\hbar^2 k^2}\right)^{1/2} \tag{8.22}$$

where \$v_k\$ is the Fourier transform of the Coulomb potential and $S_0(k)$ is the static structure factor of the non-interacting electron gas:

$$S_0(k) = \begin{cases} 1 & k > 2k_F \\ \frac{3k}{4k_F} - \frac{1}{2}\left(\frac{k}{2k_F}\right)^3 & k < 2k_F \end{cases}$$

When written in atomic units, RPA Jastrow implemented in QMCPACK has the form

$$u_{RPA}(k) = \frac{1}{2N_e}\left(-\frac{1}{S_0(k)} + \left(\frac{1}{S_0(k)^2} + \frac{12}{r_s^3 k^4}\right)^{1/2}\right) \tag{8.23}$$

Here "r_s" is again a variational parameter and $k_F \equiv (\frac{9\pi}{4r_s^3})^{1/3}$.

For both the Yukawa and Gaskell RPA Jastrows, the default value for r_s is $r_s = (\frac{3\Omega}{4\pi N_e})^{1/3}$.

`jastrow type=Two-Body function=rpa/yukawa` element:

parent elements:	`wavefunction`
child elements:	`correlation`

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**Two-body**		Must be two-body
`function`^{r}	text	**rpa/yukawa**		Must be rpa or yukawa
`name`^{r}	text	*anything*	RPA_Jee	Unique name for Jastrow
`longrange`^{o}	boolean	yes/no	yes	Use long-range part
`shortrange`^{o}	boolean	yes/no	yes	Use short-range part

parameters:

Name	Datatype	Values	Default	Description
`rs`^{o}	rs	$r_s > 0$	$\frac{3\Omega}{4\pi N_e}$	Avg. elec-elec distance
`kc`^{o}	kc	$k_c > 0$	$2\left(\frac{9\pi}{4}\right)^{1/3}\frac{4\pi N_e}{3\Omega}$	k-space cutoff

Listing 8.18: Two body RPA Jastrow with long- and short-ranged parts.

```
<jastrow name=''Jee'' type=''Two-Body'' function=''rpa''>
</jastrow>
```

8.6.5 Three-body Jastrow functions

Explicit three-body correlations can be included in the wavefunction via the three-body Jastrow factor. The three-body electron-electron-ion correlation function ($u_{\sigma\sigma' I}$) currently used in is identical to the one proposed in [[DTN04]]:

$$\begin{aligned} u_{\sigma\sigma' I}(r_{\sigma I}, r_{\sigma' I}, r_{\sigma\sigma'}) = &\sum_{\ell=0}^{M_{eI}}\sum_{m=0}^{M_{eI}}\sum_{n=0}^{M_{ee}}\gamma_{\ell mn} r_{\sigma I}^{\ell} r_{\sigma' I}^{m} r_{\sigma\sigma'}^{n} \\ &\times \left(r_{\sigma I} - \frac{r_c}{2}\right)^3 \Theta\left(r_{\sigma I} - \frac{r_c}{2}\right) \\ &\times \left(r_{\sigma' I} - \frac{r_c}{2}\right)^3 \Theta\left(r_{\sigma' I} - \frac{r_c}{2}\right) \end{aligned}$$

Here M_{eI} and M_{ee} are the maximum polynomial orders of the electron-ion and electron-electron distances, respectively, $\{\gamma_{\ell mn}\}$ are the optimizable parameters (modulo constraints), r_c is a cutoff radius, and r_{ab} are the distances between electrons or ions a and b. i.e. The correlation function is only a function of the interparticle distances and not a more complex function of the particle positions, $\mathbf{r}$. As indicated by the Θ functions, correlations are set to zero beyond a distance of $r_c/2$ in either of the electron-ion distances and the largest meaningful electron-electron distance is r_c. This is the highest-order Jastrow correlation function currently implemented.

Today, solid state applications of QMCPACK usually utilize one and two-body B-spline Jastrow functions, with calculations on heavier elements often also using the three-body term described above.

Example use case

Here is an example of H2O molecule. After optimizing one and two body Jastrow factors, add the following block in the wavefunction. The coefficients will be filled zero automatically if not given.

```
<jastrow name="J3" type="eeI" function="polynomial" source="ion0" print="yes">
  <correlation ispecies="O" especies="u" isize="3" esize="3" rcut="10">
    <coefficients id="uuO" type="Array" optimize="yes"> </coefficients>
  </correlation>
  <correlation ispecies="O" especies1="u" especies2="d" isize="3" esize="3" rcut="10">
    <coefficients id="udO" type="Array" optimize="yes"> </coefficients>
  </correlation>
  <correlation ispecies="H" especies="u" isize="3" esize="3" rcut="10">
    <coefficients id="uuH" type="Array" optimize="yes"> </coefficients>
  </correlation>
  <correlation ispecies="H" especies1="u" especies2="d" isize="3" esize="3" rcut="10">
    <coefficients id="udH" type="Array" optimize="yes"> </coefficients>
  </correlation>
</jastrow>
```

8.7 Gaussian Product Wavefunction

The Gaussian Product wavefunction implements (8.24)

$$\Psi(\vec{R}) = \prod_{i=1}^{N} \exp\left[-\frac{(\vec{R}_i - \vec{R}_i^o)^2}{2\sigma_i^2}\right] \tag{8.24}$$

where $\vec{R}_i$ is the position of the i^{th} quantum particle and $\vec{R}_i^o$ is its center. σ_i is the width of the Gaussian orbital around center i.

This variational wavefunction enhances single-particle density at chosen spatial locations with adjustable strengths. It is useful whenever such localization is physically relevant yet not captured by other parts of the trial wavefunction. For example, in an electron-ion simulation of a solid, the ions are localized around their crystal lattice sites. This single-particle localization is not captured by the ion-ion Jastrow. Therefore, the addition of this localization term will improve the wavefunction. The simplest use case of this wavefunction is perhaps the quantum harmonic oscillator (please see the "tests/models/sho" folder for examples).

Input specification

Gaussian Product Wavefunction (ionwf):

Name	Datatype	Values	Default	Description
Name	Text	ionwf	(Required)	Unique name for this wavefunction
Width	Floats	1.0 -1	(Required)	Widths of Gaussian orbitals
Source	Text	ion0	(Required)	Name of classical particle set

Additional information:

- `width` There must be one width provided for each quantum particle. If a negative width is given, then its corresponding Gaussian orbital is removed. Negative width is useful if one wants to use Gaussian wavefunction for a subset of the quantum particles.
- `source` The Gaussian centers must be specified in the form of a classical particle set. This classical particle set is likely the ion positions "ion0," hence the name "ionwf." However, arbitrary centers can be defined using a different particle set. Please refer to the examples in "tests/models/sho."

8.7.1 Example Use Case

```
<qmcsystem>
  <simulationcell>
    <parameter name="bconds">
          n n n
    </parameter>
  </simulationcell>
  <particleset name="e">
    <group name="u" size="1">
      <parameter name="mass">5.0</parameter>
      <attrib name="position" datatype="posArray" condition="0">
        0.0001 -0.0001 0.0002
      </attrib>
    </group>
  </particleset>
  <particleset name="ion0" size="1">
    <group name="H">
      <attrib name="position" datatype="posArray" condition="0">
        0 0 0
      </attrib>
    </group>
  </particleset>
  <wavefunction target="e" id="psi0">
    <ionwf name="iwf" source="ion0" width="0.8165"/>
  </wavefunction>
  <hamiltonian name="h0" type="generic" target="e">
    <extpot type="HarmonicExt" mass="5.0" energy="0.3"/>
    <estimator type="latticedeviation" name="latdev"
      target="e"    tgroup="u"
      source="ion0" sgroup="H"/>
  </hamiltonian>
</qmcsystem>
```

CHAPTER

NINE

HAMILTONIAN AND OBSERVABLES

QMCPACK is capable of the simultaneous measurement of the Hamiltonian and many other quantum operators. The Hamiltonian attains a special status among the available operators (also referred to as observables) because it ultimately generates all available information regarding the quantum system. This is evident from an algorithmic standpoint as well since the Hamiltonian (embodied in the projector) generates the imaginary time dynamics of the walkers in DMC and reptation Monte Carlo (RMC).

This section covers how the Hamiltonian can be specified, component by component, by the user in the XML format native to qmcpack. It also covers the input structure of statistical estimators corresponding to quantum observables such as the density, static structure factor, and forces.

9.1 The Hamiltonian

The many-body Hamiltonian in Hartree units is given by

$$\hat{H} = -\sum_i \frac{1}{2m_i}\nabla_i^2 + \sum_i v^{ext}(r_i) + \sum_{i<j} v^{qq}(r_i, r_j) + \sum_{i\ell} v^{qc}(r_i, r_\ell) + \sum_{\ell<m} v^{cc}(r_\ell, r_m)\,. \tag{9.1}$$

Here, the sums indexed by i/j are over quantum particles, while ℓ/m are reserved for classical particles. Often the quantum particles are electrons, and the classical particles are ions, though is not limited in this way. The mass of each quantum particle is denoted m_i, $v^{qq}/v^{qc}/v^{cc}$ are pair potentials between quantum-quantum/quantum-classical/classical-classical particles, and v^{ext} denotes a purely external potential.

QMCPACK is designed modularly so that any potential can be supported with minimal additions to the code base. Potentials currently supported include Coulomb interactions in open and periodic boundary conditions, the MPC potential, nonlocal pseudopotentials, helium pair potentials, and various model potentials such as hard sphere, Gaussian, and modified Poschl-Teller.

Reference information and examples for the `<hamiltonian/>` XML element are provided subsequently. Detailed descriptions of the input for individual potentials is given in the sections that follow.

`hamiltonian` element:

parent elements:	`simulation, qmcsystem`
child elements:	`pairpot extpot estimator constant` (deprecated)

attributes:

Name	Datatype	Values	Default	Description
name/ id^o	text	*anything*	h0	Unique id for this Hamiltonian instance
type^o	text		generic	*No current function*
role^o	text	primary/extra	extra	Designate as Hamiltonian or not
source^o	text	particleset. name	i	Identify classical particleset
target^o	text	particleset. name	e	Identify quantum particleset
default^o	boolean	yes/no	yes	Include kinetic energy term implicitly

Additional information:

- **target:** Must be set to the name of the quantum particleset. The default value is typically sufficient. In normal usage, no other attributes are provided.

Listing 9.1: All electron Hamiltonian XML element.

```
<hamiltonian target="e">
  <pairpot name="ElecElec" type="coulomb" source="e" target="e"/>
  <pairpot name="ElecIon"  type="coulomb" source="i" target="e"/>
  <pairpot name="IonIon"   type="coulomb" source="i" target="i"/>
</hamiltonian>
```

Listing 9.2: Pseudopotential Hamiltonian XML element.

```
<hamiltonian target="e">
  <pairpot name="ElecElec"  type="coulomb" source="e" target="e"/>
  <pairpot name="PseudoPot" type="pseudo"  source="i" wavefunction="psi0" format="xml
↪">
    <pseudo elementType="Li" href="Li.xml"/>
    <pseudo elementType="H" href="H.xml"/>
  </pairpot>
  <pairpot name="IonIon"    type="coulomb" source="i" target="i"/>
</hamiltonian>
```

9.2 Pair potentials

Many pair potentials are supported. Though only the most commonly used pair potentials are covered in detail in this section, all currently available potentials are listed subsequently. If a potential you desire is not listed, or is not present at all, feel free to contact the developers.

pairpot factory element:

parent elements:	hamiltonian
child elements:	type attribute

type options	coulomb	Coulomb/Ewald potential
	pseudo	Semilocal pseudopotential
	mpc	Model periodic Coulomb interaction/correction
	cpp	Core polarization potential
	skpot	*Unknown*

shared attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	*See above*	0	Select pairpot type
`name`^{r}	text	*Anything*	any	Unique name for this pairpot
`source`^{r}	text	`particleset.name`	`hamiltonian.target`	Identify interacting particles
`target`^{r}	text	`particleset.name`	`hamiltonian.target`	Identify interacting particles
`units`^{o}	text		hartree	*No current function*

Additional information:

- **type:** Used to select the desired pair potential. Must be selected from the list of type options.
- **name:** A unique name used to identify this pair potential. Block averaged output data will appear under this name in `scalar.dat` and/or `stat.h5` files.
- **source/target:** These specify the particles involved in a pair interaction. If an interaction is between classical (e.g., ions) and quantum (e.g., electrons), `source`/`target` should be the name of the classical/quantum `particleset`.
- Only `Coulomb, pseudo`, and `mpc` are described in detail in the following subsections. The older or less-used types (`cpp, skpot`) are not covered.
- Available only if `QMC_CUDA` is not defined: `skpot`.
- Available only if `OHMMS_DIM==3`: `mpc, vhxc, pseudo`.
- Available only if `OHMMS_DIM==3` and `QMC_CUDA` is not defined: `cpp`.

9.2.1 Coulomb potentials

The bare Coulomb potential is used in open boundary conditions:

$$V_c^{open} = \sum_{i<j} \frac{q_i q_j}{|r_i - r_j|} \,. \tag{9.2}$$

When periodic boundary conditions are selected, Ewald summation is used automatically:

$$V_c^{pbc} = \sum_{i<j} \frac{q_i q_j}{|r_i - r_j|} + \frac{1}{2} \sum_{L \neq 0} \sum_{i,j} \frac{q_i q_j}{|r_i - r_j + L|} \,. \tag{9.3}$$

The sum indexed by L is over all nonzero simulation cell lattice vectors. In practice, the Ewald sum is broken into short- and long-range parts in a manner optimized for efficiency (see [[NC95]]) for details.

For information on how to set the boundary conditions, consult *Specifying the system to be simulated*.

`pairpot type=coulomb` element:

parent elements:	`hamiltonian`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**coulomb**		Must be coulomb
`name/ id`^{r}	text	*anything*	ElecElec	Unique name for interaction
`source`^{r}	text	`particleset. name`	`hamiltonian. target`	Identify interacting particles
`target`^{r}	text	`particleset. name`	`hamiltonian. target`	Identify interacting particles
`pbc`^{o}	boolean	yes/no	yes	Use Ewald summation
`physical`^{o}	boolean	yes/no	yes	Hamiltonian(yes)/Observable(no)
`gpu`	boolean	yes/no	depend	Offload computation to GPU
`forces`	boolean	yes/no	no	*Deprecated*

Additional information:

- **type/source/target:** See description for the previous generic `pairpot` factory element.
- **name:** Traditional user-specified names for electron-electron, electron-ion, and ion-ion terms are `ElecElec`, `ElecIon`, and `IonIon`, respectively. Although any choice can be used, the data analysis tools expect to find columns in `*.scalar.dat` with these names.
- **pbc**: Ewald summation will not be performed if `simulationcell.bconds== n n n`, regardless of the value of `pbc`. Similarly, the `pbc` attribute can only be used to turn off Ewald summation if `simulationcell.bconds!= n n n`. The default value is recommended.
- **physical**: If `physical==yes`, this pair potential is included in the Hamiltonian and will factor into the `LocalEnergy` reported by QMCPACK and also in the DMC branching weight. If `physical==no`, then the pair potential is treated as a passive observable but not as part of the Hamiltonian itself. As such it does not contribute to the outputted `LocalEnergy`. Regardless of the value of `physical` output data will appear in `scalar.dat` in a column headed by `name`.
- **gpu**: When not specified, use the `gpu` attribute of `particleset`.

Listing 9.3: QMCPXML element for Coulomb interaction between electrons.

```
<pairpot name="ElecElec" type="coulomb" source="e" target="e"/>
```

Listing 9.4: QMCPXML element for Coulomb interaction between electrons and ions (all-electron only).

```
<pairpot name="ElecIon"  type="coulomb" source="i" target="e"/>
```

Listing 9.5: QMCPXML element for Coulomb interaction between ions.

```
<pairpot name="IonIon"   type="coulomb" source="i" target="i"/>
```

9.2.2 Pseudopotentials

QMCPACK supports pseudopotentials in semilocal form, which is local in the radial coordinate and nonlocal in angular coordinates. When all angular momentum channels above a certain threshold (ℓ_{max}) are well approximated by the same potential ($V_{\bar{\ell}} \equiv V_{loc}$), the pseudopotential separates into a fully local channel and an angularly nonlocal component:

$$V^{PP} = \sum_{ij} \left(V_{\bar{\ell}}(|r_i - \tilde{r}_j|) + \sum_{\ell \neq \bar{\ell}}^{\ell_{max}} \sum_{m=-\ell}^{\ell} |Y_{\ell m}\rangle \left[V_\ell(|r_i - \tilde{r}_j|) - V_{\bar{\ell}}(|r_i - \tilde{r}_j|) \right] \langle Y_{\ell m}| \right) . \tag{9.4}$$

Here the electron/ion index is i/j, and only one type of ion is shown for simplicity.

Evaluation of the localized pseudopotential energy $\Psi_T^{-1} V^{PP} \Psi_T$ requires additional angular integrals. These integrals are evaluated on a randomly shifted angular grid. The size of this grid is determined by ℓ_{max}. See [[MSC91]] for further detail.

uses the FSAtom pseudopotential file format associated with the "Free Software Project for Atomic-scale Simulations" initiated in 2002. See http://www.tddft.org/fsatom/manifest.php for more information. The FSAtom format uses XML for structured data. Files in this format do not use a specific identifying file extension; instead they are simply suffixed with "`.xml`." The tabular data format of CASINO is also supported.

In addition to the semilocal pseudopotential above, spin-orbit interactions can also be included through the use of spin-orbit pseudopotentials. The spin-orbit contribution can be written as

$$V^{\mathrm{SO}} = \sum_{ij} \left(\sum_{\ell=1}^{\ell_{max}-1} \frac{2}{2\ell+1} V_\ell^{\mathrm{SO}}(|r_i - \tilde{r}_j|) \sum_{m,m'=-\ell}^{\ell} |Y_{\ell m}\rangle \langle Y_{\ell m}| \vec{\ell} \cdot \vec{s} |Y_{\ell m'}\rangle \langle Y_{\ell m'}| \right) . \tag{9.5}$$

Here, $\vec{s}$ is the spin operator. For each atom with a spin-orbit contribution, the radial functions V_ℓ^{SO} can be included in the pseudopotential "`.xml`" file.

`pairpot type=pseudo` element:

parent elements:	`hamiltonian`
child elements:	`pseudo`

attributes:

Name	Datatype	Values	Default	Description
type^r	text	**pseudo**		Must be pseudo
name/id^r	text	*anything*	PseudoPot	*No current function*
source^r	text	particleset.name	i	Ion particleset name
target^r	text	particleset.name	hamiltonian.target	Electron particleset name
pbc^o	boolean	yes/no	yes*	Use Ewald summation
forces	boolean	yes/no	no	*Deprecated*
wavefunction	text	wavefunction.name	invalid	Identify wavefunction
format^r	text	xml/table	table	Select file format
algorithm^o	text	batched/non-batched	batched	Choose NLPP algorithm
DLA^o	text	yes/no	no	Use determinant localization approximation
physicalSO^o	boolean	yes/no	yes	Include the SO contribution in the local energy

Additional information:

- **type/source/target** See description for the generic pairpot factory element.
- **name:** Ignored. Instead, default names will be present in *scalar.dat output files when pseudopotentials are used. The field LocalECP refers to the local part of the pseudopotential. If nonlocal channels are present, a NonLocalECP field will be added that contains the nonlocal energy summed over all angular momentum channels.
- **pbc:** Ewald summation will not be performed if simulationcell.bconds== n n n, regardless of the value of pbc. Similarly, the pbc attribute can only be used to turn off Ewald summation if simulationcell.bconds!= n n n.
- **format:** If format==table, QMCPACK looks for *.psf files containing pseudopotential data in a tabular format. The files must be named after the ionic species provided in particleset (e.g., Li.psf and H.psf). If format==xml, additional pseudo child XML elements must be provided (see the following). These elements specify individual file names and formats (both the FSAtom XML and CASINO tabular data formats are supported).
- **algorithm** The non-batched algorithm evaluates the ratios of wavefunction components together for each quadrature point and then one point after another. The batched algorithm evaluates the ratios of quadrature points together for each wavefunction component and then one component after another. Internally, it uses VirtualParticleSet for quadrature points. Hybrid orbital representation has an extra optimization enabled when using the batched algorithm. When OpenMP offload build is enabled, the default value is batched. Otherwise, non-batched is the default.
- **DLA** Determinant localization approximation (DLA) [[ZBMAlfe19]] uses only the fermionic part of the wavefunction when calculating NLPP.
- **physicalSO** If the spin-orbit components are included in the .xml file, this flag allows control over whether the SO contribution is included in the local energy.

Listing 9.6: QMCPXML element for pseudopotential electron-ion interaction (psf files).

```
  <pairpot name="PseudoPot" type="pseudo"  source="i" wavefunction="psi0" format="psf
↪"/>
```

Listing 9.7: QMCPXML element for pseudopotential electron-ion interaction (xml files). If SOC terms present in xml, they are added to local energy

```
  <pairpot name="PseudoPot" type="pseudo"  source="i" wavefunction="psi0" format="xml
↪">
    <pseudo elementType="Li" href="Li.xml"/>
    <pseudo elementType="H" href="H.xml"/>
  </pairpot>
```

Listing 9.8: QMCPXML element for pseudopotential to accumulate the spin-orbit energy, but do not include in local energy

```
  <pairpot name="PseudoPot" type="pseudo" source="i" wavefunction="psi0" format="xml"␣
↪physicalSO="no">
    <pseudo elementType="Pb" href="Pb.xml"/>
  </pairpot>
```

Details of <pseudo/> input elements are shown in the following. It is possible to include (or construct) a full pseudopotential directly in the input file without providing an external file via `href`. The full XML format for pseudopotentials is not yet covered.

`pseudo` element:

parent elements:	`pairpot type=pseudo`
child elements:	`header local grid`

attributes:

Name	Datatype	Values	Default	Description
`elementType`/ `symbol`^{r}	text	`groupe.` `name`	none	Identify ionic species
`href`^{r}	text	*filepath*	none	Pseudopotential file path
`format`^{r}	text	xml/casino	xml	Specify file format
`cutoff`^{o}	real			Nonlocal cutoff radius
`lmax`^{o}	integer			Largest angular momentum
`nrule`^{o}	integer			Integration grid order

Listing 9.9: QMCPXML element for pseudopotential of single ionic species.

```
<pseudo elementType="Li" href="Li.xml"/>
```

9.2.3 MPC Interaction/correction

The MPC interaction is an alternative to direct Ewald summation. The MPC corrects the exchange correlation hole to more closely match its thermodynamic limit. Because of this, the MPC exhibits smaller finite-size errors than the bare Ewald interaction, though a few alternative and competitive finite-size correction schemes now exist. The MPC is itself often used just as a finite-size correction in post-processing (set `physical=false` in the input).

`pairpot type=mpc` element:

parent elements:	`hamiltonian`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**mpc**		Must be MPC
`name/ id`^{r}	text	*anything*	MPC	Unique name for interaction
`source`^{r}	text	`particleset. name`	`hamiltonian. target`	Identify interacting particles
`target`^{r}	text	`particleset. name`	`hamiltonian. target`	Identify interacting particles
`physical`^{o}	boolean	yes/no	no	Hamiltonian(yes)/observable(no)
`cutoff`	real	> 0	30.0	Kinetic energy cutoff

Remarks:

- `physical`: Typically set to `no`, meaning the standard Ewald interaction will be used during sampling and MPC will be measured as an observable for finite-size post-correction. If `physical` is `yes`, the MPC interaction will be used during sampling. In this case an electron-electron Coulomb `pairpot` element should not be supplied.
- **Developer note:** Currently the `name` attribute for the MPC interaction is ignored. The name is always reset to `MPC`.

Listing 9.10: MPC for finite-size postcorrection.

```
<pairpot type="MPC" name="MPC" source="e" target="e" ecut="60.0" physical="no"/>
```

9.3 General estimators

A broad range of estimators for physical observables are available in QMCPACK. The following sections contain input details for the total number density (`density`), number density resolved by particle spin (`spindensity`), spherically averaged pair correlation function (`gofr`), static structure factor (`sk`), static structure factor (`skall`), energy density (`energydensity`), one body reduced density matrix (`dm1b`), $S(k)$ based kinetic energy correction (`chiesa`), forward walking (`ForwardWalking`), and force (`Force`) estimators. Other estimators are not yet covered.

When an `<estimator/>` element appears in `<hamiltonian/>`, it is evaluated for all applicable chained QMC runs (e.g., VMC→DMC→DMC). Estimators are generally not accumulated during wavefunction optimization sections. If an `<estimator/>` element is instead provided in a particular `<qmc/>` element, that estimator is only evaluated for that specific section (e.g., during VMC only).

`estimator` factory element:

parent elements:	`hamiltonian, qmc`
type selector:	`type` attribute

type options	density	Density on a grid
	spindensity	Spin density on a grid
	gofr	Pair correlation function (quantum species)
	sk	Static structure factor
	SkAll	Static structure factor needed for finite size correction
	structurefactor	Species resolved structure factor
	species kinetic	Species resolved kinetic energy
	latticedeviation	Spatial deviation between two particlesets
	momentum	Momentum distribution
	energydensity	Energy density on uniform or Voronoi grid
	dm1b	One body density matrix in arbitrary basis
	chiesa	Chiesa-Ceperley-Martin-Holzmann kinetic energy correction
	Force	Family of "force" estimators (see *"Force" estimators*)
	ForwardWalking	Forward walking values for existing estimators
	orbitalimages	Create image files for orbitals, then exit
	flux	Checks sampling of kinetic energy
	localmoment	Atomic spin polarization within cutoff radius
	Pressure	*No current function*

shared attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	*See above*	0	Select estimator type
`name`^{r}	text	*anything*	any	Unique name for this estimator

9.3.1 Chiesa-Ceperley-Martin-Holzmann kinetic energy correction

This estimator calculates a finite-size correction to the kinetic energy following the formalism laid out in [[CCMH06]]. The total energy can be corrected for finite-size effects by using this estimator in conjunction with the MPC correction.

`estimator type=chiesa` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**chiesa**		Must be chiesa
`name`^{o}	text	*anything*	KEcorr	Always reset to KEcorr
`source`^{o}	text	`particleset.name`	e	Identify quantum particles
`psi`^{o}	text	`wavefunction.name`	psi0	Identify wavefunction

Listing 9.11: "Chiesa" kinetic energy finite-size postcorrection.

```
<estimator name="KEcorr" type="chiesa" source="e" psi="psi0"/>
```

9.3.2 Density estimator

The particle number density operator is given by

$$\hat{n}_r = \sum_i \delta(r - r_i) \,. \tag{9.6}$$

The `density` estimator accumulates the number density on a uniform histogram grid over the simulation cell. The value obtained for a grid cell c with volume Ω_c is then the average number of particles in that cell:

$$n_c = \int dR \, |\Psi|^2 \int_{\Omega_c} dr \sum_i \delta(r - r_i) \,. \tag{9.7}$$

`estimator type=density` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
type^r	text	**density**		Must be density
name^r	text	*anything*	any	Unique name for estimator
delta^o	real array(3)	$0 \leq v_i \leq 1$	0.1 0.1 0.1	Grid cell spacing, unit coords
x_min^o	real	> 0	0	Grid starting point in x (Bohr)
x_max^o	real	> 0	| lattice[0] |	Grid ending point in x (Bohr)
y_min^o	real	> 0	0	Grid starting point in y (Bohr)
y_max^o	real	> 0	| lattice[1] |	Grid ending point in y (Bohr)
z_min^o	real	> 0	0	Grid starting point in z (Bohr)
z_max^o	real	> 0	| lattice[2] |	Grid ending point in z (Bohr)
potential^o	boolean	yes/no	no	Accumulate local potential, *deprecated*
debug^o	boolean	yes/no	no	*No current function*

Additional information:

- name: The name provided will be used as a label in the stat.h5 file for the blocked output data. Postprocessing tools expect name="Density."
- delta: This sets the histogram grid size used to accumulate the density: delta="0.1 0.1 0.05"$\rightarrow$ $10 \times 10 \times 20$ grid, delta="0.01 0.01 0.01"$\rightarrow$ $100 \times 100 \times 100$ grid. The density grid is written to a stat.h5 file at the end of each MC block. If you request many *blocks* in a <qmc/> element, or select a large grid, the resulting stat.h5 file could be many gigabytes in size.
- *_min/*_max: Can be used to select a subset of the simulation cell for the density histogram grid. For example if a (cubic) simulation cell is 20 Bohr on a side, setting *_min=5.0 and *_max=15.0 will result in a density histogram grid spanning a $10 \times 10 \times 10$ Bohr cube about the center of the box. Use of x_min, x_max, y_min, y_max, z_min, z_max is only appropriate for orthorhombic simulation cells with open boundary conditions.
- When open boundary conditions are used, a <simulationcell/> element must be explicitly provided as the first subelement of <qmcsystem/> for the density estimator to work. In this case the molecule should be centered around the middle of the simulation cell ($L/2$) and not the origin (0 since the space within the cell, and hence the density grid, is defined from 0 to L).

Listing 9.12: QMCPXML,caption=Density estimator (uniform grid).

```
<estimator name="Density" type="density" delta="0.05 0.05 0.05"/>
```

9.3.3 Spin density estimator

The spin density is similar to the total density described previously. In this case, the sum over particles is performed independently for each spin component.

estimator type=spindensity element:

parent elements:	hamiltonian, qmc
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
type^r	text	**spindensity**		Must be spindensity
name^r	text	*anything*	any	Unique name for estimator
report^o	boolean	yes/no	no	Write setup details to stdout

parameters:

Name	Datatype	Values	Default	Description
grid^o	integer array(3)	$v_i >$		Grid cell count
dr^o	real array(3)	$v_i >$		Grid cell spacing (Bohr)
cell^o	real array(3,3)	*anything*		Volume grid exists in
corner^o	real array(3)	*anything*		Volume corner location
center^o	real array (3)	*anything*		Volume center/origin location
voronoi^o	text	particleset.name		*Under development*
test_moves^o	integer	$>= 0$	0	Test estimator with random moves

Additional information:

- name: The name provided will be used as a label in the stat.h5 file for the blocked output data. Postprocessing tools expect name="SpinDensity."
- grid: The grid sets the dimension of the histogram grid. Input like <parameter name="grid"> 40 40 40 </parameter> requests a $40 \times 40 \times 40$ grid. The shape of individual grid cells is commensurate with the supercell shape.
- dr: The dr sets the real-space dimensions of grid cell edges (Bohr units). Input like <parameter name="dr"> 0.5 0.5 0.5 </parameter> in a supercell with axes of length 10 Bohr each (but of arbitrary shape) will produce a $20 \times 20 \times 20$ grid. The inputted dr values are rounded to produce an integer number of grid cells along each supercell axis. Either grid or dr must be provided, but not both.
- cell: When cell is provided, a user-defined grid volume is used instead of the global supercell. This must be provided if open boundary conditions are used. Additionally, if cell is provided, the user must specify where the volume is located in space in addition to its size/shape (cell) using either the corner or center parameters.
- corner: The grid volume is defined as $corner + \sum_{d=1}^{3} u_d cell_d$ with $0 < u_d < 1$ ("cell" refers to either the supercell or user-provided cell).
- center: The grid volume is defined as $center + \sum_{d=1}^{3} u_d cell_d$ with $-1/2 < u_d < 1/2$ ("cell" refers to either the supercell or user-provided cell). corner/center can be used to shift the grid even if cell is not specified. Simultaneous use of corner and center will cause QMCPACK to abort.

Listing 9.13: Spin density estimator (uniform grid).

```
<estimator type="spindensity" name="SpinDensity" report="yes">
  <parameter name="grid"> 40 40 40 </parameter>
</estimator>
```

Listing 9.14: Spin density estimator (uniform grid centered about origin).

```
<estimator type="spindensity" name="SpinDensity" report="yes">
  <parameter name="grid">
    20 20 20
  </parameter>
  <parameter name="center">
    0.0 0.0 0.0
  </parameter>
  <parameter name="cell">
    10.0  0.0  0.0
     0.0 10.0  0.0
     0.0  0.0 10.0
  </parameter>
</estimator>
```

9.3.4 Pair correlation function, $g(r)$

The functional form of the species-resolved radial pair correlation function operator is

$$g_{ss'}(r) = \frac{V}{4\pi r^2 N_s N_{s'}} \sum_{i_s=1}^{N_s} \sum_{j_{s'}=1}^{N_{s'}} \delta(r - |r_{i_s} - r_{j_{s'}}|) \,, \tag{9.8}$$

where N_s is the number of particles of species s and V is the supercell volume. If $s = s'$, then the sum is restricted so that $i_s \neq j_s$.

In QMCPACK, an estimate of $g_{ss'}(r)$ is obtained as a radial histogram with a set of N_b uniform bins of width δr. This can be expressed analytically as

$$\tilde{g}_{ss'}(r) = \frac{V}{4\pi r^2 N_s N_{s'}} \sum_{i=1}^{N_s} \sum_{j=1}^{N_{s'}} \frac{1}{\delta r} \int_{r-\delta r/2}^{r+\delta r/2} dr' \delta(r' - |r_{si} - r_{s'j}|) \,, \tag{9.9}$$

where the radial coordinate r is restricted to reside at the bin centers, $\delta r/2, 3\delta r/2, 5\delta r/2, \ldots$.

`estimator type=gofr` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**gofr**		Must be gofr
`name`^{o}	text	*anything*	any	*No current function*
`num_bin`^{r}	integer	> 1	20	# of histogram bins
`rmax`^{o}	real	> 0	10	Histogram extent (Bohr)
`dr`^{o}	real	0	0.5	*No current function*
`debug`^{o}	boolean	yes/no	no	*No current function*
`target`^{o}	text	`particleset.name`	`hamiltonian.target`	Quantum particles
`source/sources`^{o}	text array	`particleset.name`	`hamiltonian.target`	Classical particles

Additional information:

- `num_bin`: This is the number of bins in each species pair radial histogram.
- `rmax`: This is the maximum pair distance included in the histogram. The uniform bin width is $\delta r =$ `rmax/num_bin`. If periodic boundary conditions are used for any dimension of the simulation cell, then the default value of `rmax` is the simulation cell radius instead of 10 Bohr. For open boundary conditions, the volume (V) used is 1.0 Bohr^3.
- `source/sources`: If unspecified, only pair correlations between each species of quantum particle will be measured. For each classical particleset specified by `source/sources`, additional pair correlations between each quantum and classical species will be measured. Typically there is only one classical particleset (e.g., `source="ion0"`), but there can be several in principle (e.g., `sources="ion0 ion1 ion2"`).
- `target`: The default value is the preferred usage (i.e., `target` does not need to be provided).
- Data is output to the `stat.h5` for each QMC subrun. Individual histograms are named according to the quantum particleset and index of the pair. For example, if the quantum particleset is named "e" and there are two species (up and down electrons, say), then there will be three sets of histogram data in each `stat.h5` file named `gofr_e_0_0`, `gofr_e_0_1`, and `gofr_e_1_1` for up-up, up-down, and down-down correlations, respectively.

Listing 9.15: Pair correlation function estimator element.

```
<estimator type="gofr" name="gofr" num_bin="200" rmax="3.0" />
```

Listing 9.16: Pair correlation function estimator element with additional electron-ion correlations.

```
<estimator type="gofr" name="gofr" num_bin="200" rmax="3.0" source="ion0" />
```

9.3.5 Static structure factor, $S(k)$

Let $\rho^e_{\mathbf{k}} = \sum_j e^{i\mathbf{k}\cdot\mathbf{r}^e_j}$ be the Fourier space electron density, with $\mathbf{r}^e_j$ being the coordinate of the j-th electron. $\mathbf{k}$ is a wavevector commensurate with the simulation cell. QMCPACK allows the user to accumulate the static electron structure factor $S(\mathbf{k})$ at all commensurate $\mathbf{k}$ such that $|\mathbf{k}| \leq (LR\_DIM\_CUTOFF)r_c$. N^e is the number of electrons, `LR_DIM_CUTOFF` is the optimized breakup parameter, and r_c is the Wigner-Seitz radius. It is defined as follows:

$$S(\mathbf{k}) = \frac{1}{N^e}\langle \rho^e_{-\mathbf{k}}\rho^e_{\mathbf{k}}\rangle \, . \tag{9.10}$$

`estimator type=sk` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	sk		Must sk
`name`^{r}	text	*anything*	any	Unique name for estimator
`hdf5`^{o}	boolean	yes/no	no	Output to `stat.h5` (yes) or `scalar.dat` (no)

Additional information:

- `name`: This is the unique name for estimator instance. A data structure of the same name will appear in `stat.h5` output files.
- `hdf5`: If `hdf5==yes`, output data for $S(k)$ is directed to the `stat.h5` file (recommended usage). If `hdf5==no`, the data is instead routed to the `scalar.dat` file, resulting in many columns of data with headings prefixed by `name` and postfixed by the k-point index (e.g., `sk_0 sk_1 ...sk_1037 ...`).
- This estimator only works in periodic boundary conditions. Its presence in the input file is ignored otherwise.
- This is not a species-resolved structure factor. Additionally, for $\mathbf{k}$ vectors commensurate with the unit cell, $S(\mathbf{k})$ will include contributions from the static electronic density, thus meaning it will not accurately measure the electron-electron density response.

Listing 9.17: Static structure factor estimator element.

```
<estimator type="sk" name="sk" hdf5="yes"/>
```

9.3.6 Static structure factor, `SkAll`

In order to compute the finite size correction to the potential energy, records of $\rho(\mathbf{k})$ is required. What sets `SkAll` apart from `sk` is that `SkAll` records $\rho(\mathbf{k})$ in addition to $s(\mathbf{k})$.

`estimator type=SkAll` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	sk		Must be sk
`name`^{r}	text	*anything*	any	Unique name for estimator
`source`^{r}	text	Ion ParticleSet name	None	-
`target`^{r}	text	Electron ParticleSet name	None	-
`hdf5`^{o}	boolean	yes/no	no	Output to `stat.h5` (yes) or `scalar.dat` (no)
`writeionion`^{o}	boolean	yes/no	no	Writes file rhok_IonIon.dat containing $s(\mathbf{k})$ for the ions

Additional information:

- `name`: This is the unique name for estimator instance. A data structure of the same name will appear in `stat.h5` output files.
- `hdf5`: If `hdf5==yes`, output data is directed to the `stat.h5` file (recommended usage). If `hdf5==no`, the data is instead routed to the `scalar.dat` file, resulting in many columns of data with headings prefixed by `rhok` and postfixed by the k-point index.
- This estimator only works in periodic boundary conditions. Its presence in the input file is ignored otherwise.

- This is not a species-resolved structure factor. Additionally, for $\mathbf{k}$ vectors commensurate with the unit cell, $S(\mathbf{k})$ will include contributions from the static electronic density, thus meaning it wil not accurately measure the electron-electron density response.

Listing 9.18: SkAll estimator element.

```
<estimator type="skall" name="SkAll" source="ion0" target="e" hdf5="yes"/>
```

9.3.7 Species kinetic energy

Record species-resolved kinetic energy instead of the total kinetic energy in the `Kinetic` column of scalar.dat. `SpeciesKineticEnergy` is arguably the simplest estimator in QMCPACK. The implementation of this estimator is detailed in `manual/estimator/estimator_implementation.pdf`.

`estimator type=specieskinetic` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	specieskinetic		Must be specieskinetic
`name`^{r}	text	*anything*	any	Unique name for estimator
`hdf5`^{o}	boolean	yes/no	no	Output to `stat.h5` (yes)

Listing 9.19: Species kinetic energy estimator element.

```
<estimator type="specieskinetic" name="skinetic" hdf5="no"/>
```

9.3.8 Lattice deviation estimator

Record deviation of a group of particles in one particle set (target) from a group of particles in another particle set (source).

`estimator type=latticedeviation` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	latticedeviation		Must be latticedeviation
`name`^{r}	text	*anything*	any	Unique name for estimator
`hdf5`^{o}	boolean	yes/no	no	Output to `stat.h5` (yes)
`per_xyz`^{o}	boolean	yes/no	no	Directionally resolved (yes)
`source`^{r}	text	e/ion0/...	no	source particleset
`sgroup`^{r}	text	u/d/...	no	source particle group
`target`^{r}	text	e/ion0/...	no	target particleset
`tgroup`^{r}	text	u/d/...	no	target particle group

Additional information:

- `source`: The "reference" particleset to measure distances from; actual reference points are determined together with `sgroup`.
- `sgroup`: The "reference" particle group to measure distances from.
- `source`: The "target" particleset to measure distances to.
- `sgroup`: The "target" particle group to measure distances to. For example, in *Listing 32* the distance from the up electron ("u") to the origin of the coordinate system is recorded.
- `per_xyz`: Used to record direction-resolved distance. In *Listing 32*, the x,y,z coordinates of the up electron will be recorded separately if `per_xyz=yes`.
- `hdf5`: Used to record particle-resolved distances in the h5 file if `gdf5=yes`.

Listing 9.20: Lattice deviation estimator element.

```
<particleset name="e" random="yes">
  <group name="u" size="1" mass="1.0">
     <parameter name="charge"              >    -1                    </parameter>
     <parameter name="mass"                >    1.0                   </parameter>
  </group>
  <group name="d" size="1" mass="1.0">
     <parameter name="charge"              >    -1                    </parameter>
     <parameter name="mass"                >    1.0                   </parameter>
  </group>
</particleset>

<particleset name="wf_center">
  <group name="origin" size="1">
    <attrib name="position" datatype="posArray" condition="0">
              0.00000000        0.00000000        0.00000000
    </attrib>
  </group>
</particleset>

<estimator type="latticedeviation" name="latdev" hdf5="yes" per_xyz="yes"
  source="wf_center" sgroup="origin" target="e" tgroup="u"/>
```

9.3.9 Energy density estimator

An energy density operator, $\hat{\mathcal{E}}_r$, satisfies

$$\int dr\hat{\mathcal{E}}_r = \hat{H}, \tag{9.11}$$

where the integral is over all space and $\hat{H}$ is the Hamiltonian. In QMCPACK, the energy density is split into kinetic and potential components

$$\hat{\mathcal{E}}_r = \hat{\mathcal{T}}_r + \hat{\mathcal{V}}_r\,, \tag{9.12}$$

with each component given by

$$\hat{\mathcal{T}}_r = \frac{1}{2}\sum_i \delta(r-r_i)\hat{p}_i^2$$

$$\hat{\mathcal{V}}_r = \sum_{i<j} \frac{\delta(r-r_i)+\delta(r-r_j)}{2}\hat{v}^{ee}(r_i,r_j) + \sum_{i\ell} \frac{\delta(r-r_i)+\delta(r-\tilde{r}_\ell)}{2}\hat{v}^{eI}(r_i,\tilde{r}_\ell) + \sum_{\ell<m} \frac{\delta(r-\tilde{r}_\ell)+\delta(r-\tilde{r}_m)}{2}\hat{v}^{II}(\tilde{r}_\ell,\tilde{r}_m)\,.$$

Here, r_i and $\tilde{r}_\ell$ represent electron and ion positions, respectively; $\hat{p}_i$ is a single electron momentum operator; and $\hat{v}^{ee}(r_i,r_j)$, $\hat{v}^{eI}(r_i,\tilde{r}_\ell)$, and $\hat{v}^{II}(\tilde{r}_\ell,\tilde{r}_m)$ are the electron-electron, electron-ion, and ion-ion pair potential operators (including nonlocal pseudopotentials, if present). This form of the energy density is size consistent; that is, the partially integrated energy density operators of well-separated atoms gives the isolated Hamiltonians of the respective atoms. For periodic systems with twist-averaged boundary conditions, the energy density is formally correct only for either a set of supercell k-points that correspond to real-valued wavefunctions or a k-point set that has inversion symmetry around a k-point having a real-valued wavefunction. For more information about the energy density, see [[KYKC13]].

In QMCPACK, the energy density can be accumulated on piecewise uniform 3D grids in generalized Cartesian, cylindrical, or spherical coordinates. The energy density integrated within Voronoi volumes centered on ion positions is also available. The total particle number density is also accumulated on the same grids by the energy density estimator for convenience so that related quantities, such as the regional energy per particle, can be computed easily.

`estimator type=EnergyDensity` element:

parent elements:	`hamiltonian, qmc`
child elements:	`reference_points, spacegrid`

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**EnergyDensity**		Must be EnergyDensity
`name`^{r}	text	*anything*		Unique name for estimator
`dynamic`^{r}	text	`particleset.name`		Identify electrons
`static`^{o}	text	`particleset.name`		Identify ions
`ion_points`^{o}	text	yes/no	no	Separate ion energy density onto point field

Additional information:

- `name`: Must be unique. A dataset with blocked statistical data for the energy density will appear in the `stat.h5` files labeled as `name`.
- **Important:** in order for the estimator to work, a traces XML input element (<traces array="yes" write="no"/>) must appear following the <qmcsystem/> element and prior to any <qmc/> element.

Listing 9.21: Energy density estimator accumulated on a $20 \times 10 \times 10$ grid over the simulation cell.

```
<estimator type="EnergyDensity" name="EDcell" dynamic="e" static="ion0">
   <spacegrid coord="cartesian">
     <origin p1="zero"/>
     <axis p1="a1" scale=".5" label="x" grid="-1 (.05) 1"/>
     <axis p1="a2" scale=".5" label="y" grid="-1 (.1) 1"/>
     <axis p1="a3" scale=".5" label="z" grid="-1 (.1) 1"/>
   </spacegrid>
</estimator>
```

Listing 9.22: Energy density estimator accumulated within spheres of radius 6.9 Bohr centered on the first and second atoms in the ion0 particleset.

```
<estimator type="EnergyDensity" name="EDatom" dynamic="e" static="ion0">
  <reference_points coord="cartesian">
    r1 1 0 0
    r2 0 1 0
    r3 0 0 1
  </reference_points>
  <spacegrid coord="spherical">
    <origin p1="ion01"/>
    <axis p1="r1" scale="6.9" label="r"     grid="0 1"/>
    <axis p1="r2" scale="6.9" label="phi"   grid="0 1"/>
    <axis p1="r3" scale="6.9" label="theta" grid="0 1"/>
  </spacegrid>
  <spacegrid coord="spherical">
    <origin p1="ion02"/>
    <axis p1="r1" scale="6.9" label="r"     grid="0 1"/>
    <axis p1="r2" scale="6.9" label="phi"   grid="0 1"/>
    <axis p1="r3" scale="6.9" label="theta" grid="0 1"/>
  </spacegrid>
</estimator>
```

Listing 9.23: Energy density estimator accumulated within Voronoi polyhedra centered on the ions.

```
<estimator type="EnergyDensity" name="EDvoronoi" dynamic="e" static="ion0">
  <spacegrid coord="voronoi"/>
</estimator>
```

The `<reference_points/>` element provides a set of points for later use in specifying the origin and coordinate axes needed to construct a spatial histogramming grid. Several reference points on the surface of the simulation cell (see Table 9.3.9), as well as the positions of the ions (see the `energydensity.static` attribute), are made available by default. The reference points can be used, for example, to construct a cylindrical grid along a bond with the origin on the bond center.

`reference_points` element:

parent elements:	`estimator type=EnergyDensity`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
coord^r	text	Cartesian/cell		Specify coordinate system

body text: The body text is a line formatted list of points with labels

Additional information:

- `coord`: If `coord=cartesian`, labeled points are in Cartesian (x,y,z) format in units of Bohr. If `coord=cell`, then labeled points are in units of the simulation cell axes.
- `body text`: The list of points provided in the body text are line formatted, with four entries per line (*label coor1 coor2 coor3*). A set of points referenced to the simulation cell is available by default (see Table 9.3.9). If `energydensity.static` is provided, the location of each individual ion is also available (e.g., if `energydensity.static=ion0`, then the location of the first atom is available with label ion01, the second with ion02, etc.). All points can be used by label when constructing spatial histogramming grids (see the following `spacegrid` element) used to collect energy densities.

label	point	description
zero	0 0 0	Cell center
a1	a_1	Cell axis 1
a2	a_2	Cell axis 2
a3	a_3	Cell axis 3
f1p	a_1/2	Cell face 1+
f1m	-a_1/2	Cell face 1-
f2p	a_2/2	Cell face 2+
f2m	-a_2/2	Cell face 2-
f3p	a_3/2	Cell face 3+
f3m	-a_3/2	Cell face 3-
cppp	$(a_1 + a_2 + a_3)/2$	Cell corner +,+,+
cppm	$(a_1 + a_2 - a_3)/2$	Cell corner +,+,-
cpmp	$(a_1 - a_2 + a_3)/2$	Cell corner +,-,+
cmpp	$(-a_1 + a_2 + a_3)/2$	Cell corner -,+,+
cpmm	$(a_1 - a_2 - a_3)/2$	Cell corner +,-,-
cmpm	$(-a_1 + a_2 - a_3)/2$	Cell corner -,+,-
cmmp	$(-a_1 - a_2 + a_3)/2$	Cell corner -,-,+
cmmm	$(-a_1 - a_2 - a_3)/2$	Cell corner -,-,-

Table 8 Reference points available by default. Vectors a_1, a_2, and a_3 refer to the simulation cell axes. The representation of the cell is centered around `zero`.

The `<spacegrid/>` element is used to specify a spatial histogramming grid for the energy density. Grids are constructed based on a set of, potentially nonorthogonal, user-provided coordinate axes. The axes are based on information available from `reference_points`. Voronoi grids are based only on nearest neighbor distances between electrons and ions. Any number of space grids can be provided to a single energy density estimator.

`spacegrid` element:

parent elements:	`estimator type=EnergyDensity`
child elements:	`origin, axis`

attributes:

Name	Datatype	Values	Default	Description
coord^r	text	Cartesian		Specify coordinate system
		cylindrical		
		spherical		
		Voronoi		

The <origin/> element gives the location of the origin for a non-Voronoi grid.

Additional information:

- p1/p2/fraction: The location of the origin is set to p1+fraction*(p2-p1). If only p1 is provided, the origin is at p1.

origin element:

parent elements:	spacegrid
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
p1^r	text	reference_point.label		Select end point
p2^o	text	reference_point.label		Select end point
fraction^o	real		0	Interpolation fraction

The <axis/> element represents a coordinate axis used to construct the, possibly curved, coordinate system for the histogramming grid. Three <axis/> elements must be provided to a non-Voronoi <spacegrid/> element.

axis element:

parent elements:	spacegrid
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
label^r	text	*See below*		Axis/dimension label
grid^r	text		"0 1"	Grid ranges/intervals
p1^r	text	reference_point.label		Select end point
p2^o	text	reference_point.label		Select end point
scale^o	real			Interpolation fraction

Additional information:

- label: The allowed set of axis labels depends on the coordinate system (i.e., spacegrid.coord). Labels are x/y/z for coord=cartesian, r/phi/z for coord=cylindrical, r/phi/theta for coord=spherical.
- p1/p2/scale: The axis vector is set to p1+scale*(p2-p1). If only p1 is provided, the axis vector is p1.
- grid: The grid specifies the histogram grid along the direction specified by label. The allowed grid points fall in the range [-1,1] for label=x/y/z or [0,1] for r/phi/theta. A grid of 10 evenly spaced points

between 0 and 1 can be requested equivalently by `grid="0 (0.1) 1"` or `grid="0 (10) 1."` Piecewise uniform grids covering portions of the range are supported, e.g., `grid="-0.7 (10) 0.0 (20) 0.5."`

- Note that `grid` specifies the histogram grid along the (curved) coordinate given by `label`. The axis specified by `p1/p2/scale` does not correspond one-to-one with `label` unless `label=x/y/z`, but the full set of axes provided defines the (sheared) space on top of which the curved (e.g., spherical) coordinate system is built.

9.3.10 One body density matrix

The N-body density matrix in DMC is $\hat{\rho}_N = |\Psi_T\rangle\langle\Psi_{FN}|$ (for VMC, substitute Ψ_T for Ψ_{FN}). The one body reduced density matrix (1RDM) is obtained by tracing out all particle coordinates but one:

$$\hat{n}_1 = \sum_n Tr_{R_n} |\Psi_T\rangle\langle\Psi_{FN}| \tag{9.13}$$

In this formula, the sum is over all electron indices and $Tr_{R_n}(*) \equiv \int dR_n \langle R_n |*| R_n\rangle$ with $R_n = [r_1, ..., r_{n-1}, r_{n+1}, ..., r_N]$. When the sum is restricted over spin-up or spin-down electrons, one obtains a density matrix for each spin species. The 1RDM computed by is partitioned in this way.

In real space, the matrix elements of the 1RDM are

$$n_1(r, r') = \langle r |\hat{n}_1| r'\rangle = \sum_n \int dR_n \Psi_T(r, R_n)\Psi^*_{FN}(r', R_n) \,. \tag{9.14}$$

A more efficient and compact representation of the 1RDM is obtained by expanding in the SPOs obtained from a Hartree-Fock or DFT calculation, $\{\phi_i\}$:

$$\begin{aligned} n_1(i,j) &= \langle\phi_i |\hat{n}_1| \phi_j\rangle \\ &= \int dR\Psi^*_{FN}(R)\Psi_T(R) \sum_n \int dr'_n \frac{\Psi_T(r'_n, R_n)}{\Psi_T(r_n, R_n)} \phi_i(r'_n)^*\phi_j(r_n) \,. \end{aligned}$$

The integration over r' in (9.15) is inefficient when one is also interested in obtaining matrices involving energetic quantities, such as the energy density matrix of [[KKR14]] or the related (and more well known) generalized Fock matrix. For this reason, an approximation is introduced as follows:

$$n_1(i,j) \approx \int dR\Psi_{FN}(R)^*\Psi_T(R) \sum_n \int dr'_n \frac{\Psi_T(r'_n, R_n)^*}{\Psi_T(r_n, R_n)^*} \phi_i(r_n)^*\phi_j(r'_n) \,. \tag{9.15}$$

For VMC, FN-DMC, FP-DMC, and RN-DMC this formula represents an exact sampling of the 1RDM corresponding to $\hat{\rho}^\dagger_N$ (see appendix A of [[KKR14]] for more detail).

`estimtor type=dm1b` element:

parent elements:	`hamiltonian, qmc`
child elements:	*None*

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**dm1b**		Must be dm1b
`name`^{r}	text	*anything*		Unique name for estimator

parameters:

Name	Datatype	Values	Default	Description
basis^r	text array	sposet.name(s)		Orbital basis
integrator^o	text	uniform_grid uniform density	uniform_grid	Integration method
evaluator^o	text	loop/matrix	loop	Evaluation method
scale^o	real	$0 < scale < 1$	1.0	Scale integration cell
center^o	real array(3)	*any point*		Center of cell
points^o	integer	> 0	10	Grid points in each dim
samples^o	integer	> 0	10	MC samples
warmup^o	integer	> 0	30	MC warmup
timestep^o	real	> 0	0.5	MC time step
use_drift^o	boolean	yes/no	no	Use drift in VMC
check_overlap^o	boolean	yes/no	no	Print overlap matrix
check_derivatives^o	boolean	yes/no	no	Check density derivatives
acceptance_ratio^o	boolean	yes/no	no	Print accept ratio
rstats^o	boolean	yes/no	no	Print spatial stats
normalized^o	boolean	yes/no	yes	basis comes norm'ed
volume_normed^o	boolean	yes/no	yes	basis norm is volume
energy_matrix^o	boolean	yes/no	no	Energy density matrix

Additional information:

- name: Density matrix results appear in stat.h5 files labeled according to name.
- basis: List sposet.name's. The total set of orbitals contained in all sposet's comprises the basis (subspace) onto which the one body density matrix is projected. This set of orbitals generally includes many virtual orbitals that are not occupied in a single reference Slater determinant.
- integrator: Select the method used to perform the additional single particle integration. Options are uniform_grid (uniform grid of points over the cell), uniform (uniform random sampling over the cell), and density (Metropolis sampling of approximate density, $\sum_{b \in \texttt{basis}} |\phi_b|^2$, is not well tested, please check results carefully!). Depending on the integrator selected, different subsets of the other input parameters are active.
- evaluator: Select for-loop or matrix multiply implementations. Matrix is preferred for speed. Both implementations should give the same results, but please check as this has not been exhaustively tested.
- scale: Resize the simulation cell by scale for use as an integration volume (active for integrator=uniform/uniform_grid).
- center: Translate the integration volume to center at this point (active for integrator=uniform/uniform_grid). If center is not provided, the scaled simulation cell is used as is.
- points: Number of grid points in each dimension for integrator=uniform_grid. For example, points=10 results in a uniform $10 \times 10 \times 10$ grid over the cell.
- samples: Sets the number of MC samples collected for each step (active for integrator=uniform/density).

- `warmup`: Number of warmup Metropolis steps at the start of the run before data collection (active for `integrator=density`).
- `timestep`: Drift-diffusion time step used in Metropolis sampling (active for `integrator=density`).
- `use_drift`: Enable drift in Metropolis sampling (active for `integrator=density`).
- `check_overlap`: Print the overlap matrix (computed via simple Riemann sums) to the log, then abort. Note that subsequent analysis based on the 1RDM is simplest if the input orbitals are orthogonal.
- `check_derivatives`: Print analytic and numerical derivatives of the approximate (sampled) density for several sample points, then abort.
- `acceptance_ratio`: Print the acceptance ratio of the density sampling to the log for each step.
- `rstats`: Print statistical information about the spatial motion of the sampled points to the log for each step.
- `normalized`: Declare whether the inputted orbitals are normalized or not. If `normalized=no`, direct Riemann integration over a $200 \times 200 \times 200$ grid will be used to compute the normalizations before use.
- `volume_normed`: Declare whether the inputted orbitals are normalized to the cell volume (default) or not (a norm of 1.0 is assumed in this case). Currently, B-spline orbitals coming from QE and HEG planewave orbitals native to QMCPACK are known to be volume normalized.
- `energy_matrix`: Accumulate the one body reduced energy density matrix, and write it to `stat.h5`. This matrix is not covered in any detail here; the interested reader is referred to [[KKR14]].

Listing 9.24: One body density matrix with uniform grid integration.

```
<estimator type="dm1b" name="DensityMatrices">
  <parameter name="basis"        >  spo_u spo_uv  </parameter>
  <parameter name="evaluator"    >  matrix        </parameter>
  <parameter name="integrator"   >  uniform_grid  </parameter>
  <parameter name="points"       >  4             </parameter>
  <parameter name="scale"        >  1.0           </parameter>
  <parameter name="center"       >  0 0 0         </parameter>
</estimator>
```

Listing 9.25: One body density matrix with uniform sampling.

```
<estimator type="dm1b" name="DensityMatrices">
  <parameter name="basis"        >  spo_u spo_uv  </parameter>
  <parameter name="evaluator"    >  matrix        </parameter>
  <parameter name="integrator"   >  uniform       </parameter>
  <parameter name="samples"      >  64            </parameter>
  <parameter name="scale"        >  1.0           </parameter>
  <parameter name="center"       >  0 0 0         </parameter>
</estimator>
```

Listing 9.26: One body density matrix with density sampling.

```
<estimator type="dm1b" name="DensityMatrices">
  <parameter name="basis"        >  spo_u spo_uv  </parameter>
  <parameter name="evaluator"    >  matrix        </parameter>
  <parameter name="integrator"   >  density       </parameter>
  <parameter name="samples"      >  64            </parameter>
  <parameter name="timestep"     >  0.5           </parameter>
  <parameter name="use_drift"    >  no            </parameter>
</estimator>
```

Listing 9.27: Example `sposet` initialization for density matrix use. Occupied and virtual orbital sets are created separately, then joined (`basis="spo_u spo_uv"`).

```
<sposet_builder type="bspline" href="../dft/pwscf_output/pwscf.pwscf.h5" tilematrix=
↪"1 0 0 0 1 0 0 0 1" meshfactor="1.0" gpu="no" precision="single">
  <sposet type="bspline" name="spo_u"  group="0" size="4"/>
  <sposet type="bspline" name="spo_d"  group="0" size="2"/>
  <sposet type="bspline" name="spo_uv" group="0" index_min="4" index_max="10"/>
</sposet_builder>
```

Listing 9.28: Example `sposet` initialization for density matrix use. Density matrix orbital basis created separately (`basis="dm_basis"`).

```
<sposet_builder type="bspline" href="../dft/pwscf_output/pwscf.pwscf.h5" tilematrix=
↪"1 0 0 0 1 0 0 0 1" meshfactor="1.0" gpu="no" precision="single">
  <sposet type="bspline" name="spo_u"  group="0" size="4"/>
  <sposet type="bspline" name="spo_d"  group="0" size="2"/>
  <sposet type="bspline" name="dm_basis" size="50" spindataset="0"/>
</sposet_builder>
```

9.4 Forward-Walking Estimators

Forward walking is a method for sampling the pure fixed-node distribution $\langle\Phi_0|\Phi_0\rangle$. Specifically, one multiplies each walker's DMC mixed estimate for the observable $\mathcal{O}$, $\frac{\mathcal{O}(\mathbf{R})\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}$, by the weighting factor $\frac{\Phi_0(\mathbf{R})}{\Psi_T(\mathbf{R})}$. As it turns out, this weighting factor for any walker $\mathbf{R}$ is proportional to the total number of descendants the walker will have after a sufficiently long projection time β.

To forward walk on an observable, declare a generic forward-walking estimator within a `<hamiltonian>` block, and then specify the observables to forward walk on and the forward-walking parameters. Here is a summary.

`estimator type=ForwardWalking` element:

parent elements:	`hamiltonian, qmc`
child elements:	`Observable`

attributes:

Name	Datatype	Values	Default	Description
`type`^{r}	text	**ForwardWalking**		Must be "ForwardWalking"
`name`^{r}	text	*anything*	any	Unique name for estimator

`Observable` element:

parent elements:	`estimator, hamiltonian, qmc`
child elements:	*None*

Name	Datatype	Values	Default	Description
name^r	text	*anything*	any	Registered name of existing estimator on which to forward walk
max^r	integer	> 0		Maximum projection time in steps (max$=\beta/\tau$)
frequency^n	text	≥ 1		Dump data only for every frequency-th to scalar.dat file

Additional information:

- **Cost**: Because histories of observables up to max time steps have to be stored, the memory cost of storing the nonforward-walked observables variables should be multiplied by max. Although this is not an issue for items such as potential energy, it could be prohibitive for observables such as density, forces, etc.
- **Naming Convention**: Forward-walked observables are automatically named FWE_name_i, where i is the forward-walked expectation value at time step i, and name is whatever name appears in the <Observable> block. This is also how it will appear in the scalar.dat file.

In the following example case, QMCPACK forward walks on the potential energy for 300 time steps and dumps the forward-walked value at every time step.

Listing 9.29: Forward-walking estimator element.

```
<estimator name="fw" type="ForwardWalking">
    <Observable name="LocalPotential" max="300" frequency="1"/>
     <!--- Additional Observable blocks go here -->
 </estimator>
```

9.5 "Force" estimators

QMCPACK supports force estimation by use of the Chiesa-Ceperly-Zhang (CCZ) estimator. Currently, open and periodic boundary conditions are supported but for all-electron calculations only.

Without loss of generality, the CCZ estimator for the z-component of the force on an ion centered at the origin is given by the following expression:

$$F_z = -Z \sum_{i=1}^{N_e} \frac{z_i}{r_i^3} [\theta(r_i - \mathcal{R}) + \theta(\mathcal{R} - r_i) \sum_{\ell=1}^{M} c_\ell r_i^\ell] \,. \tag{9.16}$$

Z is the ionic charge, M is the degree of the smoothing polynomial, $\mathcal{R}$ is a real-space cutoff of the sphere within which the bare-force estimator is smoothed, and c_ℓ are predetermined coefficients. These coefficients are chosen to minimize the weighted mean square error between the bare force estimate and the s-wave filtered estimator. Specifically,

$$\chi^2 = \int_0^{\mathcal{R}} dr\, r^m \left[f_z(r) - \tilde{f}_z(r) \right]^2 . \tag{9.17}$$

Here, m is the weighting exponent, $f_z(r)$ is the unfiltered radial force density for the z force component, and $\tilde{f}_z(r)$ is the smoothed polynomial function for the same force density. The reader is invited to refer to the original paper for a more thorough explanation of the methodology, but with the notation in hand, QMCPACK takes the following parameters.

estimator type=Force element:

parent elements:	`hamiltonian, qmc`
child elements:	`parameter`

attributes:

Name	Datatype	Values	Default	Description
`mode`^{o}	text	*See above*	bare	Select estimator type
`lrmethod`^{o}	text	ewald or srcoul	ewald	Select long-range potential breakup method
`type`^{r}	text	Force		Must be "Force"
`name`^{o}	text	*Anything*	Force-Base	Unique name for this estimator
`pbc`^{o}	boolean	yes/no	yes	Using periodic BCs or not
`addionion`^{o}	boolean	yes/no	no	Add the ion-ion force contribution to output force estimate

parameters:

Name	Datatype	Values	Default	Description
`rcut`^{o}	real	> 0	1.0	Real-space cutoff $\mathcal{R}$ in bohr
`nbasis`^{o}	integer	> 0	2	Degree of smoothing polynomial M
`weightexp`^{o}	integer	> 0	2	χ^2 weighting exponent :math`m`

Additional information:

- **Naming Convention**: The unique identifier `name` is appended with `name_X_Y` in the `scalar.dat` file, where `X` is the ion ID number and `Y` is the component ID (an integer with x=0, y=1, z=2). All force components for all ions are computed and dumped to the `scalar.dat` file.
- **Long-range breakup**: With periodic boundary conditions, it is important to converge the lattice sum when calculating Coulomb contribution to the forces. As a quick test, increase the `LR_dim_cutoff` parameter until ion-ion forces are converged. The Ewald method converges more slowly than optimized method, but the optimized method can break down in edge cases, eg. too large `LR_dim_cutoff`.
- **Miscellaneous**: Usually, the default choice of `weightexp` is sufficient. Different combinations of `rcut` and `nbasis` should be tested though to minimize variance and bias. There is, of course, a tradeoff, with larger `nbasis` and smaller `rcut` leading to smaller biases and larger variances.

The following is an example use case.

```
<simulationcell>
  ...
  <parameter name="LR_handler">  opt_breakup_original  </parameter>
  <parameter name="LR_dim_cutoff">  20  </parameter>
</simulationcell>
<hamiltonian>
  <estimator name="F" type="Force" mode="cep" addionion="yes">
    <parameter name="rcut">0.1</parameter>
    <parameter name="nbasis">4</parameter>
    <parameter name="weightexp">2</parameter>
  </estimator>
</hamiltonian>
```

9.6 Stress estimators

QMCPACK takes the following parameters.

parent elements:	`hamiltonian`

attributes:

Name	Datatype	Values	Default	Description
`mode`^{r}	text	stress	bare	Must be "stress"
`type`^{r}	text	Force		Must be "Force"
`source`^{r}	text	ion0		Name of ion particleset
`name`^{o}	text	*Anything*	ForceBase	Unique name for this estimator
`addionion`^{o}	boolean	yes/no	no	Add the ion-ion stress contribution to output

Additional information:

- **Naming Convention**: The unique identifier `name` is appended with `name_X_Y` in the `scalar.dat` file, where `X` and `Y` are the component IDs (an integer with x=0, y=1, z=2).
- **Long-range breakup**: With periodic boundary conditions, it is important to converge the lattice sum when calculating Coulomb contribution to the forces. As a quick test, increase the `LR_dim_cutoff` parameter until ion-ion stresses are converged. Check using QE "Ewald contribution", for example. The stress estimator is implemented only with the Ewald method.

The following is an example use case.

```
<simulationcell>
  ...
  <parameter name="LR_handler">  ewald  </parameter>
  <parameter name="LR_dim_cutoff">  45  </parameter>
</simulationcell>
<hamiltonian>
  <estimator name="S" type="Force" mode="stress" source="ion0"/>
</hamiltonian>
```

CHAPTER

TEN

QUANTUM MONTE CARLO METHODS

`qmc` factory element:

Parent elements	`simulation, loop`
type selector	`method` attribute

type options:

vmc	Variational Monte Carlo
linear	Wavefunction optimization with linear method
dmc	Diffusion Monte Carlo
rmc	Reptation Monte Carlo

shared attributes:

Name	Datatype	Values	Default	Description
`method`	text	listed above	invalid	QMC driver
`move`	text	pbyp, alle	pbyp	Method used to move electrons
`gpu`	text	yes/no	dep.	Use the GPU
`trace`	text		no	???
`profiling`	text	yes/no	no	Activate resume/pause control
`checkpoint`	integer	-1, 0, n	-1	Checkpoint frequency
`record`	integer	n	0	Save configuration ever n steps
`target`	text			???
`completed`	text			???
`append`	text	yes/no	no	???

Additional information:

- `move`: There are two ways to move electrons. The more used method is the particle-by-particle move. In this method, only one electron is moved for acceptance or rejection. The other method is the all-electron move; namely, all the electrons are moved once for testing acceptance or rejection.
- `gpu`: When the executable is compiled with CUDA, the target computing device can be chosen by this switch. With a regular CPU-only compilation, this option is not effective.
- `profiling`: Performance profiling tools by default profile complete application executions. This is largely unnecessary if the focus is a QMC section instead of any initialization and additional QMC sections for equilibrating walkers. Setting this flag to `yes` for the QMC sections of interest and starting the tool with data collection paused from the beginning help reducing the profiling workflow and amount of collected data. Additional restriction may be imposed by profiling tools. For example, NVIDIA profilers can only be turned on and

off once and thus only the first QMC section with `profiling="yes"` will be profiled. VTune instead allows pause and resume for unlimited times and thus multiple selected QMC sections can be profiled in a single run.

- `checkpoint`: This enables and disables checkpointing and specifying the frequency of output. Possible values are:
  - **[-1]** No checkpoint (default setting).
  - **[0]** Write the checkpoint files after the completion of the QMC section.
  - **[n]** Write the checkpoint files after every n blocks, and also at the end of the QMC section.

The particle configurations are written to a `.config.h5` file.

Listing 10.1: The following is an example of running a simulation that can be restarted.

```
<qmc method="dmc" move="pbyp"  checkpoint="0">
  <parameter name="timestep">         0.004  </parameter>
  <parameter name="blocks">           100   </parameter>
  <parameter name="steps">            400    </parameter>
</qmc>
```

The checkpoint flag instructs QMCPACK to output walker configurations. This also works in VMC. This outputs an h5 file with the name `projectid.run-number.config.h5`. Check that this file exists before attempting a restart.

To continue a run, specify the `mcwalkerset` element before your VMC/DMC block:

Listing 10.2: Restart (read walkers from previous run).

```
<mcwalkerset fileroot="BH.s002" version="0 6" collected="yes"/>
 <qmc method="dmc" move="pbyp"  checkpoint="0">
   <parameter name="timestep">         0.004  </parameter>
   <parameter name="blocks">           100   </parameter>
   <parameter name="steps">            400    </parameter>
 </qmc>
```

`BH` is the project id, and `s002` is the calculation number to read in the walkers from the previous run.

In the project id section, make sure that the series number is different from any existing ones to avoid overwriting them.

10.1 Batched drivers

Under the Exascale Computing Project effort a new set of QMC drivers was developed to eliminate the divergence of legacy CPU and GPU code paths at the QMC driver level and make the drivers CPU/GPU agnostic. The divergence came from the the fact that the CPU code path favors executing all the compute tasks within a step for one walker and then advance walker by walker. Multiple CPU threads process their own assigned walkers in parallel. In this way, walkers are not synchronized with each other and maximal throughout can be achieved on CPU. The GPU code path favors executing the same compute task over all the walkers together to maximize GPU throughput. This compute dispatch pattern minimizes the overhead of dispatching computation and host-device data transfer. However, the legacy GPU code path only leverages the OpenMP main host thread for handling all the interaction between the host and GPUs and limit the kernel dispatch capability. In brief, the CPU code path handles computation with a walker batch size of one and many batches while the GPU code path uses only one batch containing all the walkers. The new drivers that implement this flexible batching scheme are called “batched drivers”.

The batched drivers introduce a new concept, "crowd", as a sub-organization of walker population. A crowd is a subset of the walkers that are operated on as as single batch. Walkers within a crowd operate their computation in lock-step, which helps the GPU efficiency. Walkers between crowds remain fully asynchronous unless operations involving the full population are needed. With this flexible batching capability the new drivers are capable of delivering maximal performance on given hardware. In the new driver design, all the batched API calls may fallback to an existing single walker implementation. Consequently, batched drivers allow mixing and matching CPU-only and GPU-accelerated features in a way that is not feasible with the legacy GPU implementation.

For OpenMP GPU offload users, batched drivers are essential to effectively use GPUs.

10.1.1 Transition from classic drivers

Available drivers are `vmc_batch`, `dmc_batch` and `linear_batch`. There are notable changes in the driver input section when moving from classic drivers to batched drivers:

- `walkers` is not supported in any batched driver inputs. Instead, `walkers_per_rank` and `total_walkers` specify the population at the start of a driver run.
- `crowds` can added in batched drivers to specify the number of crowds.
- If a classic driver input section contains `walkers` equals 1, the same effect can be achieved by omitting the specification of `walkers_per_rank`, `total_walkers` or `crowds` in batched drivers.
- The `walkers_per_rank`, `total_walkers` or `crowds` parameters are optional. See driver-specific parameter additional information below about default values.
- When running on GPUs, tuning `walkers_per_rank` or `total_walkers` is likely needed to maximize GPU throughput, just like tuning `walkers` in the classic drivers.
- Only particle-by-particle move is supported. No all-particle move support.

10.2 Variational Monte Carlo

10.2.1 `vmc` driver

parameters:

Name	Datatype	Values	Default	Description
walkers	integer	> 0	dep.	Number of walkers per MPI task
blocks	integer	≥ 0	1	Number of blocks
steps	integer	≥ 0	1	Number of steps per block
warmupsteps	integer	≥ 0	0	Number of steps for warming up
substeps	integer	≥ 0	1	Number of substeps per step
usedrift	text	yes,no	yes	Use the algorithm with drift
timestep	real	> 0	0.1	Time step for each electron move
samples	integer	≥ 0	0	Number of walker samples for DMC/optimization
stepsbetweensamples	integer	> 0	1	Period of sample accumulation
samplesperthread	integer	≥ 0	0	Number of samples per thread
storeconfigs	integer	all values	0	Write configurations to files
blocks_between_recompute	integer	≥ 0	dep.	Wavefunction recompute frequency
spinMass	real	> 0	1.0	Effective mass for spin sampling
debug_checks	text	see additional info	dep.	Turn on/off additional recompute and checks

Additional information:

- walkers The number of walkers per MPI task. The initial default number of ixml{walkers} is one per OpenMP thread or per MPI task if threading is disabled. The number is rounded down to a multiple of the number of threads with a minimum of one per thread to ensure perfect load balancing. One walker per thread is created in the event fewer walkers than threads are requested.
- blocks This parameter is universal for all the QMC methods. The MC processes are divided into a number of blocks, each containing a number of steps. At the end of each block, the statistics accumulated in the block are dumped into files, e.g., scalar.dat. Typically, each block should have a sufficient number of steps that the I/O at the end of each block is negligible compared with the computational cost. Each block should not take so long that monitoring its progress is difficult. There should be a sufficient number of blocks to perform statistical analysis.
- warmupsteps - warmupsteps are used only for equilibration. Property measurements are not performed during warm-up steps.
- steps - steps are the number of energy and other property measurements to perform per block.
- substeps For each substep, an attempt is made to move each of the electrons once only by either particle-by-particle or an all-electron move. Because the local energy is evaluated only at each full step and not each substep, substeps are computationally cheaper and can be used to reduce the correlation between property measurements at a lower cost.
- usedrift The VMC is implemented in two algorithms with or without drift. In the no-drift algorithm, the move of each electron is proposed with a Gaussian distribution. The standard deviation is chosen as the time step input. In the drift algorithm, electrons are moved by Langevin dynamics.
- timestep The meaning of time step depends on whether or not the drift is used. In general, larger time steps reduce the time correlation but might also reduce the acceptance ratio, reducing overall statistical efficiency. For VMC, typically the acceptance ratio should be close to 50% for an efficient simulation.
- samples Separate from conventional energy and other property measurements, samples refers to storing whole electron configurations in memory ("walker samples") as would be needed by subsequent wavefunction optimization or DMC steps. *A standard VMC run to measure the energy does not need samples to be set.*

$$\texttt{samples} = \frac{\texttt{blocks} \cdot \texttt{steps} \cdot \texttt{walkers}}{\texttt{stepsbetweensamples}} \cdot \texttt{number of MPI tasks}$$

- `samplesperthread` This is an alternative way to set the target amount of samples and can be useful when preparing a stored population for a subsequent DMC calculation.

$$\texttt{samplesperthread} = \frac{\texttt{blocks} \cdot \texttt{steps}}{\texttt{stepsbetweensamples}}$$

- `stepsbetweensamples` Because samples generated by consecutive steps are correlated, having `stepsbetweensamples` larger than 1 can be used to reduces that correlation. In practice, using larger substeps is cheaper than using `stepsbetweensamples` to decorrelate samples.
- `storeconfigs` If `storeconfigs` is set to a nonzero value, then electron configurations during the VMC run are saved to files.
- `blocks_between_recompute` Recompute the accuracy critical determinant part of the wavefunction from scratch: =1 by default when using mixed precision. =0 (no recompute) by default when not using mixed precision. Recomputing introduces a performance penalty dependent on system size.
- `spinMass` Optional parameter to allow the user to change the rate of spin sampling. If spin sampling is on using `spinor` == yes in the electron ParticleSet input, the spin mass determines the rate of spin sampling, resulting in an effective spin timestep $\tau_s = \frac{\tau}{\mu_s}$. The algorithm is described in detail in [[MZG+16]] and [[MBM16]].
- `debug_checks` valid values are 'no', 'all', 'checkGL_after_moves'. If the build type is *debug*, the default value is 'all'. Otherwise, the default value is 'no'.

An example VMC section for a simple VMC run:

```
<qmc method="vmc" move="pbyp">
  <estimator name="LocalEnergy" hdf5="no"/>
  <parameter name="walkers">    256 </parameter>
  <parameter name="warmupSteps">  100 </parameter>
  <parameter name="substeps">  5 </parameter>
  <parameter name="blocks">  20 </parameter>
  <parameter name="steps">  100 </parameter>
  <parameter name="timestep">  1.0 </parameter>
  <parameter name="usedrift">   yes </parameter>
</qmc>
```

Here we set 256 `walkers` per MPI, have a brief initial equilibration of 100 `steps`, and then have 20 `blocks` of 100 `steps` with 5 `substeps` each.

The following is an example of VMC section storing configurations (walker samples) for optimization.

```
<qmc method="vmc" move="pbyp" gpu="yes">
   <estimator name="LocalEnergy" hdf5="no"/>
   <parameter name="walkers">    256 </parameter>
   <parameter name="samples">    2867200 </parameter>
   <parameter name="stepsbetweensamples">    1 </parameter>
   <parameter name="substeps">  5 </parameter>
   <parameter name="warmupSteps">  5 </parameter>
   <parameter name="blocks">  70 </parameter>
   <parameter name="timestep">  1.0 </parameter>
   <parameter name="usedrift">   no </parameter>
 </qmc>
```

10.2.2 `vmc_batch` driver (experimental)

parameters:

Name	Datatype	Values	Default	Description
`total_walkers`	integer	> 0	1	Total number of walkers over all MPI ranks
`walkers_per_rank`	integer	> 0	1	Number of walkers per MPI rank
`crowds`	integer	> 0	dep.	Number of desynchronized dwalker crowds
`blocks`	integer	≥ 0	1	Number of blocks
`steps`	integer	≥ 0	1	Number of steps per block
`warmupsteps`	integer	≥ 0	0	Number of steps for warming up
`substeps`	integer	≥ 0	1	Number of substeps per step
`usedrift`	text	yes,no	yes	Use the algorithm with drift
`timestep`	real	> 0	0.1	Time step for each electron move
`samples` (not ready)	integer	≥ 0	0	Number of walker samples for in this VMC run
`storeconfigs` (not ready)	integer	all values	0	Write configurations to files
`blocks_between_recompute`	integer	≥ 0	dep.	Wavefunction recompute frequency
`crowd_serialize_walkers`	integer	yes, no	no	Force use of single walker APIs (for testing)
`debug_checks`	text	see additional info	dep.	Turn on/off additional recompute and checks
`spin_mass`	real	≥ 0	1.0	Effective mass for spin sampling

Additional information:

- `crowds` The number of crowds that the walkers are subdivided into on each MPI rank. If not provided, it is set equal to the number of OpenMP threads.
- `walkers_per_rank` The number of walkers per MPI rank. The exact number of walkers will be generated before performing random walking. It is not required to be a multiple of the number of OpenMP threads. However, to avoid any idle resources, it is recommended to be at least the number of OpenMP threads for pure CPU runs. For GPU runs, a scan of this parameter is necessary to reach reasonable single rank efficiency and also get a balanced time to solution. If neither `total_walkers` nor `walkers_per_rank` is provided, `walkers_per_rank` is set equal to `crowds`.
- `total_walkers` Total number of walkers over all MPI ranks. if not provided, it is computed as `walkers_per_rank` times the number of MPI ranks. If both `total_walkers` and `walkers_per_rank` are provided, `total_walkers` must be equal to `walkers_per_rank` times the number MPI ranks.
- `blocks` This parameter is universal for all the QMC methods. The MC processes are divided into a number of `blocks`, each containing a number of steps. At the end of each block, the statistics accumulated in the block are dumped into files, e.g., `scalar.dat`. Typically, each block should have a sufficient number of steps that the I/O at the end of each block is negligible compared with the computational cost. Each block should not take so long that monitoring its progress is difficult. There should be a sufficient number of `blocks` to perform statistical analysis.
- `warmupsteps` - `warmupsteps` are used only for equilibration. Property measurements are not performed during warm-up steps.

- `steps` - `steps` are the number of energy and other property measurements to perform per block.
- `substeps` For each substep, an attempt is made to move each of the electrons once only by either particle-by-particle or an all-electron move. Because the local energy is evaluated only at each full step and not each substep, `substeps` are computationally cheaper and can be used to de-correlation at a low computational cost.
- `usedrift` The VMC is implemented in two algorithms with or without drift. In the no-drift algorithm, the move of each electron is proposed with a Gaussian distribution. The standard deviation is chosen as the time step input. In the drift algorithm, electrons are moved by Langevin dynamics.
- `timestep` The meaning of time step depends on whether or not the drift is used. In general, larger time steps reduce the time correlation but might also reduce the acceptance ratio, reducing overall statistical efficiency. For VMC, typically the acceptance ratio should be close to 50% for an efficient simulation.
- `samples` (not ready)
- `storeconfigs` If `storeconfigs` is set to a nonzero value, then electron configurations during the VMC run are saved to files.
- `blocks_between_recompute` Recompute the accuracy critical determinant part of the wavefunction from scratch: =1 by default when using mixed precision. =0 (no recompute) by default when not using mixed precision. Recomputing introduces a performance penalty dependent on system size.
- `debug_checks` valid values are 'no', 'all', 'checkGL_after_load', 'checkGL_after_moves', 'checkGL_after_tmove'. If the build type is *debug*, the default value is 'all'. Otherwise, the default value is 'no'.
- `spin_mass` Optional parameter to allow the user to change the rate of spin sampling. If spin sampling is on using `spinor` == yes in the electron ParticleSet input, the spin mass determines the rate of spin sampling, resulting in an effective spin timestep $\tau_s = \frac{\tau}{\mu_s}$. The algorithm is described in detail in [[MZG+16]] and [[MBM16]].

An example VMC section for a simple `vmc_batch` run:

```
<qmc method="vmc_batch" move="pbyp">
  <estimator name="LocalEnergy" hdf5="no"/>
  <parameter name="walkers_per_rank">     256 </parameter>
  <parameter name="warmupSteps">  100 </parameter>
  <parameter name="substeps">  5 </parameter>
  <parameter name="blocks">  20 </parameter>
  <parameter name="steps">  100 </parameter>
  <parameter name="timestep">  1.0 </parameter>
  <parameter name="usedrift">   yes </parameter>
</qmc>
```

Here we set 256 walkers per MPI rank, have a brief initial equilibration of 100 `steps`, and then have 20 `blocks` of 100 `steps` with 5 `substeps` each.

10.3 Wavefunction optimization

Optimizing wavefunction is critical in all kinds of real-space QMC calculations because it significantly improves both the accuracy and efficiency of computation. However, it is very difficult to directly adopt deterministic minimization approaches because of the stochastic nature of evaluating quantities with MC. Thanks to the algorithmic breakthrough during the first decade of this century and the tremendous computer power available, it is now feasible to optimize tens of thousands of parameters in a wavefunction for a solid or molecule. QMCPACK has multiple optimizers implemented based on the state-of-the-art linear method. We are continually improving our optimizers for robustness and friendliness and are trying to provide a single solution. Because of the large variation of wavefunction types

carrying distinct characteristics, using several optimizers might be needed in some cases. We strongly suggested reading recommendations from the experts who maintain these optimizers.

A typical optimization block looks like the following. It starts with method="linear" and contains three blocks of parameters.

```
<loop max="10">
 <qmc method="linear" move="pbyp" gpu="yes">
   <!-- Specify the VMC options -->
   <parameter name="walkers">              256 </parameter>
   <parameter name="samples">          2867200 </parameter>
   <parameter name="stepsbetweensamples">    1 </parameter>
   <parameter name="substeps">               5 </parameter>
   <parameter name="warmupSteps">            5 </parameter>
   <parameter name="blocks">                70 </parameter>
   <parameter name="timestep">             1.0 </parameter>
   <parameter name="usedrift">              no </parameter>
   <estimator name="LocalEnergy" hdf5="no"/>
   ...
   <!-- Specify the correlated sampling options and define the cost function -->
   <parameter name="minwalkers">            0.3 </parameter>
        <cost name="energy">               0.95 </cost>
        <cost name="unreweightedvariance"> 0.00 </cost>
        <cost name="reweightedvariance">   0.05 </cost>
   ...
   <!-- Specify the optimizer options -->
   <parameter name="MinMethod">    OneShiftOnly </parameter>
   ...
 </qmc>
</loop>

-  Loop is helpful to repeatedly execute identical optimization blocks.

-  The first part is highly identical to a regular VMC block.

-  The second part is to specify the correlated sampling options and
   define the cost function.

-  The last part is used to specify the options of different optimizers,
   which can be very distinct from one to another.
```

10.3.1 VMC run for the optimization

The VMC calculation for the wavefunction optimization has a strict requirement that `samples` or `samplesperthread` must be specified because of the optimizer needs for the stored `samples`. The input parameters of this part are identical to the VMC method.

Recommendations:

- Run the inclusive VMC calculation correctly and efficiently because this takes a significant amount of time during optimization. For example, make sure the derived `steps` per block is 1 and use larger `substeps` to control the correlation between `samples`.
- A reasonable starting wavefunction is necessary. A lot of optimization fails because of a bad wavefunction starting point. The sign of a bad initial wavefunction includes but is not limited to a very long equilibration time, low acceptance ratio, and huge variance. The first thing to do after a failed optimization is to check the information provided by the VMC calculation via `*.scalar.dat files`.

10.3.2 Correlated sampling and cost function

After generating the samples with VMC, the derivatives of the wavefunction with respect to the parameters are computed for proposing a new set of parameters by optimizers. And later, a correlated sampling calculation is performed to quickly evaluate values of the cost function on the old set of parameters and the new set for further decisions. The input parameters are listed in the following table.

`linear` method:

parameters:

Name	Datatype	Values	Default	Description
`nonlocalpp`	text	yes, no	no	include non-local PP energy in the cost function
`minwalkers`	real	0–1	0.3	Lower bound of the effective weight
`maxWeight`	real	> 1	1e6	Maximum weight allowed in reweighting

Additional information:

- `maxWeight` The default should be good.
- `nonlocalpp` The `nonlocalpp` contribution to the local energy depends on the wavefunction. When a new set of parameters is proposed, this contribution needs to be updated if the cost function consists of local energy. Fortunately, nonlocal contribution is chosen small when making a PP for small locality error. We can ignore its change and avoid the expensive computational cost. An implementation issue with GPU code is that a large amount of memory is consumed with this option.
- `minwalkers` This is a `critical` parameter. When the ratio of effective samples to actual number of samples in a reweighting step goes lower than `minwalkers`, the proposed set of parameters is invalid.

The cost function consists of three components: energy, unreweighted variance, and reweighted variance.

```
<cost name="energy">                    0.95 </cost>
<cost name="unreweightedvariance">      0.00 </cost>
<cost name="reweightedvariance">        0.05 </cost>
```

10.3.3 Optimizers

QMCPACK implements a number of different optimizers each with different priorities for accuracy, convergence, memory usage, and stability. The optimizers can be switched among “OneShiftOnly” (default), “adaptive,” “descent,” “hybrid,” and “quartic” (old) using the following line in the optimization block:

```
<parameter name="MinMethod"> THE METHOD YOU LIKE </parameter>
```

10.3.4 OneShiftOnly Optimizer

The OneShiftOnly optimizer targets a fast optimization by moving parameters more aggressively. It works with OpenMP and GPU and can be considered for large systems. This method relies on the effective weight of correlated sampling rather than the cost function value to justify a new set of parameters. If the effective weight is larger than `minwalkers`, the new set is taken whether or not the cost function value decreases. If a proposed set is rejected, the standard output prints the measured ratio of effective samples to the total number of samples and adjustment on `minwalkers` can be made if needed.

`linear` method:

parameters:

Name	Datatype	Values	Default	Description
shift_i	real	> 0	0.01	Direct stabilizer added to the Hamiltonian matrix
shift_s	real	> 0	1.00	Initial stabilizer based on the overlap matrix

Additional information:

- shift_i This is the direct term added to the diagonal of the Hamiltonian matrix. It provides more stable but slower optimization with a large value.
- shift_s This is the initial value of the stabilizer based on the overlap matrix added to the Hamiltonian matrix. It provides more stable but slower optimization with a large value. The used value is auto-adjusted by the optimizer.

Recommendations:

- Default shift_i, shift_s should be fine.
- For hard cases, increasing shift_i (by a factor of 5 or 10) can significantly stabilize the optimization by reducing the pace towards the optimal parameter set.
- If the VMC energy of the last optimization iterations grows significantly, increase minwalkers closer to 1 and make the optimization stable.
- If the first iterations of optimization are rejected on a reasonable initial wavefunction, lower the minwalkers value based on the measured value printed in the standard output to accept the move.

We recommended using this optimizer in two sections with a very small minwalkers in the first and a large value in the second, such as the following. In the very beginning, parameters are far away from optimal values and large changes are proposed by the optimizer. Having a small minwalkers makes it much easier to accept these changes. When the energy gradually converges, we can have a large minwalkers to avoid risky parameter sets.

```
<loop max="6">
 <qmc method="linear" move="pbyp" gpu="yes">
   <!-- Specify the VMC options -->
   <parameter name="walkers">               1 </parameter>
   <parameter name="samples">           10000 </parameter>
   <parameter name="stepsbetweensamples">    1 </parameter>
   <parameter name="substeps">               5 </parameter>
   <parameter name="warmupSteps">            5 </parameter>
   <parameter name="blocks">                25 </parameter>
   <parameter name="timestep">             1.0 </parameter>
   <parameter name="usedrift">              no </parameter>
   <estimator name="LocalEnergy" hdf5="no"/>
   <!-- Specify the optimizer options -->
   <parameter name="MinMethod">    OneShiftOnly </parameter>
   <parameter name="minwalkers">           1e-4 </parameter>
 </qmc>
</loop>
<loop max="12">
 <qmc method="linear" move="pbyp" gpu="yes">
   <!-- Specify the VMC options -->
   <parameter name="walkers">               1 </parameter>
   <parameter name="samples">           20000 </parameter>
   <parameter name="stepsbetweensamples">    1 </parameter>
   <parameter name="substeps">               5 </parameter>
   <parameter name="warmupSteps">            2 </parameter>
   <parameter name="blocks">                50 </parameter>
```

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```
   <parameter name="timestep">             1.0 </parameter>
   <parameter name="usedrift">              no </parameter>
   <estimator name="LocalEnergy" hdf5="no"/>
   <!-- Specify the optimizer options -->
   <parameter name="MinMethod">    OneShiftOnly </parameter>
   <parameter name="minwalkers">            0.5 </parameter>
 </qmc>
</loop>
```

For each optimization step, you will see

```
The new set of parameters is valid. Updating the trial wave function!
```

or

```
The new set of parameters is not valid. Revert to the old set!
```

Occasional rejection is fine. Frequent rejection indicates potential problems, and users should inspect the VMC calculation or change optimization strategy. To track the progress of optimization, use the command `qmca -q ev *.scalar.dat` to look at the VMC energy and variance for each optimization step.

10.3.5 Adaptive Optimizer

The default setting of the adaptive optimizer is to construct the linear method Hamiltonian and overlap matrices explicitly and add different shifts to the Hamiltonian matrix as "stabilizers." The generalized eigenvalue problem is solved for each shift to obtain updates to the wavefunction parameters. Then a correlated sampling is performed for each shift's updated wavefunction and the initial trial wavefunction using the middle shift's updated wavefunction as the guiding function. The cost function for these wavefunctions is compared, and the update corresponding to the best cost function is selected. In the next iteration, the median magnitude of the stabilizers is set to the magnitude that generated the best update in the current iteration, thus adapting the magnitude of the stabilizers automatically.

When the trial wavefunction contains more than 10,000 parameters, constructing and storing the linear method matrices could become a memory bottleneck. To avoid explicit construction of these matrices, the adaptive optimizer implements the block linear method (BLM) approach. [[ZN17]] The BLM tries to find an approximate solution $\vec{c}_{opt}$ to the standard LM generalized eigenvalue problem by dividing the variable space into a number of blocks and making intelligent estimates for which directions within those blocks will be most important for constructing $\vec{c}_{opt}$, which is then obtained by solving a smaller, more memory-efficient eigenproblem in the basis of these supposedly important block-wise directions.

`linear` method:

parameters:

Name	Datatype	Values	Default	Description
max_relative_change	real	> 0	10.0	Allowed change in cost function
max_param_change	real	> 0	0.3	Allowed change in wavefunction parameter
shift_i	real	> 0	0.01	Initial diagonal stabilizer added to the Hamiltonian matrix
shift_s	real	> 0	1.00	Initial overlap-based stabilizer added to the Hamiltonian matrix
target_shift_i	real	any	-1.0	Diagonal stabilizer value aimed for during adaptive method (disabled if ≤ 0)
cost_increase_tol	real	≥ 0	0.0	Tolerance for cost function increases
chase_lowest	text	yes, no	yes	Chase the lowest eigenvector in iterative solver
chase_closest	text	yes, no	no	Chase the eigenvector closest to initial guess
block_lm	text	yes, no	no	Use BLM
blocks	integer	> 0		Number of blocks in BLM
nolds	integer	> 0		Number of old update vectors used in BLM
nkept	integer	> 0		Number of eigenvectors to keep per block in BLM

Additional information:

- shift_i This is the initial coefficient used to scale the diagonal stabilizer. More stable but slower optimization is expected with a large value. The adaptive method will automatically adjust this value after each linear method iteration.
- shift_s This is the initial coefficient used to scale the overlap-based stabilizer. More stable but slower optimization is expected with a large value. The adaptive method will automatically adjust this value after each linear method iteration.
- target_shift_i If set greater than zero, the adaptive method will choose the update whose shift_i value is closest to this target value so long as the associated cost is within cost_increase_tol of the lowest cost. Disable this behavior by setting target_shift_i to a negative number.
- cost_increase_tol Tolerance for cost function increases when selecting the best shift.
- nblocks This is the number of blocks used in BLM. The amount of memory required to store LM matrices decreases as the number of blocks increases. But the error introduced by BLM would increase as the number of blocks increases.
- nolds In BLM, the interblock correlation is accounted for by including a small number of wavefunction update vectors outside the block. Larger would include more interblock correlation and more accurate results but also higher memory requirements.
- nkept This is the number of update directions retained from each block in the BLM. If all directions are retained in each block, then the BLM becomes equivalent to the standard LM. Retaining five or fewer directions per block is often sufficient.

Recommendations:

- Default shift_i, shift_s should be fine.
- When there are fewer than about 5,000 variables being optimized, the traditional LM is preferred because it has a lower overhead than the BLM when the number of variables is small.
- Initial experience with the BLM suggests that a few hundred blocks and a handful of and often provide a good balance between memory use and accuracy. In general, using fewer blocks should be more accurate but would

require more memory.

```
<loop max="15">
 <qmc method="linear" move="pbyp">
   <!-- Specify the VMC options -->
   <parameter name="walkers">                1 </parameter>
   <parameter name="samples">            20000 </parameter>
   <parameter name="stepsbetweensamples">    1 </parameter>
   <parameter name="substeps">               5 </parameter>
   <parameter name="warmupSteps">            5 </parameter>
   <parameter name="blocks">                50 </parameter>
   <parameter name="timestep">             1.0 </parameter>
   <parameter name="usedrift">              no </parameter>
   <estimator name="LocalEnergy" hdf5="no"/>
   <!-- Specify the correlated sampling options and define the cost function -->
        <cost name="energy">               1.00 </cost>
        <cost name="unreweightedvariance"> 0.00 </cost>
        <cost name="reweightedvariance">   0.00 </cost>
   <!-- Specify the optimizer options -->
   <parameter name="MinMethod">adaptive</parameter>
   <parameter name="max_relative_cost_change">10.0</parameter>
   <parameter name="shift_i"> 1.00 </parameter>
   <parameter name="shift_s"> 1.00 </parameter>
   <parameter name="max_param_change"> 0.3 </parameter>
   <parameter name="chase_lowest"> yes </parameter>
   <parameter name="chase_closest"> yes </parameter>
   <parameter name="block_lm"> no </parameter>
   <!-- Specify the BLM specific options if needed
     <parameter name="nblocks"> 100 </parameter>
     <parameter name="nolds"> 5 </parameter>
     <parameter name="nkept"> 3 </parameter>
   -->
 </qmc>
</loop>
```

The adaptive optimizer is also able to optimize individual excited states directly. [[ZN16]] In this case, it tries to minimize the following function:

$$\Omega[\Psi] = \frac{\langle\Psi|\omega - H|\Psi\rangle}{\left\langle\Psi|(\omega - H)^2|\Psi\right\rangle}.$$

The global minimum of this function corresponds to the state whose energy lies immediately above the shift parameter ω in the energy spectrum. For example, if ω were placed in between the ground state energy and the first excited state energy and the wavefunction ansatz was capable of a good description for the first excited state, then the wavefunction would be optimized for the first excited state. Note that if the ansatz is not capable of a good description of the excited state in question, the optimization could converge to a different state, as is known to occur in some circumstances for traditional ground state optimizations. Note also that the ground state can be targeted by this method by choosing ω to be below the ground state energy, although we should stress that this is not the same thing as a traditional ground state optimization and will in general give a slightly different wavefunction. Excited state targeting requires two additional parameters, as shown in the following table.

Excited state targeting:

parameters:

Name	Datatype	Values	Default	Description
targetExcited	text	yes, no	no	Whether to use the excited state targeting optimization
omega	real	real numbers	none	Energy shift used to target different excited states

Excited state recommendations:

- Because of the finite variance in any approximate wavefunction, we recommended setting $\omega = \omega_0 - \sigma$, where ω_0 is placed just below the energy of the targeted state and σ^2 is the energy variance.
- To obtain an unbiased excitation energy, the ground state should be optimized with the excited state variational principle as well by setting omega below the ground state energy. Note that using the ground state variational principle for the ground state and the excited state variational principle for the excited state creates a bias in favor of the ground state.

10.3.6 Descent Optimizer

Gradient descent algorithms are an alternative set of optimization methods to the OneShiftOnly and adaptive optimizers based on the linear method. These methods use only first derivatives to optimize trial wave functions and convergence can be accelerated by retaining a memory of previous derivative values. Multiple flavors of accelerated descent methods are available. They differ in details such as the schemes for adaptive adjustment of step sizes. [[ON19]] Descent algorithms avoid the construction of matrices that occurs in the linear method and consequently can be applied to larger sets of optimizable parameters. Parameters for descent are shown in the table below.

descent method:

parameters:

Name	Datatype	Values	Default	Description
flavor	text	RMSprop, Random, ADAM, AMSGrad	RMSprop	Particular type of descent method
Ramp_eta	text	yes, no	no	Whether to gradually ramp up step sizes
Ramp_num	integer	> 0	30	Number of steps over which to ramp up step size
TJF_2Body_eta	real	> 0	0.01	Step size for two body Jastrow parameters
TJF_1Body_eta	real	> 0	0.01	Step size for one body Jastrow parameters
F_eta	real	> 0	0.001	Step size for number counting Jastrow F matrix parameters
Gauss_eta	real	> 0	0.001	Step size for number counting Jastrow gaussian basis parameters
CI_eta	real	> 0	0.01	Step size for CI parameters
Orb_eta	real	> 0	0.001	Step size for orbital parameters
collection_step	real	> 0	0.01	Step number to start collecting samples for final averages
compute_step	real	> 0	0.001	Step number to start computing averaged from stored history
print_derivs	real	yes, no	no	Whether to print parameter derivatives

These descent algorithms have been extended to the optimization of the same excited state functional as the adaptive LM. [[LON20]] This also allows the hybrid optimizer discussed below to be applied to excited states. The relevant parameters are the same as for targeting excited states with the adaptive optimizer above.

Additional information and recommendations:

- It is generally advantageous to set different step sizes for different types of parameters. More nonlinear parameters such as those for number counting Jastrow factors or orbitals typically require smaller steps sizes than those for CI coefficients or traditional Jastrow parameters. There are defaults for several parameter types and a default of .001 has been chosen for all other parameters.
- The ability to gradually ramp up step sizes to their input values is useful for avoiding spikes in the average local energy during early iterations of descent optimization. This initial rise in the energy occurs as a memory of past gradients is being built up and it may be possible for the energy to recover without ramping if there are enough iterations in the optimization.
- The step sizes chosen can have a substantial influence on the quality of the optimization and the final variational energy achieved. Larger step sizes may be helpful if there is reason to think the descent optimization is not reaching the minimum energy. There are also additional hyperparameters in the descent algorithms with default values. [[ON19]] They seem to have limited influence on the effectiveness of the optimization compared to step sizes, but users can adjust them within the source code of the descent engine if they wish.
- The sampling effort for individual descent steps can be small compared that for linear method iterations as shown in the example input below. Something in the range of 10,000 to 30,000 seems sufficient for molecules with tens of electrons. However, descent optimizations may require anywhere from a few hundred to a few thousand iterations.
- For reporting quantities such as a final energy and associated uncertainty, an average over many descent steps can be taken. The parameters for `collection_step` and `compute_step` help automate this task. After the descent iteration specified by `collection_step`, a history of local energy values will be kept for determining a final error and average, which will be computed and given in the output once the iteration specified by `compute_step` is reached. For reasonable results, this procedure should use descent steps near the end of the optimization when the wave function parameters are essentially no longer changing.
- In cases where a descent optimization struggles to reach the minimum and a linear method optimization is not possible or unsatisfactory, it may be useful to try the hybrid optimization approach described in the next subsection.

```
<loop max="2000">
   <qmc method="linear" move="pbyp" checkpoint="-1" gpu="no">

   <!-- VMC inputs -->
    <parameter name="blocks">2000</parameter>
    <parameter name="steps">1</parameter>
    <parameter name="samples">20000</parameter>
    <parameter name="warmupsteps">100</parameter>
    <parameter name="timestep">0.05</parameter>

    <parameter name="MinMethod">descent</parameter>
    <estimator name="LocalEnergy" hdf5="no"/>
    <parameter name="usebuffer">yes</parameter>

    <estimator name="LocalEnergy" hdf5="no"/>

    <!-- Descent Inputs -->
      <parameter name="flavor">RMSprop</parameter>

      <parameter name="Ramp_eta">no</parameter>
      <parameter name="Ramp_num">30</parameter>
```

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```
     <parameter name="TJF_2Body_eta">.02</parameter>
      <parameter name="TJF_1Body_eta">.02</parameter>
     <parameter name="F_eta">.001</parameter>
     <parameter name="Gauss_eta">.001</parameter>
     <parameter name="CI_eta">.1</parameter>
     <parameter name="Orb_eta">.0001</parameter>

     <parameter name="collection_step">500</parameter>
     <parameter name="compute_step">998</parameter>

    <parameter name="targetExcited"> yes </parameter>
    <parameter name="targetExcited"> -11.4 </parameter>

     <parameter name="print_derivs">no</parameter>


   </qmc>
</loop>
```

10.3.7 Hybrid Optimizer

Another optimization option is to use a hybrid combination of accelerated descent and blocked linear method. It provides a means to retain the advantages of both individual methods while scaling to large numbers of parameters beyond the traditional 10,000 parameter limit of the linear method. [[ON19]] In a hybrid optimization, alternating sections of descent and BLM optimization are used. Gradient descent is used to identify the previous important directions in parameter space used by the BLM, the number of which is set by the `nold` input for the BLM. Over the course of a section of descent, vectors of parameter differences are stored and then passed to the linear method engine after the optimization changes to the BLM. One motivation for including sections of descent is to counteract noise in linear method updates due to uncertainties in its step direction and allow for a smoother movement to the minimum. There are two additional parameters used in the hybrid optimization and it requires a slightly different format of input to specify the constituent methods as shown below in the example.

`descent` method:

parameters:

Name	Datatype	Values	Default	Description
`num_updates`	integer	> 0		Number of steps for a method
`Stored_Vectors`	integer	> 0	5	Number of vectors to transfer to BLM

```
<loop max="203">
<qmc method="linear" move="pbyp" checkpoint="-1" gpu="no">
 <parameter name="Minmethod"> hybrid </parameter>

 <optimizer num_updates="100">

<parameter name="blocks">1000</parameter>
     <parameter name="steps">1</parameter>
     <parameter name="samples">20000</parameter>
     <parameter name="warmupsteps">1000</parameter>
     <parameter name="timestep">0.05</parameter>
```

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```
    <estimator name="LocalEnergy" hdf5="no"/>

    <parameter name="Minmethod"> descent </parameter>
    <parameter name="Stored_Vectors">5</parameter>
    <parameter name="flavor">RMSprop</parameter>
    <parameter name="TJF_2Body_eta">.01</parameter>
    <parameter name="TJF_1Body_eta">.01</parameter>
    <parameter name="CI_eta">.1</parameter>

    <parameter name="Ramp_eta">no</parameter>
    <parameter name="Ramp_num">10</parameter>
 </optimizer>

 <optimizer num_updates="3">

    <parameter name="blocks">2000</parameter>
    <parameter name="steps">1</parameter>
    <parameter name="samples">1000000</parameter>
    <parameter name="warmupsteps">1000</parameter>
    <parameter name="timestep">0.05</parameter>

    <estimator name="LocalEnergy" hdf5="no"/>

    <parameter name="Minmethod"> adaptive </parameter>
    <parameter name="max_relative_cost_change">10.0</parameter>
    <parameter name="max_param_change">3</parameter>
    <parameter name="shift_i">0.01</parameter>
    <parameter name="shift_s">1.00</parameter>

    <parameter name="block_lm">yes</parameter>
    <parameter name="nblocks">2</parameter>
    <parameter name="nolds">5</parameter>
    <parameter name="nkept">5</parameter>

 </optimizer>
</qmc>
</loop>
```

Additional information and recommendations:

- In the example above, the input for `loop` gives the total number of steps for the full optimization while the inputs for `num_updates` specify the number of steps in the constituent methods. For this case, the optimization would begin with 100 steps of descent using the parameters in the first `optimizer` block and then switch to the BLM for 3 steps before switching back to descent for the final 100 iterations of the total of 203.
- The design of the hybrid method allows for more than two `optimizer` blocks to be used and the optimization will cycle through the individual methods. However, the effectiveness of this in terms of the quality of optimization results is unexplored.
- It can be useful to follow a hybrid optimization with a section of pure descent optimization and take an average energy over the last few hundred iterations as the final variational energy. This approach can achieve a lower statistical uncertainty on the energy for less overall sampling effort compared to what a pure linear method optimization would require. The `collection_step` and `compute_step` parameters discussed earlier for descent are useful for setting up the descent engine to do this averaging on its own.

10.3.8 Quartic Optimizer

This is an older optimizer method retained for compatibility. We recommend starting with the newest OneShiftOnly or adaptive optimizers. The quartic optimizer fits a quartic polynomial to 7 values of the cost function obtained using reweighting along the chosen direction and determines the optimal move. This optimizer is very robust but is a bit conservative when accepting new steps, especially when large parameters changes are proposed.

`linear` method:

parameters:

Name	Datatype	Values	Default	Description
`bigchange`	real	> 0	50.0	Largest parameter change allowed
`alloweddifference`	real	> 0	1e-4	Allowed increase in energy
`exp0`	real	any value	-16.0	Initial value for stabilizer
`stabilizerscale`	real	> 0	2.0	Increase in value of `exp0` between iterations
`nstabilizers`	integer	> 0	3	Number of stabilizers to try
`max_its`	integer	> 0	1	Number of inner loops with same samples

Additional information:

- `exp0` This is the initial value for stabilizer (shift to diagonal of H). The actual value of stabilizer is 10^{exp0}.

Recommendations:

- For hard cases (e.g., simultaneous optimization of long MSD and 3-Body J), set `exp0` to 0 and do a single inner iteration (max its=1) per sample of configurations.

```
<!-- Specify the optimizer options -->
<parameter name="MinMethod">quartic</parameter>
<parameter name="exp0">-6</parameter>
<parameter name="alloweddifference"> 1.0e-4 </parameter>
<parameter name="nstabilizers"> 1 </parameter>
<parameter name="bigchange">15.0</parameter>
```

10.3.9 General Recommendations

- All electron wavefunctions are typically more difficult to optimize than pseudopotential wavefunctions because of the importance of the wavefunction near the nucleus.
- Two-body Jastrow contributes the largest portion of correlation energy from bare Slater determinants. Consequently, the recommended order for optimizing wavefunction components is two-body, one-body, three-body Jastrow factors and MSD coefficients.
- For two-body spline Jastrows, always start from a reasonable one. The lack of physically motivated constraints in the functional form at large distances can cause slow convergence if starting from zero.
- One-body spline Jastrow from old calculations can be a good starting point.
- Three-body polynomial Jastrow can start from zero. It is beneficial to first optimize one-body and two-body Jastrow factors without adding three-body terms in the calculation and then add the three-body Jastrow and optimize all the three components together.

Optimization of CI coefficients

When storing a CI wavefunction in HDF5 format, the CI coefficients and the α and β components of each CI are not in the XML input file. When optimizing the CI coefficients, they will be stored in HDF5 format. The optimization header block will have to specify that the new CI coefficients will be saved to HDF5 format. If the tag is not added coefficients will not be saved.

```
<qmc method="linear" move="pbyp" gpu="no" hdf5="yes">

The rest of the optimization block remains the same.
```

When running the optimization, the new coefficients will be stored in a `*.sXXX.opt.h5` file, where XXX coressponds to the series number. The H5 file contains only the optimized coefficients. The corresponding `*.sXXX.opt.xml` will be updated for each optimization block as follows:

```
<detlist size="1487" type="DETS" nca="0" ncb="0" nea="2" neb="2" nstates="85" cutoff=
↪"1e-2" href="../LiH.orbs.h5" opt_coeffs="LiH.s001.opt.h5"/>
```

The opt_coeffs tag will then reference where the new CI coefficients are stored.

When restarting the run with the new optimized coeffs, you need to specify the previous hdf5 containing the basis set, orbitals, and MSD, as well as the new optimized coefficients. The code will read the previous data but will rewrite the coefficients that were optimized with the values found in the *.sXXX.opt.h5 file. Be careful to keep the pair of optimized CI coefficients and Jastrow coefficients together to avoid inconsistencies.

10.3.10 Output of intermediate values

Use the following parameters to the linear optimizers to output intermediate values such as the overlap and Hamiltonian matrices.

Name	Datatype	Values	Default	Description
`output_matrices_csv`	text	yes, no	no	Output linear method matrices to CSV files
`output_matrices_hdf`	text	yes, no	no	Output linear method matrices to HDF file
`freeze_parameters`	text	yes, no	no	Do not update parameters between iterations

The `output_matrices_csv` parameter will write to <base name>.ham.s000.scalar.dat and <base name>.ovl.scalar.dat. One line per iteration of the optimizer loop. Combined with `freeze_parameters`, this allows computing error bars on the matrices for use in regression testing.

The `output_matrices_hdf` parameter will output in HDF format the matrices used in the linear method along with the shifts and the eigenvalue and eigenvector produced by QMCPACK. The file is named "<base name>.<series number>.linear_matrices.h5". It only works with the batched optimizer (`linear_batch`)

10.4 Diffusion Monte Carlo

10.4.1 dmc driver

Main input parameters are given in Table 10.4.1, additional in Table 10.4.1.

parameters:

Name	Datatype	Values	Default	Description
targetwalkers	integer	> 0	dep.	Overall total number of walkers
blocks	integer	≥ 0	1	Number of blocks
steps	integer	≥ 0	1	Number of steps per block
warmupsteps	integer	≥ 0	0	Number of steps for warming up
timestep	real	> 0	0.1	Time step for each electron move
nonlocalmoves	string	yes, no, v0, v1, v3	no	Run with T-moves
branching_cutoff_scheme	string	classic/DRV/ZSGMA/YL	classic	Branch cutoff scheme
maxcpusecs	real	≥ 0	3.6e5	Deprecated. Superseded by max_seconds
max_seconds	real	≥ 0	3.6e5	Maximum allowed walltime in seconds
blocks_between_recompute	integer	≥ 0	dep.	Wavefunction recompute frequency
spinMass	real	> 0	1.0	Effective mass for spin sampling
debug_checks	text	see additional info	dep.	Turn on/off additional recompute and checks

Table 9 Main DMC input parameters.

Name	Datatype	Values	Default	Description
energyUpdateInterval	integer	≥ 0	0	Trial energy update interval
refEnergy	real	all values	dep.	Reference energy in atomic units
feedback	double	≥ 0	1.0	Population feedback on the trial energy
sigmaBound	10	≥ 0	10	Parameter to cutoff large weights
killnode	string	yes/other	no	Kill or reject walkers that cross nodes
warmupByReconfiguration	option	yes,no	0	Warm up with a fixed population
reconfiguration	string	yes/pure/other	no	Fixed population technique
branchInterval	integer	≥ 0	1	Branching interval
substeps	integer	≥ 0	1	Branching interval
MaxAge	double	≥ 0	10	Kill persistent walkers
MaxCopy	double	≥ 0	2	Limit population growth
maxDisplSq	real	all values	-1	Maximum particle move
scaleweight	string	yes/other	yes	Scale weights (CUDA only)
checkproperties	integer	≥ 0	100	Number of steps between walker updates
fastgrad	text	yes/other	yes	Fast gradients
storeconfigs	integer	all values	0	Store configurations
use_nonblocking	string	yes/no	yes	Using nonblocking send/recv
debug_disable_branching	string	yes/no	no	Disable branching for debugging without correctness guarantee

Table 10 Additional DMC input parameters.

Additional information:

- `targetwalkers`: A DMC run can be considered a restart run or a new run. A restart run is considered to be any method block beyond the first one, such as when a DMC method block follows a VMC block. Alternatively, a user reading in configurations from disk would also considered a restart run. In the case of a restart run, the DMC driver will use the configurations from the previous run, and this variable will not be used. For a new run, if the number of walkers is less than the number of threads, then the number of walkers will be set equal to the number of threads.
- `blocks`: This is the number of blocks run during a DMC method block. A block consists of a number of DMC steps (steps), after which all the statistics accumulated in the block are written to disk.
- `steps`: This is the number of DMC steps in a block.
- `warmupsteps`: These are the steps at the beginning of a DMC run in which the instantaneous average energy is used to update the trial energy. During regular steps, E_{ref} is used.
- `timestep`: The `timestep` determines the accuracy of the imaginary time propagator. Generally, multiple time steps are used to extrapolate to the infinite time step limit. A good range of time steps in which to perform time step extrapolation will typically have a minimum of 99% acceptance probability for each step.
- `checkproperties`: When using a particle-by-particle driver, this variable specifies how often to reset all the variables kept in the buffer.
- `maxcpusecs`: Deprecated. Superseded by `max_seconds`.
- `max_seconds`: The default is 100 hours. Once the specified time has elapsed, the program will finalize the simulation even if all blocks are not completed.
- `spinMass` This is an optional parameter to allow the user to change the rate of spin sampling. If spin sampling is on using `spinor` == yes in the electron ParticleSet input, the spin mass determines the rate of spin sampling, resulting in an effective spin timestep $\tau_s = \frac{\tau}{\mu_s}$ where τ is the normal spatial timestep and μ_s is the value of the spin mass. The algorithm is described in detail in [[MZG+16]] and [[MBM16]].
- `debug_checks` valid values are 'no', 'all', 'checkGL_after_moves'. If the build type is *debug*, the default value is 'all'. Otherwise, the default value is 'no'.
- `energyUpdateInterval`: The default is to update the trial energy at every step. Otherwise the trial energy is updated every `energyUpdateInterval` step.

$$E_{\text{trial}} = \text{refEnergy} + \text{feedback} \cdot (\ln \texttt{targetWalkers} - \ln N) \,,$$

where N is the current population.

- `refEnergy`: The default reference energy is taken from the VMC run that precedes the DMC run. This value is updated to the current mean whenever branching happens.
- `feedback`: This variable is used to determine how strong to react to population fluctuations when doing population control. See the equation in energyUpdateInterval for more details.
- `useBareTau`: The same time step is used whether or not a move is rejected. The default is to use an effective time step when a move is rejected.
- `warmupByReconfiguration`: Warmup DMC is done with a fixed population.
- `sigmaBound`: This determines the branch cutoff to limit wild weights based on the sigma and `sigmaBound`.
- `killnode`: When running fixed-node, if a walker attempts to cross a node, the move will normally be rejected. If `killnode` = "yes," then walkers are destroyed when they cross a node.
- `reconfiguration`: If `reconfiguration` is "yes," then run with a fixed walker population using the reconfiguration technique.

- `branchInterval`: This is the number of steps between branching. The total number of DMC steps in a block will be `BranchInterval`*Steps.
- `substeps`: This is the same as `BranchInterval`.
- `nonlocalmoves`: Evaluate pseudopotentials using one of the nonlocal move algorithms such as T-moves.
  - no(default): Imposes the locality approximation.
  - yes/v0: Implements the algorithm in the 2006 Casula paper [[Cas06]].
  - v1: Implements the v1 algorithm in the 2010 Casula paper [[CMSF10]].
  - v2: Is **not implemented** and is **skipped** to avoid any confusion with the v2 algorithm in the 2010 Casula paper [[CMSF10]].
  - v3: (Experimental) Implements an algorithm similar to v1 but is much faster. v1 computes the transition probability before each single electron T-move selection because of the acceptance of previous T-moves. v3 mostly reuses the transition probability computed during the evaluation of nonlocal pseudopotentials for the local energy, namely before accepting any T-moves, and only recomputes the transition probability of the electrons within the same pseudopotential region of any electrons touched by T-moves. This is an approximation to v1 and results in a slightly different time step error, but it significantly reduces the computational cost. v1 and v3 agree at zero time step. This faster algorithm is the topic of a paper in preparation.

    The v1 and v3 algorithms are size-consistent and are important advances over the previous v0 non-size-consistent algorithm. We highly recommend investigating the importance of size-consistency.
- `scaleweight`: This is the scaling weight per Umrigar/Nightingale. CUDA only.
- `MaxAge`: Set the weight of a walker to min(currentweight,0.5) after a walker has not moved for `MaxAge` steps. Needed if persistent walkers appear during the course of a run.
- `MaxCopy`: When determining the number of copies of a walker to branch, set the number of copies equal to min(Multiplicity,MaxCopy).
- `fastgrad`: This calculates gradients with either the fast version or the full-ratio version.
- `maxDisplSq`: When running a DMC calculation with particle by particle, this sets the maximum displacement allowed for a single particle move. All distance displacements larger than the max are rejected. If initialized to a negative value, it becomes equal to Lattice(LR/rc).
- `sigmaBound`: This determines the branch cutoff to limit wild weights based on the sigma and `sigmaBound`.
- `storeconfigs`: If `storeconfigs` is set to a nonzero value, then electron configurations during the DMC run will be saved. This option is disabled for the OpenMP version of DMC.
- `blocks_between_recompute`: See details in *Variational Monte Carlo*.
- `branching_cutoff_scheme`: Modifies how the branching factor is computed so as to avoid divergences and stability problems near nodal surfaces.
  - classic (default): The implementation found in QMCPACK v3.0.0 and earlier. $E_{\rm cut} = \min(\max(\sigma^2 \times \mathrm{sigmaBound}, \mathrm{maxSigma}), 2.5/\tau)$, where σ^2 is the variance and $\mathrm{maxSigma}$ is set to 50 during warmup (equilibration) and 10 thereafter. $\mathrm{sigmaBound}$ is default to 10.
  - DRV: Implements the algorithm of DePasquale et al., Eq. 3 in [[DRV88]] or Eq. 9 of [[UNR93]]. $E_{\rm cut} = 2.0/\sqrt{\tau}$.
  - ZSGMA: Implements the "ZSGMA" algorithm of [[ZSG+16]] with $\alpha = 0.2$. The cutoff energy is modified by a factor including the electron count, $E_{\rm cut} = \alpha\sqrt{N/\tau}$, which greatly improves size consistency over Eq. 39 of [[UNR93]]. See Eq. 6 in [[ZSG+16]] and for an application to molecular crystals [[ZBKlimevs+18]].

– YL: An unpublished algorithm due to Ye Luo. $E_{\rm cut} = \sigma \times \min(\text{sigmaBound}, \sqrt{1/\tau})$. This option takes into account both size consistency and wavefunction quality via the term σ. sigmaBound is default to 10.

Listing 10.3: The following is an example of a very simple DMC section.

```
<qmc method="dmc" move="pbyp" target="e">
  <parameter name="blocks">100</parameter>
  <parameter name="steps">400</parameter>
  <parameter name="timestep">0.010</parameter>
  <parameter name="warmupsteps">100</parameter>
</qmc>
```

The time step should be individually adjusted for each problem. Please refer to the theory section on diffusion Monte Carlo.

Listing 10.4: The following is an example of running a simulation that can be restarted.

```
<qmc method="dmc" move="pbyp"  checkpoint="0">
  <parameter name="timestep">         0.004  </parameter>
  <parameter name="blocks">           100   </parameter>
  <parameter name="steps">            400    </parameter>
</qmc>
```

The checkpoint flag instructs QMCPACK to output walker configurations. This also works in VMC. This will output an h5 file with the name `projectid.run-number.config.h5`. Check that this file exists before attempting a restart. To read in this file for a continuation run, specify the following:

Listing 10.5: Restart (read walkers from previous run).

```
<mcwalkerset fileroot="BH.s002" version="0 6" collected="yes"/>
```

BH is the project id, and s002 is the calculation number to read in the walkers from the previous run.

Combining VMC and DMC in a single run (wavefunction optimization can be combined in this way too) is the standard way in which QMCPACK is typically run. There is no need to run two separate jobs since method sections can be stacked and walkers are transferred between them.

Listing 10.6: Combined VMC and DMC run.

```
<qmc method="vmc" move="pbyp" target="e">
  <parameter name="blocks">100</parameter>
  <parameter name="steps">4000</parameter>
  <parameter name="warmupsteps">100</parameter>
  <parameter name="samples">1920</parameter>
  <parameter name="walkers">1</parameter>
  <parameter name="timestep">0.5</parameter>
</qmc>
<qmc method="dmc" move="pbyp" target="e">
  <parameter name="blocks">100</parameter>
  <parameter name="steps">400</parameter>
  <parameter name="timestep">0.010</parameter>
  <parameter name="warmupsteps">100</parameter>
</qmc>
<qmc method="dmc" move="pbyp" target="e">
  <parameter name="warmupsteps">500</parameter>
  <parameter name="blocks">50</parameter>
  <parameter name="steps">100</parameter>
```

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```
  <parameter name="timestep">0.005</parameter>
</qmc>
```

10.4.2 `dmc_batch` driver (experimental)

parameters:

Name	Datatype	Values	Default	Description
`total_walkers`	integer	> 0	1	Total number of walkers over all MPI ranks
`walkers_per_rank`	integer	> 0	1	Number of walkers per MPI rank
`crowds`	integer	> 0	dep.	Number of desynchronized dwalker crowds
`blocks`	integer	≥ 0	1	Number of blocks
`steps`	integer	≥ 0	1	Number of steps per block
`warmupsteps`	integer	≥ 0	0	Number of steps for warming up
`timestep`	real	> 0	0.1	Time step for each electron move
`nonlocalmoves`	string	yes, no, v0, v1, v3	no	Run with T-moves
`branching_cutoff_scheme`	string	classic/DRV/ZSGMA/YLsic	classic	Branch cutoff scheme
`blocks_between_recompute`	integer	≥ 0	dep.	Wavefunction recompute frequency
`feedback`	double	≥ 0	1.0	Population feedback on the trial energy
`sigmaBound`	10	≥ 0	10	Parameter to cutoff large weights
`reconfiguration`	string	yes/pure/other	no	Fixed population technique
`storeconfigs`	integer	all values	0	Store configurations
`use_nonblocking`	string	yes/no	yes	Using nonblocking send/recv
`debug_disable_branching`	string	yes/no	no	Disable branching for debugging
`crowd_serialize_walkers`	integer	yes, no	no	Force use of single walker APIs (for testing)
`debug_checks`	text	see additional info	dep.	Turn on/off additional recompute and checks
`spin_mass`	real	≥ 0	1.0	Effective mass for spin sampling

- `crowds` The number of crowds that the walkers are subdivided into on each MPI rank. If not provided, it is set equal to the number of OpenMP threads.
- `walkers_per_rank` The number of walkers per MPI rank. This number does not have to be a multiple of the number of OpenMP threads. However, to avoid any idle resources, it is recommended to be at least the number of OpenMP threads for pure CPU runs. For GPU runs, a scan of this parameter is necessary to reach reasonable single rank efficiency and also get a balanced time to solution. For highest throughput on GPUs, expect to use hundreds of walkers_per_rank, or the largest number that will fit in GPU memory. If neither `total_walkers` nor `walkers_per_rank` is provided, `walkers_per_rank` is set equal to `crowds`.

- `total_walkers` Total number of walkers summed over all MPI ranks, or equivalently the total number of walkers in the DMC calculation. If not provided, it is computed as `walkers_per_rank` times the number of MPI ranks. If both `total_walkers` and `walkers_per_rank` are provided, which is not recommended, `total_walkers` must be consistently set equal to `walkers_per_rank` times the number MPI ranks.
- `debug_checks` valid values are 'no', 'all', 'checkGL_after_load', 'checkGL_after_moves', 'checkGL_after_tmove'. If the build type is *debug*, the default value is 'all'. Otherwise, the default value is 'no'.
- `spin_mass` Optional parameter to allow the user to change the rate of spin sampling. If spin sampling is on using `spinor` == yes in the electron ParticleSet input, the spin mass determines the rate of spin sampling, resulting in an effective spin timestep $\tau_s = \frac{\tau}{\mu_s}$. The algorithm is described in detail in [[MZG+16]] and [[MBM16]].

Listing 10.7: The following is an example of a minimal DMC section using the `dmc_batch` driver

```
<qmc method="dmc_batch" move="pbyp" target="e">
  <parameter name="walkers_per_rank">256</parameter>
  <parameter name="blocks">100</parameter>
  <parameter name="steps">400</parameter>
  <parameter name="timestep">0.010</parameter>
  <parameter name="warmupsteps">100</parameter>
</qmc>
```

10.5 Reptation Monte Carlo

Like DMC, RMC is a projector-based method that allows sampling of the fixed-node wavefunciton. However, by exploiting the path-integral formulation of Schrödinger's equation, the RMC algorithm can offer some advantages over traditional DMC, such as sampling both the mixed and pure fixed-node distributions in polynomial time, as well as not having population fluctuations and biases. The current implementation does not work with T-moves.

There are two adjustable parameters that affect the quality of the RMC projection: imaginary projection time β of the sampling path (commonly called a "reptile") and the Trotter time step τ. β must be chosen to be large enough such that $e^{-\beta\hat{H}}|\Psi_T\rangle \approx |\Phi_0\rangle$ for mixed observables, and $e^{-\frac{\beta}{2}\hat{H}}|\Psi_T\rangle \approx |\Phi_0\rangle$ for pure observables. The reptile is discretized into $M = \beta/\tau$ beads at the cost of an $\mathcal{O}(\tau)$ time-step error for observables arising from the Trotter-Suzuki breakup of the short-time propagator.

The following table lists some of the more practical

`vmc` method:

parameters:

Name	Datatype	Values	Default	Description
beta	real	> 0	dep.	Reptile project time β
timestep	real	> 0	0.1	Trotter time step τ for each electron move
beads	int	> 0	1	Number of reptile beads $M = \beta/\tau$
blocks	integer	> 0	1	Number of blocks
steps	integer	≥ 0	1	Number of steps per block
vmcpresteps	integer	≥ 0	0	Propagates reptile using VMC for given number of steps
warmupsteps	integer	≥ 0	0	Number of steps for warming up
maxAge	integer	≥ 0	0	Force accept for stuck reptile if age exceeds maxAge

Additional information:

Because of the sampling differences between DMC ensembles of walkers and RMC reptiles, the RMC block should contain the following estimator declaration to ensure correct sampling: <estimator name="RMC" hdf5="no">.

- beta or beads? One or the other can be specified, and from the Trotter time step, the code will construct an appropriately sized reptile. If both are given, beta overrides beads.
- **Mixed vs. pure observables?** Configurations sampled by the endpoints of the reptile are distributed according to the mixed distribution $f(\mathbf{R}) = \Psi_T(\mathbf{R})\Phi_0(\mathbf{R})$. Any observable that is computable within DMC and is dumped to the scalar.dat file will likewise be found in the scalar.dat file generated by RMC, except there will be an appended _m to alert the user that the observable was computed on the mixed distribution. For pure observables, care must be taken in the interpretation. If the observable is diagonal in the position basis (in layman's terms, if it is entirely computable from a single electron configuration $\mathbf{R}$, like the potential energy), and if the observable does not have an explicit dependence on the trial wavefunction (e.g., the local energy has an explicit dependence on the trial wavefunction from the kinetic energy term), then pure estimates will be correctly computed. These observables will be found in either the scalar.dat, where they will be appended with a _p suffix, or in the stat.h5 file. No mixed estimators will be dumped to the h5 file.
- **Sampling**: For pure estimators, the traces of both pure and mixed estimates should be checked. Ergodicity is a known problem in RMC. Because we use the bounce algorithm, it is possible for the reptile to bounce back and forth without changing the electron coordinates of the central beads. This might not easily show up with mixed estimators, since these are accumulated at constantly regrown ends, but pure estimates are accumulated on these central beads and so can exhibit strong autocorrelations in pure estimate traces.
- **Propagator**: Our implementation of RMC uses Moroni's DMC link action (symmetrized), with Umrigar's scaled drift near nodes. In this regard, the propagator is identical to the one QMCPACK uses in DMC.
- **Sampling**: We use Ceperley's bounce algorithm. MaxAge is used in case the reptile gets stuck, at which point the code forces move acceptance, stops accumulating statistics, and requilibrates the reptile. Very rarely will this be required. For move proposals, we use particle-by-particle VMC a total of N_e times to generate a new all-electron configuration, at which point the action is computed and the move is either accepted or rejected.

CHAPTER

ELEVEN

OUTPUT OVERVIEW

QMCPACK writes several output files that report information about the simulation (e.g., the physical properties such as the energy), as well as information about the computational aspects of the simulation, checkpoints, and restarts. The types of output files generated depend on the details of a calculation. The following list is not meant to be exhaustive but rather to highlight some salient features of the more common file types. Further details can be found in the description of the estimator of interest.

11.1 The .scalar.dat file

The most important output file is the `scalar.dat` file. This file contains the output of block-averaged properties of the system such as the local energy and other estimators. Each line corresponds to an average over $N_{walkers} * N_{steps}$ samples. By default, the quantities reported in the `scalar.dat` file include the following:

LocalEnergy The local energy.

LocalEnergy_sq The local energy squared.

LocalPotential The local potential energy.

Kinetic The kinetic energy.

ElecElec The electron-electron potential energy.

IonIon The ion-ion potential energy.

LocalECP The energy due to the pseudopotential/effective core potential.

NonLocalECP The nonlocal energy due to the pseudopotential/effective core potential.

MPC The modified periodic Coulomb potential energy.

BlockWeight The number of MC samples in the block.

BlockCPU The number of seconds to compute the block.

AcceptRatio The acceptance ratio.

QMCPACK includes a python utility, `qmca`, that can be used to process these files. Details and examples are given in *Analyzing QMCPACK data*.

11.2 The .opt.xml file

This file is generated after a VMC wavefunction optimization and contains the part of the input file that lists the optimized Jastrow factors. Conveniently, this file is already formatted such that it can easily be incorporated into a DMC input file.

11.3 The .qmc.xml file

This file contains information about the computational aspects of the simulation, for example, which parts of the code are being executed when. This file is generated only during an ensemble run in which QMCPACK runs multiple input files.

11.4 The .dmc.dat file

This file contains information similar to the `.scalar.dat` file but also includes extra information about the details of a DMC calculation, for example, information about the walker population.

Index The block number.

LocalEnergy The local energy.

Variance The variance.

Weight The number of samples in the block.

NumOfWalkers The number of walkers times the number of steps.

AvgSentWalkers The average number of walkers sent. During a DMC simulation, walkers might be created or destroyed. At every step, QMCPACK will do some load balancing to ensure that the walkers are evenly distributed across nodes.

TrialEnergy The trial energy. See *Diffusion Monte Carlo* for an explanation of trial energy.

DiffEff The diffusion efficiency.

LivingFraction The fraction of the walker population from the previous step that survived to the current step.

11.5 The .bandinfo.dat file

This file contains information from the trial wavefunction about the band structure of the system, including the available k-points. This can be helpful in constructing trial wavefunctions.

11.6 Checkpoint and restart files

11.6.1 The .cont.xml file

This file enables continuation of the run. It is mostly a copy of the input XML file with the series number incremented and the `mcwalkerset` element added to read the walkers from a config file. The `.cont.xml` file is always created, but other files it depends on are present only if checkpointing is enabled.

11.6.2 The .config.h5 file

This file contains stored walker configurations.

11.6.3 The .random.h5 file

This file contains the state of the random number generator to allow restarts. (Older versions used an XML file with a suffix of `.random.xml`).

CHAPTER

TWELVE

ANALYZING QMCPACK DATA

12.1 Using the qmca tool to obtain total energies and related quantities

The `qmca` tool is the primary means of analyzing scalar-valued data generated by QMCPACK. Output files that contain scalar-valued data are `*.scalar.dat` and `*.dmc.dat` (see *Output Overview* for a detailed description of these files). Quantities that are available for analysis in `*.scalar.dat` files include the local energy and its variance, kinetic energy, potential energy and its components, acceptance ratio, and the average CPU time spent per block, among others. The `*.dmc.dat` files provide information regarding the DMC walker population in addition to the local energy.

Basic capabilities of `qmca` include calculating mean values and associated error bars, processing multiple files at once in batched fashion, performing twist averaging, plotting mean values by series, and plotting traces (per block or step) of the underlying data. These capabilities are explained with accompanying examples in the following subsections.

To use `qmca`, installations of Python and NumPy must be present on the local machine. For graphical plotting, the matplotlib module must also be available.

An overview of all supported input flags to `qmca` can be obtained by typing `qmca` at the command line with no other inputs (also try `qmca -x` for a short list of examples):

```
>qmca
  no files provided, please see help info below

  Usage: qmca [options] [file(s)]

  Options:
    --version             show program's version number and exit
    -v, --verbose         Print detailed information (default=False).
    -q QUANTITIES, --quantities=QUANTITIES
                          Quantity or list of quantities to analyze.  See names
                          and abbreviations below (default=all).
    -u UNITS, --units=UNITS
                          Desired energy units.  Can be Ha (Hartree), Ry
                          (Rydberg), eV (electron volts), kJ_mol (k.
                          joule/mole), K (Kelvin), J (Joules) (default=Ha).
    -e EQUILIBRATION, --equilibration=EQUILIBRATION
                          Equilibration length in blocks (default=auto).
    -a, --average         Average over files in each series (default=False).
    -w WEIGHTS, --weights=WEIGHTS
                          List of weights for averaging (default=None).
    -b, --reblock         (pending) Use reblocking to calculate statistics
                          (default=False).
```

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```
    -p, --plot            Plot quantities vs. series (default=False).
    -t, --trace           Plot a trace of quantities (default=False).
    -h, --histogram       (pending) Plot a histogram of quantities
                          (default=False).
    -o, --overlay         Overlay plots (default=False).
    --legend=LEGEND       Placement of legend.  None for no legend, outside for
                          outside legend (default=upper right).
    --noautocorr          Do not calculate autocorrelation. Warning: error bars
                          are no longer valid! (default=False).
    --noac                Alias for --noautocorr (default=False).
    --sac                 Show autocorrelation of sample data (default=False).
    --sv                  Show variance of sample data (default=False).
    -i, --image           (pending) Save image files (default=False).
    -r, --report          (pending) Write a report (default=False).
    -s, --show_options    Print user provided options (default=False).
    -x, --examples        Print examples and exit (default=False).
    --help                Print help information and exit (default=False).
    -d DESIRED_ERROR, --desired_error=DESIRED_ERROR
                          Show number of samples needed for desired error bar
                          (default=none).
    -n PARTICLE_NUMBER, --enlarge_system=PARTICLE_NUMBER
                          Show number of samples needed to maintain error bar on
                          larger system: desired particle number first, current
                          particle number second (default=none)
```

12.1.1 Obtaining a statistically correct mean and error bar

A rough guess at the mean and error bar of the local energy can be obtained in the following way with `qmca`:

```
>qmca -q e qmc.s000.scalar.dat
qmc  series 0  LocalEnergy           =  -45.876150 +/- 0.017688
```

In this case the VMC energy of an 8-atom cell of diamond is estimated to be $-45.876(2)$ Hartrees (Ha). This rough guess should not be used for production-level or publication-quality estimates.

To obtain production-level results, the underlying data should first be inspected visually to ensure that all data included in the averaging can be attributed to a distribution sharing the same mean. The first steps of essentially any MC calculation (the "equilibration phase") do not belong to the equilibrium distribution and should be excluded from estimates of the mean and its error bar.

We can plot a data trace (`-t`) of the local energy in the following way:

```
>qmca -t -q e -e 0 qmc.s000.scalar.dat
```

The `-e 0` part indicates that we do not want any data to be initially excluded from the calculation of averages. The resulting plot is shown in Fig. 12.1. The unphysical equilibration period is visible on the left side of the plot.

Most of the data fluctuates around a well-defined mean (consistent variations around a flat line). This property is important to verify by plotting the trace for each QMC run.

If we exclude none of the equilibration data points, we get an erroneous estimate of $-45.870(2)$ Ha for the local energy:

```
>qmca -q e -e 0 qmc.s000.scalar.dat
qmc  series 0  LocalEnergy           =  -45.870071 +/- 0.018072
```

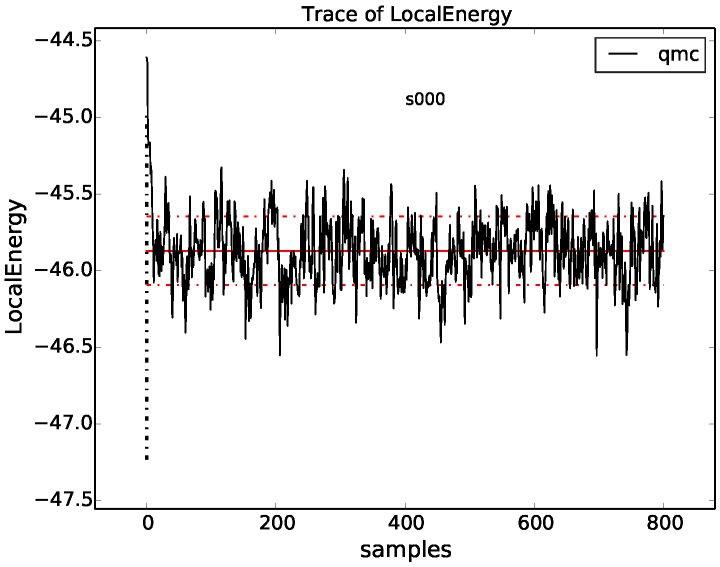


Fig. 12.1: Trace of the VMC local energy for an 8-atom cell of diamond generated with `qmca`. The x-axis ("samples") refers to the VMC block index in this case.

The equilibration period is typically estimated by eye, though a few conservative values should be checked to ensure that the mean remains unaffected. In this dataset, the equilibration appears to have been reached after 100 or so samples. After excluding the first 100 VMC blocks from the analysis we get

```
>qmca -q e -e 100 qmc.s000.scalar.dat
qmc  series 0  LocalEnergy            =  -45.877363 +/- 0.017432
```

This estimate ($-45.877(2)$ Ha) differs significantly from the $-45.870(2)$ Ha figure obtained from the full set of data, but it agrees with the rough estimate of $-45.876(2)$ Ha obtained with the abbreviated command (`qmca -q e qmc.s000.scalar.dat`). This is because `qmca` makes a heuristic guess at the equilibration period and got it reasonably correct in this case. In many cases, the heuristic guess fails and should not be relied on for quality results.

We have so far obtained a statistically correct mean. To obtain a statistically correct error bar, it is best to include $\sim$100 or more statistically independent samples. An estimate of the number of independent samples can be obtained by considering the autocorrelation time, which is essentially a measure of the number of samples that must be traversed before an uncorrelated/independent sample is reached. We can get an estimate of the autocorrelation time in the following way:

```
>qmca -q e -e 100 qmc.s000.scalar.dat --sac
qmc  series 0  LocalEnergy            =  -45.877363 +/- 0.017432    4.8
```

The flag `-sac` stands for (s)how (a)uto(c)orrelation. In this case, the autocorrelation estimate is $4.8 \approx 5$ samples. Since the total run contained 800 samples and we have excluded 100 of them, we can estimate the number of independent samples as $(800 - 100)/5 = 140$. In this case, the error bar is expected to be estimated reasonably well.

Keep in mind that the error bar represents the expected range of the mean with a certainty of only $\sim 70\%$; i.e., it is a one sigma error bar. The actual mean value will lie outside the range indicated by the error bar in 1 out of every 3 runs, and in a set of 20 runs 1 value can be expected to deviate from its estimate by twice the error bar.

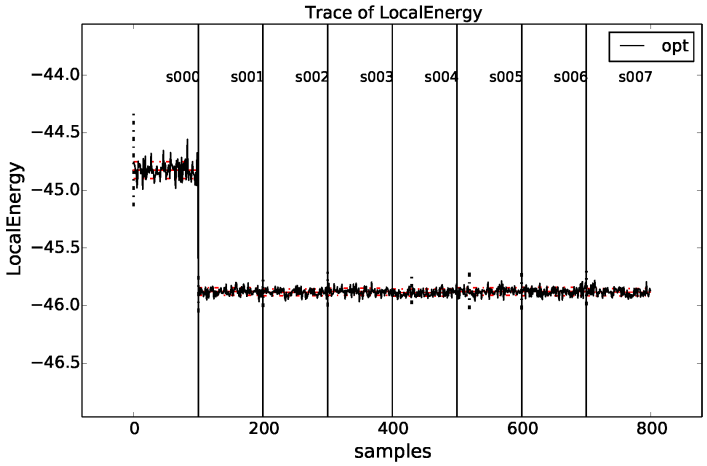


Fig. 12.2: Trace of the local energy during one- and two-body Jastrow optimizations for an 8-atom cell of diamond generated with `qmca`. Data for each optimization cycle (QMCPACK series) is separated by a vertical black line.

12.1.2 Judging wavefunction optimization

Wavefunction optimization is a highly nonlinear and sometimes sensitive process. As such, there is a risk that systematic errors encountered at this stage of the QMC process can be propagated into subsequent (expensive) DMC runs unless they are guarded against with vigilance.

In this section we again consider an 8-atom cell of diamond but now in the context of Jastrow optimization (one- and two-body terms). In optimization runs it is often preferable to use a large number of `warmupsteps` (~ 100) so that equilibration bias does not propagate into the optimization process. We can check that the added warm-up has had its intended effect by again checking the local energy trace:

```
>qmca -t -q e *scalar*
```

The resulting plot can be found in Fig. 12.2. In this case sufficient `warmupsteps` were used to exit the equilibration period before samples were collected and we can proceed without using the `-e` option with `qmca`.

After inspecting the trace, we should inspect the text output from `qmca`, now including the total energy and its variance:

```
>qmca -q ev opt*scalar.dat
                          LocalEnergy              Variance           ratio
opt  series 0  -44.823616 +/- 0.007430   7.054219 +/- 0.041998   0.1574
opt  series 1  -45.877643 +/- 0.003329   1.095362 +/- 0.041154   0.0239
opt  series 2  -45.883191 +/- 0.004149   1.077942 +/- 0.021555   0.0235
opt  series 3  -45.877524 +/- 0.003094   1.074047 +/- 0.010491   0.0234
opt  series 4  -45.886062 +/- 0.003750   1.061707 +/- 0.014459   0.0231
opt  series 5  -45.877668 +/- 0.003475   1.091585 +/- 0.021637   0.0238
opt  series 6  -45.877109 +/- 0.003586   1.069205 +/- 0.009387   0.0233
opt  series 7  -45.882563 +/- 0.004324   1.058771 +/- 0.008651   0.0231
```

The flags `-q ev` requested the energy (`e`) and the variance (`v`). For this combination of quantities, a third column (`ratio`) is printed containing the ratio of the variance and the absolute value of the local energy. The variance/energy ratio is an intensive quantity and is useful to inspect regardless of the system under study. Successful optimization of molecules and solids of any size generally result in comparable values for the variance/energy ratio.

The first line of the output (`series 0`) corresponds to the local energy and variance of the system without a Jastrow factor (all Jastrow coefficients were initialized to zero in this case), reflecting the quality of the orbitals alone. For

pseudopotential systems, a variance/energy ratio $>$ 0.20 Ha generally indicates there is a problem with the input orbitals that needs to be resolved before performing wavefunction optimization.

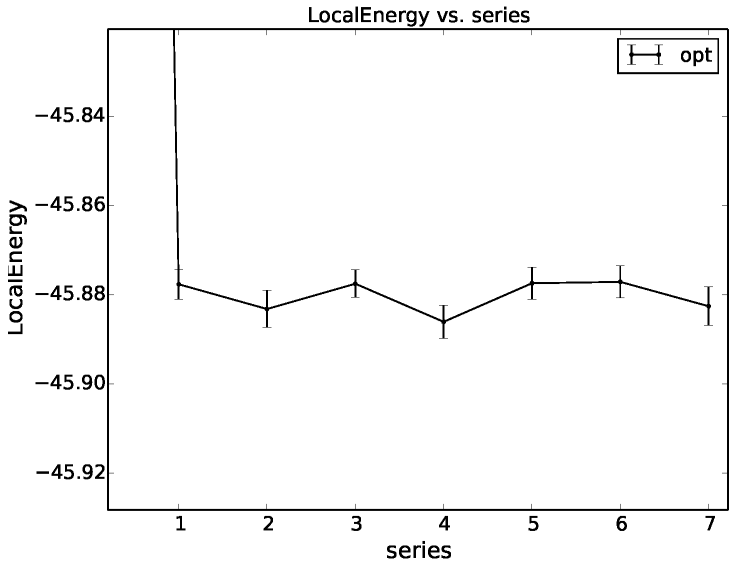
The subsequent lines correspond to energies and variances of intermediate parameterizations of the trial wavefunction during the optimization process. The output line containing `opt series 1`, for example, corresponds to the trial wavefunction parameterized during the `series 0` step (the parameters of this wavefunction would be found in an output file matching `*s000*opt.xml`). The first thing to check about the resulting optimization is again the variance/energy ratio. For pseudopotential systems, a variance/energy ratio $<$ 0.03 Ha is consistent with a trial wavefunction of production quality, and values of 0.01 Ha are rarely obtainable for standard Slater-Jastrow wavefunctions. By this metric, all parameterizations obtained for optimizations performed in series 0-6 are of comparable quality (note that the quality of the wavefunction obtained during optimization series 7 is effectively unknown).

A good way to further discriminate among the parameterizations is to plot the energy and variance as a function of series with `qmca`:

```
>qmca -p -q ev opt*scalar.dat
```

The `-p` option results in plots of means plus error bars vs. series for all requested quantities. The resulting plots for the local energy and variance are shown in Fig. 12.3. In this case, the resulting energies and variances are statistically indistinguishable for all optimization cycles.

A good way to choose the optimal wavefunction for use in DMC is to select the one with the lowest statistically significant energy within the set of optimized wavefunctions with reasonable variance (e.g., among those with a variance/energy ratio $<$ 0.03 Ha). For pseudopotential calculations, minimizing according to the total energy is recommended to reduce locality errors in DMC.



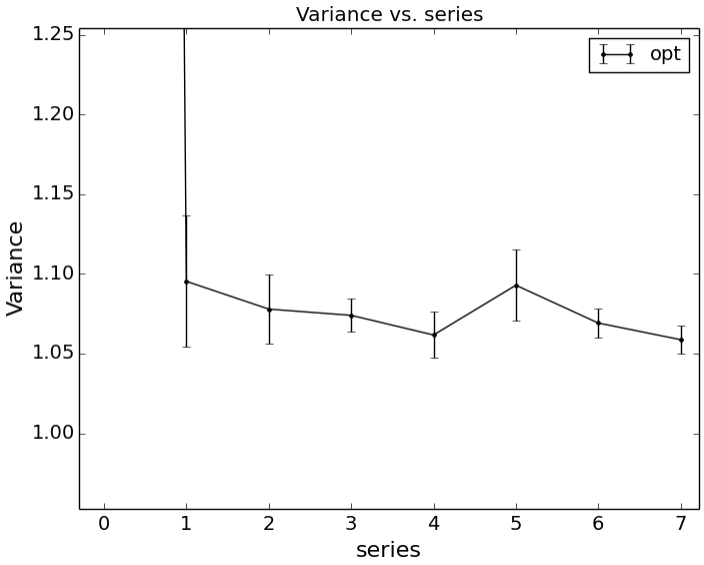


Fig. 12.3: Energy and variance vs. optimization series for an 8-atom cell of diamond as plotted by `qmca`.

12.1.3 Judging diffusion Monte Carlo runs

Judging the quality of the DMC projection process requires more care than is needed in VMC. To reduce bias, a small time step is required in the approximate projector but this also leads to slow equilibration and long autocorrelation times. Systematic errors in the projection process can also arise from statistical fluctuations due to pseudopotentials or from trial wavefunctions with larger-than-necessary variance.

To illustrate the problems that can arise with respect to slow equilibration and long autocorrelation times, we consider the 8-atom diamond system with VMC (200 blocks of 160 steps) followed by DMC (400 blocks of 5 steps) with a small time step (0.002 Ha^{-1}). A good first step in assessing the quality of any DMC run is to plot the trace of the local energy:

```
>qmca -t -q e -e 0 *scalar*
```

The resulting trace plot is shown in Fig. 12.4. As always, the DMC local energy decreases exponentially away from the VMC value, but in this case it takes a long time to do so. At least half of the DMC run is inefficiently consumed by equilibration. If we are not careful to inspect and remove the transient, the estimated DMC energy will be strongly biased by the transient as shown by the horizontal red line (estimated mean) in the figure. The autocorrelation time is also large (~ 12 blocks):

```
>qmca -q e -e 200 --sac *s001.scalar*
qmc  series 1  LocalEnergy           =  -46.045720 +/- 0.004813   11.6
```

Of the included 200 blocks, fewer than 20 contribute to the estimated error bar, indicating that we cannot trust the reported error bar. This can also be demonstrated directly from the data. If we halve the number of included samples to 100, we expect from Gaussian statistics that the error bar will grow by a factor of $\sqrt{2}$, but instead we get

```
>qmca -q e -e 300 *s001.scalar*
qmc  series 1  LocalEnergy           =  -46.048537 +/- 0.009280
```

which erroneously shows an estimated increase in the error bar by a factor of about 2. Overall, this run is simply too short to gain meaningful information.

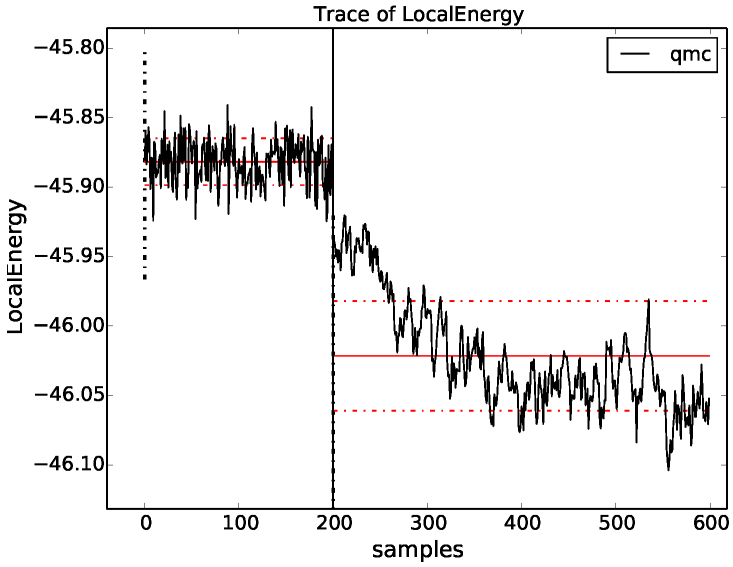


Fig. 12.4: Trace of the local energy for VMC followed by DMC with a small time step (0.002 Ha^{-1}) for an 8-atom cell of diamond generated with `qmca`.

Consider the case in which we are interested in the cohesive energy of diamond, and, after having performed a time step study of the cohesive energy, we have found that the energy difference between bulk diamond and atomic carbon converges to our required accuracy with a larger time step of 0.01 Ha^{-1}. In a production setting, a small cell could be used to determine the appropriate time step, while a larger cell would subsequently be used to obtain a converged cohesive energy, though for purposes of demonstration we still proceed here with the 8-atom cell. The new time step of 0.01 Ha^{-1} will result in a shorter autocorrelation time than the smaller time step used previously, but we would like to shorten the equilibration time further still. This can be achieved by using a larger time step (say 0.02 Ha^{-1}) in a short intermediate DMC run used to walk down the transient. The rapidly achieved equilibrium with the 0.02 Ha^{-1} time step projector will be much nearer to the 0.01 Ha^{-1} time step we seek than the original VMC equilibrium, so we can expect a shortened secondary equilibration time in the production 0.01 Ha^{-1} time step run. Note that this procedure is fully general, even if having to deal with an even shorter time step (e.g., 0.002 Ha^{-1}) for a particular problem.

We now rerun the previous example but with an intermediate DMC calculation using 40 blocks of 5 steps with a time step of 0.02 Ha^{-1}, followed by a production DMC calculation using 400 blocks of 10 steps with a time step of 0.01 Ha^{-1}. We again plot the local energy trace using `qmca`:

```
>qmca -t -q e -e 0 *scalar*
```

with the result shown in Fig. 12.5. The projection transient has been effectively contained in the short DMC run with a larger time step. As expected, the production run contains only a short equilibration period. Removing the first 20 blocks as a precaution, we obtain an estimate of the total energy in VMC and DMC:

```
>qmca -q ev -e 20 --sac qmc.*.scalar.dat
                          LocalEnergy              Variance           ratio
qmc   series 0  -45.881042 +/- 0.001283    1.0   1.076726 +/- 0.007013    1.0   0.0235
qmc   series 1  -46.040814 +/- 0.005046    3.9   1.011303 +/- 0.016807    1.1   0.0220
qmc   series 2  -46.032960 +/- 0.002077    5.2   1.014940 +/- 0.002547    1.0   0.0220
```

Notice that the variance/energy ratio in DMC (0.220 Ha) is similar to but slightly smaller than that obtained with VMC (0.235 Ha). If the DMC variance/energy ratio is ever significantly larger than with VMC, this is cause to be concerned about the correctness of the DMC run. Also notice the estimated autocorrelation time (~ 5 blocks). This leaves us

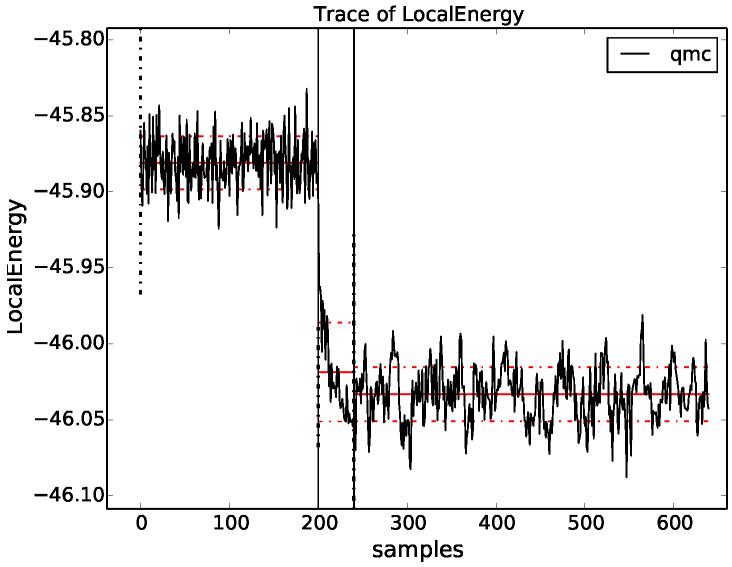


Fig. 12.5: Trace of the local energy for VMC followed by a short intermediate DMC with a large time step (0.02 Ha^{-1}) and finally a production DMC run with a time step of 0.01 Ha^{-1}. Calculations were performed in an 8-atom cell of diamond.

with an estimated ~ 76 independent samples, though we should recall that the autocorrelation time is also a statistical estimate that can be improved with more data. We can gain a better estimate of the autocorrelation time by using the `*.dmc.dat` files, which contain output data resolved per step rather than per block (there are $10\times$ more steps than blocks in this example case):

```
>qmca -q ev -e 200 --sac qmc.s002.dmc.dat
                          LocalEnergy              Variance           ratio
qmc  series 2  -46.032909 +/- 0.002068   31.2   1.015781 +/- 0.002536    1.4    0.0221
```

This results in an estimated autocorrelation time of ~ 31 steps, or ~ 3 blocks, indicating that we actually have ~ 122 independent samples, which should be sufficient to obtain a trustworthy error bar. Our final DMC total energy is estimated to be $-46.0329(2)$ Ha.

Another simulation property that should be explicitly monitored is the behavior of the DMC walker population. Data regarding the walker population is contained in the `*.dmc.dat` files. In Fig. 12.6 we show the trace of the DMC walker population for the current run:

```
>qmca -t -q nw *dmc.dat
qmc  series 1  NumOfWalkers           =  2056.905405 +/- 8.775527
qmc  series 2  NumOfWalkers           =  2050.164160 +/- 4.954850
```

Following a DMC run, the walker population should be checked for two qualities: (1) that the population is sufficiently large (a number $> 2,000$ is generally sufficient to reduce population control bias) and (2) that the population fluctuates benignly around its intended target value. In this case the target walker count (provided in the input file) was $2,048$ and we can confirm from the plot that the population is simply fluctuating around this value. Also, from the text output we have a dynamic population estimate of 2,050(5) walkers. Rapid population reductions or increases—population explosions—are indicative of problems with a run. These issues sometimes result from using a considerably poor wavefunction (see comments regarding variance/energy ratio in the preceding subsections). QMCPACK has internal guards in place that prevent the population from exceeding certain maximum and minimum bounds, so in particularly faulty runs one might see the population "stabilize" to a constant value much larger or smaller than the target. In such cases the cause(s) for the divergent population behavior needs to be investigated and resolved before proceeding

further.

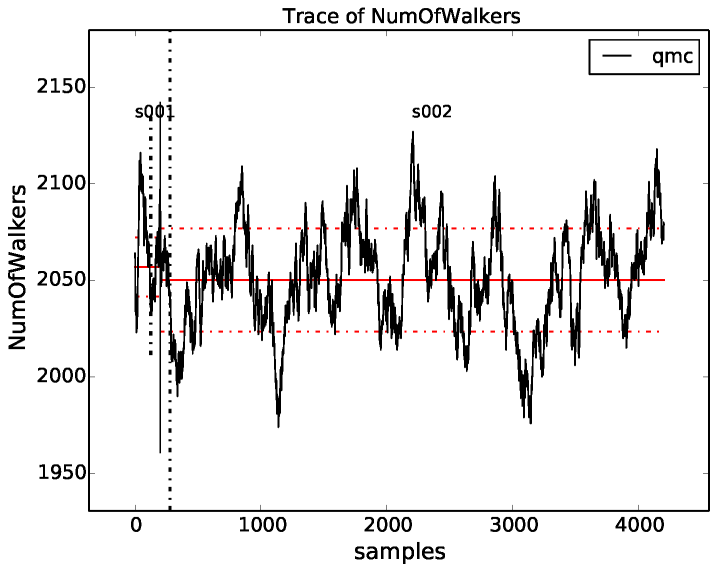


Fig. 12.6: Trace of the DMC walker population for an 8-atom cell of diamond obtained with `qmca`.

12.1.4 Obtaining other quantities

A number of other scalar-valued quantities are available with `qmca`. To obtain text output for all quantities available, simply exclude the `-q` option used in previous examples. The following example shows output for a DMC calculation of the 8-atom diamond system from the `scalar.dat` file:

```
>qmca -e 20 qmc.s002.scalar.dat
qmc  series 2
  LocalEnergy            =          -46.0330 +/-           0.0021
  Variance               =            1.0149 +/-           0.0025
  Kinetic                =            33.851 +/-            0.019
  LocalPotential         =            -79.884 +/-           0.020
  ElecElec               =          -11.4483 +/-           0.0083
  LocalECP               =           -22.615 +/-            0.029
  NonLocalECP            =            5.2815 +/-           0.0079
  IonIon                 =            -51.10 +/-             0.00
  LocalEnergy_sq         =           2120.05 +/-             0.19
  BlockWeight            =          20514.27 +/-            48.38
  BlockCPU               =            1.4890 +/-           0.0038
  AcceptRatio            =         0.9963954 +/-        0.0000055
  Efficiency             =             71.88 +/-             0.00
  TotalTime              =            565.80 +/-             0.00
  TotalSamples           =           7795421 +/-                0
```

Similarly, for the `dmc.dat` file we get

```
>qmca -e 20 qmc.s002.dmc.dat
qmc  series 2
  LocalEnergy            =          -46.0329 +/-           0.0020
  Variance               =            1.0162 +/-           0.0025
```

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```
  TotalSamples           =            8201275 +/-                0
  TrialEnergy            =          -46.0343 +/-           0.0023
  DiffEff                =          0.9939150 +/-        0.0000088
  Weight                 =            2050.23 +/-             4.82
  NumOfWalkers           =               2050 +/-                5
  LivingFraction         =           0.996427 +/-         0.000021
  AvgSentWalkers         =             0.2625 +/-           0.0011
```

Any subset of desired quantities can be obtained by using the `-q` option with either the full names of the quantities just listed

```
>qmca -q 'LocalEnergy Kinetic LocalPotential' -e 20 qmc.s002.scalar.dat
qmc  series 2
  LocalEnergy            =          -46.0330 +/-           0.0021
  Kinetic                =            33.851 +/-            0.019
  LocalPotential         =           -79.884 +/-            0.020
```

or with their corresponding abbreviations.

```
>qmca -q ekp -e 20 qmc.s002.scalar.dat
qmc  series 2
  LocalEnergy            =          -46.0330 +/-           0.0021
  Kinetic                =            33.851 +/-            0.019
  LocalPotential         =           -79.884 +/-            0.020
```

Abbreviations for each quantity can be found by typing `qmca` at the command line with no other input. This following is a current list:

```
Abbreviations and full names for quantities:
    ar              = AcceptRatio
    bc              = BlockCPU
    bw              = BlockWeight
    ce              = CorrectedEnergy
    de              = DiffEff
    e               = LocalEnergy
    ee              = ElecElec
    eff             = Efficiency
    ii              = IonIon
    k               = Kinetic
    kc              = KEcorr
    l               = LocalECP
    le2             = LocalEnergy_sq
    mpc             = MPC
    n               = NonLocalECP
    nw              = NumOfWalkers
    p               = LocalPotential
    sw              = AvgSentWalkers
    te              = TrialEnergy
    ts              = TotalSamples
    tt              = TotalTime
    v               = Variance
    w               = Weight
```

See the output overview for `scalar.dat` (*The .scalar.dat file*) and `dmc.dat` (*The .dmc.dat file*) for more information about these quantities. The data analysis aspects for these quantities are essentially the same as for the local energy as covered in the preceding subsections. Quantities that do not belong to an equilibrium distribution (e.g., `BlockCPU`) are somewhat different, though they still exhibit statistical fluctuations.

12.1.5 Processing multiple files

Batch file processing is a common use case for `qmca`. If we consider an "equation-of-state" calculation involving the 8-atom diamond cell we have used so far, we might be interested in the total energy for the various supercell volumes along the trajectory from compression to expansion. After checking the traces (`qmca -t -q e scale_*/vmc/*scalar*`) to settle on a sensible equilibration cutoff as discussed in the preceding subsections, we can obtain the total energies all at once:

```
>qmca -q ev -e 40 scale_*/vmc/*scalar*
                          LocalEnergy              Variance           ratio
scale_0.80/vmc/qmc  series 0 -44.670984 +/- 0.006051  2.542384 +/- 0.019902  0.0569
scale_0.82/vmc/qmc  series 0 -44.982818 +/- 0.005757  2.413011 +/- 0.022626  0.0536
scale_0.84/vmc/qmc  series 0 -45.228257 +/- 0.005374  2.258577 +/- 0.019322  0.0499
scale_0.86/vmc/qmc  series 0 -45.415842 +/- 0.005532  2.204980 +/- 0.052978  0.0486
scale_0.88/vmc/qmc  series 0 -45.570215 +/- 0.004651  2.061374 +/- 0.014359  0.0452
scale_0.90/vmc/qmc  series 0 -45.683684 +/- 0.005009  1.988539 +/- 0.018267  0.0435
scale_0.92/vmc/qmc  series 0 -45.751359 +/- 0.004928  1.913282 +/- 0.013998  0.0418
scale_0.94/vmc/qmc  series 0 -45.791622 +/- 0.005026  1.843704 +/- 0.014460  0.0403
scale_0.96/vmc/qmc  series 0 -45.809256 +/- 0.005053  1.829103 +/- 0.014536  0.0399
scale_0.98/vmc/qmc  series 0 -45.806235 +/- 0.004963  1.775391 +/- 0.015199  0.0388
scale_1.00/vmc/qmc  series 0 -45.783481 +/- 0.005293  1.726869 +/- 0.012001  0.0377
scale_1.02/vmc/qmc  series 0 -45.741655 +/- 0.005627  1.681776 +/- 0.011496  0.0368
scale_1.04/vmc/qmc  series 0 -45.685101 +/- 0.005353  1.682608 +/- 0.015423  0.0368
scale_1.06/vmc/qmc  series 0 -45.615164 +/- 0.005978  1.652155 +/- 0.010945  0.0362
scale_1.08/vmc/qmc  series 0 -45.543037 +/- 0.005191  1.646375 +/- 0.013446  0.0361
scale_1.10/vmc/qmc  series 0 -45.450976 +/- 0.004794  1.707649 +/- 0.048186  0.0376
scale_1.12/vmc/qmc  series 0 -45.371851 +/- 0.005103  1.686997 +/- 0.035920  0.0372
scale_1.14/vmc/qmc  series 0 -45.265490 +/- 0.005311  1.631614 +/- 0.012381  0.0360
scale_1.16/vmc/qmc  series 0 -45.161961 +/- 0.004868  1.656586 +/- 0.014788  0.0367
scale_1.18/vmc/qmc  series 0 -45.062579 +/- 0.005971  1.671998 +/- 0.019942  0.0371
scale_1.20/vmc/qmc  series 0 -44.960477 +/- 0.004888  1.651864 +/- 0.009756  0.0367
```

In this case, we are using a Jastrow factor optimized only at the equilibrium geometry (`scale_1.00`) but with radial cutoffs restricted to the Wigner-Seitz radius of the most compressed supercell (`scale_0.80`) to avoid introducing wavefunction cusps at the cell boundary (had we tried, QMCPACK would have aborted with a warning in this case). It is clear that this restricted Jastrow factor is not an optimal choice because it yields variance/energy ratios between 0.036 and 0.057 Ha. This issue is largely a result of our undersized (8-atom) supercell; larger cells should always be used in real production calculations.

Batch processing is also possible for multiple quantities. If multiple quantities are requested, an additional line is inserted to separate results from different runs:

```
>qmca -q 'e bc eff' -e 40 scale_*/vmc/*scalar*
scale_0.80/vmc/qmc  series 0
  LocalEnergy           =          -44.6710 +/-           0.0061
  BlockCPU              =           0.02986 +/-          0.00038
  Efficiency            =          38104.00 +/-             0.00

scale_0.82/vmc/qmc  series 0
  LocalEnergy           =          -44.9828 +/-           0.0058
  BlockCPU              =           0.02826 +/-          0.00013
  Efficiency            =          44483.91 +/-             0.00

scale_0.84/vmc/qmc  series 0
  LocalEnergy           =          -45.2283 +/-           0.0054
  BlockCPU              =           0.02747 +/-          0.00030
  Efficiency            =          52525.12 +/-             0.00
```

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```
scale_0.86/vmc/qmc  series 0
  LocalEnergy            =          -45.4158 +/-           0.0055
  BlockCPU               =           0.02679 +/-          0.00013
  Efficiency             =          50811.55 +/-             0.00

scale_0.88/vmc/qmc  series 0
  LocalEnergy            =          -45.5702 +/-           0.0047
  BlockCPU               =           0.02598 +/-          0.00015
  Efficiency             =          74148.79 +/-             0.00

scale_0.90/vmc/qmc  series 0
  LocalEnergy            =          -45.6837 +/-           0.0050
  BlockCPU               =           0.02527 +/-          0.00011
  Efficiency             =          65714.98 +/-             0.00

...
```

12.1.6 Twist averaging

Twist averaging can be performed straightforwardly for any output quantity listed in *Obtaining other quantities* with `qmca`. We illustrate these capabilities by repeating the 8-atom diamond DMC runs performed in Section *Judging diffusion Monte Carlo runs* at 8 real-valued supercell twist angles (a $2 \times 2 \times 2$ Monkhorst-Pack grid centered at the Γ-point). Data traces for each twist can be overlapped on the same plot:

```
>qmca -to -q e -e '30 20 30' *scalar* --legend outside
```

The `-o` option requests the plots to be overlapped; otherwise, 8 separate plots would be generated. The equilibration input `-e '30 20 30'` cuts out from the analyzed data the first 30 blocks for series 0 (VMC), 20 blocks for series 1 (intermediate DMC), and 30 blocks for series 2 (production DMC). The resulting plot is shown in Fig. 12.7.

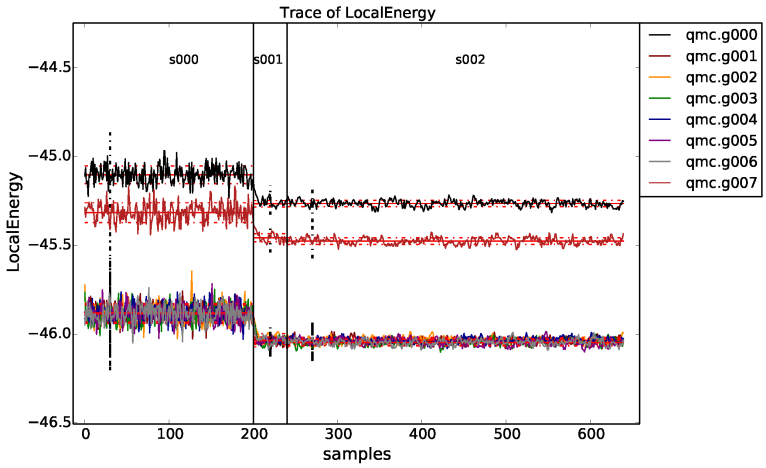

Fig. 12.7: Overlapped energy traces from VMC to DMC for an 8-supercell diamond obtained with `qmca`. Data for each twist appears in a different color.

Twist averaging is performed by providing the `-a` option. If provided on its own, uniform weights are applied to each twist angle. To obtain a trace plot with twist averaging enforced, use a command similar to the following:

```
>qmca -a -t -q e -e '30 20 30' *scalar*
```

The resulting plot is shown in Fig. 12.8. As can be seen from the trace plot, the chosen equilibration lengths are appropriate, and we proceed to obtain the twist-averaged total energy from the `scalar.dat` files

```
>qmca -a -q ev -e 30 --sac *s002.scalar*
                            LocalEnergy                Variance           ratio
avg  series 2  -45.873369 +/- 0.000753    5.3   1.028751 +/- 0.001056    1.3   0.0224
```

and also from the `dmc.dat` files

```
>qmca -a -q ev -e 300 --sac *s002.dmc*
                           LocalEnergy                Variance           ratio
avg  series 2  -45.873371 +/- 0.000741   30.5   1.028843 +/- 0.000972    1.6   0.0224
```

yielding a twist-averaged total energy of $-45.8733(8)$ Ha.

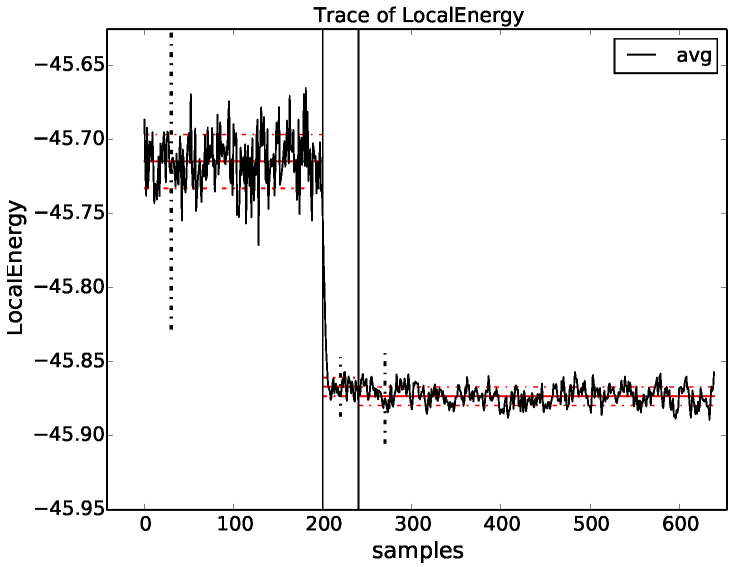

Fig. 12.8: Twist-averaged energy trace from VMC to DMC for an 8-supercell diamond obtained with `qmca`.

As can be seen from Fig. 12.7, some of the twist angles are degenerate. This is seen more clearly in the text output

```
>qmca -q ev -e 30 *s002.scalar*
                            LocalEnergy                Variance           ratio
qmc.g000  series 2  -45.264510 +/- 0.001942   1.057065 +/- 0.002318   0.0234
qmc.g001  series 2  -46.035511 +/- 0.001806   1.015992 +/- 0.002836   0.0221
qmc.g002  series 2  -46.035410 +/- 0.001538   1.015039 +/- 0.002661   0.0220
qmc.g003  series 2  -46.047285 +/- 0.001898   1.018219 +/- 0.002588   0.0221
qmc.g004  series 2  -46.034225 +/- 0.002539   1.013420 +/- 0.002835   0.0220
qmc.g005  series 2  -46.046731 +/- 0.002963   1.018337 +/- 0.004109   0.0221
qmc.g006  series 2  -46.047133 +/- 0.001958   1.021483 +/- 0.003082   0.0222
qmc.g007  series 2  -45.476146 +/- 0.002065   1.070456 +/- 0.003133   0.0235
```

The degenerate twists grouped by set are $\{0\}$, $\{1, 2, 4\}$, $\{3, 5, 6\}$, and $\{7\}$.

Alternatively, the run could have been performed at the four unique (irreducible) twist angles *only*. We will emulate this situation by analyzing data for twists 0, 1, 3, and 7 only. In a production setting with irreducibly weighted twists, the run would be performed on these twists alone; we reuse the uniform twist data for illustration purposes only.

We can use `qmca` to perform twist averaging with different weights applied to each twist:

```
>qmca -a -w '1 3 3 1' -q ev -e 30 *g000*2*sc* *g001*2*sc* *g003*2*sc* *g007*2*sc*
                            LocalEnergy              Variance           ratio
avg  series 2  -45.873631 +/- 0.001044   1.028769 +/- 0.001520   0.0224
```

yielding a total energy value of $-45.874(1)$ Ha, in agreement with the uniform weighted twist average performed previously.

The decision of whether or not to perform irreducible weighted twist averaging should be made on the basis of efficiency. The relative efficiency of irreducible vs. uniform weighted twist averaging depends on the irreducible weights and the ratio of the lengths of the available sampling and equilibration periods. A formula for the relative efficiency of these two cases is derived and discussed in more detail in *Appendix A: Derivation of twist averaging efficiency*.

12.1.7 Setting output units

Estimates outputted by `qmca` are in Hartree units by default. The output units for energetic quantities can be changed by using the `-u` option.

Energy in Hartrees:

```
>qmca -q e -u Ha -e 20 qmc.s002.scalar.dat
qmc  series 2  LocalEnergy           =  -46.032960 +/- 0.002077
```

Energy in electron volts:

```
>qmca -q e -u eV -e 20 qmc.s002.scalar.dat
qmc  series 2  LocalEnergy           =  -1252.620565 +/- 0.056521
```

Energy in Rydbergs:

```
>qmca -q e -u rydberg -e 20 qmc.s002.scalar.dat
qmc  series 2  LocalEnergy           =  -92.065919 +/- 0.004154
```

Energy in kilojoules per mole:

```
>qmca -q e -u kj_mol -e 20 qmc.s002.scalar.dat
qmc  series 2  LocalEnergy           =  -120859.512998 +/- 5.453431
```

12.1.8 Speeding up trace plotting

When working with many files or files with many entries, `qmca` might take a long time to produce plots. The time delay is actually due to the autocorrelation time estimate used to calculate error bars. The calculation time for the autocorrelation scales as $\mathcal{O}(M^2)$, with M being the number of statistical samples. If you are interested only in plotting traces and not in the estimated error bars, the autocorrelation time estimation can be turned off with the `-noac` option:

```
>qmca -t -q e -e 20 --noac qmc.s002.scalar.dat
```

Note that the resulting error bars printed to the console will be underestimated and are not meaningful. Do *not* use `-noac` in conjunction with the `-p` plotting option as these plots are of no use without meaningful error bars.

12.1.9 Short usage examples

Plotting a trace of the local energy:

```
>qmca -t -q e *scalar*
```

Applying an equilibration cutoff to VMC data (series 0):

```
>qmca -q e -e 30 *s000.scalar*
```

Applying the same equilibration cutoff to VMC and DMC data (series 0, 1, 2):

```
>qmca -q e -e 20 *scalar*
```

Applying different equilibration cutoffs to VMC and DMC data (series 0, 1, 2):

```
>qmca -q e -e '30 20 40' *scalar*
```

Obtaining the energy, variance, and variance/energy ratio for all series:

```
>qmca -q ev -e 30 *scalar*
```

Overlaying plots of mean + error bar for energy and variance for separate two- and three-body Jastrow optimization runs:

```
>qmca -po -q ev ./optJ2/*scalar* ./optJ3/*scalar*
```

Obtaining the acceptance ratio:

```
>qmca -q ar -e 30 *scalar*
```

Obtaining the average DMC walker population:

```
>qmca -q nw -e 400 *s002.dmc.dat
```

Obtaining the MC efficiency:

```
>qmca -q eff -e 30 *scalar*
```

Obtaining the total wall clock time per series:

```
>qmca -q tt -e 0 *scalar*
```

Obtaining the average wall clock time spent per block:

```
>qmca -q bc -e 0 *scalar*
```

Obtaining a subset of desired quantities:

```
>qmca -q 'e v ar eff' -e 30 *scalar*
```

Obtaining all available quantities:

```
>qmca -e 30 *scalar*
```

Obtaining the twist-averaged total energy with uniform weights:

```
>qmca -a -q e -e 40 *g*s002.scalar.dat
```

Obtaining the twist-averaged total energy with specific weights:

```
>qmca -a -w '1 3 3 1' -q e -e 40 *g*s002.scalar.dat
```

Obtaining the local, kinetic, and potential energies in eV:

```
>qmca -q ekp -e 30 -u eV *scalar*
```

12.1.10 Production quality checklist

1. Inspect the trace plots (`-t` option) for any oddities in the data. Typical behavior is a short equilibration period followed by benign fluctuations around a clear mean value. There should not be any large spikes in the data. This applies to *all* runs (VMC, optimization, DMC, etc.).
2. Remove all equilibration steps (`-e` option) from the data by inspecting the trace plot.
3. Check the quality of the orbitals (standalone Jastrow-less VMC or sometimes the first `scalar` file produced during optimization) by inspecting the variance/energy ratio `qmca -q ev *scalar*`. For pseudopotential systems without a Jastrow, the variance/energy ratio should not exceed 0.2 Ha; otherwise, there is a problem with the orbitals.
4. Check the quality of the optimized Jastrow factor by inspecting the variance/energy ratio. For pseudopotential systems with a Jastrow, the variance/energy ratio should not exceed 0.04 Ha for pseudopotential systems. A good Jastrow is indicated by a variance/energy ratio in the range of $0.01 - 0.03$ Ha. A value less than 0.01 Ha is difficult to achieve.
5. Confirm that the optimization has converged by plotting the energy and variance vs. optimization series (`qmca -p -q ev *scalar*`). Do not assume that optimization has converged in only a few cycles. Use at least 10 cycles with about 100,000 samples unless you already have experience with the system in question.
6. Optimize Jastrow factors according to energy minimization to reduce locality errors arising from the use of nonlocal pseudopotentials in DMC. A good approach is to optimize with a few cycles of variance minimization followed by several cycles of energy minimization.
7. Occasionally try optimizing with more samples and/or cycles to see if improved results are obtained.
8. If using a B-spline representation of the orbitals, converge the VMC energy and variance with respect to the mesh size (controlled via meshfactor). This is best done in the presence of any Jastrow factor to reduce noise. Consider using the hybrid LMTO representation of the orbitals as this can reduce both the VMC/DMC variance and the DMC time step error, in addition to saving memory.
9. Check the variance/energy ratio of all production VMC and DMC calculations. In all cases, the DMC ratio should be slightly less than the VMC ratio and both should abide the preceding guidelines, i.e., the ratio should be less than 0.04 Ha for pseudopotential systems. The production ratio should also be consistent with what is observed during wavefunction optimization.
10. Be aware of population control bias in DMC. Run with a population of $\sim 2,000$ or greater. Occasionally repeat a run using a larger population to explicitly confirm that population control bias is small.
11. Check the stability of the DMC walker population by plotting the trace of the population size (`qmca -t -q nw *dmc.dat`). Verify that the average walker population is consistent with the requested value provided in the input.
12. In DMC, perform a time step study to obtain either (1) extrapolated results or (2) a time step for future production where an energy difference shows convergence (e.g., a band gap or defect formation energy). For pseudopo-

tential systems, converged time steps for many systems are in the range of $0.002 - 0.01$ Ha^{-1}, but the actual converged time step must be explicitly checked.

13. In periodic systems, converge the total energy with respect to the size of the twist/k-point grid. Results for smaller systems can easily be transferred to larger ones (e.g., a $2 \times 2 \times 2$ twist grid in a $2 \times 2 \times 2$ tiled cell is equivalent to a $1 \times 1 \times 1$ twist grid in a $4 \times 4 \times 4$ tiled cell).

14. In periodic systems, perform finite-size extrapolation including two body corrections (needed for cohesive energy/phase stability studies) unless it can be shown that finite-size effects cancel for the energy difference in question (e.g., some defect formation energies).

12.2 Using the qmc-fit tool for statistical time step extrapolation and curve fitting

The `qmc-fit` tool is used to provide statistical estimates of curve-fitting parameters based on QMCPACK data. Although `qmc-fit` will eventually support many types of fitted curves (e.g., Morse potential binding curves and various equation-of-state fitting curves), it is currently limited to estimating fitting parameters related to time step extrapolation.

12.2.1 The jackknife statistical technique

The `qmc-fit` tool obtains estimates of fitting parameter means and associated error bars via the "jack-knife" technique. This technique is a powerful and general tool to obtain meaningful error bars for any quantity that is related in a nonlinear fashion to an underlying set of statistical data. For this reason, we give a brief overview of the jackknife technique before proceeding with usage instructions for the `qmc-fit` tool.

Consider N statistical variables $\{x_n\}_{n=1}^{N}$ that have been outputted by one or more simulation runs. If we have M samples of each of the N variables, then the mean values of each these variables can be estimated in the standard way, that is, $\bar{x}_n \approx \frac{1}{M}\sum_{m=1}^{M} x_{nm}$.

Suppose we are interested in P statistical quantities $\{y_p\}_{p=1}^{P}$ that are related to the original N variables by a known multidimensional function F:

$$y_1, y_2, \ldots, y_P = F(x_1, x_2, \ldots, x_N) \quad \text{or}$$
$$\vec{y} = F(\vec{x})\,.$$

The relationship implied by F is completely general. For example, the $\{x_n\}$ might be elements of a matrix with $\{y_p\}$ being the eigenvalues, or F might be a fitting procedure for N energies at different time steps with P fitting parameters. An approximate guess at the mean value of $\vec{y}$ can be obtained by evaluating F at the mean value of $\vec{x}$ (i.e. $F(\bar{x}_1 \ldots \bar{x}_N)$), but with this approach we have no way to estimate the statistical error bar of any $\bar{y}_p$.

In the jackknife procedure, the statistical variability intrinsic to the underlying data $\{x_n\}$ is used to obtain estimates of the mean and error bar of $\{y_p\}$. We first construct a new set of x statistical data by taking the average over all samples but one:

$$\tilde{x}_{nm} = \frac{1}{N-1}(N\bar{x}_n - x_{nm}) \qquad m \in [1, M]\,. \tag{12.1}$$

The result is a distribution of approximate x mean values. These are used to construct a distribution of approximate means for y:

$$\tilde{y}_{1m}, \ldots, \tilde{y}_{Pm} = F(\tilde{x}_{1m}, \ldots, \tilde{x}_{Nm}) \qquad m \in [1, M]\,. \tag{12.2}$$

Estimates for the mean and error bar of the quantities of interest can finally be obtained using the following formulas:

$$\begin{aligned} \bar{y}_p &= \frac{1}{M}\sum_{m=1}^{M} \tilde{y}_{pm} \,. \\ \sigma_{y_p} &= \sqrt{\frac{M-1}{M}\left(\sum_{m=1}^{M} \tilde{y}_{pm}^2 - M\bar{y}_p^2\right)} \,. \end{aligned} \tag{12.3}$$

12.2.2 Performing time step extrapolation

In this section, we use a 32-atom supercell of MnO as an example system for time step extrapolation. Data for this system has been collected in DMC using the following sequence of time steps: 0.04, 0.02, 0.01, 0.005, 0.0025, 0.00125 Ha^{-1}. For a typical production pseudopotential study, time steps in the range of $0.02 - 0.002$ Ha^{-1} are usually sufficient and it is recommended to increase the number of steps/blocks by a factor of two when the time step is halved. To perform accurate statistical fitting, we must first understand the equilibration and autocorrelation properties of the inputted local energy data. After plotting the local energy traces (`qmca -t -q e -e 0 ./qmc*/*scalar*`), it is clear that an equilibration period of 30 blocks is reasonable. Approximate autocorrelation lengths are also obtained with `qmca`:

```
>qmca -e 30 -q e --sac ./qmc*/qmc.g000.s002.scalar.dat
./qmc_tm_0.00125/qmc.g000 series 2 LocalEnergy = -3848.234513 +/- 0.055754  1.7
./qmc_tm_0.00250/qmc.g000 series 2 LocalEnergy = -3848.237614 +/- 0.055432  2.2
./qmc_tm_0.00500/qmc.g000 series 2 LocalEnergy = -3848.349741 +/- 0.069729  2.8
./qmc_tm_0.01000/qmc.g000 series 2 LocalEnergy = -3848.274596 +/- 0.126407  3.9
./qmc_tm_0.02000/qmc.g000 series 2 LocalEnergy = -3848.539017 +/- 0.075740  2.4
./qmc_tm_0.04000/qmc.g000 series 2 LocalEnergy = -3848.976424 +/- 0.075305  1.8
```

The autocorrelation must be removed from the data before jackknifing, so we will reblock the data by a factor of 4.

The `qmc-fit` tool can be used in the following way to obtain a linear time step fit of the data:

```
>qmc-fit ts -e 30 -b 4 -s 2 -t '0.00125 0.0025 0.005 0.01 0.02 0.04' ./qmc*/*scalar*
fit function  : linear
fitted formula: (-3848.193 +/- 0.037) + (-18.95 +/- 1.95)*t
intercept     : -3848.193 +/- 0.037  Ha
```

The input arguments are as follows: `ts` indicates we are performing a time step fit, `-e 30` is the equilibration period removed from each set of scalar data, `-b 4` indicates the data will be reblocked by a factor of 4 (e.g., a file containing 400 entries will be block averaged into a new set of 100 before jackknife fitting), `-s 2` indicates that the time step data begins with series 2 (scalar files matching `*s000*` or `*s001*` are to be excluded), and `-t` '0.00125 0.0025 0.005 0.01 0.02 0.04' provides a list of time step values corresponding to the inputted scalar files. The `-e` and `-b` options can receive a list of file-specific values (same format as `-t`) if desired. As can be seen from the text output, the parameters for the linear fit are printed with error bars obtained with jackknife resampling and the zero time step "intercept" is $-3848.19(4)$ Ha. In addition to text output, the previous command will result in a plot of the fit with the zero time step value shown as a red dot, as shown in the top panel of Fig. 12.9.

Different fitting functions are supported via the `-f` option. Currently supported options include `linear` ($a + bt$), `quadratic` ($a + bt + ct^2$), and `sqrt` ($a + b\sqrt{t} + ct$). Results for a quadratic fit are shown subsequently and in the bottom panel of Fig. 12.9.

```
>qmc-fit ts -f quadratic -e30 -b4 -s2 -t '0.00125 0.0025 0.005 0.01 0.02 0.04' ./qmc*/
↪*scalar*
fit function  : quadratic
fitted formula: (-3848.245 +/- 0.047) + (-7.25 +/- 8.33)*t + (-285.00 +/- 202.39)*t^2
intercept     : -3848.245 +/- 0.047  Ha
```

In this case, we find a zero time step estimate of $-3848.25(5)$ Ha^{-1}. A time step of 0.04 Ha^{-1} might be on the large side to include in time step extrapolation, and it is likely to have an outsize influence in the case of linear extrapolation. Upon excluding this point, linear extrapolation yields a zero timestep value of $-3848.22(4)$ Ha^{-1}. Note that quadratic extrapolation can result in intrinsically larger uncertainty in the extrapolated value. For example, when the 0.04 Ha^{-1} point is excluded, the uncertainty grows by 50% and we obtain an estimated value of $-3848.28(7)$ instead.

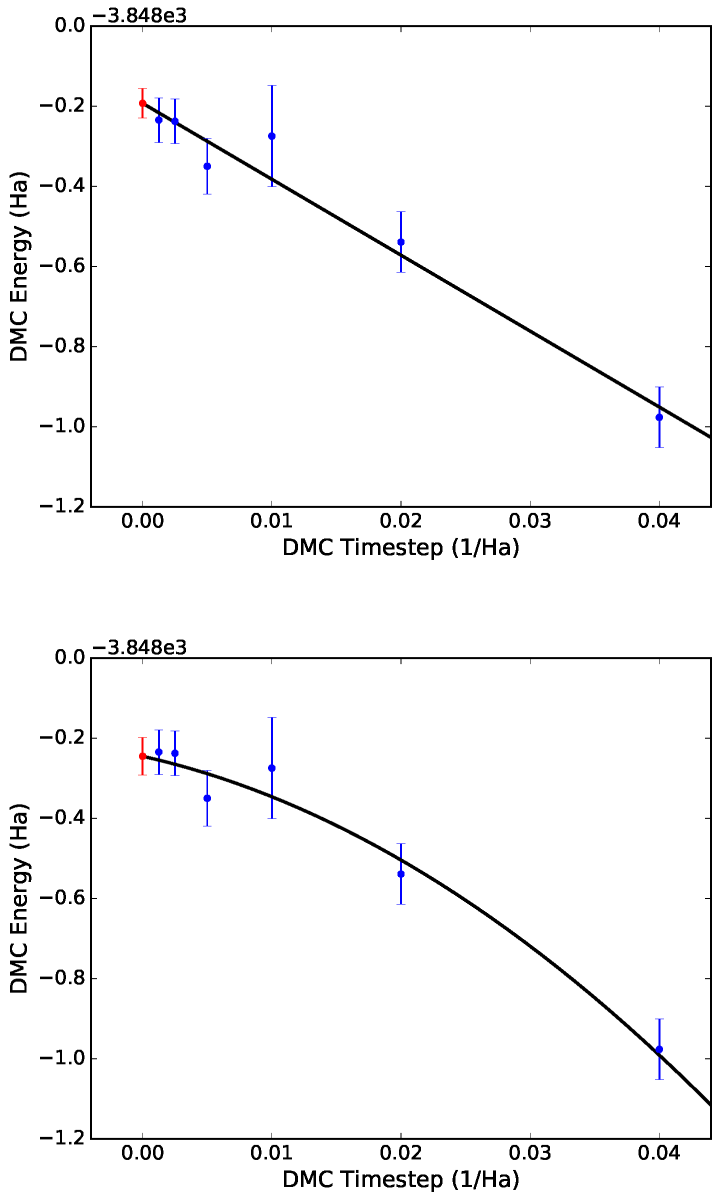

Fig. 12.9: Linear (top) and quadratic (bottom) time step fits to DMC data for a 32-atom supercell of MnO obtained with `qmc-fit`. Zero time step estimates are indicated by the red data point on the left side of either panel.

12.3 Using the qdens tool to obtain electron densities

The `qdens` tool is provided to post-process the heavy density data produced by QMCPACK and output the mean density (with and without errorbars) in file formats viewable with, e.g., XCrysDen or VESTA. The tool currently works only with the `SpinDensity` estimator in QMCPACK.

Note: this tool is provisional and may be changed or replaced at any time. The planned successor to this tool (`qstat`) will expand access to other observables and will retain at least the non-plotting capabilities of `qdens`.

To use `qdens`, Nexus must be installed along with NumPy and H5Py. A short list of example use cases are covered in the next section. Current input flags are:

```
>qdens

Usage: qdens [options] [file(s)]

Options:
  --version             show program's version number and exit
  -h, --help            Print help information and exit (default=False).
  -v, --verbose         Print detailed information (default=False).
  -f FORMATS, --formats=FORMATS
                        Format or list of formats for density file output.
                        Options: dat, xsf, chgcar (default=None).
  -e EQUILIBRATION, --equilibration=EQUILIBRATION
                        Equilibration length in blocks (default=0).
  -r REBLOCK, --reblock=REBLOCK
                        Block coarsening factor; use estimated autocorrelation
                        length (default=None).
  -a, --average         Average over files in each series (default=False).
  -w WEIGHTS, --weights=WEIGHTS
                        List of weights for averaging (default=None).
  -i INPUT, --input=INPUT
                        QMCPACK input file containing structure and grid
                        information (default=None).
  -s STRUCTURE, --structure=STRUCTURE
                        File containing atomic structure (default=None).
  -g GRID, --grid=GRID  Density grid dimensions (default=None).
  -c CELL, --cell=CELL  Simulation cell axes (default=None).
  --lineplot=LINEPLOT   Produce a line plot along the selected dimension: 0,
                        1, or 2 (default=None).
  --noplot              Do not show plots interactively (default=False).
```

12.3.1 Usage examples

Process a single file, excluding the first 40 blocks, and produce XSF files:

```
qdens -v -e 40 -f xsf -i qmc.in.xml qmc.s000.stat.h5
```

Process files for all available series:

```
qdens -v -e 40 -f xsf -i qmc.in.xml *stat.h5
```

Combine groups of 10 adjacent statistical blocks together (appropriate if the estimated autocorrelation time is about 10 blocks):

```
qdens -v -e 40 -r 10 -f xsf -i qmc.in.xml qmc.s000.stat.h5
```

Apply different equilibration lengths and reblocking factors to each series (below is appropriate if there are three series, e.g. `s000`, `s001`, and `s002`):

```
qdens -v -e '20 20 40' -r '4 4 8' -f xsf -i qmc.in.xml *stat.h5
```

Produce twist averaged densities (also works with multiple series and reblocking):

```
qdens -v -a -e 40 -f xsf -i qmc.g000.twistnum_0.in.xml qmc.g*.s000.stat.h5
```

Twist averaging with arbitrary weights can be performed via the `-w` option in a fashion identical to `qmca`.

12.3.2 Files produced

Look for files with names and extensions similar to:

```
qmc.s000.SpinDensity_u.xsf
qmc.s000.SpinDensity_u-err.xsf
qmc.s000.SpinDensity_u+err.xsf

qmc.s000.SpinDensity_d.xsf
qmc.s000.SpinDensity_d-err.xsf
qmc.s000.SpinDensity_d+err.xsf

qmc.s000.SpinDensity_u+d.xsf
qmc.s000.SpinDensity_u+d-err.xsf
qmc.s000.SpinDensity_u+d+err.xsf

qmc.s000.SpinDensity_u-d.xsf
qmc.s000.SpinDensity_u-d-err.xsf
qmc.s000.SpinDensity_u-d+err.xsf
```

Files postfixed with `u` relate to the up electron density, `d` to down, `u+d` to the total charge density, and `u-d` to the difference between up and down electron densities.

Files without `err` in the name contain only the mean, whereas files with `+err`/`-err` in the name contain the mean plus/minus the estimated error bar. Please use caution in interpreting the error bars as their accuracy depends crucially on a correct estimation of the autocorrelation time by the user (see `-r` option) and having a sufficient number of blocks remaining following any reblocking.

When twist averaging, the group tag (e.g. `g000` or similar) will be replaced with `avg` in the names of the outputted files.

CHAPTER

THIRTEEN

PERIODIC LCAO FOR SOLIDS

13.1 Introduction

QMCPACK implements the linear combination of atomic orbitals (LCAO) and Gaussian basis sets in periodic boundary conditions. This method uses orders of magnitude less memory than the real-space spline wavefunction. Although the spline scheme enables very fast evaluation of the wavefunction, it might require too much on-node memory for a large complex cell. The periodic Gaussian evaluation provides a fallback that will definitely fit in available memory but at significantly increased computational expense. Well-designed Gaussian basis sets should be used to accurately represent the wavefunction, typically including both diffuse and high angular momentum functions.

The current implementation is not highly optimized for efficiency but can handle real and complex trial wavefunctions generated by PySCF [[SBB+18]], but other codes such as Crystal can be interfaced on request. Supercell tiling is handled outside QMCPACK through a proper PySCF input generated by Nexus and the Supercell geometry and coefficients of the molecular orbotals are constructed in the converter provided by QMCPACK. This is different from the plane wave/spline route where the tiling is provided in QMCPACK.

LCAO schemes use physical considerations to construct a highly efficient basis set compared with plane waves. Typically only a few tens of basis functions per atom are required compared with thousands of plane waves. Many forms of LCAO schemes exist and are being implemented in QMCPACK. The details of the already-implemented methods are described in the following section.

GTOs: The Gaussian basis functions follow a radial-angular decomposition of

$$\phi(\mathbf{r}) = R_l(r)Y_{lm}(\theta,\phi)\,, \tag{13.1}$$

where $Y_{lm}(\theta,\phi)$ is a spherical harmonic, l and m are the angular momentum and its z component, and r,θ,ϕ are spherical coordinates. In practice, they are atom centered and the l expansion typically includes 1–3 additional channels compared with the formally occupied states of the atom (e.g., 4–6 for a nickel atom with occupied s, p, and d electron shells.

The evaluation of GTOs within PBC differs slightly from evaluating GTOs in open boundary conditions (OBCs). The orbitals are evaluated at a distance r in the primitive cell (similar to OBC), and then the contributions of the periodic images are added by evaluating the orbital at a distance $r + T$, where T is a translation of the cell lattice vector. This requires loops over the periodic images until the contributions are orbitals Φ. In the current implementation, the number of periodic images is an input parameter named `PBCimages`, which takes three integers corresponding to the number of periodic images along the supercell axes (X, Y and Z axes for a cubic cell). By default these parameters are set to `PBCimages= 8 8 8`, but they **require manual convergence checks**. Convergence checks can be performed by checking the total energy convergence with respect to `PBCimages`, similar to checks performed for plane wave cutoff energy and B-spline grids. Use of diffuse Gaussians might require these parameters to be increased, while sharply localized Gaussians might permit a decrease. The cost of evaluating the wavefunction increases sharply as `PBCimages` is increased. This input parameter will be replaced by a tolerance factor and numerical screening in the future.

13.2 Generating and using periodic Gaussian-type wavefunctions using PySCF

Similar to any QMC calculation, using periodic GTOs requires the generation of a periodic trial wavefunction. QMCPACK is currently interfaced to PySCF, which is a multipurpose electronic structure written mainly in Python with key numerical functionality implemented via optimized C and C++ libraries [[SBB+18]]. Such a wavefunction can be generated according to the following example for a $2 \times 1 \times 1$ supercell using tiling (kpoints) and a supertwist shifted away from Γ, leading to a complex wavefunction.

Listing 13.1: Example PySCF input for single k-point calculation for a $2 \times 1 \times 1$ carbon supercell.

```
#! /usr/bin/env python3
import numpy
import h5py
from pyscf.pbc import gto, scf, dft, df
from pyscf.pbc import df

cell = gto.Cell()
cell.a             = '''
         3.37316115       3.37316115       0.00000000
         0.00000000       3.37316115       3.37316115
         3.37316115       0.00000000       3.37316115'''
cell.atom = '''
   C        0.00000000       0.00000000       0.00000000
   C        1.686580575      1.686580575      1.686580575
            '''
cell.basis         = 'bfd-vdz'
cell.ecp           = 'bfd'
cell.unit          = 'B'
cell.drop_exponent = 0.1
cell.verbose       = 5
cell.charge        = 0
cell.spin          = 0
cell.build()


sp_twist=[0.07761248, 0.07761248, -0.07761248]

kmesh=[2,1,1]
kpts=[[ 0.07761248,  0.07761248, -0.07761248],[ 0.54328733,  0.54328733, -0.54328733]]


mf = scf.KRHF(cell,kpts)
mf.exxdiv = 'ewald'
mf.max_cycle = 200

e_scf=mf.kernel()

ener = open('e_scf','w')
ener.write('%s\n' % (e_scf))
print('e_scf',e_scf)
ener.close()

title="C_diamond-tiled-cplx"
from PyscfToQmcpack import savetoqmcpack
```

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```
savetoqmcpack(cell,mf,title=title,kmesh=kmesh,kpts=kpts,sp_twist=sp_twist)
```

Note that the last three lines of the file

```
title="C_diamond-tiled-cplx"
from PyscfToQmcpack import savetoqmcpack
savetoqmcpack(cell,mf,title=title,kmesh=kmesh,kpts=kpts,sp_twist=sp_twist)
```

contain the title (name of the HDF5 to be used in QMCPACK) and the call to the converter. The title variable will be the name of the HDF5 file where all the data needed by QMCPACK will be stored. The function *savetoqmcpack* will be called at the end of the calculation and will generate the HDF5 similarly to the non-periodic PySCF calculation in *convert4qmc*. The function is distributed with QMCPACK and is located in the qmcpack/src/QMCTools directory under the name *PyscfToQmcpack.py*. Note that you need to specify the supertwist coordinates that was used with the provided kpoints. The supertwist must match the coordinates of the K-points otherwise the phase factor for the atomic orbital will be incorrect and incorrect results will be obtained. (For more details on how to generate tiling with PySCF and Nexus, refer to the Nexus guide or the 2019 QMCPACK Workshop material available on github: https://github.com/QMCPACK/qmcpack_workshop_2019 under **qmcpack_workshop_2019/day2_nexus/pyscf/04_pyscf_diamond_hf_qmc/**

For the converter in the script to be called properly, you need to specify the path to the file in your PYTHONPATH such as

```
export PYTHONPATH=QMCPACK_PATH/src/QMCTools:$PYTHONPATH
```

To generate QMCPACK input files, you will need to run `convert4qmc` exactly as specified in *convert4qmc* for both cases:

```
convert4qmc -pyscf C_diamond-tiled-cplx
```

This tool can be used with any option described in convert4qmc. Since the HDF5 contains all the information needed, there is no need to specify any other specific tag for periodicity. A supercell at Γ-point or using multiple k-points will work without further modification.

Running convert4qmc will generate 3 input files:

Listing 13.2: C_diamond-tiled-cplx.structure.xml. This file contains the geometry of the system.

```
<?xml version="1.0"?>
<qmcsystem>
  <simulationcell>
    <parameter name="lattice">
  6.74632230000000e+00  6.74632230000000e+00  0.00000000000000e+00
  0.00000000000000e+00  3.37316115000000e+00  3.37316115000000e+00
  3.37316115000000e+00  0.00000000000000e+00  3.37316115000000e+00
</parameter>
    <parameter name="bconds">p p p</parameter>
    <parameter name="LR_dim_cutoff">15</parameter>
  </simulationcell>
  <particleset name="ion0" size="4">
    <group name="C">
      <parameter name="charge">4</parameter>
      <parameter name="valence">4</parameter>
      <parameter name="atomicnumber">6</parameter>
    </group>
    <attrib name="position" datatype="posArray">
```

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```
  0.0000000000e+00  0.0000000000e+00  0.0000000000e+00
  1.6865805750e+00  1.6865805750e+00  1.6865805750e+00
  3.3731611500e+00  3.3731611500e+00  0.0000000000e+00
  5.0597417250e+00  5.0597417250e+00  1.6865805750e+00
</attrib>
    <attrib name="ionid" datatype="stringArray">
 C C C C
</attrib>
  </particleset>
  <particleset name="e" random="yes" randomsrc="ion0">
    <group name="u" size="8">
      <parameter name="charge">-1</parameter>
    </group>
    <group name="d" size="8">
      <parameter name="charge">-1</parameter>
    </group>
  </particleset>
</qmcsystem>
```

As one can see, for both examples, the two-atom primitive cell has been expanded to contain four atoms in a $2 \times 1 \times 1$ carbon cell.

Listing 13.3: C_diamond-tiled-cplx.wfj.xml. This file contains the trial wavefunction.

```
<?xml version="1.0"?>
<qmcsystem>
  <wavefunction name="psi0" target="e">
    <determinantset type="MolecularOrbital" name="LCAOBSet" source="ion0" transform=
↪"yes" twist="0.07761248  0.07761248  -0.07761248" href="C_diamond-tiled-cplx.h5"␣
↪PBCimages="8  8  8">
      <slaterdeterminant>
        <determinant id="updet" size="8">
          <occupation mode="ground"/>
          <coefficient size="52" spindataset="0"/>
        </determinant>
        <determinant id="downdet" size="8">
          <occupation mode="ground"/>
          <coefficient size="52" spindataset="0"/>
        </determinant>

      </slaterdeterminant>
    </determinantset>
    <jastrow name="J2" type="Two-Body" function="Bspline" print="yes">
      <correlation size="10" speciesA="u" speciesB="u">
        <coefficients id="uu" type="Array"> 0 0 0 0 0 0 0 0 0 0</coefficients>
      </correlation>
      <correlation size="10" speciesA="u" speciesB="d">
        <coefficients id="ud" type="Array"> 0 0 0 0 0 0 0 0 0 0</coefficients>
      </correlation>
    </jastrow>
    <jastrow name="J1" type="One-Body" function="Bspline" source="ion0" print="yes">
      <correlation size="10" cusp="0" elementType="C">
        <coefficients id="eC" type="Array"> 0 0 0 0 0 0 0 0 0 0</coefficients>
      </correlation>
    </jastrow>
```

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```
  </wavefunction>
</qmcsystem>
```

This file contains information related to the trial wavefunction. It is identical to the input file from an OBC calculation to the exception of the following tags:

*.wfj.xml specific tags:

tag	tag type	default	description
`twist`	3 doubles	(0 0 0)	Coordinate of the twist to compute
`href`	string	default	Name of the HDF5 file generated by PySCF and used for convert4qmc
`PBCimages`	3 Integer	8 8 8	Number of periodic images to evaluate the orbitals

Other files containing QMC methods (such as optimization, VMC, and DMC blocks) will be generated and will behave in a similar fashion regardless of the type of SPO in the trial wavefunction.

CHAPTER

FOURTEEN

SELECTED CONFIGURATION INTERACTION

A direct path towards improving the accuracy of a QMC calculation is through a better trial wavefunction. Although using a multireference wavefunction can be straightforward in theory, in actual practice methods such as CASSCF are not always intuitive and often require being an expert in either the method or the code generating the wavefunction. An alternative is to use a selected configuration of interaction method (selected CI) such as CIPSI (configuration interaction using a perturbative selection done iteratively). This provides a direct route to systematically improving the wavefunction.

14.1 Theoretical background

The principle behind selected CI is rather simple and was first published in 1955 by R. K. Nesbet [[Nes55]]. The first calculations on atoms were performed by Diner, Malrieu, and Claverie [[DMC67]] in 1967 and became computationally viable for larger molecules in 2013 by Caffarel et al. [[EG13]].

As described by Caffarel et al. in [[EG13]], multideterminantal expansions of the ground-state wavefunction Ψ_T are written as a linear combination of Slater determinants

$$\sum_k c_k \sum_q d_{k,q} D_{k,q\uparrow}(r^\uparrow) D_{k,q\downarrow}(r^\downarrow) \,, \tag{14.1}$$

where each determinant corresponds to a given occupation by the N_α and N_β electrons of $N = N_\alpha + N_\beta$ orbitals among a set of M spin-orbitals $\{\phi_1, ., \phi_M\}$ (restricted case). When no symmetries are considered, the maximum number of such determinants is

$$\left(\begin{array}{c} M \\ N_\alpha \end{array} \right) . \left(\begin{array}{c} M \\ N_\beta \end{array} \right) , \tag{14.2}$$

a number that grows factorially with M and N. The best representation of the exact wavefunction in the determinantal basis is the full configuration interaction (FCI) wavefunction written as

$$|\Psi_0\rangle = \sum_i c_i |D_i\rangle \,, \tag{14.3}$$

where c_i are the ground-state coefficients obtained by diagonalizing the matrix, $H_{ij} = \langle D_i|H|D_j\rangle$, within the full orthonormalized set $\langle D_i||D_j\rangle = \delta_{ij}$ of determinants $|D_i\rangle$. CIPSI provides a convenient method to build up to this full wavefunction with a single criteria.

A CIPSI wavefunction is built iteratively starting from a reference wavefunction, usually Hartree-Fock or CASSCF, by adding all single and double excitations and then iteratively selecting relevant determinants according to some criteria. Detailed iterative steps can be found in the reference by Caffarel et al. and references within [[EG13]], [[SAGC16]], [[SGCL0]] and [[GSLC17]] and are summarized as follows:

- Step 1: Define a reference wavefunction:

$$|\Psi\rangle = \sum_{i \in D} c_i |i\rangle \qquad E_{var} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | | \Psi \rangle}. \tag{14.4}$$

- Step 2: Generate external determinants $|\alpha\rangle$: New determinants are added by generating all single and double excitations from determinants $i \in D$ such as:

$$\langle \Psi_0^{(n)} | H | D_{i_c} \rangle \neq 0 \, . \tag{14.5}$$

- Step 3: Evaluate the second-order perturbative contribution to each determinant $|\alpha\rangle$:

$$\Delta E = \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E_{var} - \langle \alpha | \hat{H} | \alpha \rangle} \, . \tag{14.6}$$

- Step 4: Select the determinants with the largest contributions and add them to the Hamiltonian.
- Step 5: Diagonalize the Hamiltonian within the new added determinants and update the wavefunction and the the value of E_{var}.
- Step 6: Iterate until reaching convergence.

Repeating this process leads to a multireference trial wavefunction of high quality that can be used in QMC.

$$\Psi_T(r) = e^{J(r)} \sum_k c_k \sum_q d_{k,q} D_{k,q\uparrow}(r^\uparrow) D_{k,q\downarrow}(r^\downarrow) \, . \tag{14.7}$$

The linear coefficients c_k are then optimized with the presence of the Jastrow function.

Note the following:

- When all determinants $|\alpha\rangle$ are selected, the full configuration interaction result is obtained.
- CIPSI can be seen as a deterministic counterpart of FCIQMC.
- In practice, any wavefunction method can be made multireference with CIPSI. For instance, a multireference coupled cluster (MRCC) with CIPSI is implemented in QP. [[GGMS17]]
- At any time, with CIPSI selection, $E_{PT_2} = \sum_\alpha \Delta E_\alpha$ estimates the distance to the FCI solution.

14.1.1 CIPSI wavefunction interface

The CIPSI method is implemented in the QP code:cite:*QP* developed by the Caffarel group. Once the trial wavefunction is generated, QP is able to produce output readable by the QMCPACK converter as described in *convert4qmc*. QP can be installed with multiple plugins for different levels of theory in quantum chemistry. When installing the "QMC" plugin, QP can save the wavefunction in a format readable by the QMCPACK converter.

In the following we use the $C_2O_2H_3N$ molecule (Fig. 14.1) as an example of how to run a multireference calculation with CIPSI as a trial wavefunction for . The choice of this molecule is motivated by its multireference nature. Although the molecule remains small enough for CCSD(T) calculations with aug-cc-pVTZ basis set, the D1 diagnostic shows a very high value for $C_2O_2H_3N$, suggesting a multireference character. Therefore, an accurate reference for the system is not available, and it becomes difficult to trust the quality of a single-determinant wavefunction even when using the DFT-B3LYP exchange and correlation functional. Therefore, in the following, we show an example of how to systematically improve the nodal surface by increasing the number of determinants in the trial wavefunction.

The following steps show how to run from Hartree-Fock to selected CI using QP2, convert the wavefunction to a QMCPACK trial wavefunction, and analyze the result.

- Step 1: Generate the QP input file. QP takes for input an XYZ file containing the geometry of the molecule such as:

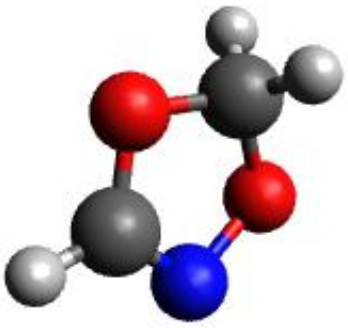

Fig. 14.1: $C_2O_2H_3N$ molecule.

8			
C2O2H3N			
C	1.067070	-0.370798	0.020324
C	-1.115770	-0.239135	0.081860
O	-0.537581	1.047619	-0.091020
N	0.879629	0.882518	0.046830
H	-1.525096	-0.354103	1.092299
H	-1.868807	-0.416543	-0.683862
H	2.035229	-0.841662	0.053363
O	-0.025736	-1.160835	-0.084319

The input file is generated through the following command line:

```
qp_create_ezfio C2O2H3N.xyz -b cc-pvtz
```

This means that we will be simulating the molecule in all electrons within the cc-pVTZ basis set. Other options are, of course, possible such as using ECPs, different spin multiplicities, etc. For more details, see the QP tutorial at https://quantumpackage.github.io/qp2/

A directory called `C2O2H3N.ezfio` is created and contains all the relevant data to run the SCF Hartree-Fock calculation. Note that because of the large size of molecular orbitals (MOs) (220), it is preferable to run QP in parallel. QP parallelization is based on a master/slave process that allows a master node to manage the work load between multiple MPI processes through the LibZMQ library. In practice, the run is submitted to one master node and is then submitted to as many nodes as necessary to speed up the calculations. If a slave node dies before the end of its task, the master node will resubmit the workload to another available node. If more nodes are added at any time during the simulation, the master node will use them to reduce the time to solution.

- Step 2: Run Hartree-Fock. To save the integrals on disk and avoid recomputing them later, edit the `ezfio` directory with the following command:

```
qp_edit C2O2H3N.ezfio
```

This will generate a temporary file showing all the contents of the simulation and opens an editor to allow modification of their values. Look for `io_ao_one_e_integrals` and modify its value from `None` to `Write`.

To run a simulation with QP, use the binary texttt{qp_run} with the desired level of theory, in this case Hartree-Fock (scf).

```
mpirun -np 1 qp_run scf C2O2H3N.ezfio &> C2O2H3N-SCF.out
```

If run in serial, the evaluation of the integrals and the Hamiltonian diagonalization would take a substantial amount of computer time. We recommend adding a few more slave nodes to help speed up the calculation.

```
mpirun -np 20 qp_run -s scf C2O2H3N.ezfio &> C2O2H3N-SCF-Slave.out
```

The total Hartree-Fock energy of the system in cc-pVTZ is *:math:`E_{HF}=-283.0992`*Ha.

- Step 3: Freeze core electrons. To avoid making excitation from the core electrons, freeze the core electrons and do only the excitations from the valence electrons.

```
qp_set_frozen_core C2O2H3N.ezfio
```

This will will automatically freeze the orbitals from 1 to 5, leaving the remaining orbitals active.

- Step 4: Transform atomic orbitals (AOs) to MOs. This step is the most costly, especially given that its implementation in QP is serial. We recommend completing it in a separate run and on one node.

```
qp_run four_idx_transform C2O2H3N.ezfio
```

The MO integrals are now saved on disk, and unless the orbitals are changed, they will not be recomputed.

- Step 5: CIPSI At this point the wavefunction is ready for the selected CI. By default, QP has two convergence criteria: the number of determinants (set by default to 1M) or the value of PT2 (set by default to 1.10^{-4}Ha). For this molecule, the total number of determinants in the FCI space is $2.07e+88$ determinants. Although this number is completely out of range of what is possible to compute, we will set the limit of determinants in QP to 5M determinants and see whether the nodal surface of the wavefunction is converged enough for the DMC. At this point it is important to remember that the main value of CIPSI compared with other selected CI methods, is that the value of PT2 is evaluated directly at each step, giving a good estimate of the error to the FCI energy. This allows us to conclude that when the E+PT2 energy is converged, the nodal surface is also probably converged. Similar to the SCF runs, FCI runs have to be submitted in parallel with a master/slave process:

```
mpirun -np 1 qp_run fci C2O2H3N.ezfio &> C2O2H3N-FCI.out &
sleep 300
mpirun -np 199 qp_run -s fci C2O2H3N.ezfio &> C2O2H3N-FCI-Slave.out
wait
```

- Step 6 (optional): Natural orbitals Although this step is optional, it is important to note that using natural orbitals instead of Hartree-Fock orbitals will always improve the quality of the wavefunction and the nodal surface by reducing the number of needed determinants for the same accuracy. When a full convergence to the FCI limit is attainable, this step will not lead to any change in the energy but will only reduce the total number of determinants. However, if a full convergence is not possible, this step can significantly increase the accuracy of the calculation at the same number of determinants.

```
qp_run save_natorb C2O2H3N.ezfio
```

At this point, the orbitals are modified, a new AO $\rightarrow$MO transformation is required, and steps 3 and 4 need to be run again.

- Step 7: Analyze the CIPSI results. Fig. 14.2 shows the evolution of the variational energy and the energy corrected with PT2 as a function of the number of determinants up to 4M determinants. Although it is clear that the raw variational energy is far from being converged, the Energy + PT2 appears converged around 0.4M determinants.

- Step 8: Truncate the number of determinants. Although using all the 4M determinants from CIPSI always guarantees that all important determinants are kept in the wavefunction, practically, such a large number of

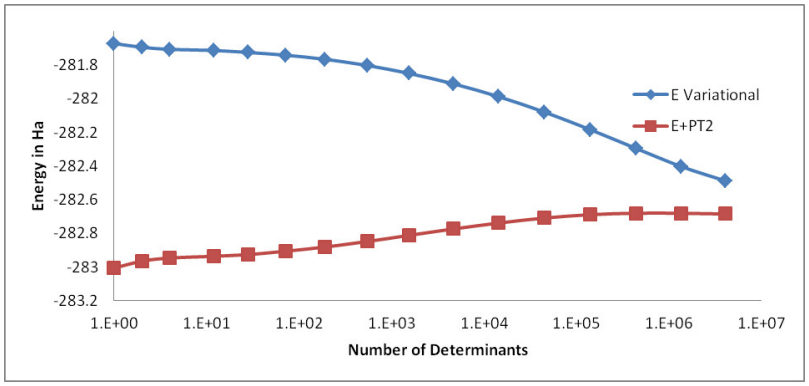

Fig. 14.2: Evolution of the variational energy and the Energy + PT2 as a function of the number of determinants for the $C_2O_2H_3N$ molecule.

determinants would make any QMC calculation prohibitively expensive because the cost of evaluating a determinant in DMC grows as $\sqrt{N_{det}}$, where N_{det} is the number of determinants in the trial wavefunction. To truncate the number of determinants, we follow the method described by Scemama et al. [[SGCL0]] where the wavefunction is truncated by independently removing spin-up and spin-down determinants whose contribution to the norm of the wavefunction is below a user-defined threshold, ϵ. For this step, we choose to truncate the determinants whose coefficients are below, 1.10^{-3}, 1.10^{-4}, 1.10^{-5}, and 1.10^{-6}, translating to 239, 44539, 541380, and 908128 determinants, respectively.

To truncate the determinants in QP, edit the `ezfio` file as follows:

```
qp_edit C2O2H3N.ezfio
```

Then look for `ci\_threshold` and modify the value according to the desired threshold. Use the following run to truncate the determinants:

```
qp_run truncate_wf_spin C2O2H3N.ezfio
```

Method	N_det	Energy
Hartree-Fock	1	-281.6729
Natural orbitals	1	-281.6735
E_Variational	438,753	-282.2951
E_Variational	4,068,271	-282.4882
E+PT2	438,753	-282.6809
E+PT2	4,068,271	-282.6805

Table 14.1.1 Energies of $C_2O_2H_3N$ using orbitals from Hartree-Fock, natural orbitals, and 0.4M and 4M determinants

- Save the wavefunction for QMCPACK. The wavefunction in QP is now ready to be converted to QMCPACK format. Save the wavefunction into QMCPACK format and then convert the wavefunction using the `convert4qmc` tool.

```
qp_run save_for_qmcpack C2O2H3N.ezfio
convert4qmc -orbitals QP2QMCPACK.h5 -multidets QP2QMCPACK.h5 -addCusp -production
```

Note that QP2 produces an HDF5 file in the QMCPACK format, named QP2QMCPACK. Such file can be used fir single determinants or multideterminants calculations. Since we are running all-electron calculations, orbitals in QMC need to be corrected for the electron-nuclearcusp condition. This is done by adding the option `-addCusp` to `convert4qmc`, which adds a tag forcing QMCPACK to run the correction or read them from a

file if pre-computed. When running multiple DMC runs with different truncation thresholds, only the number of determinants is varied and the orbitals remain unchanged from one calculation to another and the cusp correction needs to be run only once.

- Step 10: Run QMCPACK. At this point, running a multideterminant DMC becomes identical to running a regular DMC with QMCPACK; After correcting the orbitals for the cusp, optimize the Jastrow functions and then run the DMC. It is important, however, to note a few items:

  (1) QMCPACK allows reoptimization of the coefficients of the determinants during the Jastrow optimization step. Although this has proven to lower the energy significantly when the number of determinants is below 10k, a large number of determinants from CIPSI is often too large to optimize conveniently. Keeping the coefficients of the determinants from CIPSI unoptimized is an alternative strategy.

  (2) The large determinant expansion and the Jastrows are both trying to recover the missing correlations from the system. When optimizing the Jastrows, we recommend first optimizing J1 and J2 without the J3, and then with the added J3. Trying to initially optimize J1, J2, and J3 at the same time could lead to numerical instabilities.

  (3) The parameters of the Jastrow function will need to be optimized for each truncation scheme and usually cannot be reused efficiently from one truncation scheme to another.

- Step 11: Analyze the DMC results from QMCPACK. From Table 14.1.1, we can see that increasing the number of determinants from 0.5M to almost 1M keeps the energy within error bars and does not improve the quality of the nodal surface. We can conclude that the DMC energy is converged at 0.54M determinants. Note that this number of determinants also corresponds to the convergence of E+PT2 in CIPSI calculations, confirming for this case that the convergence of the nodal surface can follow the convergence of E+PT2 instead of the more difficult variational energy.

N_det	DMC	CISPI
1	-283.0696 (6)	-283.0063
239	-283.0730 (9)	-282.9063
44,539	-283.078 (1)	-282.7339
541,380	-283.088 (1)	-282.6772
908,128	-283.089 (1)	-282.6775

Table 12 DMC Energies and CIPSI(E+PT2) of $C_2O_2H_3N$ in function of the number of determinants in the trial wavefunction.

As mentioned in previous sections, DMC is variational relative to the exact nodal surface. A nodal surface is "better" if it lowers DMC energy. To assess the quality of the nodal surface from CIPSI, we compare these DMC results to other single-determinant calculations from multiple nodal surfaces and theories. Fig. 14.3 shows the energy of the $C_2O_2H_3N$ molecule as a function of different single-determinant trial wavefunctions with an aug-cc-pVTZ basis set, including Hartree-Fock, DFT-PBE, and hybrid functionals B3LYP and PBE0. The last four points in the plot show the systematic improvement of the nodal surface as a function of the number of determinants.

When the DMC-CIPSI energy is converged with respect to the number of determinants, its nodal surface is still lower than the best SD-DMC (B3LYP) by 6(1) mHa. When compared with CCSD(T) with the same basis set, $E_{CCSD(T)}$ is 4 mHa higher than DMC-CIPSI and 2 mHa lower than DMC-B3LYP. Although 6 (1) mHa can seem very small, it is important to remember that CCSD(T) cannot correctly describe multireference systems; therefore, it is impossible to assess the correctness of the single-determinant–DMC result, making CIPSI-DMC calculations an ideal benchmark tool for multireference systems.

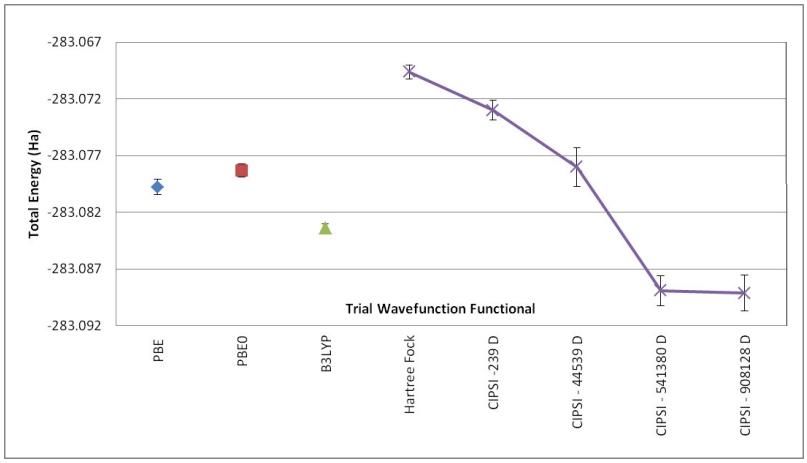

Fig. 14.3: DMC energy of the $C_2O_2H_3N$ molecule as a function of different single-determinant trial wavefunctions with aug-ccp-VTZ basis set using nodal surfaces from Hartree-Fock, DFT-PBE, and DFT with hybrid functionals PBE0 and P3LYP. As indicated, the CIPSI trial wavefunction contains 239, 44539, 514380, and 908128 determinants (D).

CHAPTER

FIFTEEN

SPIN-ORBIT CALCULATIONS IN QMC

15.1 Introduction

In order to introduce relativistic effects in real materials, in principle the full Dirac equation must be solved where the resulting wave function is a four-component spinor. For the valence electrons that participate in chemistry, the single particle spinors can be well approximated by two-component spinors as two of the components are negligible. Note that this is not true for the deeper core electrons, where all four components contribute. In light of this fact, relativistic pseudopotentials have been developed to remove the core electrons while providing an effective potential for the valence electrons [[DC12]]. This allows relativistic effects to be studied in QMC methods using two-component spinor wave functions.

In QMCPACK, spin-orbit interactions have been implemented following the methodology described in [[MZG+16]] and [[MBM16]]. We briefly describe some of the details below.

15.2 Single-Particle Spinors

The single particle spinors used in QMCPACK take the form

$$\begin{aligned} \phi(\mathbf{r}, s) = \\ \phi^{\uparrow}(\mathbf{r})\chi^{\uparrow}(s) + \phi^{\downarrow}(\mathbf{r})\chi^{\downarrow}(s) \\ = \\ \phi^{\uparrow}(\mathbf{r})e^{is} + \phi^{\downarrow}(\mathbf{r})e^{-is}\,, \end{aligned} \tag{15.1}$$

where s is the spin variable and using the complex spin representation. In order to carry out spin-orbit calculations in solids, the single-particle spinors can be obtained using Quantum ESPRESSO. After carrying out the spin-orbit calculation in QE (with flags `noncolin` = .true., `lspinorb` = .true., and a relativistic `.UPF` pseudopotential), the spinors can be obtained by using the converter *convertpw4qmc*:

```
convertpw4qmc data-file-schema.xml
```

where the `data-file-schema.xml` file is output from your QE calculation. This will produce an `eshdf.h5` file which contains the up and down components of the spinors per k-point.

15.3 Trial Wavefunction

Using the generated single particle spinors, we build the many-body wavefunction in a similar fashion to the normal non-relativistic calculations, namely

$$\Psi_T(\mathbf{R},\mathbf{S}) = e^J \sum_\alpha c_\alpha \det_\alpha \left[\phi_i(\mathbf{r}_j, s_j)\right] \ , \tag{15.2}$$

where we now utilize determinants of spinors, as opposed to the usual product of up and down determinants. An example xml input block for the trial wave function is show below:

Listing 15.1: wavefunction specification for a single determinant trial wave function

```
<?xml version="1.0"?>
<qmcsystem>
  <wavefunction name="psi0" target="e">
    <sposet_builder name="spo_builder" type="bspline" href="eshdf.h5" tilematrix=
↪"100010001" twistnum="0" source="ion0" size="10">
      <sposet type="bspline" name="myspo" size="10">
        <occupation mode="ground"/>
      </sposet>
    </sposet_builder>
    <determinantset>
      <slaterdeterminant>
        <determinant id="det" group="u" sposet="myspo" size="10"/>
      </slaterdeterminant>
    </determinantset>
    <jastrow type="One-Body" name="J1" function="bspline" source="ion0" print="yes">
        <correlation elementType="O" size="8" cusp="0.0">
           <coefficients id="eO" type="Array">
           </coefficients>
        </correlation>
     </jastrow>
    <jastrow type="Two-Body" name="J2" function="bspline" print="yes">
      <correlation speciesA="u" speciesB="u" size="8">
        <coefficients id="uu" type="Array">
        </coefficients>
      </correlation>
    </jastrow>
  </wavefunction>
</qmcsystem>
```

We note that we only specify an "up" determinant, since we no longer need a product of up and down determinants. In the Jastrow specification, we only need to provide the jastrow terms for the same spin as there is no longer a distinction between the up and down spins.

We also make a small modification in the particleset specification:

Listing 15.2: specification for the electron particle when performing spin-orbit calculations

```
<particleset name="e" random="yes" randomsrc="ion0" spinor="yes">
   <group name="u" size="10" mass="1.0">
      <parameter name="charge"              >    -1                    </parameter>
      <parameter name="mass"                >    1.0                   </parameter>
   </group>
</particleset>
```

Note that we only provide a single electron group to represent all electrons in the system, as opposed to the usual separation of up and down electrons. The additional keyword `spinor=yes` is the *only* required keyword for spinors. This will be used internally to determine which movers to use in QMC drivers (e.g. VMCUpdatePbyP vs SOVMCUpdatePbyP) and which SPOSets to use in the trial wave function (spinors vs. normal orbitals)

note: In the current implementation, spinor wavefunctions are only supported at the single determinant level. Multi-determinant spinor wave functions will be supported in a future release.

15.4 QMC Methods

In this formalism, the spin degree of freedom becomes a continuous variable similar to the spatial degrees of freedom. In order to sample the spins, we introduce a *spin kinetic energy* operator

$$T_s = \sum_{i=1}^{N_e} -\frac{1}{2\mu_s}\left[\frac{\partial^2}{\partial s_i^2} + 1\right] , \tag{15.3}$$

where μ_s is a spin mass. This operator vanishes when acting on an arbitrary spinor or anti-symmetric product of spinors due to the offset. This avoids any unphysical contribution to the local energy. However, this does contribute to the Green's function in DMC,

$$G(\mathbf{R}'\mathbf{S}' \leftarrow \mathbf{R}\mathbf{S}; \tau, \mu_s) \propto G(\mathbf{R}' \leftarrow \mathbf{R}; \tau) \exp\left[-\frac{\mu_s}{2\tau}\left|\mathbf{S}' - \mathbf{S} - \frac{\tau}{\mu_s}\mathbf{v}_\mathbf{S}(\mathbf{S})\right|^2\right] , \tag{15.4}$$

where $G(\mathbf{R}' \leftarrow \mathbf{R}; \tau)$ is the usual Green's function for the spatial evolution and the *spin kinetic energy* operator introduces a Green's function for the spin variables. Note that this includes a contribution from the *spin drift* $\mathbf{v}_\mathbf{S}(\mathbf{S}) = \nabla_\mathbf{S} \ln \Psi_T(\mathbf{S})$.

In both the VMC and DMC methods, there are no required changes to a typical input

```
<qmc method="vmc/dmc">
  <parameter name="steps"    >    50   </parameter>
  <parameter name="blocks"   >    50   </parameter>
  <parameter name="walkers"  >    10   </parameter>
  <parameter name="timestep" >  0.01   </parameter>
</qmc>
```

Whether or not spin moves are used is determined internally by the `spinor=yes` flag in particleset.

By default, the spin mass μ_s (which controls the rate of spin sampling relative to the spatial sampling) is set to 1.0. This can be changed by adding an additional parameter to the QMC input

```
<parameter name="spinMass" > 0.25 </parameter>
```

A larger/smaller spin mass corresponds to slower/faster spin sampling relative to the spatial coordinates.

15.5 Spin-Orbit Effective Core Potentials

The spin-orbit contribution to the Hamiltonian can be introduced through the use of Effective Core Potentials (ECPs). As described in [[MBM16]], the relativistic (semilocal) ECPs take the general form

$$W^{\mathrm{RECP}} = W_{LJ}(r) + \sum_{\ell j m_j} W_{\ell j}(r)|\ell j m_j\rangle\langle \ell j m_j| , \tag{15.5}$$

where the projectors $|\ell j m_j\rangle$ are the so-called spin spherical harmonics. An equivalent formulation is to decouple the fully relativistic effective core potential (RECP) into *averaged relativistic* (ARECP) and *spin-orbit* (SORECP) contributions:

$$\begin{aligned} W^{\mathrm{RECP}} = \\ W^{\mathrm{ARECP}} + W^{\mathrm{SOECP}} \\ W^{\mathrm{ARECP}} = \\ W_L^{\mathrm{ARECP}}(r) + \sum_{\ell m_\ell} W_\ell^{ARECP}(r) |\ell m_\ell\rangle\langle \ell m_\ell| \\ W^{\mathrm{SORECP}} = \\ \sum_\ell \frac{2}{2\ell+1} \Delta W_\ell^{\mathrm{SORECP}}(r) \sum_{m_\ell, m'_\ell} |\ell m_\ell\rangle\langle \ell m_\ell| \vec{\ell}\cdot\vec{s} |\ell m'_\ell\rangle\langle \ell m'_\ell| \,. \end{aligned} \tag{15.6}$$

Note that the W^{ARECP} takes exactly the same form as the semilocal pseudopotentials used in standard QMC calculations. In the pseudopotential `.xml` file format, the $W_\ell^{\mathrm{ARECP}}(r)$ terms are tabulated as usual. If spin-orbit terms are included in the `.xml` file, the file must tabulate the entire radial spin-orbit prefactor $\frac{2}{2\ell+1}\Delta W_\ell^{\mathrm{SORECP}}(r)$. We note the following relations between the two representations of the relativistic potentials

$$\begin{aligned} W_\ell^{\mathrm{ARECP}}(r) = \\ \frac{\ell+1}{2\ell+1} W^{\mathrm{RECP}}_{\ell, j=\ell+1/2}(r) + \frac{\ell}{2\ell+1} W^{\mathrm{RECP}}_{\ell, j=\ell-1/2}(r) \\ \Delta W_\ell^{\mathrm{SORECP}}(r) = \\ W^{\mathrm{RECP}}_{\ell, j=\ell+1/2}(r) - W^{\mathrm{RECP}}_{\ell, j=\ell-1/2}(r) \end{aligned} \tag{15.7}$$

The structure of the spin-orbit `.xml` is

```
<?xml version="1.0" encoding="UTF-8"?>
<pseudo>
  <header ... relativistic="yes" ... />
  <grid ... />
  <semilocal units="hartree" format="r*V" npots-down="4" npots-up="0" l-local="3"␣
↪npots="2">
    <vps l="s" .../>
    <vps l="p" .../>
    <vps l="d" .../>
    <vps l="f" .../>
    <vps_so l="p" .../>
    <vps_so l="d" .../>
  </semilocal>
</pseudo>
```

This is included in the Hamiltonian in the same way as the usual pseudopotentials. If the `<vps_so>` elements are found, the spin-orbit contributions will be present in the calculation. By default, the spin-orbit terms *will be* included in the local energy. In order to accumulate the spin-orbit energy, but exclude it from the local energy (and therefore will not be propogated into the walker weights in DMC for example), the `physicalSO` flag should be set to no in the Hamiltonian input. A typical application will include the SOC terms in the local energy, and an example input block is given as

```
<hamiltonian name="h0" type="generic" target="e">
  <pairpot name="ElecElec" type="coulomb" source="e" target="e" physical="true"/>
  <pairpot name="IonIon" type="coulomb" source=ion0" target="ion0" physical="true"/>
  <pairpot name="PseudoPot" type="pseudo" source="i" wavefunction="psi0" format="xml">
    <pseudo elementType="Pb" href="Pb.xml"/>
  </pairpot>
</hamiltonian>
```

The contribution from the spin-orbit will be printed to the `.stat.h5` and `.scalar.dat` files for post-processing. An example output is shown below

```
LocalEnergy              =           -3.4419 +/-           0.0014
Variance                 =            0.1132 +/-           0.0013
Kinetic                  =            1.1252 +/-           0.0027
LocalPotential           =           -4.5671 +/-           0.0028
ElecElec                 =            1.6881 +/-           0.0025
LocalECP                 =           -6.5021 +/-           0.0062
NonLocalECP              =            0.3286 +/-           0.0025
LocalEnergy_sq           =           11.9601 +/-           0.0086
SOECP                    =          -0.08163 +/-           0.0003
```

The `NonLocalECP` represents the W^{ARECP}, `SOECP` represents the W^{SORECP}, and the sum is the full W^{RECP} contribution.

CHAPTER

SIXTEEN

AUXILIARY-FIELD QUANTUM MONTE CARLO

The AFQMC method is an orbital-space formulation of the imaginary-time propagation algorithm. We refer the reader to one of the review articles on the method [[PZ04], [Zha13], [ZK03]] for a detailed description of the algorithm. It uses the Hubbard-Stratonovich transformation to express the imaginary-time propagator, which is inherently a 2-body operator, as an integral over 1-body propagators, which can be efficiently applied to an arbitrary Slater determinant. This transformation allows us to represent the interacting many-body system as an average over a noninteracting system (e.g., Slater determinants) in a time-dependent fluctuating external field (the Auxiliary fields). The walkers in this case represent nonorthogonal Slater determinants, whose time average represents the desired quantum state. QMCPACK currently implements the phaseless AFQMC algorithm of Zhang and Krakauer [[ZK03]], where a trial wavefunction is used to project the simulation to the real axis, controlling the fermionic sign problem at the expense of a bias. This approximation is similar in spirit to the fixed-node approximation in real-space DMC but applied in the Hilbert space where the AFQMC random walk occurs.

16.1 Input

The input for an AFQMC calculation is fundamentally different to the input for other real-space algorithms in QMCPACK. The main source of input comes from the Hamiltonian matrix elements in an appropriate single particle basis. This must be evaluated by an external code and saved in a format that QMCPACK can read. More details about file formats follow. The input file has six basic xml-blocks: `AFQMCInfo`, `Hamiltonian`, `Wavefunction`, `WalkerSet`, `Propagator`, and `execute`. The first five define input structures required for various types of calculations. The `execute` block represents actual calculations and takes as input the other blocks. Nonexecution blocks are parsed first, followed by a second pass where execution blocks are parsed (and executed) in order. *Listing 51* shows an example of a minimal input file for an AFQMC calculation. Table 16.5 shows a brief description of the most important parameters in the calculation. All xml sections contain a "name" argument used to identify the resulting object within QMCPACK. For example, in the example, multiple Hamiltonian objects with different names can be defined. The one actually used in the calculation is the one passed to "execute" as ham.

Listing 16.1: Sample input file for AFQMC.

```
<?xml version="1.0"?>
<simulation method="afqmc">
  <project id="Carbon" series="0"/>

  <AFQMCInfo name="info0">
    <parameter name="NMO">32</parameter>
    <parameter name="NAEA">16</parameter>
    <parameter name="NAEB">16</parameter>
  </AFQMCInfo>

  <Hamiltonian name="ham0" info="info0">
    <parameter name="filename">fcidump.h5</parameter>
```

(continues on next page)

(continued from previous page)

```
  </Hamiltonian>

  <Wavefunction name="wfn0" type="MSD" info="info0">
    <parameter name="filetype">hdf5</parameter>
    <parameter name="filename">wfn.h5</parameter>
  </Wavefunction>

  <WalkerSet name="wset0">
    <parameter name="walker_type">closed</parameter>
  </WalkerSet>

  <Propagator name="prop0" info="info0">
  </Propagator>

  <execute wset="wset0" ham="ham0" wfn="wfn0" prop="prop0" info="info0">
    <parameter name="timestep">0.005</parameter>
    <parameter name="blocks">10000</parameter>
    <parameter name="nWalkers">20</parameter>
    <Estimator name="back_propagation">
      <parameter name="naverages">4</parameter>
      <parameter name="nsteps">400</parameter>
      <parameter name="path_restoration">true</parameter>
      <onerdm/>
      <diag2rdm/>
      <twordm/>
      <ontop2rdm/>
      <realspace_correlators/>
      <correlators/>
      <genfock/>
    </Estimator>
  </execute>

</simulation>
```

The following list includes all input sections for AFQMC calculations, along with a detailed explanation of accepted parameters. Since the code is under active development, the list of parameters and their interpretation might change in the future.

`AFQMCInfo`: Input block that defines basic information about the calculation. It is passed to all other input blocks to propagate the basic information: `<AFQMCInfo name="info0">`

- **NMO**. Number of molecular orbitals, i.e., number of states in the single particle basis.
- **NAEA**. Number of active electrons-alpha, i.e., number of spin-up electrons.
- **NAEB**. Number of active electrons-beta, i.e., number of spin-down electrons.

`Hamiltonian`: Controls the object that reads, stores, and manages the `hamiltonian`. `<Hamiltonian name="ham0" type="SparseGeneral" info="info0">`

- **filename**. Name of file with the `Hamiltonian`. This is a required parameter.
- **cutoff_1bar**. Cutoff applied to integrals during reading. Any term in the Hamiltonian smaller than this value is set to zero. (For filetype="hdf5", the cutoff is applied only to the 2-electron integrals). Default: 1e-8
- **cutoff_decomposition**. Cutoff used to stop the iterative cycle in the generation of the Cholesky decomposition of the 2-electron integrals. The generation of Cholesky vectors is stopped when the maximum error in the diagonal reaches this value. In case of an eigenvalue factorization, this becomes the cutoff applied to the eigenvalues. Only eigenvalues above this value are kept. Default: 1e-6

- **nblocks**. This parameter controls the distribution of the 2-electron integrals among processors. In the default behavior (nblocks=1), all nodes contain the entire list of integrals. If nblocks > 1, the of nodes in the calculation will be split in nblocks groups. Each node in a given group contains the same subset of integrals and subsequently operates on this subset during any further operation that requires the hamiltonian. The maximum number of groups is NMO. Currently only works for filetype="hdf5" and the file must contain integrals. Not yet implemented for input hamiltonians in the form of Cholesky vectors or for ASCII input. Coming soon! Default: No distribution
- **printEig**. If "yes", prints additional information during the Cholesky decomposition. Default: no
- **fix_2eint**. If this is set to "yes", orbital pairs that are found not to be positive definite are ignored in the generation of the Cholesky factorization. This is necessary if the 2-electron integrals are not positive definite because of round-off errors in their generation. Default: no

`Wavefunction`: controls the object that manages the trial wavefunctions. This block expects a list of xml-blocks defining actual trial wavefunctions for various roles. `<Wavefunction name="wfn0" type="MSD/PHMSD" info="info0">`

- **filename**. Name of file with wavefunction information.
- **cutoff**. cutoff applied to the terms in the calculation of the local energy. Only terms in the Hamiltonian above this cutoff are included in the evaluation of the energy. Default: 1e-6
- **nnodes**. Defines the parallelization of the local energy evaluation and the distribution of the `Hamiltonian` matrix (not to GPU)
- **nbatch_qr**. This turns on(>=1)/off(==0) batched QR calculation. -1 means all the walkers in the batch. Default: 0 (CPU) / -1 (GPU)

`WalkerSet`: Controls the object that handles the set of walkers. `<WalkerSet name="wset0">`

- **walker_type**. Type of walker set: closed or collinear. Default: collinear
- **pop_control**. Population control algorithm. Options: "simple": Uses a simple branching scheme with a fluctuating population. Walkers with weight above max_weight are split into multiple walkers of weight reset_weight. Walkers with weight below min_weight are killed with probability (weight/min_weight); "pair": Fixed-population branching algorithm, based on QWalk's branching algorithm. Pairs of walkers with weight above/below max_weight/min_weight are combined into 2 walkers with weights equal to $(w_1 + w_2)/2$. The probability of replicating walker w1 (larger weight) occurs with probability $w_1/(w_1 + w_2)$, otherwise walker w2 (lower weight) is replicated; "comb": Fixed-population branching algorithm based on the Comb method. Will be available in the next release. Default: "pair"
- **min_weight**. Weight at which walkers are possibly killed (with probability weight/min_weight). Default: 0.05
- **max_weight**. Weight at which walkers are replicated. Default: 4.0
- **reset_weight**. Weight to which replicated walkers are reset to. Default: 1.0

`Propagator`: Controls the object that manages the propagators. `<Propagator name="prop0" info="info0">`

- **cutoff**. Cutoff applied to Cholesky vectors. Elements of the Cholesky vectors below this value are set to zero. Only meaningful with sparse hamiltonians. Default: 1e-6
- **substractMF**. If "yes", apply mean-field subtraction based on the ImpSamp trial wavefunction. Must set to "no" to turn it off. Default: yes
- **vbias_bound**. Upper bound applied to the vias potential. Components of the vias potential above this value are truncated there. The bound is currently applied to $\sqrt{\tau}v_{bias}$, so a larger value must be used as either the time step or the fluctuations increase (e.g. from running a larger system or using a poor trial wavefunction). Default: 3.0
- **apply_constrain**. If "yes", apply the phaseless constrain to the walker propagation. Currently, setting this to "no" produces unknown behavior, since free propagation algorithm has not been tested. Default: yes

- **hybrid**. If "yes", use hybrid propagation algorithm. This propagation scheme doesn't use the local energy during propagation, leading to significant speed ups when its evaluation cost is high. The local energy of the ImpSamp trial wavefunction is never evaluated. To obtain energy estimates in this case, you must define an Estimator xml-block with the `Wavefunction` block. The local energy of this trial wavefunction is evaluated and printed. It is possible to use a previously defined trial wavefunction in the Estimator block, just set its "name" argument to the name of a previously defined wavefunction. In this case, the same object is used for both roles. Default: no
- **nnodes**. Controls the parallel propagation algorithm. If nnodes > 1, the nodes in the simulation are split into groups of nnodes nodes, each group working collectively to propagate their walkers. Default: 1 (Serial algorithm)
- **nbatch**. This turns on(>=1)/off(==0) batched calculation of density matrices and overlaps. -1 means all the walkers in the batch. Default: 0 (CPU) / -1 (GPU)
- **nbatch_qr**. This turns on(>=1)/off(==0) batched QR calculation. -1 means all the walkers in the batch. Default: 0 (CPU) / -1 (GPU)

`execute`: Defines an execution region. `<execute wset="wset0" ham="ham0" wfn="wfn0" prop="prop0" info="info0">`

- **nWalkers**. Initial number of walkers per core group (see ncores). This sets the number of walkers for a given group of "ncores" on a node; the total number of walkers in the simulation depends on the total number of nodes and on the total number of cores on a node in the following way: $\#_walkers_total = nWalkers * \#_nodes * \#_cores_total/ncores$. Default: 5
- **timestep**. Time step in 1/a.u. Default: 0.01
- **blocks**. Number of blocks. Slow operations occur once per block (e.g., write to file, slow observables, checkpoints), Default: 100
- **step**. Number of steps within a block. Operations that occur at the step level include load balance, orthogonalization, branching, etc. Default: 1
- **substep**. Number of substeps within a step. Only walker propagation occurs in a substep. Default: 1
- **ortho**. Number of steps between orthogonalization. Default: 1
- **ncores**. Number of nodes in a task group. This number defines the number of cores on a node that share the parallel work associated with a distributed task. This number is used in the `Wavefunction` and `Propagator` task groups. The walker sets are shares by the ncores on a given node in the task group.
- **checkpoint**. Number of blocks between checkpoint files are generated. If a value smaller than 1 is given, no file is generated. If **hdf_write_file** is not set, a default name is used. **Default: 0**
- **hdf_write_file**. If set (and checkpoint>0), a checkpoint file with this name will be written.
- **hdf_read_file**. If set, the simulation will be restarted from the given file.

Within the `Estimators` xml block has an argument **name**: the type of estimator we want to measure. Currently available estimators include: "basic", "energy", "mixed_one_rdm", and "back_propagation".

The basic estimator has the following optional parameters:

- **timers**. print timing information. Default: true

The back_propagation estimator has the following parameters:

- **ortho**. Number of back-propagation steps between orthogonalization. Default: 10
- **nsteps**. Maximum number of back-propagation steps. Default: 10
- **naverages**. Number of back propagation calculations to perform. The number of steps will be chosed equally distributed in the range 0,nsteps. Default: 1

- **block_size**. Number of blocks to use in the internal average of the back propagated estimator. This is used to block data and reduce the size of the output. Default: 1
- **nskip**. Number of blocks to skip at the start of the calculation for equilibration purposes. Default: 0
- **path_restoration**. Use full path restoration. Can result in better back propagated results. Default false.

The following observables can be computed with the back_propagated estimator

- **onerdm**. One-particle reduced density matrix.
- **twordm**. Full Two-particle reduced density matrix.
- **diag2rdm**. Diagonal part of the two-particle reduced density matrix.
- **ontop2rdm**. On top two-particle reduced density matrix.
- **realspace_correlators**. Charge-Charge, and spin-spin correlation functions in real space.
- **correlators**. Charge-Charge, and spin-spin correlation functions in real space centered about atomic sites.
- **genfock**. Generalized Fock matrix.

Real space correlation functions require a real space grid. Details coming soon..

16.2 Hamiltonian File formats

QMCPACK offers three factorization approaches which are appropriate in different settings. The most generic approach implemented is based on the modified-Cholesky factorization [[ADVFerre+09], [BL77], [KdMerasP03], [PKVZ11], [PZK13]] of the ERI tensor:

$$v_{pqrs} = V_{(pr),(sq)} \approx \sum_{n}^{N_{\text{chol}}} L_{pr,n} L^{*}_{sq,n}, \tag{16.1}$$

where the sum is truncated at $N_{\text{chol}} = x_c M$, x_c is typically between 5 and 10, M is the number of basis functions and we have assumed that the single-particle orbitals are in general complex. The storage requirement is thus naively $\mathcal{O}(M^3)$. Note we follow the usual definition of $v_{pqrs} = \langle pq|rs\rangle = (pr|qs)$. With this form of factorization QMCPACK allows for the integrals to be stored in either dense or sparse format.

The dense case is the simplest and is only implemented for Hamiltonians with *real* integrals (and basis functions, i.e. not the homegeneous electron gas which has complex orbitals but real integrals). The file format is given as follows:

Listing 16.2: Sample Dense Cholesky QMCPACK Hamtiltonian.

```
$ h5dump -n afqmc.h5
HDF5 "afqmc.h5" {
    FILE_CONTENTS {
        group      /
        group      /Hamiltonian
        group      /Hamiltonian/DenseFactorized
        dataset    /Hamiltonian/DenseFactorized/L
        dataset    /Hamiltonian/dims
        dataset    /Hamiltonian/hcore
        dataset    /Hamiltonian/Energies
    }
}
```

where the datasets are given by the following

- `/Hamiltonian/DenseFactorized/L` Contains the $[M^2, N_{\text{nchol}}]$ dimensional matrix representatation of $L_{pr,n}$.

- `/Hamiltonian/dims` Descriptor array of length 8 containing $[0, 0, 0, M, N_\alpha, N_\beta, 0, N_{\text{nchol}}]$. Note that N_α and N_β are somewhat redundant and will be read from the input file and wavefunction. This allows for the Hamiltonian to be used with different (potentially spin polarized) wavefunctions.
- `/Hamiltonian/hcore` Contains the $[M, M]$ dimensional one-body Hamiltonian matrix elements h_{pq}.
- `/Hamiltonian/Energies` Array containing $[E_{II}, E_{\text{core}}]$. E_{II} should contain ion-ion repulsion energy and any additional constant terms which have to be added to the total energy. E_{core} is deprecated and not used.

Typically the Cholesky matrix is sparse, particularly if written in the non-orthogonal AO basis (not currently supported in QMCPACK). In this case only a small number of non-zero elements (denoted nnz below) need to be stored which can reduce the memory overhead considerably. Internally QMCPACK stores this matrix in the CSR format, and the HDF5 file format is reflective of this. For large systems and, more generally when running in parallel, it is convenient to chunk the writing/reading of the Cholesky matrix into blocks of size $[M^2, \frac{N_{\text{chol}}}{N_{\text{blocks}}}]$ (if interpreted as a dense array). This is achieved by writing these blocks to different data sets in the file. For the sparse case the Hamtiltonian file format is given as follows:

Listing 16.3: Sample Sparse Cholesky QMCPACK Hamtiltonian.

```
$ h5dump -n afqmc.h5
HDF5 "afqmc.h5" {
    FILE_CONTENTS {
        group      /
        group      /Hamiltonian
        group      /Hamiltonian/Factorized
        dataset    /Hamiltonian/Factorized/block_sizes
        dataset    /Hamiltonian/Factorized/index_0
        dataset    /Hamiltonian/Factorized/vals_0
        dataset    /Hamiltonian/ComplexIntegrals
        dataset    /Hamiltonian/dims
        dataset    /Hamiltonian/hcore
        dataset    /Hamiltonian/Energies
    }
}
```

- `/Hamiltonian/Factorized/block_sizes` Contains the number of elements in each block of the sparse representation of the Cholesky matrix $L_{pr,n}$. In this case there is 1 block.
- `/Hamiltonian/Factorized/index_0` $[2 \times nnz]$ dimensional array, containing the indices of the non-zero values of $L_{ik,n}$. The row indices are stored in the even entries, and the column indices in the odd entries.
- `/Hamiltonian/Factorized/vals_0` $[nnz]$ length array containing non-zero values of $L_{pr,n}$ for chunk 0.
- `/Hamiltonian/dims` Descriptor array of length 8 containing $[0, nnz, N_{\text{block}}, M, N_\alpha, N_\beta, 0, N_{\text{nchol}}]$.
- `/Hamiltonian/ComplexIntegrals` Length 1 array that specifies if integrals are complex valued. 1 for complex integrals, 0 for real integrals.
- `/Hamiltonian/hcore` Contains the $[M, M]$ dimensional one-body Hamiltonian matrix elements h_{pq}. Due to its small size this is written as a dense 2D-array.
- `/Hamiltonian/Energies` Array containing $[E_{II}, E_{\text{core}}]$. E_{II} should contain ion-ion repulsion energy and any additional constant terms which have to be added to the total energy. E_{core} is deprecated and not used.

To reduce the memory overhead of storing the three-index tensor we recently adapted the tensor-hypercontraction [[HPMartinez12], [HPSMartinez12], [PHMartinezS12]] (THC) approach for use in AFQMCcite{MaloneISDF2019}.

Within the THC approach we can approximate the orbital products entering the ERIs as

$$\varphi_p^*(\mathbf{r})\varphi_r(\mathbf{r}) \approx \sum_{\mu}^{N_\mu} \zeta_\mu(\mathbf{r})\varphi_p^*(\mathbf{r}_\mu)\varphi_r(\mathbf{r}_\mu), \tag{16.2}$$

where $\varphi_p(\mathbf{r})$ are the one-electron orbitals and $\mathbf{r}_\mu$ are a set of specially selected interpolating points, $\zeta_\mu(\mathbf{r})$ are a set of interpolating vectors and $N_\mu = x_\mu M$. We can then write the ERI tensor as a product of rank-2 tensors

$$v_{pqrs} \approx \sum_{\mu\nu} \varphi_p^*(\mathbf{r}_\mu)\varphi_r(\mathbf{r}_\mu)M_{\mu\nu}\varphi_q^*(\mathbf{r}_\nu)\varphi_s(\mathbf{r}_\nu), \tag{16.3}$$

where

$$M_{\mu\nu} = \int d\mathbf{r}d\mathbf{r}'\zeta_\mu(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\zeta_\nu^*(\mathbf{r}'). \tag{16.4}$$

We also require the half-rotated versions of these quantities which live on a different set of $\tilde{N}_\mu$ interpolating points $\tilde{\mathbf{r}}_\mu$ (see [[MZM19]]). The file format for THC factorization is as follows:

Listing 16.4: Sample Sparse Cholesky QMCPACK Hamtiltonian.

```
$ h5dump -n afqmc.h5
HDF5 "afqmc.h5" {
    FILE_CONTENTS {
        group      /
        group      /Hamiltonian
        group      /Hamiltonian/THC
        dataset    /Hamiltonian/THC/Luv
        dataset    /Hamiltonian/THC/Orbitals
        dataset    /Hamiltonian/THC/HalfTransformedMuv
        dataset    /Hamiltonian/THC/HalfTransformedFullOrbitals
        dataset    /Hamiltonian/THC/HalfTransformedOccOrbitals
        dataset    /Hamiltonian/THC/dims
        dataset    /Hamiltonian/ComplexIntegrals
        dataset    /Hamiltonian/dims
        dataset    /Hamiltonian/hcore
        dataset    /Hamiltonian/Energies
    }
}
```

- `/Hamiltonian/THC/Luv` Cholesky factorization of the $M_{\mu\nu}$ matrix given in (16.4).
- `/Hamiltonian/THC/Orbitals` $[M, N_\mu]$ dimensional array of orbitals evaluated at chosen interpolating points $\varphi_i(\mathbf{r}_\mu)$.
- `/Hamiltonian/THC/HalfTransformedMuv` $[\tilde{N}_\mu, \tilde{N}_\mu]$ dimensional array containing half-transformed $\tilde{M}_{\mu\nu}$.
- `/Hamiltonian/THC/HalfTransformedFullOrbitals` $[M, \tilde{N}_\mu]$ dimensional array containing orbital set computed at half-transformed interpolating points $\varphi_i(\tilde{\mathbf{r}}_\mu)$.
- `/Hamiltonian/THC/HalfTransformedOccOrbitals` $[N_\alpha + N_\beta, \tilde{N}_\mu]$ dimensional array containing half-rotated orbital set computed at half-transformed interpolating points $\varphi_a(\tilde{\mathbf{r}}_\mu) = \sum_p A_{pa}^*\varphi_p(\tilde{\mathbf{r}}_\mu)$, where $\mathbf{A}$ is the Slater-Matrix of the (currently single-determinant) trial wavefunction.
- `/Hamiltonian/THC/dims` Descriptor array containing $[M, N_\mu, \tilde{N}_\mu]$.
- `/Hamiltonian/ComplexIntegrals` Length 1 array that specifies if integrals are complex valued. 1 for complex integrals, 0 for real integrals.

- `/Hamiltonian/dims` Descriptor array of length 8 containing $[0, 0, 0, M, N_\alpha, N_\beta, 0, 0]$.
- `/Hamiltonian/hcore` Contains the $[M, M]$ dimensional one-body Hamiltonian matrix elements h_{ij}.
- `/Hamiltonian/Energies` Array containing $[E_{II}, E_{\text{core}}]$. E_{II} should contain ion-ion repulsion energy and any additional constant terms which have to be added to the total energy (such as the electron-electron interaction Madelung contribution of $\frac{1}{2}N\xi$). E_{core} is deprecated and not used.

Finally, we have implemented an explicitly k-point dependent factorization for periodic systems [[MZM20], [MZC19]]

$$(\mathbf{k}_p p \mathbf{k}_r r | \mathbf{k}_q q \mathbf{k}_s s) = \sum_n L^{\mathbf{Q},\mathbf{k}}_{pr,n} L^{\mathbf{Q},\mathbf{k}'\,*}_{sq,n} \tag{16.5}$$

where $\mathbf{k}$, $\mathbf{k}'$ and $\mathbf{Q}$ are vectors in the first Brillouin zone. The one-body Hamiltonian is block diagonal in $\mathbf{k}$ and in (16.5) we have used momentum conservation $(\mathbf{k}_p - \mathbf{k}_r + \mathbf{k}_q - \mathbf{k}_s) = \mathbf{G}$ with $\mathbf{G}$ being some vector in the reciprocal lattice of the simulation cell. The convention for the Cholesky matrix $L^{\mathbf{Q},\mathbf{k}}_{pr,\gamma}$ is as follows: $\mathbf{k}_r = \mathbf{k}_p - \mathbf{Q}$, so the vector $\mathbf{k}$ labels the k-point of the first band index, p, while the k-point vector of the second band index, r, is given by $\mathbf{k} - \mathbf{Q}$. Electron repulsion integrals at different $\mathbf{Q}$ vectors are zero by symmetry, resulting in a reduction in the number of required $\mathbf{Q}$ vectors. For certain $\mathbf{Q}$ vectors that satisfy $\mathbf{Q} \neq -\mathbf{Q}$ (this is not satisfied at the origin and at high symmetry points on the edge of the 1BZ), we have $L^{\mathbf{Q},\mathbf{k}\,*}_{sq,\gamma} = L^{-\mathbf{Q},\mathbf{k}-\mathbf{Q}}_{qs,\gamma}$, which requires us to store Cholesky vectors for either one of the $(\mathbf{Q}, -\mathbf{Q})$ pair, but not both.

In what follows let $m_{\mathbf{k}}$ denote the number of basis functions for basis functions of a given k-point (these can in principle differ for different k-points due to linear dependencies), $n^\alpha_{\mathbf{k}}$ the number of α electrons in a given k-point and $n^{\mathbf{Q}_n}_{\text{chol}}$ the number of Cholesky vectors for momentum transfer $\mathbf{Q}_n$. The file format for this factorization is as follows (for a $2 \times 2 \times 2$ k-point mesh, for denser meshes generally there will be far fewer symmetry inequivalent momentum transfer vectors than there are k-points):

Listing 16.5: Sample Dense k-point dependent Cholesky QMCPACK Hamtiltonian.

```
$ h5dump -n afqmc.h5
HDF5 "afqmc.h5" {
    FILE_CONTENTS {
        group      /
        group      /Hamiltonian
        group      /Hamiltonian/KPFactorized
        dataset    /Hamiltonian/KPFactorized/L0
        dataset    /Hamiltonian/KPFactorized/L1
        dataset    /Hamiltonian/KPFactorized/L2
        dataset    /Hamiltonian/KPFactorized/L3
        dataset    /Hamiltonian/KPFactorized/L4
        dataset    /Hamiltonian/KPFactorized/L5
        dataset    /Hamiltonian/KPFactorized/L6
        dataset    /Hamiltonian/KPFactorized/L7
        dataset    /Hamiltonian/NCholPerKP
        dataset    /Hamiltonian/MinusK
        dataset    /Hamiltonian/NMOPerKP
        dataset    /Hamiltonian/QKTok2
        dataset    /Hamiltonian/H1_kp0
        dataset    /Hamiltonian/H1_kp1
        dataset    /Hamiltonian/H1_kp2
        dataset    /Hamiltonian/H1_kp3
        dataset    /Hamiltonian/H1_kp4
        dataset    /Hamiltonian/H1_kp5
        dataset    /Hamiltonian/H1_kp6
        dataset    /Hamiltonian/H1_kp7
        dataset    /Hamiltonian/ComplexIntegrals
```

(continues on next page)

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```
        dataset    /Hamiltonian/KPoints
        dataset    /Hamiltonian/dims
        dataset    /Hamiltonian/Energies
    }
}
```

- `/Hamiltonian/KPFactorized/L[n]` This series of datasets store elements of the Cholesky tensors $L[\mathbf{Q}_n, \mathbf{k}, pr, n]$. Each data set is of dimension $[N_k, m_{\mathbf{k}} \times m_{\mathbf{k}'}, n_{\mathrm{chol}}^{\mathbf{Q}_n}]$, where, again, k is the k-point associated with basis function p, the k-point of basis function r is defined via the mapping `QKtok2`.
- `/Hamiltonian/NCholPerKP` N_k length array giving number of Cholesky vectors per k-point.
- `/Hamiltonian/MinusK`: N_k length array mapping a k-point to its inverse: $\mathbf{k}_i$+`MinusK[i]` $= \mathbf{0} \mod \mathbf{G}$.
- `/Hamiltonian/NMOPerKP`: N_k length array listing number of basis functions per k-point.
- `/Hamiltonian/QKTok2`: $[N_k, N_k]$ dimensional array. `QKtok2[i,j]` yields the k point index satisfying $\mathbf{k} = \mathbf{Q}_i - \mathbf{k}_j + \mathbf{G}$.
- `/Hamiltonian/dims`: Descriptor array of length 8 containing $[0, 0, 0, M, N_\alpha, N_\beta, 0, 0]$.
- `/Hamiltonian/H1_kp[n]` Contains the $[m_{\mathbf{k}_n}, m_{\mathbf{k}_n}]$ dimensional one-body Hamiltonian matrix elements $h_{(\mathbf{k}_n p)(\mathbf{k}_n q)}$.
- `/Hamiltonian/ComplexIntegrals` Length 1 array that specifies if integrals are complex valued. 1 for complex integrals, 0 for real integrals.
- `/Hamiltonian/KPoints` $[N_k, 3]$ Dimensional array containing k-points used to sample Brillouin zone.
- `/Hamiltonian/dims` Descriptor array of length 8 containing $[0, 0, N_k, M, N_\alpha, N_\beta, 0, N_{\mathrm{nchol}}]$. Note that M is the total number of basis functions, i.e. $M = \sum_{\mathbf{k}} m_{\mathbf{k}}$, and likewise for the number of electrons.
- `/Hamiltonian/Energies` Array containing $[E_{II}, E_{\mathrm{core}}]$. E_{II} should contain ion-ion repulsion energy and any additional constant terms which have to be added to the total energy (such as the electron-electron interaction Madelung contribution of $\frac{1}{2}N\xi$). E_{core} is deprecated and not used.

Complex integrals should be written as an array with an additional dimension, e.g., a 1D array should be written as a 2D array with `array_hdf5[:,0]=real(1d_array)` and `array_hdf5[:,1]=imag(1d_array)`. The functions `afqmctools.utils.misc.from_qmcpack_complex` and `afqmctools.utils.misc.to_qmcpack_complex` can be used to transform qmcpack format to complex valued numpy arrays of the appropriate shape and vice versa.

Finally, if using external tools to generate this file format, we provide a sanity checker script in `utils/afqmctools/bin/test_afqmc_input.py` which will raise errors if the format does not conform to what is being used internally.

16.3 Wavefunction File formats

AFQMC allows for two types of multi-determinant trial wavefunctions: non-orthogonal multi Slater determinants (NOMSD) or SHCI/CASSCF style particle-hole multi Slater determinants (PHMSD).

The file formats are described below

16.3.1 NOMSD

```
h5dump -n wfn.h5

HDF5 "wfn.h5" {
    FILE_CONTENTS {
        group      /
        group      /Wavefunction
        group      /Wavefunction/NOMSD
        dataset    /Wavefunction/NOMSD/Psi0_alpha
        dataset    /Wavefunction/NOMSD/Psi0_beta
        group      /Wavefunction/NOMSD/PsiT_0
        dataset    /Wavefunction/NOMSD/PsiT_0/data_
        dataset    /Wavefunction/NOMSD/PsiT_0/dims
        dataset    /Wavefunction/NOMSD/PsiT_0/jdata_
        dataset    /Wavefunction/NOMSD/PsiT_0/pointers_begin_
        dataset    /Wavefunction/NOMSD/PsiT_0/pointers_end_
        group      /Wavefunction/NOMSD/PsiT_1
        dataset    /Wavefunction/NOMSD/PsiT_1/data_
        dataset    /Wavefunction/NOMSD/PsiT_1/dims
        dataset    /Wavefunction/NOMSD/PsiT_1/jdata_
        dataset    /Wavefunction/NOMSD/PsiT_1/pointers_begin_
        dataset    /Wavefunction/NOMSD/PsiT_1/pointers_end_
        dataset    /Wavefunction/NOMSD/ci_coeffs
        dataset    /Wavefunction/NOMSD/dims
    }
}
```

Note that the α components of the trial wavefunction are stored under `PsiT_{2n}` and the β components are stored under `PsiT_{2n+1}`.

- `/Wavefunction/NOMSD/Psi0_alpha` $[M, N_\alpha]$ dimensional array α component of initial walker wavefunction.
- `/Wavefunction/NOMSD/Psi0_beta` $[M, N_\beta]$ dimensional array for β initial walker wavefunction.
- `/Wavefunction/NOMSD/PsiT_{2n}/data_` Array of length nnz containing non-zero elements of n-th α component of trial wavefunction walker wavefunction. Note the **conjugate transpose** of the Slater matrix is stored.
- `/Wavefunction/NOMSD/PsiT_{2n}/dims` Array of length 3 containing $[M, N_\alpha, nnz]$ where nnz is the number of non-zero elements of this Slater matrix
- `/Wavefunction/NOMSD/PsiT_{2n}/jdata_` CSR indices array.
- `/Wavefunction/NOMSD/PsiT_{2n}/pointers_begin_` CSR format begin index pointer array.
- `/Wavefunction/NOMSD/PsiT_{2n}/pointers_end_` CSR format end index pointer array.
- `/Wavefunction/NOMSD/ci_coeffs` N_D length array of ci coefficients. Stored as complex numbers.
- `/Wavefunction/NOMSD/dims` Integer array of length 5 containing $[M, N_\alpha, N_\beta,$ walker_type , $N_D]$

16.3.2 PHMSD

```
h5dump -n wfn.h5

HDF5 "wfn.h5" {
    FILE_CONTENTS {
        group      /
        group      /Wavefunction
        group      /Wavefunction/PHMSD
        dataset    /Wavefunction/PHMSD/Psi0_alpha
        dataset    /Wavefunction/PHMSD/Psi0_beta
        dataset    /Wavefunction/PHMSD/ci_coeffs
        dataset    /Wavefunction/PHMSD/dims
        dataset    /Wavefunction/PHMSD/occs
        dataset    /Wavefunction/PHMSD/type
    }
}
```

- `/Wavefunction/NOMSD/Psi0_alpha` $[M, N_\alpha]$ dimensional array α component of initial walker wavefunction.
- `/Wavefunction/NOMSD/Psi0_beta` $[M, N_\beta]$ dimensional array for β initial walker wavefunction.
- `/Wavefunction/PHMSD/ci_coeffs` N_D length array of ci coefficients. Stored as complex numbers.
- `/Wavefunction/PHMSD/dims` Integer array of length 5 containing $[M, N_\alpha, N_\beta,$ walker_type $, N_D]$
- `/Wavefunction/PHMSD/occs` Integer array of length $(N_\alpha + N_\beta) * N_D$ describing the determinant occupancies. For example if $(N_\alpha = N_\beta = 2)$ and $N_D = 2$, $M = 4$, and if $|\Psi_T\rangle = |0,1\rangle|0,1\rangle + |0,1\rangle|0,2\rangle >$ then occs = $[0, 1, 4, 5, 0, 1, 4, 6]$. Note that β occupancies are displacd by M.
- `/Wavefunction/PHMSD/type` integer 0/1. 1 implies trial wavefunction is written in different basis than the underlying basis used for the integrals. If so a matrix of orbital coefficients is required to be written in the NOMSD format. If 0 then assume wavefunction is in same basis as integrals.

16.4 Current Feature Implementation Status

The current status of features available in QMCPACK is as follows:

Table 16.1: Code features available on CPU

Hamiltonian	SD	NOMSD	PHMSD	Real Build	Complex Build
Sparse	Yes	Yes	Yes	Yes	Yes
Dense	Yes	Yes	No	Yes	No
k-point	Yes	No	No	No	Yes
THC	Yes	No	No	Yes	Yes

Table 16.2: Code features available on GPU

Hamiltonian	SD	NOMSD	PHMSD	Real Build	Complex Build
Sparse	No	No	No	No	No
Dense	Yes	No	No	Yes	No
k-point	Yes	No	No	No	Yes
THC	Yes	No	No	Yes	Yes

16.5 Advice/Useful Information

AFQMC calculations are computationally expensive and require some care to obtain reasonable performance. The following is a growing list of useful advice for new users, followed by a sample input for a large calculation.

- Generate Cholesky-decomposed integrals with external codes instead of the 2-electron integrals directly. The generation of the Cholesky factorization is faster and consumes less memory.
- Use the hybrid algorithm for walker propagation. Set steps/substeps to adequate values to reduce the number of energy evaluations. This is essential when using large multideterminant expansions.
- Adjust cutoffs in the wavefunction and propagator bloxks until desired accuracy is reached. The cost of the calculation will depend on these cutoffs.
- Adjust ncores/nWalkers to obtain better efficiency. Larger nWalkers will lead to more efficient linear algebra operations but will increase the time per step. Larger ncores will reduce the time per step but will reduce efficiency because of inefficiencies in the parallel implementation. For large calculations, values between 6–12 for both quantities should be reasonable, depending on architecture.

Listing 16.6: Example of sections of an AFQMC input file for a large calculation.

```
...

  <Hamiltonian name="ham0" type="SparseGeneral" info="info0">
    <parameter name="filename">fcidump.h5</parameter>
    <parameter name="cutoff_1bar">1e-6</parameter>
    <parameter name="cutoff_decomposition">1e-5</parameter>
  </Hamiltonian>

  <Wavefunction name="wfn0" type="MSD" info="info0">
    <parameter name="filetype">ascii</parameter>
    <parameter name="filename">wfn.dat</parameter>
  </Wavefunction>

  <WalkerSet name="wset0">
    <parameter name="walker_type">closed</parameter>
  </WalkerSet>

  <Propagator name="prop0" info="info0">
    <parameter name="hybrid">yes</parameter>
  </Propagator>

  <execute wset="wset0" ham="ham0" wfn="wfn0" prop="prop0" info="info0">
    <parameter name="ncores">8</parameter>
    <parameter name="timestep">0.01</parameter>
    <parameter name="blocks">10000</parameter>
    <parameter name="steps">10</parameter>
    <parameter name="substeps">5</parameter>
    <parameter name="nWalkers">8</parameter>
    <parameter name="ortho">5</parameter>
  </execute>
```

`afqmc` method

parameters in `AFQMCInfo`

Name	Datatype	Values	Default	Description
NMO	integer	≥ 0	no	Number of molecular orbitals
NAEA	integer	≥ 0	no	Number of active electrons of spin-up
NAEB	integer	≥ 0	no	Number of active electrons of spin-down

parameters in `Hamiltonian`

Name	Datatype	Values	Default	Description
info	argument			Name of `AFQMCInfo` block
filename	string		no	Name of file with the hamiltonian
filetype	string	hdf5	yes	Native HDF5-based format of QMCPACK

parameters in `Wavefunction`

Name	Datatype	Values	Default	Description
info	argument			name of `AFQMCInfo` block
type	argument	MSD, PHMSD	no	Linear combination of (assumed non-orthogonal) Slater determinants
filetype	string	ascii, hdf5	no	CI-type multi-determinant wave function

parameters in `WalkerSet`

Name	Datatype	Values	Default	Description
walker_type	string	collinear	yes	Request a collinear walker set.
		closed	no	Request a closed shell (doubly-occupied) walker set.

parameters in `Propagator`

Name	Datatype	Values	Default	Description
type	argument	afqmc	afqmc	Type of propagator
info	argument			Name of `AFQMCInfo` block
hybrid	string	yes		Use hybrid propagation algorithm.
		no		Use local energy based propagation algorithm.

parameters in `execute`

Name	Datatype	Values	Default	Description
wset	argument			
ham	argument			
wfn	argument			
prop	argument			
info	argument			Name of `AFQMCInfo` block
nWalkers	integer	≥ 0	5	Initial number of walkers per task group
timestep	real	> 0	0.01	Time step in 1/a.u.
blocks	integer	≥ 0	100	Number of blocks
step	integer	> 0	1	Number of steps within a block
substep	integer	> 0	1	Number of substeps within a step
ortho	integer	> 0	1	Number of steps between walker orthogonalization.

16.6 AFQMCTOOLS

The `afqmctools` library found in `qmcpack/utils/afqmctools` provides a number of tools to interface electronic structure codes with AFQMC in QMCPACK. Currently PYSCF is the best supported package and is capable of generating both molecular and solid state input for AFQMC.

In what follows we will document the most useful routines from a user's perspective.

afqmctools has to be in your PYTHONPATH.

16.6.1 pyscf_to_afqmc.py

This is the main script to convert PYSCF output into QMCPACK input. The command line options are as follows:

```
> pyscf_to_afqmc.py -h

usage: pyscf_to_afqmc.py [-h] [-i CHK_FILE] [-o HAMIL_FILE] [-w WFN_FILE]
                         [-q QMC_INPUT] [-t THRESH] [-k] [--density-fit] [-a]
                         [-c CAS] [-d] [-n NDET_MAX] [-r] [-p]
                         [--low LOW_THRESH] [--high HIGH_THRESH] [--dense]
                         [-v]

optional arguments:
  -h, --help            show this help message and exit
  -i CHK_FILE, --input CHK_FILE
                        Input pyscf .chk file.
  -o HAMIL_FILE, --output HAMIL_FILE
                        Output file name for QMCPACK hamiltonian.
  -w WFN_FILE, --wavefunction WFN_FILE
                        Output file name for QMCPACK wavefunction. By default
                        will write to hamil_file.
  -q QMC_INPUT, --qmcpack-input QMC_INPUT
                        Generate skeleton QMCPACK input xml file.
  -t THRESH, --cholesky-threshold THRESH
                        Cholesky convergence threshold.
  -k, --kpoint          Generate explicit kpoint dependent integrals.
  --density-fit         Use density fitting integrals stored in input pyscf
                        chkpoint file.
  -a, --ao, --ortho-ao  Transform to ortho AO basis. Default assumes we work
                        in MO basis
  -c CAS, --cas CAS     Specify a CAS in the form of N,M.
  -d, --disable-ham     Disable hamiltonian generation.
  -n NDET_MAX, --num-dets NDET_MAX
                        Set upper limit on number of determinants to generate.
  -r, --real-ham        Write integrals as real numbers.
  -p, --phdf            Use parallel hdf5.
  --low LOW_THRESH      Lower threshold for non-integer occupanciesto include
                        in multi-determinant exansion.
  --high HIGH_THRESH    Upper threshold for non-integer occupanciesto include
                        in multi-determinant exansion.
  --dense               Write dense Hamiltonian.
  -v, --verbose         Verbose output.
```

examples on how to generate AFQMC input from PYSCF simulations are available in *AFQMC Tutorials*

16.6.2 afqmc_to_fcidump.py

This script is useful for converting AFQMC hamiltonians to the FCIDUMP format.

```
> afqmc_to_fcidump.py

usage: afqmc_to_fcidump.py [-h] [-i INPUT_FILE] [-o OUTPUT_FILE] [-s SYMM]
                                                    [-t TOL] [-c] [--complex-paren] [-
↪v]

optional arguments:
  -h, --help            show this help message and exit
  -i INPUT_FILE, --input INPUT_FILE
                                                    Input AFQMC hamiltonian file.
  -o OUTPUT_FILE, --output OUTPUT_FILE
                                                    Output file for FCIDUMP.
  -s SYMM, --symmetry SYMM
                                                    Symmetry of integral file (1,4,8).
  -t TOL, --tol TOL     Cutoff for integrals.
  -c, --complex         Whether to write integrals as complex numbers.
  --complex-paren       Whether to write FORTRAN format complex numbers.
  -v, --verbose         Verbose output.
```

16.6.3 fcidump_to_afqmc.py

This script is useful for converting Hamiltonians in the FCIDUMP format to the AFQMC file format.

```
> fcidump_to_afqmc.py -h

usage: fcidump_to_afqmc.py [-h] [-i INPUT_FILE] [-o OUTPUT_FILE]
                                                    [--write-complex] [-t THRESH] [-s␣
↪SYMM] [-v]

optional arguments:
  -h, --help            show this help message and exit
  -i INPUT_FILE, --input INPUT_FILE
                                                    Input FCIDUMP file.
  -o OUTPUT_FILE, --output OUTPUT_FILE
                                                    Output file name for PAUXY data.
  --write-complex       Output integrals in complex format.
  -t THRESH, --cholesky-threshold THRESH
                                                    Cholesky convergence threshold.
  -s SYMM, --symmetry SYMM
                                                    Symmetry of integral file (1,4,8).
  -v, --verbose         Verbose output.
```

16.6.4 Writing a Hamiltonian

`write_qmcpack_sparse` and `write_qmcpack_dense` can be used to write either sparse or dense qmcpack Hamiltonians.

```
import numpy
from afqmctools.hamiltonian.io import write_qmcpack_sparse, write_qmcpack_dense

nmo = 50
nchol = 37
nelec = (3,3)
enuc = -108.3
# hcore and eri should obey the proper symmetry in real applications
# h_ij
hcore = numpy.random.random((nmo,nmo))
# L_{(ik),n}
chol = numpy.random.random((nmo*nmo, nchol))
write_qmcpack_dense(hcore, chol, nelec, nmo, enuc,
                    real_chol=True,
                    filename='hamil_dense.h5')
write_qmcpack_sparse(hcore, chol, nelec, nmo, enuc,
                    real_chol=True,
                    filename='hamil_sparse.h5')
```

Note the `real_chol` parameter controls whether the integrals are written as real or complex numbers. Complex numbers should be used if `-DENABLE_QMC_COMPLEX=1`, while the dense Hamiltonian is only available for real builds.

16.6.5 Writing a wavefunction

`write_qmcpack_wfn` can be used to write either NOMSD or PHMSD wavefunctions:

```
import numpy
from afqmctools.wavefunction.mol import write_qmcpack_wfn

# NOMSD
ndet = 100
nmo = 50
nelec = (3, 7)
wfn = numpy.array(numpy.random.random((ndet, nmo, sum(nelec))), dtype=numpy.
↪complex128)
coeffs = numpy.array(numpy.random.random((ndet)), dtype=numpy.complex128)
uhf = True
write_qmcpack_wfn('wfn.h5', (coeffs, wfn), uhf, nelec, nmo)
```

By default the first term in the expansion will be used as the initial walker wavefunction. To use another wavefunction we can pass a value to the `init` parameter:

```
init = numpy.array(numpy.random.random((nmo,sum(nelec)), dtype=numpy.complex128)
write_qmcpack_wfn('wfn.h5', (coeffs, wfn), uhf, nelec, nmo, init=[init,init])
```

Particle-hole wavefunction (PHMSD) from SHCI or CASSCF calculations are also written using the same function:

```
import numpy
from afqmctools.wavefunction.mol import write_qmcpack_wfn

```

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```
# PHMSD
ndet = 2
nmo = 4
nelec = (2,2)
uhf = True
# |psi_T> = 1/sqrt(2)(|0,1>|0,1> + |0,1>|0,2>)
coeffs = numpy.array([0.707,0.707], dtype=numpy.complex128)
occa = numpy.array([(0,1), (0,1)])
occb = numpy.array([(0,1), (0,2)])
write_qmcpack_wfn('wfn.h5', (coeffs, occa, occb), uhf, nelec, nmo)
```

16.6.6 Analyzing Estimators

The `afqmctools.analysis.average` module can be used to perform simple error analysis for estimators computed with AFQMC.

Warning: Autocorrelation is not accounted for. Use with caution.

average_one_rdm Returns P[s,i,j] = $\langle c_{is}^\dagger c_{js} \rangle$ as a (nspin, M, M) dimensional array.

average_two_rdm Gamma[s1s2,i,k,j,l] = $\langle c_i^\dagger c_j^\dagger c_l c_k \rangle$. For closed shell systems, returns [(a,a,a,a),(a,a,b,b)]. For collinear systems, returns [(a,a,a,a),(a,a,b,b),(b,b,b,b)].

average_diag_two_rdm Returns $\langle c_{is}^+ c_{jt}^+ c_{jt} c_{is} \rangle$ as a (2M,2M) dimensional array.

average_on_top_pdm Returns $n_2(\mathbf{r}, \mathbf{r})$ for a given real space grid.

average_realspace_correlations Returns $\langle C(\mathbf{r}_1) C(\mathbf{r}_2) \rangle$ and $\langle S(\mathbf{r}_1) S(\mathbf{r}_2) \rangle$ for a given set of points in real space. $\hat{C} = (\hat{n}_\uparrow + \hat{n}_\downarrow)$, $\hat{S} = (\hat{n}_\uparrow - \hat{n}_\downarrow)$

average_atom_correlations Returns $\langle C(I) \rangle$, $\langle S(I) \rangle$, $\langle C(I) C(J) \rangle$, $\langle S(I) S(J) \rangle$ for a given set of atomic sites I, J. $\hat{C} = (\hat{n}_\uparrow + \hat{n}_\downarrow)$, $\hat{S} = (\hat{n}_\uparrow - \hat{n}_\downarrow)$

average_gen_fock Returns generalized Fock matrix $F_\pm$. The parameter `fock_type` is used to specify F_+ (`fock_type='plus'`) or F_- (`fock_type='minus'`)

get_noons Get natural orbital occupation numbers from one-rdm.

As an example the following will extract the back propagated one rdm for the maximum propagation time, and skip 10 blocks as the equilibration phase.

```
from afqmctools.analysis.average import average_one_rdm

P, Perr = average_one_rdm('qmc.s000.stat.h5', estimator='back_propagated', eqlb=10)
```

CHAPTER

SEVENTEEN

EXAMPLES

WARNING: THESE EXAMPLES ARE NOT CONVERGED! YOU MUST CONVERGE PARAMETERS (SIMULATION CELL SIZE, JASTROW PARAMETER NUMBER/CUTOFF, TWIST NUMBER, DMC TIME STEP, DFT PLANE WAVE CUTOFF, DFT K-POINT MESH, ETC.) FOR REAL CALCUATIONS!

The following examples should run in serial on a modern workstation in a few hours.

17.1 Using QMCPACK directly

In `examples/molecules` are the following examples. Each directory also contains a `README` file with more details.

Directory	Description
`H2O`	H2O molecule from GAMESS orbitals
`He`	Helium atom with simple wavefunctions

17.2 Using Nexus

For more information about Nexus, see the User Guide in `nexus/documentation`.

For Python to find the Nexus library, the PYTHONPATH environment variable should be set to `<QMCPACK source>/nexus/library`. For these examples to work properly, the executables for QE and QMCPACK either need to be on the path, or the paths in the script should be adjusted.

These examples can be found under the `nexus/examples/qmcpack` directory.

Directory	Description
`diamond`	Bulk diamond with VMC
`graphene`	Graphene sheet with DMC
`c20`	C20 cage molecule
`oxygen_dimer`	Binding curve for O_2 molecule
`H2O`	H_2O molecule with QE orbitals
`LiH`	LiH crystal with QE orbitals

CHAPTER

EIGHTEEN

LAB 1: MC STATISTICAL ANALYSIS

18.1 Topics covered in this lab

This lab focuses on the basics of analyzing data from MC calculations. In this lab, participants will use data from VMC calculations of a simple 1-electron system with an analytically soluble system (the ground state of the hydrogen atom) to understand how to interpret an MC situation. Most of these analyses will also carry over to DMC simulations. Topics covered include:

- Averaging MC variables
- The statisical error bar of mean values
- The effects of autocorrelation and variance on the error bar
- The relationship between MC time step and autocorrelation
- The use of blocking to reduce autocorrelation
- The significance of the acceptance ratio
- The significance of the sample size
- How to determine whether an MC run was successful
- The relationship between wavefunction quality and variance
- Gauging the efficiency of MC runs
- The cost of scaling up to larger system sizes

18.2 Lab directories and files

```
labs/lab1_qmc_statistics/
│
├── atom                                - H atom VMC calculation
│   ├── H.s000.scalar.dat                  - H atom VMC data
│   └── H.xml                              - H atom VMC input file
│
├── autocorrelation                     - varying autocorrelation
│   ├── H.dat                              - data for gnuplot
│   ├── H.plt                              - gnuplot for time step vs. E_L, tau_c
│   ├── H.s000.scalar.dat                  - H atom VMC data: time step = 10
│   ├── H.s001.scalar.dat                  - H atom VMC data: time step =  5
│   ├── H.s002.scalar.dat                  - H atom VMC data: time step =  2
│   ├── H.s003.scalar.dat                  - H atom VMC data: time step =  1
```

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```
    ├── H.s004.scalar.dat              - H atom VMC data: time step =  0.5
    ├── H.s005.scalar.dat              - H atom VMC data: time step =  0.2
    ├── H.s006.scalar.dat              - H atom VMC data: time step =  0.1
    ├── H.s007.scalar.dat              - H atom VMC data: time step =  0.05
    ├── H.s008.scalar.dat              - H atom VMC data: time step =  0.02
    ├── H.s009.scalar.dat              - H atom VMC data: time step =  0.01
    ├── H.s010.scalar.dat              - H atom VMC data: time step =  0.005
    ├── H.s011.scalar.dat              - H atom VMC data: time step =  0.002
    ├── H.s012.scalar.dat              - H atom VMC data: time step =  0.001
    ├── H.s013.scalar.dat              - H atom VMC data: time step =  0.0005
    ├── H.s014.scalar.dat              - H atom VMC data: time step =  0.0002
    ├── H.s015.scalar.dat              - H atom VMC data: time step =  0.0001
    └── H.xml                          - H atom VMC input file

├── average                           - Python scripts for average/std. dev.
    ├── average.py                        - average five E_L from H atom VMC
    ├── stddev2.py                        - standard deviation using (E_L)^2
    └── stddev.py                         - standard deviation around the mean

├── basis                             - varying basis set for orbitals
    ├── H__exact.s000.scalar.dat          - H atom VMC data using STO basis
    ├── H_STO-2G.s000.scalar.dat          - H atom VMC data using STO-2G basis
    ├── H_STO-3G.s000.scalar.dat          - H atom VMC data using STO-3G basis
    └── H_STO-6G.s000.scalar.dat          - H atom VMC data using STO-6G basis

├── blocking                          - varying block/step ratio
    ├── H.dat                             - data for gnuplot
    ├── H.plt                             - gnuplot for N_block vs. E, tau_c
    ├── H.s000.scalar.dat                 - H atom VMC data 50000:1 blocks:steps
    ├── H.s001.scalar.dat                 - "  "    "    "  25000:2 blocks:steps
    ├── H.s002.scalar.dat                 - "  "    "    "  12500:4 blocks:steps
    ├── H.s003.scalar.dat                 - "  "    "    "  6250: 8 blocks:steps
    ├── H.s004.scalar.dat                 - "  "    "    "  3125:16 blocks:steps
    ├── H.s005.scalar.dat                 - "  "    "    "  2500:20 blocks:steps
    ├── H.s006.scalar.dat                 - "  "    "    "  1250:40 blocks:steps
    ├── H.s007.scalar.dat                 - "  "    "    "  1000:50 blocks:steps
    ├── H.s008.scalar.dat                 - "  "    "    "  500:100 blocks:steps
    ├── H.s009.scalar.dat                 - "  "    "    "  250:200 blocks:steps
    ├── H.s010.scalar.dat                 - "  "    "    "  125:400 blocks:steps
    ├── H.s011.scalar.dat                 - "  "    "    "  100:500 blocks:steps
    ├── H.s012.scalar.dat                 - "  "    "    "  50:1000 blocks:steps
    ├── H.s013.scalar.dat                 - "  "    "    "  40:1250 blocks:steps
    ├── H.s014.scalar.dat                 - "  "    "    "  20:2500 blocks:steps
    ├── H.s015.scalar.dat                 - "  "    "    "  10:5000 blocks:steps
    └── H.xml                           - H atom VMC input file

├── blocks                            -  varying total number of blocks
    ├── H.dat                             - data for gnuplot
    ├── H.plt                             - gnuplot for N_block vs. E
    ├── H.s000.scalar.dat                 - H atom VMC data    500 blocks
    ├── H.s001.scalar.dat                 - "  "    "    "    2000 blocks
    ├── H.s002.scalar.dat                 - "  "    "    "    8000 blocks
    ├── H.s003.scalar.dat                 - "  "    "    "   32000 blocks
    ├── H.s004.scalar.dat                 - "  "    "    "  128000 blocks
    └── H.xml                             - H atom VMC input file

├── dimer                           - comparing no and simple Jastrow factor
```

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```
    ├── H2_STO___no_jastrow.s000.scalar.dat - H dimer VMC data without Jastrow
    └── H2_STO_with_jastrow.s000.scalar.dat - H dimer VMC data with Jastrow

├── docs                                  - documentation
    ├── Lab_1_MC_Analysis.pdf               - this document
    └── Lab_1_Slides.pdf                    - slides presented in the lab

├── nodes                                 - varying number of computing nodes
    ├── H.dat                               - data for gnuplot
    ├── H.plt                               - gnuplot for N_node vs. E
    ├── H.s000.scalar.dat                   - H atom VMC data with  32 nodes
    ├── H.s001.scalar.dat                   - H atom VMC data with 128 nodes
    └── H.s002.scalar.dat                   - H atom VMC data with 512 nodes

├── problematic                           - problematic VMC run
    └── H.s000.scalar.dat                   - H atom VMC data with a problem

└── size                                   - scaling with number of particles
    ├── 01________H.s000.scalar.dat         - H atom VMC data
    ├── 02________H2.s000.scalar.dat        - H dimer "   "
    ├── 06________C.s000.scalar.dat         - C atom  "   "
    ├── 10______CH4.s000.scalar.dat         - methane "   "
    ├── 12________C2.s000.scalar.dat        - C dimer "   "
    ├── 16_____C2H4.s000.scalar.dat         - ethene  "
    ├── 18___CH4CH4.s000.scalar.dat         - methane dimer VMC data
    ├── 32_C2H4C2H4.s000.scalar.dat         - ethene dimer   "   "
    ├── nelectron_tcpu.dat                  - data for gnuplot
    └── Nelectron_tCPU.plt                  - gnuplot for N_elec vs. t_CPU
```

18.3 Atomic units

QMCPACK operates in Ha atomic units to reduce the number of factors in the Schrödinger equation. Thus, the unit of length is the bohr (5.291772 $\times 10^{-11}$ m = 0.529177 Å); the unit of energy is the Ha (4.359744 $\times 10^{-18}$ J = 27.211385 eV). The energy of the ground state of the hydrogen atom in these units is -0.5 Ha.

18.4 Reviewing statistics

We will practice taking the average (mean) and standard deviation of some MC data by hand to review the basic definitions.

Enter Python's command line by typing `python [Enter]`. You will see a prompt ">>>."

The mean of a dataset is given by:

$$\overline{x} = \frac{1}{N} \sum_{i=1}^{N} x_i \,. \tag{18.1}$$

To calculate the average of five local energies from an MC calculation of the ground state of an electron in the hydrogen atom, input (truncate at the thousandths place if you cannot copy and paste; script versions are also available in the `average` directory):

```
(
(-0.45298911858) +
(-0.45481953564) +
(-0.48066105923) +
(-0.47316713469) +
(-0.46204733302)
)/5.
```

Then, press [Enter] to get:

```
>>> ((-0.45298911858) + (-0.45481953564) + (-0.48066105923) +
(-0.47316713469) + (-0.4620473302))/5.
-0.46473683566800006
```

To understand the significance of the mean, we also need the standard deviation around the mean of the data (also called the error bar), given by:

$$\sigma = \sqrt{\frac{1}{N(N-1)} \sum_{i=1}^{N} (x_i - \overline{x})^2} \,. \tag{18.2}$$

To calculate the standard deviation around the mean (-0.464736835668) of these five data points, put in:

```
( (1./(5.*(5.-1.))) * (
(-0.45298911858-(-0.464736835668))**2 + \\
(-0.45481953564-(-0.464736835668))**2 +
(-0.48066105923-(-0.464736835668))**2 +
(-0.47316713469-(-0.464736835668))**2 +
(-0.46204733302-(-0.464736835668))**2 )
)**0.5
```

Then, press [Enter] to get:

```
>>> ( (1./(5.*(5.-1.))) * ( (-0.45298911858-(-0.464736835668))**2 +
(-0.45481953564-(-0.464736835668))**2 + (-0.48066105923-(-0.464736835668))**2 +
(-0.47316713469-(-0.464736835668))**2 + (-0.46204733302-(-0.464736835668))**2
) )**0.5
0.0053303187464332066
```

Thus, we might report this data as having a value -0.465 +/- 0.005 Ha. This calculation of the standard deviation assumes that the average for this data is fixed, but we can continually add MC samples to the data, so it is better to use an estimate of the error bar that does not rely on the overall average. Such an estimate is given by:

$$\tilde{\sigma} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left[(x^2)_i - (x_i)^2 \right]} \,. \tag{18.3}$$

To calculate the standard deviation with this formula, input the following, which includes the square of the local energy calculated with each corresponding local energy:

```
( (1./(5.-1.)) * (
(0.60984565298-(-0.45298911858)**2) + \\
(0.61641291630-(-0.45481953564)**2) +
(1.35860151160-(-0.48066105923)**2) + \\
(0.78720769003-(-0.47316713469)**2) +
(0.56393677687-(-0.46204733302)**2) )
)**0.5
```

and press [Enter] to get:

```
>>> ((1./(5.-1.))*((0.60984565298-(-0.45298911858)**2)+
(0.61641291630-(-0.45481953564)**2)+(1.35860151160-(-0.48066105923)**2)+
(0.78720769003-(-0.47316713469)**2)+(0.56393677687-(-0.46204733302)**2))
)**0.5
0.84491636672906634
```

This much larger standard deviation, acknowledging that the mean of this small data set is not the average in the limit of infinite sampling, more accurately reports the value of the local energy as -0.5 +/- 0.8 Ha.

Type quit() and press [Enter] to exit the Python command line.

18.5 Inspecting MC Data

QMCPACK outputs data from MC calculations into files ending in scalar.dat. Several quantities are calculated and written for each block of MC steps in successive columns to the right of the step index.

Change directories to atom, and open the file ending in scalar.dat with a text editor (e.g., **vi *.scalar.dat** or **emacs *.scalar.dat**. If possible, adjust the terminal so that lines do not wrap. The data will begin as follows (broken into three groups to fit on this page):

```
#   index    LocalEnergy          LocalEnergy_sq       LocalPotential      ...
          0   -4.5298911858e-01    6.0984565298e-01   -1.1708693521e+00
          1   -4.5481953564e-01    6.1641291630e-01   -1.1863425644e+00
          2   -4.8066105923e-01    1.3586015116e+00   -1.1766446209e+00
          3   -4.7316713469e-01    7.8720769003e-01   -1.1799481122e+00
          4   -4.6204733302e-01    5.6393677687e-01   -1.1619244081e+00
          5   -4.4313854290e-01    6.0831516179e-01   -1.2064503041e+00
          6   -4.5064926960e-01    5.9891422196e-01   -1.1521370176e+00
          7   -4.5687452611e-01    5.8139614676e-01   -1.1423627617e+00
          8   -4.5018503739e-01    8.4147849706e-01   -1.1842075439e+00
          9   -4.3862013841e-01    5.5477715836e-01   -1.2080979177e+00
```

The first line begins with a #, indicating that this line does not contain MC data but rather the labels of the columns. After a blank line, the remaining lines consist of the MC data. The first column, labeled index, is an integer indicating which block of MC data is on that line. The second column contains the quantity usually of greatest interest from the simulation: the local energy. Since this simulation did not use the exact ground state wavefunction, it does not produce -0.5 Ha as the local energy although the value lies within about 10%. The value of the local energy fluctuates from block to block, and the closer the trial wavefunction is to the ground state the smaller these fluctuations will be. The next column contains an important ingredient in estimating the error in the MC average—the square of the local energy—found by evaluating the square of the Hamiltonian.

```
...    Kinetic              Coulomb              BlockWeight          ...
        7.1788023352e-01   -1.1708693521e+00    1.2800000000e+04
        7.3152302871e-01   -1.1863425644e+00    1.2800000000e+04
        6.9598356165e-01   -1.1766446209e+00    1.2800000000e+04
        7.0678097751e-01   -1.1799481122e+00    1.2800000000e+04
        6.9987707508e-01   -1.1619244081e+00    1.2800000000e+04
        7.6331176120e-01   -1.2064503041e+00    1.2800000000e+04
        7.0148774798e-01   -1.1521370176e+00    1.2800000000e+04
        6.8548823555e-01   -1.1423627617e+00    1.2800000000e+04
        7.3402250655e-01   -1.1842075439e+00    1.2800000000e+04
        7.6947777925e-01   -1.2080979177e+00    1.2800000000e+04
```

The fourth column from the left consists of the values of the local potential energy. In this simulation, it is identical to the Coulomb potential (contained in the sixth column) because the one electron in the simulation has only the potential energy coming from its interaction with the nucleus. In many-electron simulations, the local potential energy contains contributions from the electron-electron Coulomb interactions and the nuclear potential or pseudopotential. The fifth column contains the local kinetic energy value for each MC block, obtained from the Laplacian of the wavefunction. The sixth column shows the local Coulomb interaction energy. The seventh column displays the weight each line of data has in the average (the weights are identical in this simulation).

```
...     BlockCPU            AcceptRatio
        6.0178991748e-03    9.8515625000e-01
        5.8323097461e-03    9.8562500000e-01
        5.8213412744e-03    9.8531250000e-01
        5.8330412549e-03    9.8828125000e-01
        5.8108362256e-03    9.8625000000e-01
        5.8254170264e-03    9.8625000000e-01
        5.8314813086e-03    9.8679687500e-01
        5.8258469971e-03    9.8726562500e-01
        5.8158433545e-03    9.8468750000e-01
        5.7959401123e-03    9.8539062500e-01
```

The eighth column shows the CPU time (in seconds) to calculate the data in that line. The ninth column from the left contains the acceptance ratio (1 being full acceptance) for MC steps in that line's data. Other than the block weight, all quantities vary from line to line.

Exit the text editor (**[Esc] :q! [Enter]** in vi, **[Ctrl]-x [Ctrl]-c** in emacs).

18.6 Averaging quantities in the MC data

QMCPACK includes the qmca Python tool to average quantities in the `scalar.dat` file (and also the `dmc.dat` file of DMC simulations). Without any flags, qmca will output the average of each column with a quantity in the `scalar.dat` file as follows.

Execute qmca by `qmca *.scalar.dat`, which for this data outputs:

```
H  series 0
LocalEnergy            =          -0.45446 +/-           0.00057
Variance               =             0.529 +/-             0.018
Kinetic                =            0.7366 +/-            0.0020
LocalPotential         =           -1.1910 +/-            0.0016
Coulomb                =           -1.1910 +/-            0.0016
LocalEnergy_sq         =             0.736 +/-             0.018
BlockWeight            =    12800.00000000 +/-       0.00000000
BlockCPU               =        0.00582002 +/-       0.00000067
AcceptRatio            =          0.985508 +/-         0.000048
Efficiency             =        0.00000000 +/-       0.00000000
```

After one blank, qmca prints the title of the subsequent data, gleaned from the data file name. In this case, `H.s000.scalar.dat` became "H series 0." Everything before the first "`.s`" will be interpreted as the title, and the number between "`.s`" and the next "." will be interpreted as the series number.

The first column under the title is the name of each quantity qmca averaged. The column to the right of the equal signs contains the average for the quantity of that line, and the column to the right of the plus-slash-minus is the statistical error bar on the quantity. All quantities calculated from MC simulations have and must be reported with a statistical error bar!

Two new quantities not present in the `scalar.dat` file are computed by qmca from the data—variance and efficiency. We will look at these later in this lab.

To view only one value, **qmca** takes the **-q (quantity)** flag. For example, the output of `qmca -q LocalEnergy *.scalar.dat` in this directory produces a single line of output:

```
H  series 0  LocalEnergy = -0.454460 +/- 0.000568
```

Type `qmca --help` to see the list of all quantities and their abbreviations.

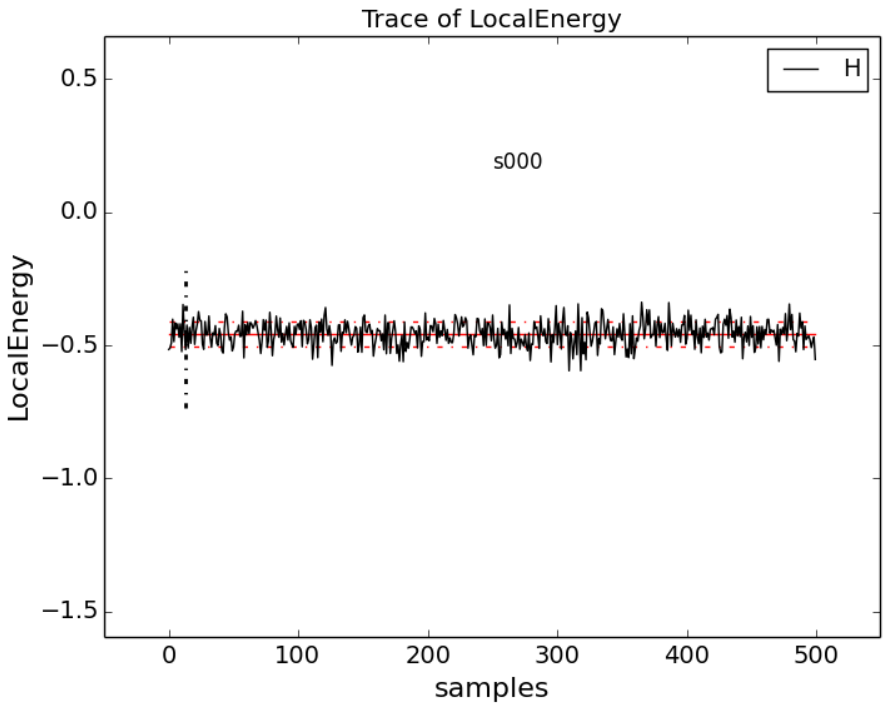
18.7 Evaluating MC simulation quality

There are several aspects of a MC simulation to consider in deciding how well it went. Besides the deviation of the average from an expected value (if there is one), the stability of the simulation in its sampling, the autocorrelation between MC steps, the value of the acceptance ratio (accepted steps over total proposed steps), and the variance in the local energy all indicate the quality of an MC simulation. We will look at these one by one.

18.7.1 Tracing MC quantities

Visualizing the evolution of MC quantities over the course of the simulation by a *trace* offers a quick picture of whether the random walk had the expected behavior. qmca plots traces with the -t flag.

Type `qmca -q e -t H.s000.scalar.dat`, which produces a graph of the trace of the local energy:

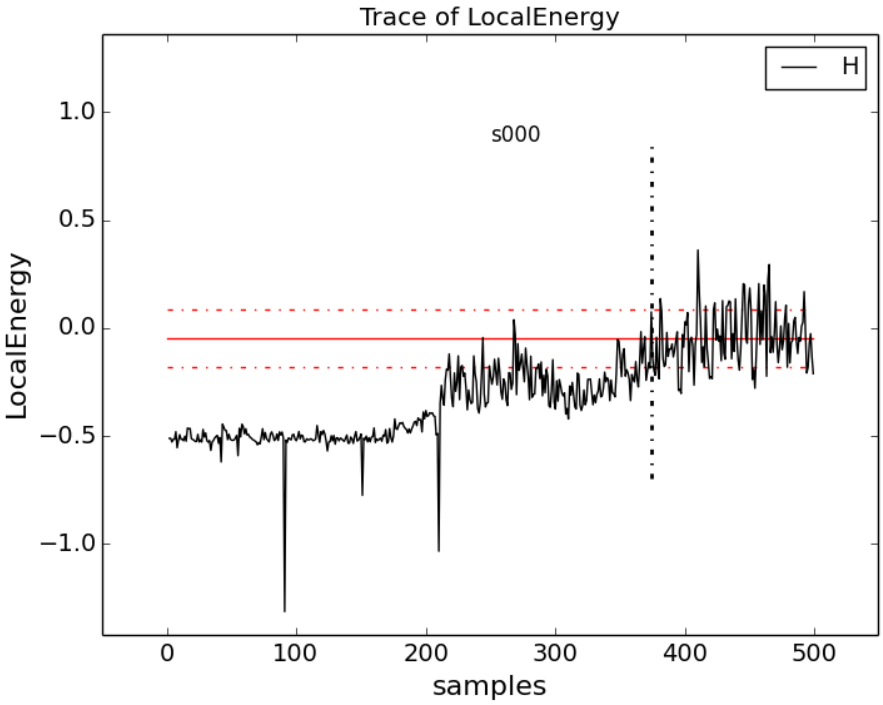


The solid black line connects the values of the local energy at each MC block (labeled "samples"). The average value is marked with a horizontal, solid red line. One standard deviation above and below the average are marked with horizontal, dashed red lines.

The trace of this run is largely centered on the average with no large-scale oscillations or major shifts, indicating a good-quality MC run.

Try tracing the kinetic and potential energies, seeing that their behavior is comparable with the total local energy.

Change to directory `problematic` and type `qmca -q e -t H.s000.scalar.dat` to produce this graph:



Here, the local energy samples cluster around the expected -0.5 Ha for the first 150 samples or so and then begin to oscillate more wildly and increase erratically toward 0, indicating a poor-quality MC run.

Again, trace the kinetic and potential energies in this run and see how their behavior compares with the total local energy.

18.7.2 Blocking away autocorrelation

Autocorrelation occurs when a given MC step biases subsequent MC steps, leading to samples that are not statistically independent. We must take this autocorrelation into account to obtain accurate statistics. qmca outputs autocorrelation when given the –sac flag.

Change to directory `autocorrelation` and type `qmca -q e --sac H.s000.scalar.dat`.

```
H  series 0  LocalEnergy = -0.454982 +/- 0.000430    1.0
```

The value after the error bar on the quantity is the autocorrelation (1.0 in this case).

Proposing too small a step in configuration space, the MC *time step*, can lead to autocorrelation since the new samples will be in the neighborhood of previous samples. Type `grep timestep H.xml` to see the varying time step values in this QMCPACK input file (`H.xml`):

```
<parameter name="timestep">10</parameter>
<parameter name="timestep">5</parameter>
<parameter name="timestep">2</parameter>
<parameter name="timestep">1</parameter>
<parameter name="timestep">0.5</parameter>
<parameter name="timestep">0.2</parameter>
<parameter name="timestep">0.1</parameter>
```

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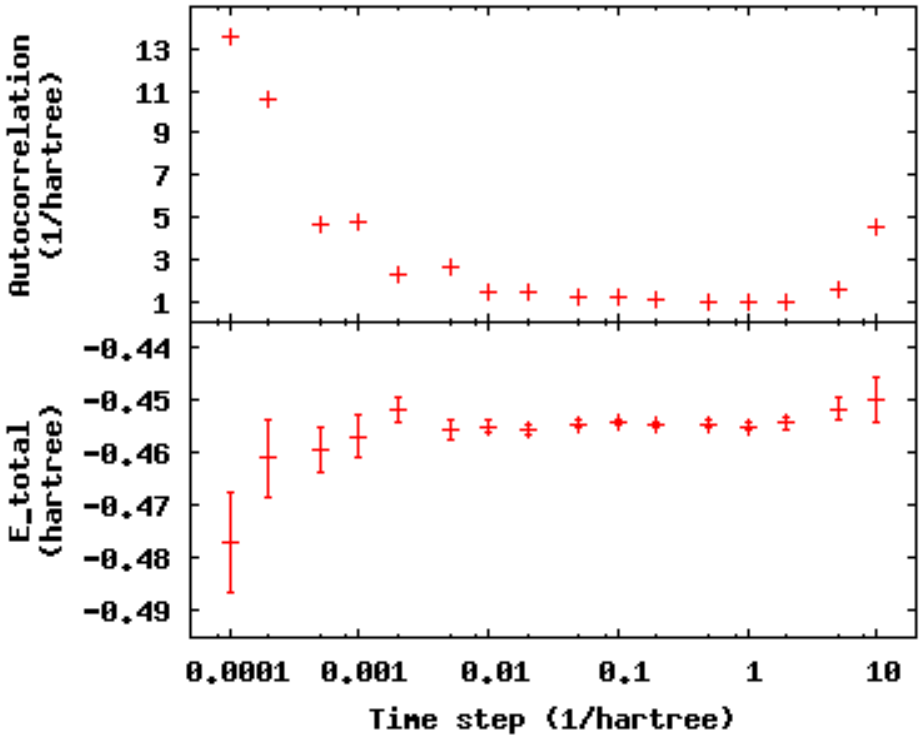
```
<parameter name="timestep">0.05</parameter>
<parameter name="timestep">0.02</parameter>
<parameter name="timestep">0.01</parameter>
<parameter name="timestep">0.005</parameter>
<parameter name="timestep">0.002</parameter>
<parameter name="timestep">0.001</parameter>
<parameter name="timestep">0.0005</parameter>
<parameter name="timestep">0.0002</parameter>
<parameter name="timestep">0.0001</parameter>
```

Generally, as the time step decreases, the autocorrelation will increase (caveat: very large time steps will also have increasing autocorrelation). To see this, type `qmca -q e --sac *.scalar.dat` to see the energies and autocorrelation times, then plot with gnuplot by inputting `gnuplot H.plt`:

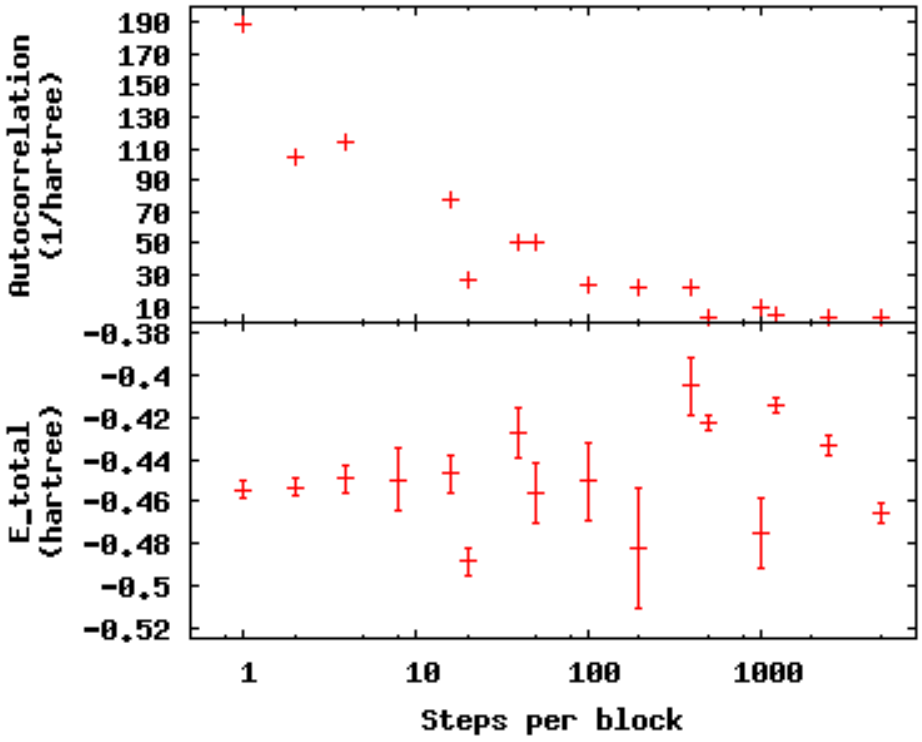


The error bar also increases with the autocorrelation.

Press `q [Enter]` to quit gnuplot.

To get around the bias of autocorrelation, we group the MC steps into blocks, take the average of the data in the steps of each block, and then finally average the averages in all the blocks. QMCPACK outputs the block averages as each line in the `scalar.dat` file. (For DMC simulations, in addition to the `scalar.dat`, QMCPACK outputs the quantities at each step to the `dmc.dat` file, which permits reblocking the data differently from the specification in the input file.)

Change directories to `blocking`. Here we look at the time step of the last dataset in the `autocorrelation` directory. Verify this by typing `grep timestep H.xml` to see that all values are set to 0.001. Now to see how we will vary the blocking, type `grep -A1 blocks H.xml`. The parameter "steps" indicates the number of steps per block, and the parameter "blocks" gives the number of blocks. For this comparison, the total number of MC steps (equal to the product of "steps" and "blocks") is fixed at 50,000. Now check the effect of blocking on autocorrelation—type `qmca -q e --sac *scalar.dat` to see the data and `gnuplot H.plt` to visualize the data:



The greatest number of steps per block produces the smallest autocorrelation time. The larger number of blocks over which to average at small step-per-block number masks the corresponding increase in error bar with increasing autocorrelation.

Press `q [Enter]` to quit gnuplot.

18.7.3 Balancing autocorrelation and acceptance ratio

Adjusting the time step value also affects the ratio of accepted steps to proposed steps. Stepping nearby in configuration space implies that the probability distribution is similar and thus more likely to result in an accepted move. Keeping the acceptance ratio high means the algorithm is efficiently exploring configuration space and not sticking at particular configurations. Return to the `autocorrelation` directory. Refresh your memory on the time steps in this set of simulations by `grep timestep H.xml`. Then, type `qmca -q ar *scalar.dat` to see the acceptance ratio as it varies with decreasing time step:

```
H  series 0  AcceptRatio = 0.047646 +/- 0.000206
H  series 1  AcceptRatio = 0.125361 +/- 0.000308
H  series 2  AcceptRatio = 0.328590 +/- 0.000340
H  series 3  AcceptRatio = 0.535708 +/- 0.000313
H  series 4  AcceptRatio = 0.732537 +/- 0.000234
H  series 5  AcceptRatio = 0.903498 +/- 0.000156
H  series 6  AcceptRatio = 0.961506 +/- 0.000083
H  series 7  AcceptRatio = 0.985499 +/- 0.000051
H  series 8  AcceptRatio = 0.996251 +/- 0.000025
H  series 9  AcceptRatio = 0.998638 +/- 0.000014
H  series 10  AcceptRatio = 0.999515 +/- 0.000009
H  series 11  AcceptRatio = 0.999884 +/- 0.000004
H  series 12  AcceptRatio = 0.999958 +/- 0.000003
H  series 13  AcceptRatio = 0.999986 +/- 0.000002
```

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```
H  series 14  AcceptRatio = 0.999995 +/- 0.000001
H  series 15  AcceptRatio = 0.999999 +/- 0.000000
```

By series 8 (time step = 0.02), the acceptance ratio is in excess of 99%.

Considering the increase in autocorrelation and subsequent increase in error bar as time step decreases, it is important to choose a time step that trades off appropriately between acceptance ratio and autocorrelation. In this example, a time step of 0.02 occupies a spot where the acceptance ratio is high (99.6%) and autocorrelation is not appreciably larger than the minimum value (1.4 vs. 1.0).

18.7.4 Considering variance

Besides autocorrelation, the dominant contributor to the error bar is the *variance* in the local energy. The variance measures the fluctuations around the average local energy, and, as the fluctuations go to zero, the wavefunction reaches an exact eigenstate of the Hamiltonian. qmca calculates this from the local energy and local energy squared columns of the `scalar.dat`.

Type `qmca -q v H.s009.scalar.dat` to calculate the variance on the run with time step balancing autocorrelation and acceptance ratio:

```
H  series 9  Variance = 0.513570 +/- 0.010589
```

Just as the total energy does not tell us much by itself, neither does the variance. However, comparing the ratio of the variance with the energy indicates how the magnitude of the fluctuations compares with the energy itself. Type `qmca -q ev H.s009.scalar.dat` to calculate the energy and variance on the run side by side with the ratio:

```
                    LocalEnergy              Variance        ratio
H  series 0  -0.454460 +/- 0.000568   0.529496 +/- 0.018445   1.1651
```

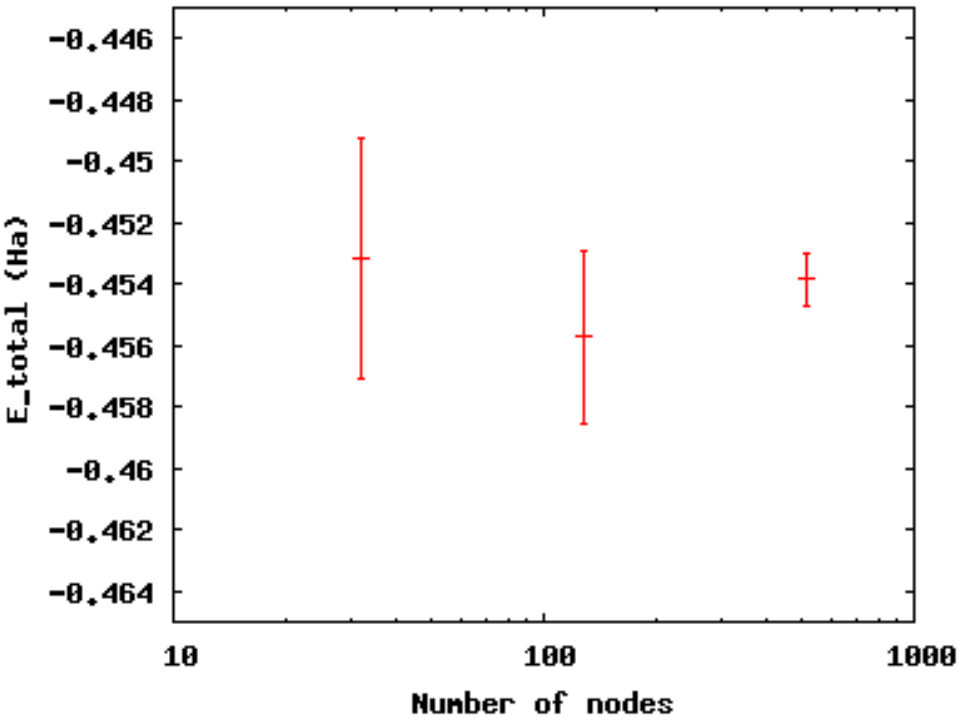
The very high ration of 1.1651 indicates the square of the fluctuations is on average larger than the value itself. In the next section, we will approach ways to improve the variance that subsequent labs will build on.

18.8 Reducing statistical error bars

18.8.1 Increasing MC sampling

Increasing the number of MC samples in a dataset reduces the error bar as the inverse of the square root of the number of samples. There are two ways to increase the number of MC samples in a simulation: (1) running more samples in parallel and (2) increasing the number of blocks (with fixed number of steps per block, this increases the total number of MC steps).

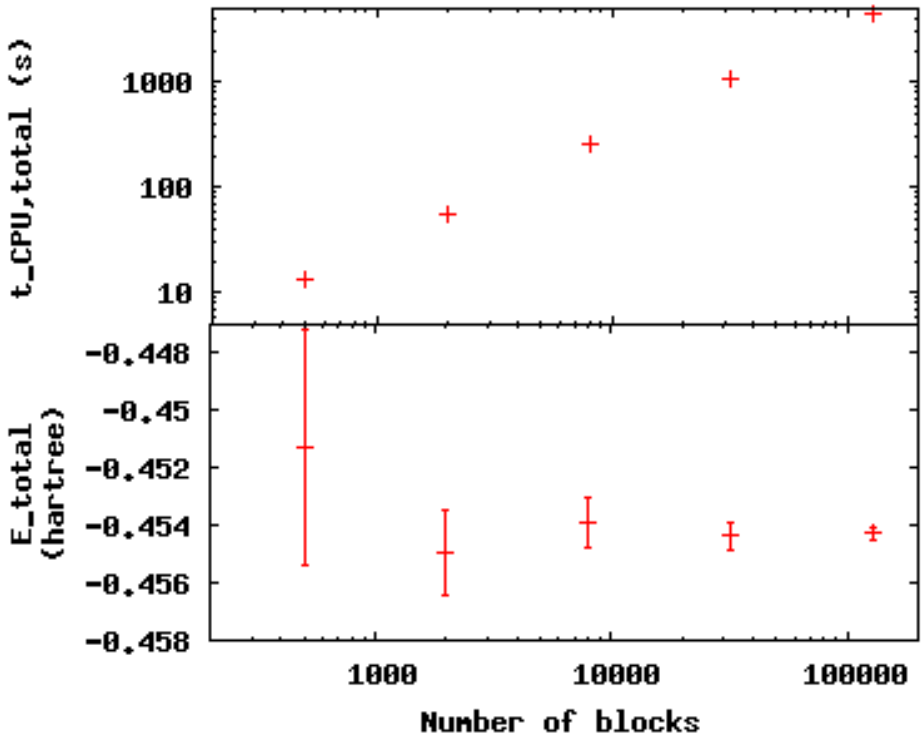
To see the effect of running more samples in parallel, change to the directory `nodes`. The series here increases the number of nodes by factors of four from 32 to 128 to 512. Type `qmca -q ev *scalar.dat` and note the change in the error bar on the local energy as the number of nodes. Visualize this with **gnuplot H.plt**:



Increasing the number of blocks, unlike running in parallel, increases the total CPU time of the simulation.

Press `q [Enter]` to quit gnuplot.

To see the effect of increasing the block number, change to the directory `blocks`. To see how we will vary the number of blocks, type `grep -A1 blocks H.xml`. The number of steps remains fixed, thus increasing the total number of samples. Visualize the tradeoff by inputting `gnuplot H.plt`:



Press `q [Enter]` to quit gnuplot.

18.8.2 Improving the basis sets

In all of the previous examples, we are using the sum of two Gaussian functions (STO-2G) to approximate what should be a simple decaying exponential for the wavefunction of the ground state of the hydrogen atom. The sum of multiple copies of a function varying each copy's width and amplitude with coefficients is called a *basis set*. As we add Gaussians to the basis set, the approximation improves, the variance goes toward zero, and the energy goes to -0.5 Ha. In nearly every other case, the exact function is unknown, and we add basis functions until the total energy does not change within some threshold.

Change to the directory `basis` and look at the total energy and variance as we change the wavefunction by typing `qmca -q ev H_`:

```
                        LocalEnergy              Variance          ratio
H_STO-2G   series 0  -0.454460 +/- 0.000568   0.529496 +/- 0.018445   1.1651
H_STO-3G   series 0  -0.465386 +/- 0.000502   0.410491 +/- 0.010051   0.8820
H_STO-6G   series 0  -0.471332 +/- 0.000491   0.213919 +/- 0.012954   0.4539
H__exact   series 0  -0.500000 +/- 0.000000   0.000000 +/- 0.000000   -0.0000
```

qmca also puts out the ratio of the variance to the local energy in a column to the right of the variance error bar. A typical high-quality value for this ratio is lower than 0.1 or so—none of these few-Gaussian wavefunctions satisfy that rule of thumb.

Use qmca to plot the trace of the local energy, kinetic energy, and potential energy of H__exact. The total energy is constantly -0.5 Ha even though the kinetic and potential energies fluctuate from configuration to configuration.

18.8.3 Adding a Jastrow factor

Another route to reducing the variance is the introduction of a Jastrow factor to account for electron-electron correlation (not the statistical autocorrelation of MC steps but the physical avoidance that electrons have of one another). To do this, we will switch to the hydrogen dimer with the exact ground state wavefunction of the atom (STO basis)—this will not be exact for the dimer. The ground state energy of the hydrogen dimer is -1.174 Ha.

Change directories to `dimer` and put in `qmca -q ev *scalar.dat` to see the result of adding a simple, one-parameter Jastrow to the STO basis for the hydrogen dimer at experimental bond length:

```
                              LocalEnergy              Variance
H2_STO___no_jastrow  series 0  -0.876548 +/- 0.005313   0.473526 +/- 0.014910
H2_STO_with_jastrow  series 0  -0.912763 +/- 0.004470   0.279651 +/- 0.016405
```

The energy reduces by 0.044 +/- 0.006 HA and the variance by 0.19 +/- 0.02. This is still 20% above the ground state energy, and subsequent labs will cover how to improve on this with improved forms of the wavefunction that capture more of the physics.

18.9 Scaling to larger numbers of electrons

18.9.1 Calculating the efficiency

The inverse of the product of CPU time and the variance measures the *efficiency* of an MC calculation. Use qmca to calculate efficiency by typing `qmca -q eff *scalar.dat` to see the efficiency of these two H_2 calculations:

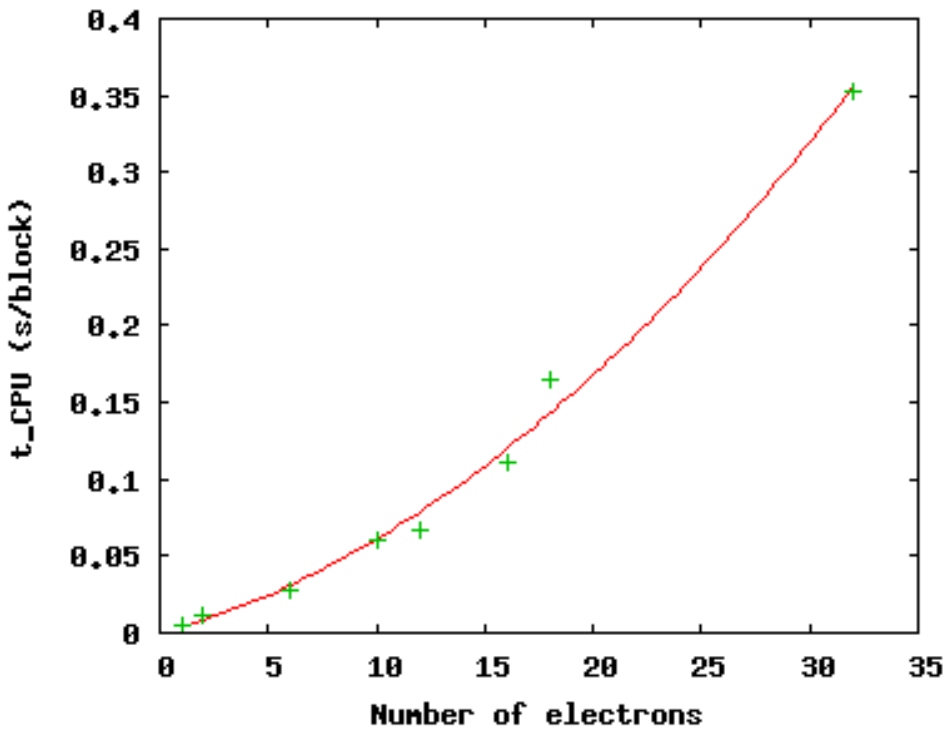
```
H2_STO___no_jastrow  series 0  Efficiency = 16698.725453 +/- 0.000000
H2_STO_with_jastrow  series 0  Efficiency = 52912.365609 +/- 0.000000
```

The Jastrow factor increased the efficiency in these calculations by a factor of three, largely through the reduction in variance (check the average block CPU time to verify this claim).

18.9.2 Scaling up

To see how MC scales with increasing particle number, change directories to `size`. Here are the data from runs of increasing numbers of electrons for H, H_2, C, CH_4, C_2, C_2H_4, $(CH_4)_2$, and $(C_2H_4)_2$ using the STO-6G basis set for the orbitals of the Slater determinant. The file names begin with the number of electrons simulated for those data.

Use `qmca -q bc *scalar.dat` to see that the CPU time per block increases with the number of electrons in the simulation; then plot the total CPU time of the simulation by **gnuplot Nelectron_tCPU.plt**:



The green pluses represent the CPU time per block at each electron number. The red line is a quadratic fit to those data. For a fixed basis set size, we expect the time to scale quadratically up to 1,000s of electrons, at which point a cubic scaling term may become dominant. Knowing the scaling allows you to roughly project the calculation time for a larger number of electrons.

Press `q [Enter]` to quit gnuplot.

This is not the whole story, however. The variance of the energy also increases with a fixed basis set as the number of particles increases at a faster rate than the energy decreases. To see this, type `qmca -q ev *scalar.dat`:

```
             LocalEnergy                 Variance
01_________H  series 0  -0.471352 +/- 0.000493      0.213020 +/- 0.012950
02________H2  series 0  -0.898875 +/- 0.000998      0.545717 +/- 0.009980
06________C  series 0  -37.608586 +/- 0.020453   184.322000 +/- 45.481193
10_______CH4  series 0  -38.821513 +/- 0.022740   169.797871 +/- 24.765674
12________C2  series 0  -72.302390 +/- 0.037691   491.416711 +/- 106.090103
16_____C2H4  series 0  -75.488701 +/- 0.042919   404.218115 +/- 60.196642
18___CH4CH4  series 0  -58.459857 +/- 0.039309   498.579645 +/- 92.480126
32_C2H4C2H4  series 0  -91.567283 +/- 0.048392   632.114026 +/- 69.637760
```

The increase in variance is not uniform, but the general trend is upward with a fixed wavefunction form and basis set. Subsequent labs will address how to improve the wavefunction to keep the variance manageable.

CHAPTER

NINETEEN

LAB 2: QMC BASICS

19.1 Topics covered in this lab

This lab focuses on the basics of performing quality QMC calculations. As an example, participants test an oxygen pseudopotential within DMC by calculating atomic and dimer properties, a common step prior to production runs. Topics covered include:

- Converting pseudopotentials into QMCPACK's FSATOM format
- Generating orbitals with QE
- Converting orbitals into QMCPACK's ESHDF format with pw2qmcpack
- Optimizing Jastrow factors with QMCPACK
- Removing DMC time step errors via extrapolation
- Automating QMC workflows with Nexus
- Testing pseudopotentials for accuracy

19.2 Lab outline

1. Download and conversion of oxygen atom pseudopotential
2. DMC time step study of the neutral oxygen atom
    1. DFT orbital generation with QE
    2. Orbital conversion with
    3. Optimization of Jastrow correlation factor with QMCPACK
    4. DMC run with multiple time steps
3. DMC time step study of the first ionization potential of oxygen
    1. Repetition of a-d above for ionized oxygen atom
4. Automated DMC calculations of the oxygen dimer binding curve

19.3 Lab directories and files

```
%
labs/lab2_qmc_basics/
|
├── oxygen_atom           - oxygen atom calculations
|   ├── O.q0.dft.in          - Quantum ESPRESSO input for DFT run
|   ├── O.q0.p2q.in          - pw2qmcpack.x input for orbital conversion run
|   ├── O.q0.opt.in.xml      - QMCPACK input for Jastrow optimization run
|   ├── O.q0.dmc.in.xml      - QMCPACK input file for neutral O DMC
|   ├── ip_conv.py           - tool to fit oxygen IP vs timestep
|   └── reference            - directory w/ completed runs
|
├── oxygen_dimer          - oxygen dimer calculations
|   ├── dimer_fit.py         - tool to fit dimer binding curve
|   ├── O_dimer.py           - automation script for dimer calculations
|   ├── pseudopotentials     - directory for pseudopotentials
|   └── reference            - directory w/ completed runs
|
└── your_system           - performing calculations for an arbitrary system (yours)
    ├── example.py           - example nexus file for periodic diamond
    ├── pseudopotentials     - directory containing C pseudopotentials
    └── reference            - directory w/ completed runs
```

19.4 Obtaining and converting a pseudopotential for oxygen

First enter the `oxygen_atom` directory:

```
cd labs/lab2_qmc_basics/oxygen_atom/
```

Throughout the rest of the lab, locations are specified with respect to `labs/lab2_qmc_basics` (e.g., `oxygen_atom`).

We use a potential from the Burkatzki-Filippi-Dolg pseudopotential database. Although the full database is available in QMCPACK distribution (`trunk/pseudopotentials/BFD/`), we use a BFD pseudopotential to illustrate the process of converting and testing an external potential for use with QMCPACK. To obtain the pseudopotential, go to http://www.burkatzki.com/pseudos/index.2.html and click on the "Select Pseudopotential" button. Next click on oxygen in the periodic table. Click on the empty circle next to "V5Z" (a large Gaussian basis set) and click on "Next." Select the Gamess format and click on "Retrive Potential." Helpful information about the pseudopotential will be displayed. The desired portion is at the bottom (the last 7 lines). Copy this text into the editor of your choice (e.g., `emacs` or `vi`) and save it as `O.BFD.gamess` (be sure to include a new line at the end of the file). To transform the pseudopotential into the FSATOM XML format used by QMCPACK, use the `ppconvert` tool:

```
ppconvert --gamess_pot O.BFD.gamess --s_ref "1s(2)2p(4)" \
 --p_ref "1s(2)2p(4)" --d_ref "1s(2)2p(4)" --xml O.BFD.xml
```

Observe the notation used to describe the reference valence configuration for this helium-core PP: `1s(2)2p(4)`. The `ppconvert` tool uses the following convention for the valence states: the first s state is labeled `1s` (`1s`, `2s`, `3s`, ...), the first p state is labeled `2p` (`2p`, `3p`, ...), and the first d state is labeled `3d` (`3d`, `4d`, ...). Copy the resulting xml file into the `oxygen_atom` directory.

Note: The command to convert the PP into QE's UPF format is similar (both formats are required):

```
ppconvert --gamess_pot O.BFD.gamess --s_ref "1s(2)2p(4)" \
 --p_ref "1s(2)2p(4)" --d_ref "1s(2)2p(4)" --log_grid --upf O.BFD.upf
```

For reference, the text of `O.BFD.gamess` should be:

```
O-QMC GEN 2 1
3
6.00000000 1 9.29793903
55.78763416 3 8.86492204
-38.81978498 2 8.62925665
1
38.41914135 2 8.71924452
```

The full QMCPACK pseudopotential is also included in `oxygen_atom/reference/O.BFD.*`.

19.5 DFT with QE to obtain the orbital part of the wavefunction

With the pseudopotential in hand, the next step toward a QMC calculation is to obtain the Fermionic part of the wavefunction, in this case a single Slater determinant constructed from DFT-LDA orbitals for a neutral oxygen atom. If you had trouble with the pseudopotential conversion step, preconverted pseudopotential files are located in the `oxygen_atom/reference` directory.

QE input for the DFT-LDA ground state of the neutral oxygen atom can be found in `O.q0.dft.in` and also in *Listing 58*. Setting `wf_collect=.true.` instructs QE to write the orbitals to disk at the end of the run. Option `wf_collect=.true.` could be a potential problem in large simulations; therefore, we recommend avoiding it and using the converter pw2qmcpack in parallel (see details in *pw2qmcpack.x*). Note that the plane-wave energy cutoff has been set to a reasonable value of 300 Ry here (`ecutwfc=300`). This value depends on the pseudopotentials used, and, in general, should be selected by running DFT → (orbital conversion) → VMC with increasing energy cutoffs until the lowest VMC total energy and variance is reached.

Listing 19.1: QE input file for the neutral oxygen atom (`O.q0.dft.in`)

```
&CONTROL
   calculation       = 'scf'
   restart_mode      = 'from_scratch'
   prefix            = 'O.q0'
   outdir            = './'
   pseudo_dir        = './'
   disk_io           = 'low'
   wf_collect        = .true.
/

&SYSTEM
   celldm(1)         = 1.0
   ibrav             = 0
   nat               = 1
   ntyp              = 1
   nspin             = 2
   tot_charge        = 0
   tot_magnetization = 2
   input_dft         = 'lda'
   ecutwfc           = 300
   ecutrho           = 1200
   nosym             = .true.
```

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```
   occupations       = 'smearing'
   smearing          = 'fermi-dirac'
   degauss           = 0.0001
/

&ELECTRONS
   diagonalization   = 'david'
   mixing_mode       = 'plain'
   mixing_beta       = 0.7
   conv_thr          = 1e-08
   electron_maxstep  = 1000
/


ATOMIC_SPECIES
   O  15.999 O.BFD.upf

ATOMIC_POSITIONS alat
   O     9.44863067       9.44863161       9.44863255

K_POINTS automatic
   1 1 1  0 0 0

CELL_PARAMETERS cubic
        18.89726133       0.00000000       0.00000000
         0.00000000      18.89726133       0.00000000
         0.00000000       0.00000000      18.89726133
```

Run QE by typing

```
mpirun -np 4 pw.x -input O.q0.dft.in >&O.q0.dft.out&
```

The DFT run should take a few minutes to complete. If desired, you can track the progress of the DFT run by typing "`tail -f O.q0.dft.out`." Once finished, you should check the LDA total energy in `O.q0.dft.out` by typing "`grep '! ' O.q0.dft.out`." The result should be close to

```
!    total energy              =     -31.57553905 Ry
```

The orbitals have been written in a format native to QE in the `O.q0.save` directory. We will convert them into the ESHDF format expected by QMCPACK by using the `pw2qmcpack.x` tool. The input for `pw2qmcpack.x` can be found in the file `O.q0.p2q.in` and also in *Listing 59*.

Listing 19.2: `pw2qmcpack.x` input file for orbital conversion (`O.q0.p2q.in`)

```
&inputpp
  prefix     = 'O.q0'
  outdir     = './'
  write_psir = .false.
/
```

Perform the orbital conversion now by typing the following:

```
mpirun -np 1 pw2qmcpack.x<O.q0.p2q.in>&O.q0.p2q.out&
```

Upon completion of the run, a new file should be present containing the orbitals for QMCPACK: `O.q0.pwscf.h5`. Template XML files for particle (`O.q0.ptcl.xml`) and wavefunction (`O.q0.wfs.xml`) inputs to QMCPACK

should also be present.

19.6 Optimization with QMCPACK to obtain the correlated part of the wavefunction

The wavefunction we have obtained to this point corresponds to a noninteracting Hamiltonian. Once the Coulomb pair potential is switched on between particles, it is known analytically that the exact wavefunction has cusps whenever two particles meet spatially and, in general, the electrons become correlated. This is represented in the wavefunction by introducing a Jastrow factor containing at least pair correlations:

$$\Psi_{Slater-Jastrow} = e^{-J}\Psi_{Slater} \tag{19.1}$$

$$J = \sum_{\sigma\sigma'}\sum_{i<j} u_2^{\sigma\sigma'}(|r_i - r_j|) + \sum_{\sigma}\sum_{iI} u_1^{\sigma I}(|r_i - r_I|)\,. \tag{19.2}$$

Here σ is a spin variable while r_i and r_I represent electron and ion coordinates, respectively. The introduction of J into the wavefunction is similar to F12 methods in quantum chemistry, though it has been present in essentially all QMC studies since the first applications the method (circa 1965).

How are the functions $u_2^{\sigma\sigma'}$ and u_1^{σ} obtained? Generally, they are approximated by analytical functions with several unknown parameters that are determined by minimizing the energy or variance directly within VMC. This is effective because the energy and variance reach a global minimum only for the true ground state wavefunction (Energy $= E \equiv \langle\Psi|\hat{H}|\Psi\rangle$, Variance $= V \equiv \langle\Psi|(\hat{H}-E)^2|\Psi\rangle$). For this exercise, we will focus on minimizing the variance.

First, we need to update the template particle and wavefunction information in `O.q0.ptcl.xml` and `O.q0.wfs.xml`. We want to simulate the O atom in open boundary conditions (the default is periodic). To do this, open `` `O.q0.ptcl.xml `` with your favorite text editor (e.g., `emacs` or `vi`) and replace

```
<parameter name="bconds">
   p p p
</parameter>
<parameter name="LR_dim_cutoff">
   15
</parameter>
```

with

```
<parameter name="bconds">
   n n n
</parameter>
```

Next we will select Jastrow factors appropriate for an atom. In open boundary conditions, the B-spline Jastrow correlation functions should cut off to zero at some distance away from the atom. Open `O.q0.wfs.xml` and add the following cutoffs (`rcut` in Bohr radii) to the correlation factors:

```
...
<correlation speciesA="u" speciesB="u" size="8" rcut="10.0">
...
<correlation speciesA="u" speciesB="d" size="8" rcut="10.0">
...
<correlation elementType="O" size="8" rcut="5.0">
...
```

These terms correspond to $u_2^{\uparrow\uparrow}/u_2^{\downarrow\downarrow}$, $u_2^{\uparrow\downarrow}$, and $u_1^{\uparrow O}/u_1^{\downarrow O}$, respectively. In each case, the correlation function (u_*) is represented by piecewise continuous cubic B-splines. Each correlation function has eight parameters, which are just the values of u on a uniformly spaced grid up to `rcut`. Initially the parameters (`coefficients`) are set to zero:

```
<correlation speciesA="u" speciesB="u" size="8" rcut="10.0">
  <coefficients id="uu" type="Array">
     0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
  </coefficients>
</correlation>
```

Finally, we need to assemble particle, wavefunction, and pseudopotential information into the main QMCPACK input file (`O.q0.opt.in.xml`) and specify inputs for the Jastrow optimization process. Open `O.q0.opt.in.xml` and write in the location of the particle, wavefunction, and pseudopotential files ("`<!-- ... -->`" are comments):

```
...
<!-- include simulationcell and particle information from pw2qmcpqack -->
<include href="O.q0.ptcl.xml"/>
...
<!-- include wavefunction information from pw2qmcpqack -->
<include href="O.q0.wfs.xml"/>
...
<!-- O pseudopotential read from "O.BFD.xml" -->
<pseudo elementType="O" href="O.BFD.xml"/>
...
```

The relevant portion of the input describing the linear optimization process is

```
<loop max="MAX">
  <qmc method="linear" move="pbyp" checkpoint="-1">
    <cost name="energy"              >  ECOST    </cost>
    <cost name="unreweightedvariance">  UVCOST   </cost>
    <cost name="reweightedvariance"  >  RVCOST   </cost>
    <parameter name="timestep"       >  TS       </parameter>
    <parameter name="samples"        >  SAMPLES  </parameter>
    <parameter name="warmupSteps"    >  50       </parameter>
    <parameter name="blocks"         >  200      </parameter>
    <parameter name="subSteps"       >  1        </parameter>
    <parameter name="nonlocalpp"     >  yes      </parameter>
    <parameter name="useBuffer"      >  yes      </parameter>
    ...
  </qmc>
</loop>
```

An explanation of each input variable follows. The remaining variables control specialized internal details of the linear optimization algorithm. The meaning of these inputs is beyond the scope of this lab, and reasonable results are often obtained keeping these values fixed.

energy Fraction of trial energy in the cost function.

unreweightedvariance Fraction of unreweighted trial variance in the cost function. Neglecting the weights can be more robust.

reweightedvariance Fraction of trial variance (including the full weights) in the cost function.

timestep Time step of the VMC random walk, determines spatial distance moved by each electron during MC steps. Should be chosen such that the acceptance ratio of MC moves is around 50% (30–70% is often acceptable). Reasonable values are often between 0.2 and 0.6 Ha^{-1}.

samples Total number of MC samples collected for optimization; determines statistical error bar of cost function. It is often efficient to start with a modest number of samples (50k) and then increase as needed. More samples may be required if the wavefunction contains a large number of variational parameters. MUST be be a multiple of the number of threads/cores.

warmupSteps Number of MC steps discarded as a warmup or equilibration period of the random walk. If this is too small, it will bias the optimization procedure.

blocks Number of average energy values written to output files. Should be greater than 200 for meaningful statistical analysis of output data (e.g., via `qmca`).

subSteps Number of MC steps in between energy evaluations. Each energy evaluation is expensive, so taking a few steps to decorrelate between measurements can be more efficient. Will be less efficient with many substeps.

nonlocalpp,useBuffer If `nonlocalpp="no,"` then the nonlocal part of the pseudopotential is not included when computing the cost function. If `useBuffer="yes,"` then temporary data is stored to speed up nonlocal pseudopotential evaluation at the expense of memory consumption.

loop max Number of times to repeat the optimization. Using the resulting wavefunction from the previous optimization in the next one improves the results. Typical choices range between 8 and 16.

The cost function defines the quantity to be minimized during optimization. The three components of the cost function, energy, unreweighted variance, and reweighted variance should sum to one. Dedicating 100% of the cost function to unreweighted variance is often a good choice. Another common choice is to try 90/10 or 80/20 mixtures of reweighted variance and energy. Using 100% energy minimization is desirable for reducing DMC pseudopotential localization errors, but the optimization process is less stable and should be attempted only after first performing several cycles of, for example, variance minimization (the entire `loop` section can be duplicated with a different cost function each time).

Replace `MAX`, `EVCOST`, `UVCOST`, `RVCOST`, `TS`, and `SAMPLES` in the `loop` with appropriate starting values in the `O.q0.opt.in.xml` input file. Perform the optimization run by typing

```
mpirun -np 4 qmcpack O.q0.opt.in.xml >&O.q0.opt.out&
```

The run should take only a few minutes for reasonable values of loop `max` and `samples`.

The log file output will appear in `O.q0.opt.out`. The beginning of each linear optimization will be marked with text similar to

```
=========================================================
  Start QMCFixedSampleLinearOptimize
  File Root O.q0.opt.s011 append = no
=========================================================
```

At the end of each optimization section the change in cost function, new values for the Jastrow parameters, and elapsed wall clock time are reported:

```
OldCost: 7.0598901869e-01 NewCost: 7.0592576381e-01 Delta Cost:-6.3254886314e-05
...
 <optVariables href="O.q0.opt.s011.opt.xml">
uu_0 6.9392504232e-01 1 1  ON 0
uu_1 4.9690781460e-01 1 1  ON 1
uu_2 4.0934542375e-01 1 1  ON 2
uu_3 3.7875640157e-01 1 1  ON 3
uu_4 3.7308380014e-01 1 1  ON 4
uu_5 3.5419786809e-01 1 1  ON 5
uu_6 4.3139019377e-01 1 1  ON 6
uu_7 1.9344371667e-01 1 1  ON 7
ud_0 3.9219009713e-01 1 1  ON 8
ud_1 1.2352664647e-01 1 1  ON 9
ud_2 4.4048945133e-02 1 1  ON 10
ud_3 2.1415676741e-02 1 1  ON 11
ud_4 1.5201803731e-02 1 1  ON 12
ud_5 2.3708169445e-02 1 1  ON 13
```

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```
ud_6 3.4279064930e-02 1 1  ON 14
ud_7 4.3334583596e-02 1 1  ON 15
eO_0 -7.8490123937e-01 1 1  ON 16
eO_1 -6.6726618338e-01 1 1  ON 17
eO_2 -4.8753453838e-01 1 1  ON 18
eO_3 -3.0913993774e-01 1 1  ON 19
eO_4 -1.7901872177e-01 1 1  ON 20
eO_5 -8.6199000697e-02 1 1  ON 21
eO_6 -4.0601160841e-02 1 1  ON 22
eO_7 -4.1358075061e-03 1 1  ON 23
 </optVariables>
...
 QMC Execution time = 2.8218972974e+01 secs
```

The cost function should decrease during each linear optimization (`Delta cost < 0`). Try "`grep OldCost *opt.out`." You should see something like this:

```
OldCost: 1.2655186572e+00 NewCost: 7.2443875597e-01 Delta Cost:-5.4107990118e-01
OldCost: 7.2229830632e-01 NewCost: 6.9833678217e-01 Delta Cost:-2.3961524143e-02
OldCost: 8.0649629434e-01 NewCost: 8.0551871147e-01 Delta Cost:-9.7758287036e-04
OldCost: 6.6821241388e-01 NewCost: 6.6797703487e-01 Delta Cost:-2.3537901148e-04
OldCost: 7.0106275099e-01 NewCost: 7.0078055426e-01 Delta Cost:-2.8219672877e-04
OldCost: 6.9538522411e-01 NewCost: 6.9419186712e-01 Delta Cost:-1.1933569922e-03
OldCost: 6.7709626744e-01 NewCost: 6.7501251165e-01 Delta Cost:-2.0837557922e-03
OldCost: 6.6659923822e-01 NewCost: 6.6651737755e-01 Delta Cost:-8.1860671682e-05
OldCost: 7.7828995609e-01 NewCost: 7.7735482525e-01 Delta Cost:-9.3513083900e-04
OldCost: 7.2717974404e-01 NewCost: 7.2715201115e-01 Delta Cost:-2.7732880747e-05
OldCost: 6.9400639873e-01 NewCost: 6.9257183689e-01 Delta Cost:-1.4345618444e-03
OldCost: 7.0598901869e-01 NewCost: 7.0592576381e-01 Delta Cost:-6.3254886314e-05
```

Blocked averages of energy data, including the kinetic energy and components of the potential energy, are written to `scalar.dat` files. The first is named "`O.q0.opt.s000.scalar.dat`," with a series number of zero (`s000`). In the end there will be `MAX` of them, one for each series.

When the job has finished, use the `qmca` tool to assess the effectiveness of the optimization process. To look at just the total energy and the variance, type "`qmca -q ev O.q0.opt*scalar*`." This will print the energy, variance, and the variance/energy ratio in Hartree units:

```
                LocalEnergy               Variance           ratio
O.q0.opt  series 0  -15.739585 +/- 0.007656   0.887412 +/- 0.010728   0.0564
O.q0.opt  series 1  -15.848347 +/- 0.004089   0.318490 +/- 0.006404   0.0201
O.q0.opt  series 2  -15.867494 +/- 0.004831   0.292309 +/- 0.007786   0.0184
O.q0.opt  series 3  -15.871508 +/- 0.003025   0.275364 +/- 0.006045   0.0173
O.q0.opt  series 4  -15.865512 +/- 0.002997   0.278056 +/- 0.006523   0.0175
O.q0.opt  series 5  -15.864967 +/- 0.002733   0.278065 +/- 0.004413   0.0175
O.q0.opt  series 6  -15.869644 +/- 0.002949   0.273497 +/- 0.006141   0.0172
O.q0.opt  series 7  -15.868397 +/- 0.003838   0.285451 +/- 0.007570   0.0180
...
```

Plots of the data can also be obtained with the "`-p`" option ("`qmca -p -q ev O.q0.opt*scalar*`").

Identify which optimization series is the "best" according to your cost function. It is likely that multiple series are similar in quality. Note the `opt.xml` file corresponding to this series. This file contains the final value of the optimized Jastrow parameters to be used in the DMC calculations of the next section of the lab.

Questions and Exercises

1. What is the acceptance ratio of your optimization runs? (use "texttqmca -q ar O.q0.opt*scalar*") Do you expect

the MC sampling to be efficient?

2. How do you know when the optimization process has converged?
3. (optional) Optimization is sometimes sensitive to initial guesses of the parameters. If you have time, try varying the initial parameters, including the cutoff radius (`rcut`) of the Jastrow factors (remember to change `id` in the `<project/>` element). Do you arrive at a similar set of final Jastrow parameters? What is the lowest variance you are able to achieve?

19.7 DMC timestep extrapolation I: neutral oxygen atom

The DMC algorithm contains two biases in addition to the fixed node and pseudopotential approximations that are important to control: time step and population control bias. In this section we focus on estimating and removing time step bias from DMC calculations. The essential fact to remember is that the bias vanishes as the time step goes to zero, while the needed computer time increases inversely with the time step.

In the same directory you used to perform wavefunction optimization (`oxygen_atom`) you will find a sample DMC input file for the neutral oxygen atom named `O.q0.dmc.in.xml`. Open this file in a text editor and note the differences from the optimization case. Wavefunction information is no longer included from `pw2qmcpack` but instead should come from the optimization run:

```
<!-- OPT_XML is from optimization, e.g. O.q0.opt.s008.opt.xml -->
<include href="OPT_XML"/>
```

Replace "`OPT_XML`" with the `opt.xml` file corresponding to the best Jastrow parameters you found in the last section (this is a file name similar to `O.q0.opt.s008.opt.xml`).

The QMC calculation section at the bottom is also different. The linear optimization blocks have been replaced with XML describing a VMC run followed by DMC. Descriptions of the input keywords follow.

timestep Time step of the VMC/DMC random walk. In VMC choose a time step corresponding to an acceptance ratio of about 50%. In DMC the acceptance ratio is often above 99%.

warmupSteps Number of MC steps discarded as a warmup or equilibration period of the random walk.

steps Number of MC steps per block. Physical quantities, such as the total energy, are averaged over walkers and steps.

blocks Number of blocks. This is also the number of average energy values written to output files. The number should be greater than 200 for meaningful statistical analysis of output data (e.g., via `qmca`). The total number of MC steps each walker takes is `blocks`×`steps`.

samples VMC only. This is the number of walkers used in subsequent DMC runs. Each DMC walker is initialized with electron positions sampled from the VMC random walk.

nonlocalmoves DMC only. If yes/no, use the locality approximation/T-moves for nonlocal pseudopotentials. T-moves generally improve the stability of the algorithm and restore the variational principle for small systems (T-moves version 1).

The purpose of the VMC run is to provide initial electron positions for each DMC walker. Setting `walkers` $= 1$ in the VMC block ensures there will be only one VMC walker per execution thread. There will be a total of 4 VMC walkers in this case (see `O.q0.dmc.qsub.in`). We want the electron positions used to initialize the DMC walkers to be decorrelated from one another. A VMC walker will often decorrelate from its current position after propagating for a few Ha $^{-1}$ in imaginary time (in general, this is system dependent). This leads to a rough rule of thumb for choosing `blocks` and `steps` for the VMC run (`vwalkers` $= 4$ here):

$$\texttt{VBLOCKS} \times \texttt{VSTEPS} \geq \frac{\texttt{DWALKERS}}{\texttt{VWALKERS}} \frac{5\ \text{Ha}^{-1}}{\texttt{VTIMESTEP}} \tag{19.3}$$

Fill in the VMC XML block with appropriate values for these parameters. There should be more than one DMC walker per thread and enough walkers in total to avoid population control bias. The general rule of thumb is to have more than $\sim 2,000$ walkers, although the dependence of the total energy on population size should be explicitly checked from time to time.

To study time step bias, we will perform a sequence of DMC runs over a range of time steps (0.1 Ha^{-1} is too large, and time steps below 0.002 Ha^{-1} are probably too small). A common approach is to select a fairly large time step to begin with and then decrease the time step by a factor of two in each subsequent DMC run. The total amount of imaginary time the walker population propagates should be the same for each run. A simple way to accomplish this is to choose input parameters in the following way

$$\begin{aligned} \texttt{timestep}_n &= \texttt{timestep}_{n-1}/2 \\ \texttt{warmupSteps}_n &= \texttt{warmupSteps}_{n-1} \times 2 \\ \texttt{blocks}_n &= \texttt{blocks}_{n-1} \\ \texttt{steps}_n &= \texttt{steps}_{n-1} \times 2 \end{aligned}$$

Each DMC run will require about twice as much computer time as the one preceding it. Note that the number of blocks is kept fixed for uniform statistical analysis. `blocks` $\times$ `steps` $\times$ `timestep` ~ 60 Ha^{-1} is sufficient for this system.

Choose an initial DMC time step and create a sequence of N time steps according to (19.4). Make N copies of the DMC XML block in the input file.

```
<qmc method="dmc" move="pbyp">
   <parameter name="warmupSteps"          >    DWARMUP          </parameter>
   <parameter name="blocks"               >    DBLOCKS          </parameter>
   <parameter name="steps"                >    DSTEPS           </parameter>
   <parameter name="timestep"             >    DTIMESTEP        </parameter>
   <parameter name="nonlocalmoves"        >    yes              </parameter>
</qmc>
```

Fill in `DWARMUP`, `DBLOCKS`, `DSTEPS`, and `DTIMESTEP` for each DMC run according to (19.4). Start the DMC time step extrapolation run by typing:

```
mpirun -np 4 qmcpack O.q0.dmc.in.xml >&O.q0.dmc.out&
```

The run should take only a few minutes to complete.

QMCPACK will create files prefixed with `O.q0.dmc`. The log file is `O.q0.dmc.out`. As before, block-averaged data is written to `scalar.dat` files. In addition, DMC runs produce `dmc.dat` files, which contain energy data averaged only over the walker population (one line per DMC step). The `dmc.dat` files also provide a record of the walker population at each step.

Use the `PlotTstepConv.pl` to obtain a linear fit to the time step data (type "`PlotTstepConv.pl O.q0.dmc.in.xml 40`"). You should see a plot similar to Fig. 19.1. The tail end of the text output displays the parameters for the linear fit. The "a" parameter is the total energy extrapolated to zero time step in Hartree units.

```
...
Final set of parameters            Asymptotic Standard Error
=======================            ==========================

a               = -15.8925         +/- 0.0007442    (0.004683%)
b               = -0.0457479       +/- 0.0422       (92.24%)
...
```

Questions and Exercises

1. What is the $\tau \to 0$ extrapolated value for the total energy?

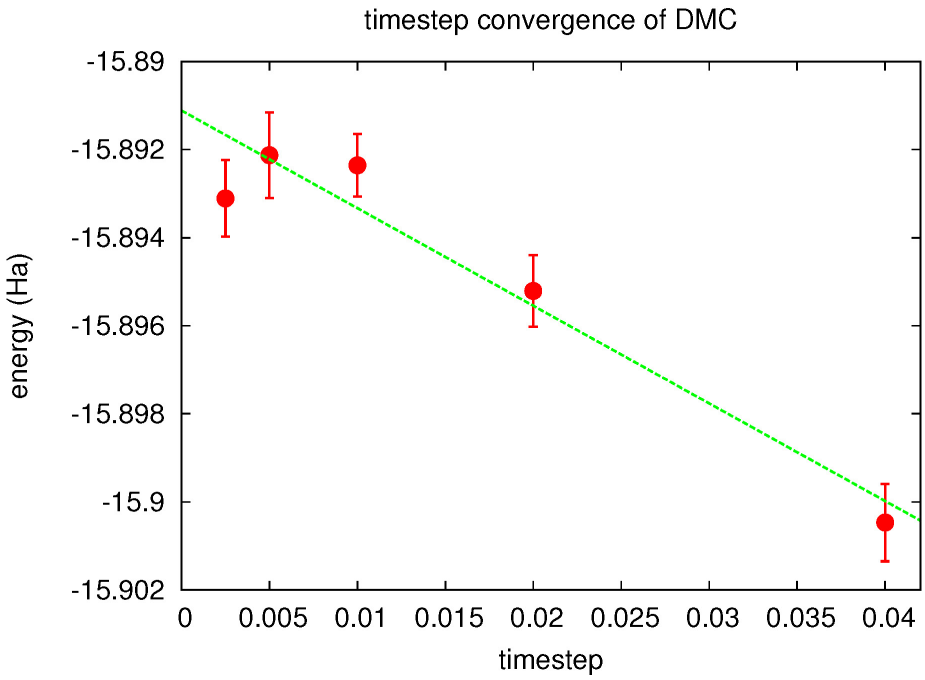

Fig. 19.1: Linear fit to DMC timestep data from `PlotTstepConv.pl`.

2. What is the maximum time step you should use if you want to calculate the total energy to an accuracy of 0.05 eV? For convenience, 1 Ha $= 27.2113846$ eV.
3. What is the acceptance ratio for this (bias < 0.05 eV) run? Does it follow the rule of thumb for sensible DMC (acceptance ratio $> 99\%$) ?
4. Check the fluctuations in the walker population (`qmca -t -q nw O.q0.dmc*dmc.dat -noac`). Does the population seem to be stable?
5. (Optional) Study population control bias for the oxygen atom. Select a few population sizes. Copy `O.q0.dmc.in.xml` to a new file and remove all but one DMC run (select a single time step). Make one copy of the new file for each population, set "textttsamples," and choose a unique `id` in `<project/>`. Use `qmca` to study the dependence of the DMC total energy on the walker population. How large is the bias compared with time step error? What bias is incurred by following the "rule of thumb" of a couple thousand walkers? Will population control bias generally be an issue for production runs on modern parallel machines?

19.8 DMC time step extrapolation II: oxygen atom ionization potential

In this section, we will repeat the calculations of the previous two sections (optimization, time step extrapolation) for the $+1$ charge state of the oxygen atom. Comparing the resulting first ionization potential (IP) with experimental data will complete our first test of the BFD oxygen pseudopotential. In actual practice, higher IPs could also be tested before performing production runs.

Obtaining the time step extrapolated DMC total energy for ionized oxygen should take much less (human) time than for the neutral case. For convenience, the necessary steps are summarized as follows.

1. Obtain DFT orbitals with QE.
   (a) Copy the DFT input (`O.q0.dft.in`) to `O.q1.dft.in`

(b) Edit `O.q1.dft.in` to match the +1 charge state of the oxygen atom.

```
...
prefix            = 'O.q1'
...
tot_charge        = 1
tot_magnetization = 3
...
```

(c) Perform the DFT run: `mpirun -np 4 pw.x -input O.q1.dft.in >&O.q1.dft.out&`

2. Convert the orbitals to ESHDF format.

(a) Copy the pw2qmcpack input (`O.q0.p2q.in`) to `O.q1.p2q.in`

(b) Edit `O.q1.p2q.in` to match the file prefix used in DFT.

```
...
prefix = 'O.q1'
...
```

(c) Perform the orbital conversion run: `mpirun -np 1 pw2qmcpack.x<O.q1.p2q.in>&O.q1.p2q.out&`

3. Optimize the Jastrow factor with QMCPACK.

(a) Copy the optimization input (`O.q0.opt.in.xml`) to `O.q1.opt.in.xml`

(b) Edit `O.q1.opt.in.xml` to match the file prefix used in DFT.

```
...
<project id="O.q1.opt" series="0">
...
<include href="O.q1.ptcl.xml"/>
...
<include href="O.q1.wfs.xml"/>
...
```

(c) Edit the particle XML file (`O.q1.ptcl.xml`) to have open boundary conditions.

```
<parameter name="bconds">
  n n n
</parameter>
```

(d) Add cutoffs to the Jastrow factors in the wavefunction XML file (`O.q1.wfs.xml`)

```
...
<correlation speciesA="u" speciesB="u" size="8" rcut="10.0">
...
<correlation speciesA="u" speciesB="d" size="8" rcut="10.0">
...
<correlation elementType="O" size="8" rcut="5.0">
...
```

(e) Perform the Jastrow optimization run: `mpirun -np 4 qmcpack O.q1.opt.in.xml >&O.q1.opt.out&`

(f) Identify the optimal set of parameters with `qmca ([your opt.xml])`.

4. DMC time step study with QMCPACK

(a) Copy the DMC input (`O.q0.dmc.in.xml`) to `O.q1.dmc.in.xml`

(b) Edit `O.q1.dmc.in.xml` to use the DFT prefix and the optimal Jastrow.

```
...
<project id="O.q1.dmc" series="0">
...
<include href="O.q1.ptcl.xml"/>
...
<include href="[your opt.xml]"/>
...
```

(c) Perform the DMC run: `mpirun -np 4 qmcpack O.q1.dmc.in.xml >&O.q1.dmc.out&`

(d) Obtain the DMC total energy extrapolated to zero time step with `PlotTstepConv.pl`.

The aforementioned process, which excludes additional steps for orbital generation and conversion, can become tedious to perform by hand in production settings where many calculations are often required. For this reason, automation tools are introduced for calculations involving the oxygen dimer in *Automated binding curve of the oxygen dimer* of the lab.

Questions and Exercises

1. What is the $\tau \to 0$ extrapolated DMC value for the first ionization potential of oxygen?
2. How does the extrapolated value compare with the experimental IP? Go to http://physics.nist.gov/PhysRefData/ASD/ionEnergy.html and enter "`O I`" in the box labeled "`Spectra`" and click on the "`Retrieve Data`" button.
3. What can we conclude about the accuracy of the pseudopotential? What factors complicate this assessment?
4. Explore the sensitivity of the IP to the choice of time step. Type `./ip_conv.py` to view three time step extrapolation plots: two for the $q = 0$, one for total energies, and one for the IP. Is the IP more, less, or similarly sensitive to time step than the total energy?
5. What is the maximum time step you should use if you want to calculate the ionization potential to an accuracy of 0.05 eV? What factor of CPU time is saved by assessing time step convergence on the IP (a total energy difference) vs. a single total energy?
6. Are the acceptance ratio and population fluctuations reasonable for the $q = 1$ calculations?

19.9 DMC workflow automation with Nexus

Production QMC projects are often composed of many similar workflows. The simplest of these is a single DMC calculation involving four different compute jobs:

1. Orbital generation via QE or GAMESS.
2. Conversion of orbital data via `pw2qmcpack.x` or `convert4qmc`.
3. Optimization of Jastrow factors via QMCPACK.
4. DMC calculation via QMCPACK.

Simulation workflows quickly become more complex with increasing costs in terms of human time for the researcher. Automation tools can decrease both human time and error if used well.

The set of automation tools we will be using is known as Nexus [[Kro16]], which is distributed with QMCPACK. Nexus is capable of generating input files, submitting and monitoring compute jobs, passing data between simulations (relaxed structures, orbital files, optimized Jastrow parameters, etc.), and data analysis. The user interface to Nexus

is through a set of functions defined in the Python programming language. User scripts that execute simple workflows resemble input files and do not require programming experience. More complex workflows require only basic programming constructs (e.g. for loops and if statements). Nexus input files/scripts should be easier to navigate than QMCPACK input files and more efficient than submitting all the jobs by hand.

Nexus is driven by simple user-defined scripts that resemble keyword-driven input files. An example Nexus input file that performs a single VMC calculation (with pregenerated orbitals) follows. Take a moment to read it over and especially note the comments (prefixed with "\#") explaining most of the contents. If the input syntax is unclear you may want to consult portions of *Appendix A: Basic Python constructs*, which gives a condensed summary of Python constructs. An additional example and details about the inner workings of Nexus can be found in the reference publication [[Kro16]].

```
#! /usr/bin/env python3

# import Nexus functions
from nexus import settings,job,get_machine,run_project
from nexus import generate_physical_system
from nexus import generate_qmcpack,vmc

settings(                               # Nexus settings
    pseudo_dir    = './pseudopotentials', # location of PP files
    runs          = '',                   # root directory for simulations
    results       = '',                   # root directory for simulation results
    status_only   = 0,                    # show simulation status, then exit
    generate_only = 0,                    # generate input files, then exit
    sleep         = 3,                    # seconds between checks on sim. progress
    machine       = 'ws4',                # workstation with 4 cores
    )

qmcjob = job(                           # specify job parameters
    cores   = 4,                          # use 4 MPI tasks
    threads = 1,                          # 1 OpenMP thread per node
    app     = 'qmcpack'                   # use QMCPACK executable (assumed in PATH)
    )

qmc_calcs = [                           # list QMC calculation methods
    vmc(                                  #   VMC
        walkers     =   1,                #     1 walker
        warmupsteps =  50,                #    50 MC steps for warmup
        blocks      = 200,                #   200 blocks
        steps       =  10,                #    10 steps per block
        timestep    =  .4                 #   0.4 1/Ha timestep
        )]

dimer = generate_physical_system(     # make a dimer system
    type       = 'dimer',                 # system type is dimer
    dimer      = ('O','O'),               # dimer is two oxygen atoms
    separation = 1.2074,                  # separated by 1.2074 Angstrom
    Lbox       = 15.0,                    # simulation box is 15 Angstrom
    units      = 'A',                     # Angstrom is dist. unit
    net_spin   = 2,                       # nup-ndown is 2
    O          = 6                        # pseudo-oxygen has 6 valence el.
    )

qmc = generate_qmcpack(                 # make a qmcpack simulation
    identifier   = 'example',             # prefix files with 'example'
    path         = 'scale_1.0',           # run in ./scale_1.0 directory
    system       = dimer,                 # run the dimer system
```

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```
    job          = qmcjob,                # set job parameters
    input_type   = 'basic',               # basic qmcpack inputs given below
    pseudos      = ['O.BFD.xml'],         # list of PP's to use
    orbitals_h5  = 'O2.pwscf.h5',         # file with orbitals from DFT
    bconds       = 'nnn',                 # open boundary conditions
    jastrows     = [],                    # no jastrow factors
    calculations = qmc_calcs              # QMC calculations to perform
    )

run_project(qmc)                        # write input file and submit job
```

19.10 Automated binding curve of the oxygen dimer

In this section we will use Nexus to calculate the DMC total energy of the oxygen dimer over a series of bond lengths. The equilibrium bond length and binding energy of the dimer will be determined by performing a polynomial fit to the data (Morse potential fits should be preferred in production tests). Comparing these values with corresponding experimental data provides a second test of the BFD pseudopotential for oxygen.

Enter the `oxygen_dimer` directory. Copy your BFD pseudopotential from the atom runs into `oxygen_dimer/pseudopotentials` (be sure to move both files: `.upf` and `.xml`). Open `O_dimer.py` with a text editor. The overall format is similar to the example file shown in the last section. The main difference is that a full workflow of runs (DFT orbital generation, orbital conversion, optimization and DMC) are being performed rather than a single VMC run.

As in the example in the last section, the oxygen dimer is generated with the `generate_physical_ system` function:

```
dimer = generate_physical_system(
    type       = 'dimer',
    dimer      = ('O','O'),
    separation = 1.2074*scale,
    Lbox       = 10.0,
    units      = 'A',
    net_spin   = 2,
    O          = 6
    )
```

Similar syntax can be used to generate crystal structures or to specify systems with arbitrary atomic configurations and simulation cells. Notice that a "`scale`" variable has been introduced to stretch or compress the dimer.

Next, objects representing a QE (PWSCF) run and subsequent orbital conversion step are constructed with respective `generate_*` functions:

```
dft = generate_pwscf(
    identifier   = 'dft',
    ...
    input_dft    = 'lda',
    ...
    )
sims.append(dft)

# describe orbital conversion run
p2q = generate_pw2qmcpack(
    identifier   = 'p2q',
```

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```
    ...
    dependencies = (dft,'orbitals'),
    )
sims.append(p2q)
```

Note the `dependencies` keyword. This keyword is used to construct workflows out of otherwise separate runs. In this case, the dependency indicates that the orbital conversion run must wait for the DFT to finish before starting.

Objects representing QMCPACK simulations are then constructed with the `generate_qmcpack` function:

```
opt = generate_qmcpack(
    identifier   = 'opt',
    ...
    jastrows     = [('J1','bspline',8,5.0),
                    ('J2','bspline',8,10.0)],
    calculations = [
        loop(max=12,
             qmc=linear(
                energy               = 0.0,
                unreweightedvariance = 1.0,
                reweightedvariance   = 0.0,
                timestep             = 0.3,
                samples              = 61440,
                warmupsteps          = 50,
                blocks               = 200,
                substeps             = 1,
                nonlocalpp           = True,
                usebuffer            = True,
                walkers              = 1,
                minwalkers           = 0.5,
                maxweight            = 1e9,
                usedrift             = False,
                minmethod            = 'quartic',
                beta                 = 0.025,
                exp0                 = -16,
                bigchange            = 15.0,
                alloweddifference    = 1e-4,
                stepsize             = 0.2,
                stabilizerscale      = 1.0,
                nstabilizers         = 3,
                )
             )
        ],
    dependencies = (p2q,'orbitals'),
    )
sims.append(opt)

qmc = generate_qmcpack(
    identifier   = 'qmc',
    ...
    jastrows     = [],
    calculations = [
        vmc(
            walkers     =   1,
            warmupsteps =  30,
            blocks      =  20,
            steps       =  10,
```

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```
            substeps     =   2,
            timestep     =  .4,
            samples      = 2048
            ),
        dmc(
            warmupsteps   = 100,
            blocks        = 400,
            steps         =  32,
            timestep      = 0.01,
            nonlocalmoves = True,
            )
        ],
    dependencies = [(p2q,'orbitals'),(opt,'jastrow')],
    )
sims.append(qmc)
```

Shared details such as the run directory, job, pseudopotentials, and orbital file have been omitted (`...`). The "`opt`" run will optimize a 1-body B-spline Jastrow with 8 knots having a cutoff of 5.0 Bohr and a B-spline Jastrow (for up-up and up-down correlations) with 8 knots and cutoffs of 10.0 Bohr. The Jastrow list for the DMC run is empty, and the previous use of `dependencies` indicates that the DMC run depends on the optimization run for the Jastrow factor. Nexus will submit the "`opt`" run first, and upon completion it will scan the output, select the optimal set of parameters, pass the Jastrow information to the "`qmc`" run, and then submit the DMC job. Independent job workflows are submitted in parallel when permitted. No input files are written or job submissions made until the "`run_project`" function is reached:

```
run_project(sims)
```

All of the simulation objects have been collected into a list (`sims`) for submission.

As written, `O_dimer.py` will perform calculations only at the equilibrium separation distance of 1.2074 {AA} since the list of scaling factors (representing stretching or compressing the dimer) contains only one value (`scales = [1.00]`). Modify the file now to perform DMC calculations across a range of separation distances with each DMC run using the Jastrow factor optimized at the equilibrium separation distance. Specifically, you will want to change the list of scaling factors to include both compression (`scale<1.0`) and stretch (`scale>1.0`):

```
scales = [1.00,0.90,0.95,1.05,1.10]
```

Note that "`1.00`" is left in front because we are going to optimize the Jastrow factor first at the equilibrium separation and reuse this Jastrow factor for all other separation distances. This procedure is used because it can reduce variations in localization errors (due to pseudopotentials in DMC) along the binding curve.

Change the `status_only` parameter in the "`settings`" function to `1` and type "`./O_dimer.py`" at the command line. This will print the status of all simulations:

```
Project starting
  checking for file collisions
  loading cascade images
    cascade 0 checking in
    cascade 10 checking in
    cascade 4 checking in
    cascade 13 checking in
    cascade 7 checking in
  checking cascade dependencies
    all simulation dependencies satisfied

  cascade status
```

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```
    setup, sent_files, submitted, finished, got_output, analyzed
    000000  dft      ./scale_1.0
    000000  p2q      ./scale_1.0
    000000  opt      ./scale_1.0
    000000  qmc      ./scale_1.0
    000000  dft      ./scale_0.9
    000000  p2q      ./scale_0.9
    000000  qmc      ./scale_0.9
    000000  dft      ./scale_0.95
    000000  p2q      ./scale_0.95
    000000  qmc      ./scale_0.95
    000000  dft      ./scale_1.05
    000000  p2q      ./scale_1.05
    000000  qmc      ./scale_1.05
    000000  dft      ./scale_1.1
    000000  p2q      ./scale_1.1
    000000  qmc      ./scale_1.1
    setup, sent_files, submitted, finished, got_output, analyzed
```

In this case, five simulation "cascades" (workflows) have been identified, each one starting and ending with "`dft`" and "`qmc`" runs, respectively. The six status flags `setup`, `sent_files`, `submitted`, `finished`, `got_output`, `analyzed`) each shows `0`, indicating that no work has been done yet.

Now change "`status_only`" back to `0`, set "`generate_only`" to `1`, and run `O_dimer.py` again. This will perform a dry run of all simulations. The dry run should finish in about 20 seconds:

```
Project starting
  checking for file collisions
  loading cascade images
    cascade 0 checking in
    cascade 10 checking in
    cascade 4 checking in
    cascade 13 checking in
    cascade 7 checking in
  checking cascade dependencies
    all simulation dependencies satisfied

  starting runs:
  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~
  poll 0  memory 91.03 MB
    Entering ./scale_1.0 0
      writing input files  0 dft
    Entering ./scale_1.0 0
      sending required files  0 dft
      submitting job  0 dft
  ...
  poll 1  memory 91.10 MB
  ...
    Entering ./scale_1.0 0
      Would have executed:
        export OMP_NUM_THREADS=1
        mpirun -np 4 pw.x -input dft.in

  poll 2  memory 91.10 MB
    Entering ./scale_1.0 0
      copying results  0 dft
    Entering ./scale_1.0 0
```

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```
    analyzing  0 dft
  ...
  poll 3  memory 91.10 MB
    Entering ./scale_1.0 1
      writing input files  1 p2q
    Entering ./scale_1.0 1
      sending required files  1 p2q
      submitting job  1 p2q
  ...
    Entering ./scale_1.0 1
      Would have executed:
        export OMP_NUM_THREADS=1
        mpirun -np 1 pw2qmcpack.x<p2q.in

  poll 4  memory 91.10 MB
    Entering ./scale_1.0 1
      copying results  1 p2q
    Entering ./scale_1.0 1
      analyzing  1 p2q
  ...
  poll 5  memory 91.10 MB
    Entering ./scale_1.0 2
      writing input files  2 opt
    Entering ./scale_1.0 2
      sending required files  2 opt
      submitting job  2 opt
  ...
    Entering ./scale_1.0 2
      Would have executed:
        export OMP_NUM_THREADS=1
        mpirun -np 4 qmcpack opt.in.xml

  poll 6  memory 91.16 MB
    Entering ./scale_1.0 2
      copying results  2 opt
    Entering ./scale_1.0 2
      analyzing  2 opt
  ...
  poll 7  memory 93.00 MB
    Entering ./scale_1.0 3
      writing input files  3 qmc
    Entering ./scale_1.0 3
      sending required files  3 qmc
      submitting job  3 qmc
  ...
    Entering ./scale_1.0 3
      Would have executed:
        export OMP_NUM_THREADS=1
        mpirun -np 4 qmcpack qmc.in.xml
  ...
  poll 17  memory 93.06 MB
Project finished
```

Nexus polls the simulation status every 3 seconds and sleeps in between. The "`scale_`" directories should now contain several files:

```
scale_1.0
   dft.in
   O.BFD.upf
   O.BFD.xml
   opt.in.xml
   p2q.in
   pwscf_output
   qmc.in.xml
   sim_dft/
       analyzer.p
       input.p
       sim.p
   sim_opt/
       analyzer.p
       input.p
       sim.p
   sim_p2q/
       analyzer.p
       input.p
       sim.p
   sim_qmc/
       analyzer.p
       input.p
       sim.p
```

Take a minute to inspect the generated input (`dft.in`, `p2q.in`, `opt.in.xml`, `qmc.in.xml`). The pseudopotential files (`O.BFD.upf` and `O.BFD.xml`) have been copied into each local directory. Four additional directories have been created: `sim_dft`, `sim_p2q`, `sim_opt` and `sim_qmc`. The `sim.p` files in each directory contain the current status of each simulation. If you run `O_dimer.py` again, it should not attempt to rerun any of the simulations:

```
Project starting
  checking for file collisions
  loading cascade images
    cascade 0 checking in
    cascade 10 checking in
    cascade 4 checking in
    cascade 13 checking in
    cascade 7 checking in
  checking cascade dependencies
    all simulation dependencies satisfied

  starting runs:
  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
  poll 0  memory 64.25 MB
Project finished
```

This way you can continue to add to the `O_dimer.py` file (e.g., adding more separation distances) without worrying about duplicate job submissions.

Now submit the jobs in the dimer workflow. Reset the state of the simulations by removing the `sim.p` files ("`rm ./scale*/sim*/sim.p`"), set "`generate_only`" to `0`, and rerun `O_dimer.py`. It should take about 20 minutes for all the jobs to complete. You may wish to open another terminal to monitor the progress of the individual jobs while the current terminal runs `O_dimer.py` in the foreground. You can begin the following first exercise once the optimization job completes.

Questions and Exercises

1. Evaluate the quality of the optimization at `scale=1.0` using the `qmca` tool. Did the optimization succeed?

How does the variance compare with the neutral oxygen atom? Is the wavefunction of similar quality to the atomic case?

2. Evaluate the traces of the local energy and the DMC walker population for each separation distance with the `qmca` tool. Are there any anomalies in the runs? Is the acceptance ratio reasonable? Is the wavefunction of similar quality across all separation distances?

3. Use the `dimer_fit.py` tool located in `oxygen_dimer` to fit the oxygen dimer binding curve. To get the binding energy of the dimer, we will need the DMC energy of the atom. Before performing the fit, answer: What DMC time step should be used for the oxygen atom results? The tool accepts three arguments (`./dimer_fit.py P N E Eerr`), `P` is the prefix of the DMC input files (should be "`qmc`" at this point), `N` is the order of the fit (use 2 to start),``E`` and `Eerr` are your DMC total energy and error bar, respectively, for the oxygen atom (in electron volts). A plot of the dimer data will be displayed, and text output will show the DMC equilibrium bond length and binding energy as well as experimental values. How accurately does your fit to the DMC data reproduce the experimental values? What factors affect the accuracy of your results?

4. Refit your data with a fourth-order polynomial. How do your predictions change with a fourth-order fit? Is a fourth-order fit appropriate for the available data?

5. Add new "`scale`" values to the list in `O_dimer.py` that interpolate between the original set (e.g., expand to). Perform the DMC calculations and redo the fits. How accurately does your fit to the DMC data reproduce the experimental values? Should this pseudopotential be used in production calculations?

6. (Optional) Perform optimization runs at the extreme separation distances corresponding to `scale=[0.90,1.10]`. Are the individually optimized wavefunctions of significantly better quality than the one imported from `scale=1.00`? Why? What form of Jastrow factor might give an even better improvement?

19.11 (Optional) Running your system with QMCPACK

This section covers a fairly simple route to get started on QMC calculations of an arbitrary system of interest using the Nexus workflow management system to set up input files and optionally perform the runs. The example provided in this section uses QE (PWSCF) to generate the orbitals forming the Slater determinant part of the trial wavefunction. PWSCF is a natural choice for solid-state systems, and it can be used for surface/slab and molecular systems as well, albeit at the price of describing additional vacuum space with plane waves.

To start out, you will need PPs for each element in your system in both the UPF (PWSCF) and FSATOM/XML (QMCPACK) formats. A good place to start is the BFD pseudopotential database (http://www.burkatzki.com/pseudos/index.2.html), which we have already used in our study of the oxygen atom. The database does not contain PPs for the fourth and fifth row transition metals or any of the lanthanides or actinides. If you need a PP that is not in the BFD database, you may need to generate and test one manually (e.g., with OPIUM, http://opium.sourceforge.net/). Otherwise, use `ppconvert` as outlined in *Obtaining and converting a pseudopotential for oxygen* to obtain PPs in the formats used by PWSCF and QMCPACK. Enter the `your_system` lab directory and place the converted PPs in `your_system/pseudopotentials`.

Before performing production calculations (more than just the initial setup in this section), be sure to converge the plane-wave energy cutoff in PWSCF as these PPs can be rather hard, sometimes requiring cutoffs in excess of 300 Ry. Depending on the system under study, the amount of memory required to represent the orbitals (QMCPACK uses 3D B-splines) can become prohibitive, forcing you to search for softer PPs.

Beyond PPs, all that is required to get started are the atomic positions and the dimensions/shape of the simulation cell. The Nexus file `example.py` illustrates how to set up PWSCF and QMCPACK input files by providing minimal information regarding the physical system (an 8-atom cubic cell of diamond in the example). Most of the contents should be familiar from your experience with the automated calculations of the oxygen dimer binding curve in *Automated binding curve of the oxygen dimer* (if you have skipped ahead you may want to skim that section for relevant information). The most important change is the expanded description of the physical system:

```
# details of your physical system (diamond conventional cell below)
my_project_name = 'diamond_vmc'    # directory to perform runs
my_dft_pps      = ['C.BFD.upf']    # pwscf pseudopotentials
my_qmc_pps      = ['C.BFD.xml']    # qmcpack pseudopotentials

#  generate your system
#    units      :  'A'/'B' for Angstrom/Bohr
#    axes       :  simulation cell axes in cartesian coordinates (a1,a2,a3)
#    elem       :  list of atoms in the system
#    pos        :  corresponding atomic positions in cartesian coordinates
#    kgrid      :  Monkhorst-Pack grid
#    kshift     :  Monkhorst-Pack shift (between 0 and 0.5)
#    net_charge :  system charge in units of e
#    net_spin   :  # of up spins - # of down spins
#    C = 4      :  (pseudo) carbon has 4 valence electrons
my_system = generate_physical_system(
    units      = 'A',
    axes       = [[ 3.57000000e+00, 0.00000000e+00, 0.00000000e+00],
                  [ 0.00000000e+00, 3.57000000e+00, 0.00000000e+00],
                  [ 0.00000000e+00, 0.00000000e+00, 3.57000000e+00]],
    elem       = ['C','C','C','C','C','C','C','C'],
    pos        = [[ 0.00000000e+00, 0.00000000e+00, 0.00000000e+00],
                  [ 8.92500000e-01, 8.92500000e-01, 8.92500000e-01],
                  [ 0.00000000e+00, 1.78500000e+00, 1.78500000e+00],
                  [ 8.92500000e-01, 2.67750000e+00, 2.67750000e+00],
                  [ 1.78500000e+00, 0.00000000e+00, 1.78500000e+00],
                  [ 2.67750000e+00, 8.92500000e-01, 2.67750000e+00],
                  [ 1.78500000e+00, 1.78500000e+00, 0.00000000e+00],
                  [ 2.67750000e+00, 2.67750000e+00, 8.92500000e-01]],
    kgrid      = (1,1,1),
    kshift     = (0,0,0),
    net_charge = 0,
    net_spin   = 0,
    C          = 4       # one line like this for each atomic species
    )

my_bconds       = 'ppp'  #  ppp/nnn for periodic/open BC's in QMC
                         #  if nnn, center atoms about (a1+a2+a3)/2
```

If you have a system you would like to try with QMC, make a copy of `example.py` and fill in the relevant information about the PPs, simulation cell axes, and atomic species/positions. Otherwise, you can proceed with `example.py` as it is.

Set "`generate_only`" to `1` and type "`./example.py`" or similar to generate the input files. All files will be written to "`./diamond_vmc`" ("`./[my_project_name]`" if you have changed "`my_project_name`" in the file). The input files for PWSCF, pw2qmcpack, and QMCPACK are `scf.in`, `pw2qmcpack.in`, and `vmc.in.xml`, respectively. Take some time to inspect the generated input files. If you have questions about the file contents, or run into issues with the generation process, feel free to consult with a lab instructor.

If desired, you can submit the runs directly with `example.py`. To do this, first reset the Nexus simulation record by typing "`rm ./diamond_vmc/sim*/sim.p`" or similar and set "`generate_only`" back to `0`. Next rerun `example.py` (you may want to redirect the text output).

Alternatively the runs can be submitted by hand:

```
mpirun -np 4 pw.x<scf.in>&scf.out&

(wait until JOB DONE appears in scf.out)
```

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```
mpirun -np 1 pw2qmcpack.x<p2q.in>&p2q.out&
```

Once the conversion process has finished, the orbitals should be located in the file `diamond_vmc/pwscf_output/pwscf.pwscf.h5`. Open `diamond_vmc/vmc.in.xml` and replace "`MISSING.h5`" with "`./pwscf_output/pwscf.pwscf.h5`". Next submit the VMC run:

```
mpirun -np 4 qmcpack vmc.in.xml>&vmc.out&
```

Note: If your system is large, the preceding process may not complete within the time frame of this lab. Working with a stripped down (but relevant) example is a good idea for exploratory runs.

Once the runs have finished, you may want to begin exploring Jastrow optimization and DMC for your system. Example calculations are provided at the end of `example.py` in the commented out text.

19.12 Appendix A: Basic Python constructs

Basic Python data types (`int`, `float`, `str`, `tuple`, `list`, `array`, `dict`, `obj`) and programming constructs (`if` statements, `for` loops, functions w/ keyword arguments) are briefly overviewed in the following. All examples can be executed interactively in Python. To do this, type "`python`" at the command line and paste any of the shaded text below at the >>> prompt. For more information about effective use of Python, consult the detailed online documentation: https://docs.python.org/2/.

19.12.1 Intrinsic types: `int, float, str`

```
#this is a comment
i=5                     # integer
f=3.6                   # float
s='quantum/monte/carlo' # string
n=None                  # represents "nothing"

f+=1.4                  # add-assign (-,*,/ also): 5.0
2**3                    # raise to a power: 8
str(i)                  # int to string: '5'
s+'/simulations'        # joining strings: 'quantum/monte/carlo/simulations'
'i={0}'.format(i)       # format string: 'i=5'
```

19.12.2 Container types: `tuple, list, array, dict, obj`

```
from numpy import array  # get array from numpy module
from generic import obj  # get obj from Nexus' generic module

t=('A',42,56,123.0)      # tuple

l=['B',3.14,196]         # list

a=array([1,2,3])         # array

d={'a':5,'b':6}          # dict
```

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```
o=obj(a=5,b=6)           # obj

                         # printing
print(t)                 #  ('A', 42, 56, 123.0)
print(l)                 #  ['B', 3.1400000000000001, 196]
print(a)                 #  [1 2 3]
print(d)                 #  {'a': 5, 'b': 6}
print(o)                 #    a               = 5
                         #    b               = 6

len(t),len(l),len(a),len(d),len(o) #number of elements: (4, 3, 3, 2, 2)

t[0],l[0],a[0],d['a'],o.a  #element access: ('A', 'B', 1, 5, 5)

s = array([0,1,2,3,4])   # slices: works for tuple, list, array
s[:]                     #   array([0, 1, 2, 3, 4])
s[2:]                    #   array([2, 3, 4])
s[:2]                    #   array([0, 1])
s[1:4]                   #   array([1, 2, 3])
s[0:5:2]                 #   array([0, 2, 4])

                         # list operations
l2 = list(l)             #   make independent copy
l.append(4)              #   add new element: ['B', 3.14, 196, 4]
l+[5,6,7]                #   addition: ['B', 3.14, 196, 4, 5, 6, 7]
3*[0,1]                  #   multiplication:  [0, 1, 0, 1, 0, 1]

b=array([5,6,7])         # array operations
a2 = a.copy()            #   make independent copy
a+b                      #   addition: array([ 6, 8, 10])
a+3                      #   addition: array([ 4, 5, 6])
a*b                      #   multiplication: array([ 5, 12, 21])
3*a                      #   multiplication: array([3, 6, 9])

                         # dict/obj operations
d2 = d.copy()            #   make independent copy
d['c'] = 7               #   add/assign element
d.keys()                 #   get element names: ['a', 'c', 'b']
d.values()               #   get element values: [5, 7, 6]

                         # obj-specific operations
o.c = 7                  #   add/assign element
o.set(c=7,d=8)           #   add/assign multiple elements
```

An important feature of Python to be aware of is that assignment is most often by reference, that is, new values are not always created. This point is illustrated with an `obj` instance in the following example, but it also holds for `list`, `array`, `dict`, and others.

```
>>> o = obj(a=5,b=6)
>>>
>>> p=o
>>>
>>> p.a=7
>>>
>>> print(o)
  a               = 7
```

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```
  b                = 6

>>> q=o.copy()
>>>
>>> q.a=9
>>>
>>> print(o)
  a                = 7
  b                = 6
```

Here `p` is just another name for `o`, while `q` is a fully independent copy of it.

19.12.3 Conditional Statements: `if/elif/else`

```
a = 5
if a is None:
    print('a is None')
elif a==4:
    print('a is 4')
elif a<=6 and a>2:
    print('a is in the range (2,6]')
elif a<-1 or a>26:
    print('a is not in the range [-1,26]')
elif a!=10:
    print('a is not 10')
else:
    print('a is 10')
#end if
```

The "`\#end if`" is not part of Python syntax, but you will see text like this throughout Nexus for clear encapsulation.

19.12.4 Iteration: `for`

```
from generic import obj

l = [1,2,3]
m = [4,5,6]
s = 0
for i in range(len(l)):  # loop over list indices
    s += l[i] + m[i]
#end for

print(s)                 # s is 21

s = 0
for v in l:              # loop over list elements
    s += v
#end for

print(s)                 # s is 6

o = obj(a=5,b=6)
s = 0
```

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```
for v in o:                 # loop over obj elements
    s += v
#end for

print(s)                    # s is 11

d = {'a':5,'b':4}
for n,v in o.items():# loop over name/value pairs in obj
    d[n] += v
#end for

print(d)                    # d is {'a': 10, 'b': 10}
```

19.12.5 Functions: `def`, argument syntax

```
def f(a,b,c=5):             # basic function, c has a default value
    print(a,b,c)
#end def f

f(1,b=2)                    # prints: 1 2 5


def f(*args,**kwargs):      # general function, returns nothing
    print(args)             #     args: tuple of positional arguments
    print(kwargs)           #   kwargs: dict of keyword arguments
#end def f

f('s',(1,2),a=3,b='t')      # 2 pos., 2 kw. args, prints:
                            #   ('s', (1, 2))
                            #   {'a': 3, 'b': 't'}

l = [0,1,2]
f(*l,a=6)                   # pos. args from list, 1 kw. arg, prints:
                            #   (0, 1, 2)
                            #   {'a': 6}
o = obj(a=5,b=6)
f(*l,**o)                   # pos./kw. args from list/obj, prints:
                            #   (0, 1, 2)
                            #   {'a': 5, 'b': 6}

f(                          # indented kw. args, prints
    blocks   = 200,         #   ()
    steps    = 10,          #   {'steps': 10, 'blocks': 200, 'timestep': 0.01}
    timestep = 0.01
    )

o = obj(                    # obj w/ indented kw. args
    blocks   = 100,
    steps    =  5,
    timestep = 0.02
    )

f(**o)                      # kw. args from obj, prints:
                            #   ()
                            #   {'timestep': 0.02, 'blocks': 100, 'steps': 5}
```

CHAPTER

TWENTY

LAB 3: ADVANCED MOLECULAR CALCULATIONS

20.1 Topics covered in this lab

This lab covers molecular QMC calculations with wavefunctions of increasing sophistication. All of the trial wavefunctions are initially generated with the GAMESS code. Topics covered include:

- Generating single-determinant trial wavefunctions with GAMESS (HF and DFT)
- Generating multideterminant trial wavefunctions with GAMESS (CISD, CASCI, and SOCI)
- Optimizing wavefunctions (Jastrow factors and CSF coefficients) with QMC
- DMC time step and walker population convergence studies
- Systematic progressions of Jastrow factors in VMC
- Systematic convergence of DMC energies with multideterminant wavefunctions
- Influence of orbitals basis choice on DMC energy

20.2 Lab directories and files

```
abs/lab3_advanced_molecules/exercises
│
├── ex1_first-run-hartree-fock    - basic work flow from Hatree-Fock to DMC
│   ├── gms                        - Hatree-Fock calculation using GAMESS
│   │   ├── h2o.hf.inp               - GAMESS input
│   │   ├── h2o.hf.dat               - GAMESS punch file containing orbitals
│   │   └── h2o.hf.out               - GAMESS output with orbitals and other info
│   ├── convert                    - Convert GAMESS wavefunction to QMCPACK format
│   │   ├── h2o.hf.out               - GAMESS output
│   │   ├── h2o.ptcl.xml             - converted particle positions
│   │   └── h2o.wfs.xml              - converted wave function
│   ├── opt                        - VMC optimization
│   │   └── optm.xml                 - QMCPACK VMC optimization input
│   ├── dmc_timestep               - Check DMC timestep bias
│   │   └── dmc_ts.xml               - QMCPACK DMC input
│   └── dmc_walkers                - Check DMC population control bias
│       └── dmc_wk.xml               - QMCPACK DMC input template
│
├── ex2_slater-jastrow-wf-options - explore jastrow and orbital options
│   ├── jastrow                    - Jastrow options
│   │   ├── 12j                      - no 3-body Jastrow
│   │   ├── 1j                       - only 1-body Jastrow
```

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```
│   │   └── 2j                        - only 2-body Jastrow
│   └── orbitals                     - Orbital options
│       ├── pbe                       - PBE orbitals
│       │   └── gms                     - DFT calculation using GAMESS
│       │       └── h2o.pbe.inp          - GAMESS DFT input
│       ├── pbe0                      - PBE0  orbitals
│       ├── blyp                      - BLYP  orbitals
│       └── b3lyp                     - B3LYP orbitals
│
├── ex3_multi-slater-jastrow
│   ├── cisd                        - CISD wave function
│   │   ├── gms                       - CISD calculation using GAMESS
│   │   │   ├── h2o.cisd.inp             - GAMESS input
│   │   │   ├── h2o.cisd.dat             - GAMESS punch file containing orbitals
│   │   │   └── h2o.cisd.out             - GAMESS output with orbitals and other info
│   │   └── convert                   - Convert GAMESS wavefunction to QMCPACK format
│   │       └── h2o.hf.out              - GAMESS output
│   ├── casci                       - CASCI wave function
│   │   └── gms                       - CASCI calculation using GAMESS
│   └── soci                        - SOCI wave function
│       ├── gms                       - SOCI calculation using GAMESS
│       ├── thres0.01                 - VMC optimization with few determinants
│       └── thres0.0075               - VMC optimization with more determinants
│
└── pseudo
    ├── H.BFD.gamess              - BFD pseudopotential for H in GAMESS format
    ├── O.BFD.CCT.gamess          - BFD pseudopotential for O in GAMESS format
    ├── H.xml                     - BFD pseudopotential for H in QMCPACK format
    └── O.xml                     - BFD pseudopotential for H in QMCPACK format
```

20.3 Exercise #1: Basics

The purpose of this exercise is to show how to generate wavefunctions for QMCPACK using GAMESS and to optimize the resulting wavefunctions using VMC. This will be followed by a study of the time step and walker population dependence of DMC energies. The exercise will be performed on a water molecule at the equilibrium geometry.

20.4 Generation of a Hartree-Fock wavefunction with GAMESS

From the top directory, go to "`ex1_first-run-hartree-fock/gms`." This directory contains an input file for a HF calculation of a water molecule using BFD ECPs and the corresponding cc-pVTZ basis set. The input file should be named: "h2o.hf.inp." Study the input file. See Section *Appendix A: GAMESS input* for a more detailed description of the GAMESS input syntax. However, there will be a better time to do this soon, so we recommend continuing with the exercise at this point. After you are done, execute GAMESS with this input and store the standard output in a file named "h2o.hf.output." Finally, in the "convert" folder, use `convert4qmc` to generate the QMCPACK `particleset` and `wavefunction` files. It is always useful to rename the files generated by `convert4qmc` to something meaningful since by default they are called `sample.Gaussian-G2.xml` and `sample.Gaussian-G2.ptcl.xml`. In a standard computer (without cross-compilation), these tasks can be accomplished by the following commands.

```
cd ${TRAINING TOP}/ex1_first-run-hartree-fock/gms
jobrun_vesta rungms h2o.hf
cd ../convert
```

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```
cp ../gms/h2o.hf.output
jobrun_vesta convert4qmc -gamess h2o.hf.output -add3BodyJ
mv sample.Gaussian-G2.xml h2o.wfs.xml
mv sample.Gaussian-G2.ptcl.xml h2o.ptcl.xml
```

The HF energy of the system is -16.9600590022 Ha. To search for the energy in the output file quickly, you can use

```
grep "TOTAL ENERGY =" h2o.hf.output
```

As the job runs on VESTA, it is a good time to review Section :ref`lab-adv-mol-convert4qmc`, "Appendix B: convert4qmc," which contains a description on the use of the converter.

20.4.1 Optimize the wavefunction

When execution of the previous steps is completed, there should be two new files called `h2o.wfs.xml` and `h2o.ptcl.xml`. Now we will use VMC to optimize the Jastrow parameters in the wavefunction. From the top directory, go to "`ex1_first-run-hartree-fock/opt`." Copy the xml files generated in the previous step to the current directory. This directory should already contain a basic QMCPACK input file for an optimization calculation (`optm.xml`) Open `optm.xml` with your favorite text editor and modify the name of the files that contain the `wavefunction` and `particleset` XML blocks. These files are included with the commands:

```
<include href=ptcl.xml/>
<include href=wfs.xml/>
```

(the particle set must be defined before the wavefunction). The name of the particle set and wavefunction files should now be `h2o.ptcl.xml` and `h2o.wfs.xml`, respectively. Study both files and submit when you are ready. Notice that the location of the ECPs has been set for you; in your own calculations you have to make sure you obtain the ECPs from the appropriate libraries and convert them to QMCPACK format using ppconvert. While these calculations finish is a good time to study *Appendix C: Wavefunction optimization XML block*, which contains a review of the main parameters in the optimization XML block. The previous steps can be accomplished by the following commands:

```
cd ${TRAINING TOP}/ex1_first-run-hartree-fock/opt
cp ../convert/h2o.wfs.xml ./
cp ../convert/h2o.ptcl.xml ./
# edit optm.xml to include the correct ptcl.xml and wfs.xml
jobrun_vesta qmcpack optm.xml
```

Use the analysis tool `qmca` to analyze the results of the calculation. Obtain the VMC energy and variance for each step in the optimization and plot it using your favorite program. Remember that `qmca` has built-in functions to plot the analyzed data.

```
qmca -q e *scalar.dat -p
```

The resulting energy as a function of the optimization step should look qualitatively similar to Fig. 20.1. The energy should decrease quickly as a function of the number of optimization steps. After 6–8 steps, the energy should be converged to ∼2–3 mHa. To improve convergence, we would need to increase the number of samples used during optimization (You can check this for yourself later.). With optimized wavefunctions, we are in a position to perform VMC and DMC calculations. The modified wavefunction files after each step are written in a file named `ID.sNNN.opt.xml`, where ID is the identifier of the calculation defined in the input file (this is defined in the project XML block with parameter "id") and NNN is a series number that increases with every executable xml block in the input file.

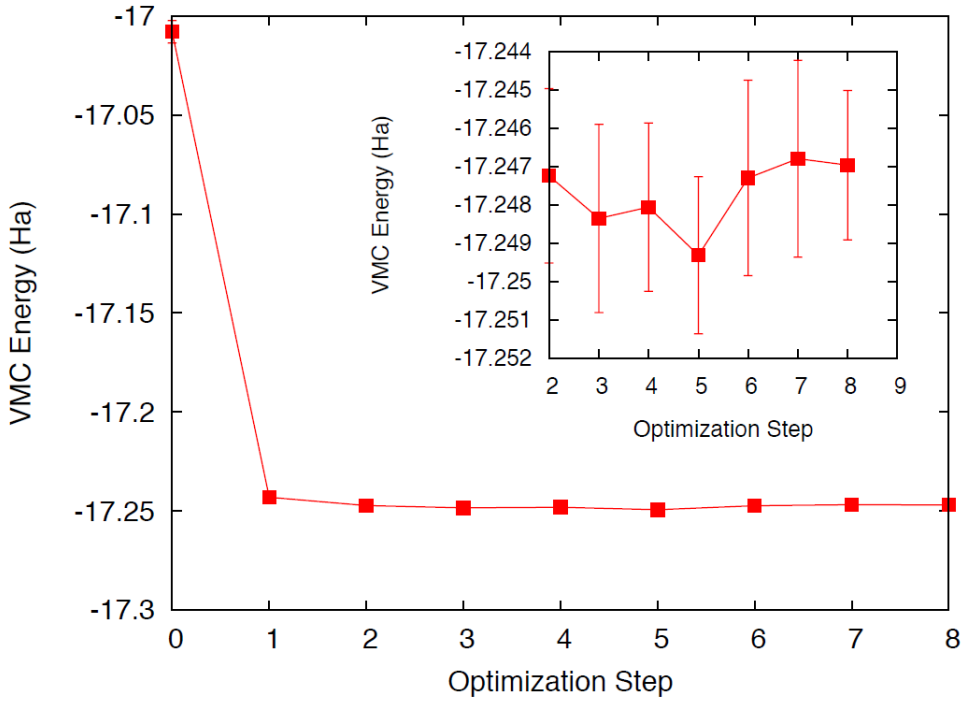

Fig. 20.1: VMC energy as a function of optimization step.

20.4.2 Time-step study

Now we will study the dependence of the DMC energy with time step. From the top directory, go to "`ex1_first-run-hartree-fock/dmc_timestep`." This folder contains a basic XML input file (`dmc_ts.xml`) that performs a short VMC calculation and three DMC calculations with varying time steps (0.1, 0.05, 0.01). Link the `particleset` and the last `optimization` file from the previous folder (the file called `jopt-h2o.sNNN.opt.xml` with the largest value of NNN). Rename the optimized `wavefunction` file to any suitable name if you wish (for example, `h2o.opt.xml`) and change the name of the `particleset` and `wavefunction` files in the input file. An optimized wavefunction can be found in the reference files (same location) in case it is needed.

The main steps needed to perform this exercise are:

```
cd \$\{TRAINING TOP\}/ex1_first-run-hartree-fock/dmc_timestep
cp ../opt/h2o.ptcl.xml ./
cp ../opt/jopt-h2o.s007.opt.xml h2o.opt.wfs.xml
# edit dmc_ts.xml to include the correct ptcl.xml and wfs.xml
jobrun_vesta qmcpack dmc_ts.xml
```

While these runs complete, go to *Appendix D: VMC and DMC XML block* and review the basic VMC and DMC input blocks. Notice that in the current DMC blocks the time step is decreased as the number of blocks is increased. Why is this?

When the simulations are finished, use `qmca` to analyze the output files and plot the DMC energy as a function of time step. Results should be qualitatively similar to those presented in Fig. 20.2; in this case we present more time steps with well converged results to better illustrate the time step dependence. In realistic calculations, the time step must be chosen small enough so that the resulting error is below the desired accuracy. Alternatively, various calculations can be performed and the results extrapolated to the zero time-step limit.

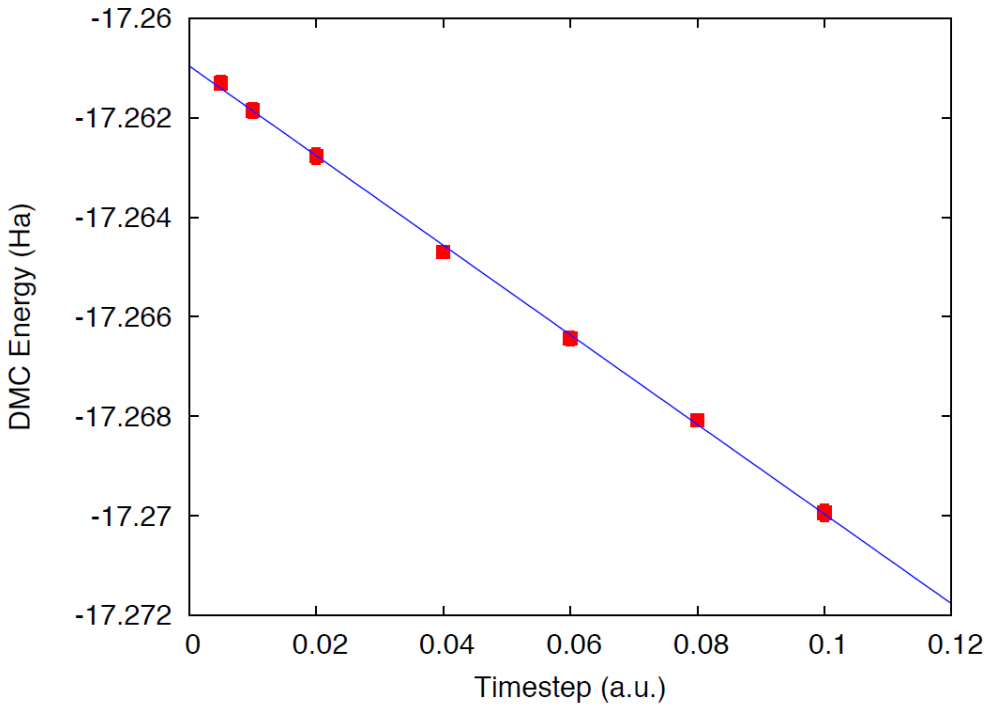

Fig. 20.2: DMC energy as a function of time step.

20.4.3 Walker population study

Now we will study the dependence of the DMC energy with the number of walkers in the simulation. Remember that, in principle, the DMC distribution is reached in the limit of an infinite number of walkers. In practice, the energy and most properties converge to high accuracy with ∼100–1,000 walkers. The actual number of walkers needed in a calculation will depend on the accuracy of the VMC wavefunction and on the complexity and size of the system. Also notice that using too many walkers is not a problem; at worse it will be inefficient since it will cost more computer time than necessary. In fact, this is the strategy used when running QMC calculations on large parallel computers since we can reduce the statistical error bars efficiently by running with large walker populations distributed across all processors.

From the top directory, go to "`ex1_first-run-hartree-fock/dmc_walkers`." Copy the optimized `wavefunction` and `particleset` files used in the previous calculations to the current folder; these are the files generated during step 2 of this exercise. An optimized `wavefunction` file can be found in the reference files (same location) in case it is needed. The directory contains a sample DMC input file and submission script. Create three directories named NWx, with x values of 120,240,480, and copy the input file to each one. Go to "NW120," and, in the input file, change the name of the `wavefunction` and `particleset` files (in this case they will be located one directory above, so use "`../dmc_timestep/h2.opt.xml`," for example); change the PP directory so that it points to one directory above; change "targetWalkers" to 120; and change the number of steps to 100, the time step to 0.01, and the number of blocks to 400. Notice that "targetWalkers" is one way to set the desired (average) number of walkers in a DMC calculation. One can alternatively set "samples" in the `<qmc method="vmc"` block to carry over de-correlated VMC configurations as DMC walkers. For your own simulations, we generally recommend setting ∼2*(#threads) walkers per node (slightly smaller than this value).

The main steps needed to perform this exercise are

```
cd ${TRAINING TOP}/ex1_first-run-hartree-fock/dmc_walkers
cp ../opt/h2o.ptcl.xml ./
```

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```
cp ../opt/jopt-h2o.s007.opt.xml h2o.opt.wfs.xml
# edit dmc_wk.xml to include the correct ptcl.xml and wfs.xml and
#  use the correct pseudopotential directory
mkdir NW120
cp dmc_wk.xml NW120
# edit dmc_wk.xml to use the desired number of walkers,
#  and collect the desired amount of statistics
jobrun_vesta qmcpack dmc_wk.xml
# repeat for NW240, NW480
```

Repeat the same procedure in the other folders by setting (targetWalkers=240, steps=100, timestep=0.01, blocks=200) in NW240 and (targetWalkers=480, steps=100, timestep=0.01, blocks=100) in NW480. When the simulations complete, use `qmca` to analyze and plot the energy as a function of the number of walkers in the calculation. As always, Fig. 20.3 shows representative results of the energy dependence on the number of walkers for a single water molecule. As shown, less than 240 walkers are needed to obtain an accuracy of 0.1 mHa.

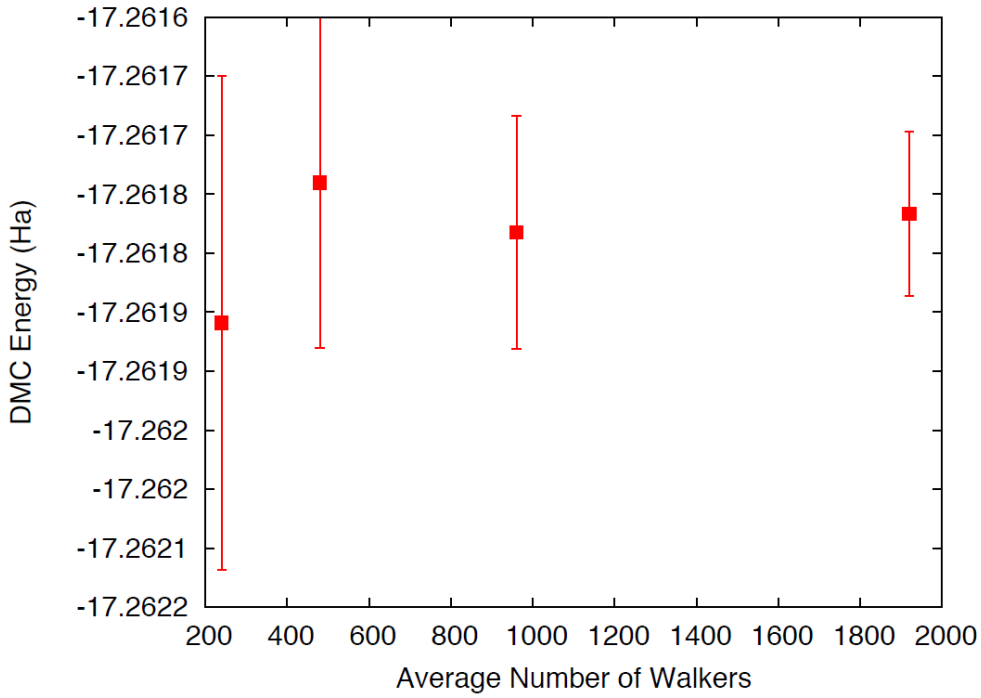

Fig. 20.3: DMC energy as a function of the average number of walkers.

20.5 Exercise #2: Slater-Jastrow wavefunction options

From this point on in the tutorial we assume familiarity with the basic parameters in the optimization, VMC, and DMC XML input blocks of QMCPACK. In addition, we assume familiarity with the submission system. As a result, the folder structure will not contain any prepared input or submission files, so you will need to generate them using input files from exercise 1. In the case of QMCPACK sample files, you will find `optm.xml`, `vmc dmc.xml`, and `submit.csh files`. Some of the options in these files can be left unaltered, but many of them will need to be tailored to the particular calculation.

In this exercise we will study the dependence of the DMC energy on the choices made in the wavefunction ansatz.

In particular, we will study the influence/dependence of the VMC energy with the various terms in the Jastrow. We will also study the influence of the VMC and DMC energies on the SPOs used to form the Slater determinant in single-determinant wavefunctions. For this we will use wavefunctions generated with various exchange-correlation functionals in DFT. Finally, we will optimize a simple multideterminant wavefunction and study the dependence of the energy on the number of configurations used in the expansion. All of these exercises will be performed on the water molecule at equilibrium.

20.5.1 Influence of Jastrow on VMC energy with HF wavefunction

In this section we will study the dependence of the VMC energy on the various Jastrow terms (e.g., 1-body, 2-body and 3-body. From the top directory, go to "`ex2_slater-jastrow-wf-options/jastrow.`" We will compare the single-determinant VMC energy using a 2-body Jastrow term, both 1- and 2-body terms, and finally 1-, 2- and 3-body terms. Since we are interested in the influence of the Jastrow, we will use the HF orbitals calculated in exercise #1. Make three folders named 2j, 12j, and 123j. For both 2j and 12j, copy the input file `optm.xml` from "`ex1_first-run-hartree-fock/opt.`" This input file performs both wavefunction optimization and a VMC calculation. Remember to correct relative paths to the PP directory. Copy the un-optimized HF `wavefunction` and `particleset` files from "`ex1_first-run-hartree-fock/convert`"; if you followed the instructions in exercise #1 these should be named `h2o.wfs.xml` and `h2o.ptcl.xml`. Otherwise, you can obtained them from the REFERENCE files. Modify the `h2o.wfs.xml` file to remove the appropriate Jastrow blocks. For example, for a 2-body Jastrow (only), you need to eliminate the Jastrow blocks named `<jastrow name="J1"` and `<jastrow name="J3."` In the case of 12j, remove only `<jastrow name="J3."` Recommended settings for the optimization run are nodes=32, threads=16, blocks=250, samples=128000, time-step=0.5, 8 optimization loops. Recommended settings in the VMC section are walkers=16, blocks=1000, steps=1, substeps=100. Notice that samples should always be set to blocks*threads per node*nodes = 32*16*250=128000. Repeat the process in both 2j and 12j cases. For the 123j case, the wavefunction has already been optimized in the previous exercise. Copy the optimized HF wavefunction and the particleset from "`ex1_first-run-hartree-fock/opt.`" Copy the input file from any of the previous runs and remove the optimization block from the input, just leave the VMC step. In all three cases, modify the submission script and submit the run.

Because these simulations will take several minutes to complete, this is an excellent opportunity to go to *Appendix E: Wavefunction XML block* and review the wavefunction XML block used by QMCPACK. When the simulations are completed, use `qmca` to analyze the output files. Using your favorite plotting program (e.g., gnu plot), plot the energy and variance as a function of the Jastrow form. Fig. 20.4 shows a typical result for this calculation. As can be seen, the VMC energy and variance depends strongly on the form of the Jastrow. Since the DMC error bar is directly related to the variance of the VMC energy, improving the Jastrow will always lead to a reduction in the DMC effort. In addition, systematic approximations (time step, number of walkers, etc.) are also reduced with improved wavefunctions.

20.5.2 Generation of wavefunctions from DFT using GAMESS

In this section we will use GAMESS to generate wavefunctions for QMCPACK from DFT calculations. From the top folder, go to "`ex2_slater-jastrow-wf-options/orbitals`." To demonstrate the variation in DMC energies with the choice of DFT orbitals, we will choose the following set of exchange-correlation functionals (PBE, PBE0, BLYP, B3LYP). For each functional, make a directory using your preferred naming convention (e.g., the name of the functional). Go into each folder and copy a GAMESS input file from "`ex1_first-run-hartree-fock/gms`." Rename the file with your preferred naming convention; we suggest using `h2o.[dft].inp`, where [dft] is the name of the functional used in the calculation. At this point, this input file should be identical to the one used to generate the HF wavefunction in exercise #1. To perform a DFT calculation we only need to add "DFTTYP" to the `$CONTRL ... $END` section and set it to the desired functional type, for example, "DFTTYP=PBE" for a PBE functional. This variable must be set to (PBE, PBE0, BLYP, B3LYP) to obtain the appropriate functional in GAMESS. For a complete list of implemented functionals, see the GAMESS input manual.

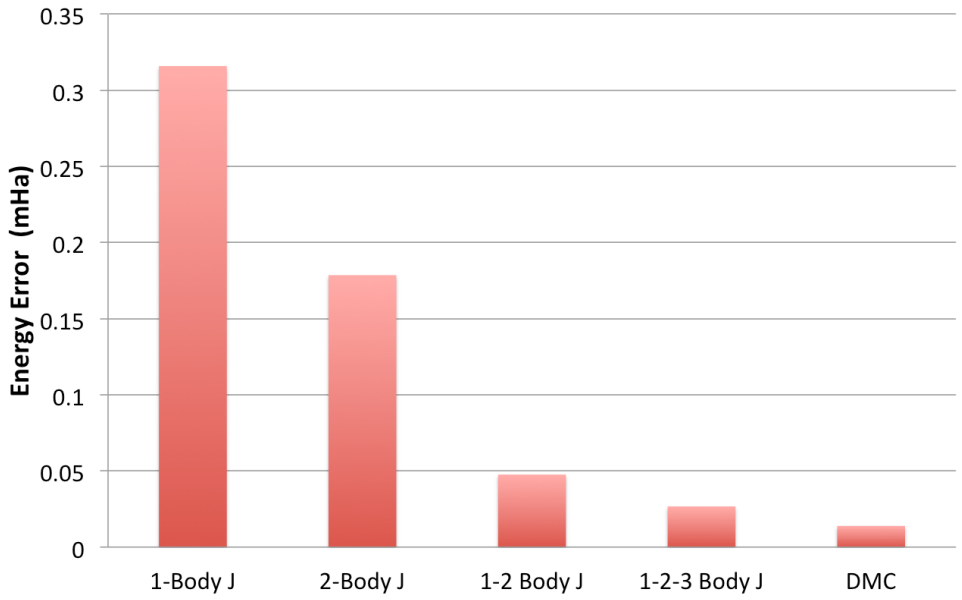

Fig. 20.4: VMC energy as a function of Jastrow type.

20.5.3 Optimization and DMC calculations with DFT wavefunctions

In this section we will optimize the wavefunction generated in the previous step and perform DMC calculations. From the top directory, go to "`ex2_slater-jastrow-wf-options/orbitals`." The steps required to achieve this are identical to those used to optimize the wavefunction with HF orbitals. Make individual folders for each calculation and obtain the necessary files to perform optimization, for example, VMC and DMC calculations from "for `ex1_first-run-hartree-fock/opt`" and "`ex1_first-run-hartree-fock/dmc_ts`." For each functional, make the appropriate modifications to the input files and copy the `particleset` and `wavefunction` files from the appropriate directory in "`ex2_slater-jastrow-wf-options/orbitals/[dft]`." We recommend the following settings: nodes=32, threads=16, (in optimization) blocks=250, samples=128000, timestep=0.5, 8 optimization loops, (in VMC) walkers=16, blocks=100, steps=1, substeps=100, (in DMC) blocks 400, targetWalkers=960, and timestep=0.01. Submit the runs and analyze the results using `qmca`.

How do the energies compare against each other? How do they compare against DMC energies with HF orbitals?

20.6 Exercise #3: Multideterminant wavefunctions

In this exercise we will study the dependence of the DMC energy on the set of orbitals and the type of configurations included in a multideterminant wavefunction.

20.6.1 Generation of a CISD wavefunctions using GAMESS

In this section we will use GAMESS to generate a multideterminant wavefunction with configuration interaction with single and double excitations (CISD). In CISD, the Schrodinger equation is solved exactly on a basis of determinants including the HF determinant and all its single and double excitations.

Go to "`ex3_multi-slater-jastrow/cisd/gms`" and you will see input and output files named `h2o.cisd.inp` and `h2o.cisd.out`. Because of technical problems with GAMESS in the BGQ architecture of VESTA, we are unable to use CISD properly in GAMESS. Consequently, the output of the calculation is already provided in the directory.

There will be time in the next step to study the GAMESS input files and the description in *Appendix A: GAMESS input*. Since the output is already provided, the only action needed is to use the converter to generate the appropriate QMCPACK files.

```
jobrun_vesta convert4qmc h2o.cisd.out -ci h2o.cisd.out \
-readInitialGuess 57 -threshold 0.0075
```

We used the PRTMO=.T. flag in the GUESS section to include orbitals in the output file. You should read these orbitals from the output (-readInitialGuess 40). The highest occupied orbital in any determinant should be 34, so reading 40 orbitals is a safe choice. In this case, it is important to rename the XML files with meaningful names, for example, `h2o.cisd.wfs.xml`. A threshold of 0.0075 is sufficient for the calculations in the training.

20.6.2 Optimization of a multideterminant wavefunction

In this section we will optimize the wavefunction generated in the previous step. There is no difference in the optimization steps if a single determinant and a multideterminant wavefunction. QMCPACK will recognize the presence of a multideterminant wavefunction and will automatically optimize the linear coefficients by default. Go to "`ex3_multi-slater-jastrow/cisd`" and make a folder called `thres0.01`. Copy the `particleset` and `wavefunction` files created in the previous step to the current directory. With your favorite text editor, open the `wavefunction` file `h2o.wfs.xml`. Look for the multideterminant XML block and change the "cutoff" parameter in detlist to 0.01. Then follow the same steps used in Section 9.4.3, "Optimization and DMC calculations with DFT wavefunctions" to optimize the wavefunction. Similar to this case, design a QMCPACK input file that performs wavefunction optimization followed by VMC and DMC calculations. Submit the calculation.

This is a good time to review the GAMESS input file description in *Appendix A: GAMESS input*, go to the previous directory and make a new folder named `thres0.0075`. Repeat the previous steps to optimize the wavefunction with a cutoff of 0.01, but use a cutoff of 0.0075 this time. This will increase the number of determinants used in the calculation. Notice that the "cutoff" parameter in the XML should be less than the "-threshold 0.0075" flag passed to the converted, which is further bounded by the PRTTOL flag in the GAMESS input.

After the wavefunction is generated, we are ready to optimize. Instead of starting from an un-optimized wavefunction, we can start from the optimized wavefunction from thres0.01 to speed up convergence. You will need to modify the file and change the cutoff in detlist to 0.0075 with a text editor. Repeat the optimization steps and submit the calculation.

When you are done, use `qmca` to analyze the results. Compare the energies at these two coefficient cutoffs with the energies obtained with DFT orbitals. Because of the time limitations of this tutorial, it is not practical to optimize the wavefunctions with a smaller cutoff since this would require more samples and longer runs due to the larger number of optimizable parameters. Fig. 20.5 shows the results of such exercise: the DMC energy as a function of the cutoff in the wavefunction. As can be seen, a large improvement in the energy is obtained as the number of configurations is increased.

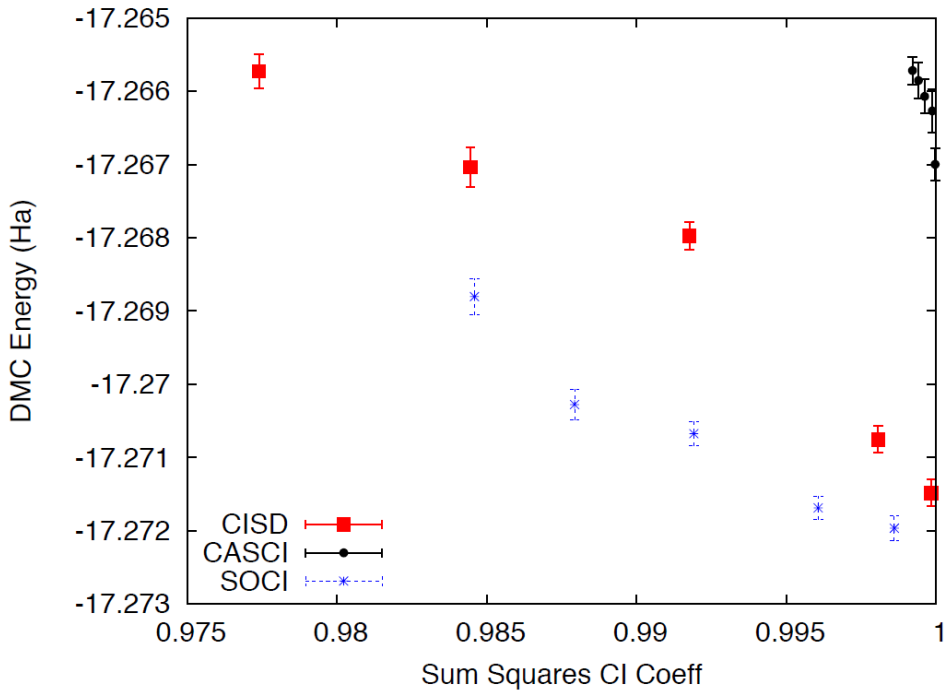

Fig. 20.5: DMC energy as a function of the sum of the square of CI coefficients from CISD.

20.6.3 CISD, CASCI, and SOCI

Go to "`ex3_multi-slater-jastrow`" and inspect the folders for the remaining wavefunction types: CASCI and SOCI. Follow the steps in the previous exercise and obtain the optimized wavefunctions for these determinant choices. Notice that the SOCI GAMESS output is not included because it is large. Already converted XML inputs can be found in "`ex3_multi-slater-jastrow/soci/thres*`."

A CASCI wavefunction is produced from a CI calculation that includes all the determinants in a complete active space (CAS) calculation, in this case using the orbitals from a previous CASSCF calculation. In this case we used a CAS(8,8) active space that includes all determinants generated by distributing 8 electrons in the lowest 8 orbitals. A SOCI calculation is similar to the CAS-CI calculation, but in addition to the determinants in the CAS it also includes all single and double excitations from all of them, leading to a much larger determinant set. Since you now have considerable experience optimizing wavefunctions and calculating DMC energies, we will leave it to you to complete the remaining tasks on your own. If you need help, refer to previous exercises in the tutorial. Perform optimizations for both wavefunctions using cutoffs in the CI expansion of 0.01 an 0.0075. If you have time, try to optimize the wavefunctions with a cutoff of 0.005. Analyze the results and plot the energy as a function of cutoff for all three cases: CISD, CAS-CI, and SOCI.

Fig. 20.5 shows the result of similar calculations using more samples and smaller cutoffs. The results should be similar to those produced in the tutorial. For reference, the exact energy of the water molecule with ECPs is approximately -17.276 Ha. From the results of the tutorial, how does the selection of determinants relate to the expected DMC energy? What about the choice in the set of orbitals?

20.7 Appendix A: GAMESS input

In this section we provide a brief description of the GAMESS input needed to produce trial wavefunction for QMC calculations with QMCPACK. We assume basic familiarity with GAMESS input structure, particularly regarding the input of atomic coordinates and the definition of Gaussian basis sets. This section focuses on generation of the output files needed by the converter tool, `convert4qmc`. For a description of the converter, see *Appendix B: convert4qmc*.

Only a subset of the methods available in GAMESS can be used to generate wavefunctions for QMCPACK, and we restrict our description to these. For a complete description of all the options and methods available in GAMESS, please refer to the official documentation at "http://www.msg.ameslab.gov/gamess/documentation.html."

Currently, `convert4qmc` can process output for the following methods in GAMESS (in SCFTYP): RHF, ROHF, and MCSCF. Both HF and DFT calculations (any DFT type) can be used in combination with RHF and ROHF calculations. For MCSCF and CI calculations, ALDET, ORMAS, and GUGA drivers can be used (details follow).

20.7.1 HF input

The following input will perform a restricted HF calculation on a closed-shell singlet (multiplicity=1). This will generate RHF orbitals for any molecular system defined in `$DATA ... $END`.

```
$CONTRL SCFTYP=RHF RUNTYP=ENERGY MULT=1
ISPHER=1 EXETYP=RUN COORD=UNIQUE MAXIT=200 $END
$SYSTEM MEMORY=150000000 $END
$GUESS GUESS=HUCKEL $END
$SCF DIRSCF=.TRUE. $END
$DATA
...
Atomic Coordinates and basis set
...
$END
```

Main options:

1. SCFTYP: Type of SCF method, options: RHF, ROHF, MCSCF, UHF and NONE.
2. RUNTYP: Type of run. For QMCPACK wavefunction generation this should always be ENERGY.
3. MULT: Multiplicity of the molecule.
4. ISPHER: Use spherical harmonics (1) or Cartesian basis functions (-1).
5. COORD: Input structure for the atomic coordinates in $DATA.

20.7.2 DFT calculations

The main difference between the input for a RHF/ROHF calculation and a DFT calculation is the definition of the DFTTYP parameter. If this is set in the $CONTROL section, a DFT calculation will be performed with the appropriate functional. Notice that although the default values are usually adequate, DFT calculations have many options involving the integration grids and accuracy settings. Make sure you study the input manual to be aware of these. Refer to the input manual for a list of the implemented exchange-correlation functionals.

20.7.3 MCSCF

MCSCF calculations are performed by setting SCFTYP=MCSCF in the CONTROL section. If this option is set, an MCSCF section must be added to the input file with the options for the calculation. An example section for the water molecule used in the tutorial follows.

```
$MCSCF CISTEP=GUGA MAXIT=1000 FULLNR=.TRUE. ACURCY=1.0D-5 $END
```

The most important parameter is CISTEP, which defines the CI package used. The only options compatible with QMCPACK are: ALDET, GUGA, and ORMAS. Depending on the package used, additional input sections are needed.

20.7.4 CI

Configuration interaction (full CI, truncated CI, CAS-CI, etc) calculations are performed by setting `SCFTYP=NONE` and `CITYP=GUGA,ALDET,ORMAS`. Each one of these packages requires further input sections, which are typically slightly different from the input sections needed for MCSCF runs.

20.7.5 GUGA: Unitary group CI package

The GUGA package is the only alternative if one wants CSFs with GAMESS. We subsequently provide a very brief description of the input sections needed to perform MCSCF, CASCI, truncated CI, and SOCI with this package. For a complete description of these methods and all the options available, please refer to the GAMESS input manual.

GUGA-MCSCF

The following input section performs a CASCI calculation with a CAS that includes 8 electrons in 8 orbitals (4 DOC and 4 VAL), for example, CAS(8,8). NMCC is the number of frozen orbitals (doubly occupied orbitals in all determinants), NDOC is the number of double occupied orbitals in the reference determinant, NVAL is the number of singly occupied orbitals in the reference (for spin polarized cases), and NVAL is the number of orbitals in the active space. Since FORS is set to .TRUE., all configurations in the active space will be included. ISTSYM defines the symmetry of the desired state.

```
$MCSCF CISTEP=GUGA MAXIT=1000 FULLNR=.TRUE. ACURCY=1.0D-5 $END
$DRT GROUP=C2v NMCC=0 NDOC=4 NALP=0 NVAL=4 ISTSYM=1 MXNINT= 500000 FORS=.TRUE. $END
```

GUGA-CASCI

The following input section performs a CASCI calculation with a CAS that includes 8 electrons in 8 orbitals (4 DOC and 4 VAL), for example, CAS(8,8). NFZC is the number of frozen orbitals (doubly occupied orbitals in all determinants). All other parameters are identical to those in the MCSCF input section.

```
$CIDRT GROUP=C2v NFZC=0 NDOC=4 NALP=0 NVAL=4 NPRT=2 ISTSYM=1 FORS=.TRUE. MXNINT=␣
↪500000 $END
$GUGDIA PRTTOL=0.001 CVGTOL=1.0E-5 ITERMX=1000 $END
```

GUGA-truncated CI

The following input sections will lead to a truncated CI calculation. In this particular case it will perform a CISD calculation since IEXCIT is set to 2. Other values in IEXCIT will lead to different CI truncations; for example, IEXCIT=4 will lead to CISDTQ. Notice that only the lowest 30 orbitals will be included in the generation of the excited determinants in this case. For a full CISD calculation, NVAL should be set to the total number of virtual orbitals.

```
$CIDRT GROUP=C2v NFZC=0 NDOC=4 NALP=0 NVAL=30 NPRT=2 ISTSYM=1 IEXCIT=2 MXNINT= 500000
↪$END
$GUGDIA PRTTOL=0.001 CVGTOL=1.0E-5 ITERMX=1000 $END
```

GUGA-SOCI

The following input section performs a SOCI calculation with a CAS that includes 8 electrons in 8 orbitals (4 DOC and 4 VAL), for example, CAS(8,8). Since SOCI is set to .TRUE., all single and double determinants from all determinants in the CAS(8,8) will be included.

```
$CIDRT GROUP=C2v NFZC=0 NDOC=4 NALP=0 NVAL=4 NPRT=2 ISTSYM=1 SOCI=.TRUE. NEXT=30␣
↪MXNINT= 500000 $END
$GUGDIA PRTTOL=0.001 CVGTOL=1.0E-5 ITERMX=1000 $END
```

20.7.6 ECP

To use ECPs in GAMESS, you must define a {$ECP ... $END} block. There must be a definition of a potential for every atom in the system, including symmetry equivalent ones. In addition, they must appear in the particular order expected by GAMESS. The following example shows an ECP input block for a single water molecule using BFD ECPs. To turn on the use of ECPs, the option "ECP=READ" must be added to the CONTROL input block.

```
$ECP
O-QMC GEN 2 1
3
6.00000000 1 9.29793903
55.78763416 3 8.86492204
-38.81978498 2 8.62925665
1
38.41914135 2 8.71924452
H-QMC GEN 0 0
3
1.000000000000 1 25.000000000000
25.000000000000 3 10.821821902641
-8.228005709676 2 9.368618758833
H-QMC
$END
```

20.8 Appendix B: convert4qmc

To generate the particleset and wavefunction XML blocks required by QMCPACK in calculations with molecular systems, the converter `convert4qmc` must be used. The converter will read the standard output from the appropriate quantum chemistry calculation and will generate all the necessary input for QMCPACK. In the following, we describe the main options of the converter for GAMESS output. In general, there are three ways to use the converter depending on the type of calculation performed. The minimum syntax for each option is shown subsequently. For a description of the XML files produced by the converter, see *Appendix E: Wavefunction XML block*.

1. For all single-determinant calculations (HF and DFT with any DFTTYP):

```
convert4qmc -gamess single det.out
```

   - single det.out is the standard output generated by GAMESS.

2. *(This option is not recommended. Use the following option to avoid mistakes.)* For multideterminant calculations where the orbitals and configurations are read from different files (e.g., when using orbitals from a MCSCF run and configurations from a subsequent CI run):

```
convert4qmc -gamess orbitals multidet.out -ci cicoeff
multidet.out
```

   - orbitals_multidet.out is the standard output from the calculation that generates the orbitals. cicoeff multidet.out is the standard output from the calculation that calculates the CI expansion.

3. For multideterminant calculations where the orbitals and configurations are read from the same file, using PRTMO=.T. in the GUESS input block:

```
convert4qmc -gamess multi det.out -ci multi det.out
-readInitialGuess Norb
```

   - multi_det.out is the standard output from the calculation that calculates the CI expansion.

Options:

- **-gamess file.out**: Standard output of GAMESS calculation. With the exception of determinant configurations and coefficients in multideterminant calculations, everything else is read from this file including atom coordinates, basis sets, SPOs, ECPs, number of electrons, multiplicity, etc.
- **-ci file.out**: In multideterminant calculations, determinant configurations and coefficients are read from this file. Notice that SPOs are NOT read from this file. Recognized CI packages are ALDET, GUGA, and ORMAS. Output produced with the GUGA package MUST have the option "NPRT=2" in the CIDRT or DRT input blocks.
- **-threshold cutoff**: Cutoff in multideterminant expansion. Only configurations with coefficients above this value are printed.
- **-zeroCI**: Sets to zero the CI coefficients of all determinants, with the exception of the first one.
- **-readInitialGuess Norb**: Reads Norb initial orbitals ("INITIAL GUESS ORBITALS") from GAMESS output. These are orbitals generated by the GUESS input block and printed with the option "PRTMO=.T.". Notice that this is useful only in combination with the option "GUESS=MOREAD" and in cases where the orbitals are not modified in the GAMESS calculation, e.g. CI runs. This is the recommended option in all CI calculations.
- **-NaturalOrbitals Norb**: Read Norb "NATURAL ORBITALS" from GAMESS output. The natural orbitals must exists in the output, otherwise the code aborts.
- **-add3BodyJ**: Adds 3-body Jastrow terms (e-e-I) between electron pairs (both same spin and opposite spin terms) and all ion species in the system. The radial function is initialized to zero, and the default cutoff is 10.0 bohr. The converter will add a 1- and 2-body Jastrow to the wavefunction block by default.

20.8.1 Useful notes

- The type of SPOs read by the converter depends on the type of calculation and on the options used. By default, when neither -readInitialGuess nor -NaturalOrbitals are used, the following orbitals are read in each case (notice that -readInitialGuess or -NaturalOrbitals are mutually exclusive):
  - RHF and ROHF: "EIGENVECTORS"
  - MCSCF: "MCSCF OPTIMIZED ORBITALS"
  - GUGA, ALDET, ORMAS: Cannot read orbitals without -readInitialGuess or -NaturalOrbitals options.
- The SPOs and printed CI coefficients in MCSCF calculations are not consistent in GAMESS. The printed CI coefficients correspond to the next-to-last iteration; they are not recalculated with the final orbitals. So to get appropriate CI coefficients from MCSCF calculations, a subsequent CI (no SCF) calculation is needed to produce consistent orbitals. In principle, it is possible to read the orbitals from the MCSCF output and the CI coefficients and configurations from the output of the following CI calculations. This could lead to problems in principle since GAMESS will rotate initial orbitals by default to obtain an initial guess consistent with the symmetry of the molecule. This last step is done by default and can change the orbitals reported in the MCSCF calculation before the CI is performed. To avoid this problem, we highly recommend using the preceding option #3 to read all the information from the output of the CI calculation; this requires the use of "PRTMO=.T." in the GUESS input block. Since the orbitals are printed after any symmetry rotation, the resulting output will always be consistent.

20.9 Appendix C: Wavefunction optimization XML block

Listing 20.1: Sample XML optimization block.

```
<loop max="10">
  <qmc method="linear" move="pbyp" checkpoint="-1" gpu="no">
  <parameter name="blocks">     10  </parameter>
    <parameter name="warmupsteps"> 25 </parameter>
    <parameter name="steps"> 1 </parameter>
    <parameter name="substeps"> 20 </parameter>
    <parameter name="timestep"> 0.5 </parameter>
    <parameter name="samples"> 10240  </parameter>
    <cost name="energy">                    0.95 </cost>
    <cost name="unreweightedvariance">      0.0 </cost>
    <cost name="reweightedvariance">        0.05 </cost>
    <parameter name="useDrift">  yes </parameter>
    <parameter name="bigchange">10.0</parameter>
    <estimator name="LocalEnergy" hdf5="no"/>
    <parameter name="usebuffer"> yes </parameter>
    <parameter name="nonlocalpp"> yes </parameter>
    <parameter name="MinMethod">quartic</parameter>
    <parameter name="exp0">-6</parameter>
    <parameter name="alloweddifference"> 1.0e-5 </parameter>
    <parameter name="stepsize">  0.15 </parameter>
    <parameter name="nstabilizers"> 1 </parameter>
  </qmc>
</loop>
```

Options:

- bigchange: (default 50.0) Largest parameter change allowed
- usebuffer: (default no) Save useful information during VMC

- nonlocalpp: (default no) Include nonlocal energy on 1-D min
- MinMethod: (default quartic) Method to calculate magnitude of parameter change quartic: fit quartic polynomial to four values of the cost function obtained using reweighting along chosen direction linemin: direct line minimization using reweighting rescale: no 1-D minimization. Uses Umrigars suggestions.
- stepsize: (default 0.25) Step size in either quartic or linemin methods.
- alloweddifference: (default 1e-4) Allowed increase in energy
- exp0: (default -16.0) Initial value for stabilizer (shift to diagonal of H). Actual value of stabilizer is 10 exp0
- nstabilizers: (default 3) Number of stabilizers to try
- stabilizaterScale: (default 2.0) Increase in value of exp0 between iterations.
- max its: (default 1) Number of inner loops with same sample
- minwalkers: (default 0.3) Minimum value allowed for the ratio of effective samples to actual number of walkers in a reweighting step. The optimization will stop if the effective number of walkers in any reweighting calculation drops below this value. Last set of acceptable parameters are kept.
- maxWeight: (defaul 1e6) Maximum weight allowed in reweighting. Any weight above this value will be reset to this value.

Recommendations:

- Set samples to equal to (#threads)*blocks.
- Set steps to 1. Use substeps to control correlation between samples.
- For cases where equilibration is slow, increase both substeps and warmupsteps.
- For hard cases (e.g., simultaneous optimization of long MSD and 3-Body J), set exp0 to 0 and do a single inner iteration (max its=1) per sample of configurations.

20.10 Appendix D: VMC and DMC XML block

Listing 20.2: Sample XML blocks for VMC and DMC calculations.

```
<qmc method="vmc" move="pbyp" checkpoint="-1">
  <parameter name="useDrift">yes</parameter>
  <parameter name="warmupsteps">100</parameter>
  <parameter name="blocks">100</parameter>
  <parameter name="steps">1</parameter>
  <parameter name="substeps">20</parameter>
  <parameter name="walkers">30</parameter>
  <parameter name="timestep">0.3</parameter>
  <estimator name="LocalEnergy" hdf5="no"/>
</qmc>
<qmc method="dmc" move="pbyp" checkpoint="-1">
  <parameter name="nonlocalmoves">yes</parameter>
  <parameter name="targetWalkers">1920</parameter>
  <parameter name="blocks">100</parameter>
  <parameter name="steps">100</parameter>
  <parameter name="timestep">0.1</parameter>
  <estimator name="LocalEnergy" hdf5="no"/>
</qmc>
```

General Options:

- **move**: (default "walker") Type of electron move. Options: "pbyp" and "walker."
- **checkpoint**: (default "-1") (If > 0) Generate checkpoint files with given frequency. The calculations can be restarted/continued with the produced checkpoint files.
- **useDrift**: (default "yes") Defines the sampling mode. useDrift = "yes" will use Langevin acceleration to sample the VMC and DMC distributions, while useDrift="no" will use random displacements in a box.
- **warmupSteps**: (default 0) Number of steps warmup steps at the beginning of the calculation. No output is produced for these steps.
- **blocks**: (default 1) Number of blocks (outer loop).
- **steps**: (default 1) Number of steps per blocks (middle loop).
- **sub steps**: (default 1) Number of substeps per step (inner loop). During substeps, the local energy is not evaluated in VMC calculations, which leads to faster execution. In VMC calculations, set substeps to the average autocorrelation time of the desired quantity.
- **time step**: (default 0.1) Electronic time step in bohr.
- **samples**: (default 0) Number of walker configurations saved during the current calculation.
- **walkers**: (default #threads) In VMC, sets the number of walkers per node. The total number of walkers in the calculation will be equal to walkers*(# nodes).

Options unique to DMC:

- **targetWalkers**: (default #walkers from previous calculation, e.g., VMC). Sets the target number of walkers. The actual population of walkers will fluctuate around this value. The walkers will be distributed across all the nodes in the calculation. On a given node, the walkers are split across all the threads in the system.
- **nonlocalmoves**: (default "no") Set to "yes" to turns on the use of Casula's T-moves.

20.11 Appendix E: Wavefunction XML block

Listing 20.3: Basic framework for a single-determinant determinantset XML block.

```
  <wavefunction name="psi0" target="e">
    <determinantset type="MolecularOrbital" name="LCAOBSet"
     source="ion0" transform="yes">
      <basisset name="LCAOBSet">
        <atomicBasisSet name="Gaussian-G2" angular="cartesian" type="Gaussian"␣
↪elementType="O" normalized="no">
        ...
        </atomicBasisSet>
      </basisset>
      <slaterdeterminant>
        <determinant id="updet" size="4">
          <occupation mode="ground"/>
          <coefficient size="57" id="updetC">
          ...
          </coefficient>
        </determinant>
        <determinant id="downdet" size="4">
          <occupation mode="ground"/>
          <coefficient size="57" id="downdetC">
          ...
```

(continues on next page)

(continued from previous page)

```
        </coefficient>
      </determinant>
    </slaterdeterminant>

  </determinantset>

  <jastrow name="J2" type="Two-Body" function="Bspline" print="yes">
  ...
  </jastrow>

</wavefunction>
```

In this section we describe the basic format of a QMCPACK wavefunction XML block. Everything listed in this section is generated by the appropriate converter tools. Little to no modification is needed when performing standard QMC calculations. As a result, this section is meant mainly for illustration purposes. Only experts should attempt to modify these files (with very few exceptions like the cutoff of CI coefficients and the cutoff in Jastrow functions) since changes can lead to unexpected results.

A QMCPACK wavefunction XML block is a combination of a determinantset, which contains the antisymmetric part of the wavefunction and one or more Jastrow blocks. The syntax of the antisymmetric block depends on whether the wavefunction is a single determinant or a multideterminant expansion. *Listing 62* shows the general structure of the single-determinant case. The determinantset block is composed of a basisset block, which defines the atomic orbital basis set, and a slaterdeterminant block, which defines the SPOs and occupation numbers of the Slater determinant. *Listing 63* shows a (piece of a) sample of a slaterdeterminant block. The slaterdeterminant block consists of two determinant blocks, one for each electron spin. The parameter "size" in the determinant block refers to the number of SPOs present while the "size" parameter in the coefficient block refers to the number of atomic basis functions per SPO.

Listing 20.4: Sample XML block for the single Slater determinant case.

```
    <slaterdeterminant>
      <determinant id="updet" size="5">
        <occupation mode="ground"/>
        <coefficient size="134" id="updetC">
  9.55471000000000e-01 -3.87000000000000e-04  6.51140000000000e-02  2.17700000000000e-
↪03
  1.43900000000000e-03  4.00000000000000e-06 -4.58000000000000e-04 -5.20000000000000e-
↪05
  -2.40000000000000e-05  6.00000000000000e-06 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -5.26000000000000e-04  2.63000000000000e-04  2.
↪63000000000000e-04
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00 -1.
↪27000000000000e-04
```

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```
  6.30000000000000e-05  6.30000000000000e-05 -0.00000000000000e+00 -0.
↪00000000000000e+00
  -0.00000000000000e+00 -3.20000000000000e-05  1.60000000000000e-05  1.
↪60000000000000e-05
  -0.00000000000000e+00 -0.00000000000000e+00 -0.00000000000000e+00  7.
↪00000000000000e-06
```

Listing 64 shows the general structure of the multideterminant case. Similar to the single-determinant case, the determinantset must contain a basisset block. This definition is identical to the one described previously. In this case, the definition of the SPOs must be done independently from the definition of the determinant configurations; the latter is done in the sposet block, while the former is done on the multideterminant block. Notice that two sposet sets must be defined, one for each electron spin. The name of each sposet set is required in the definition of the multideterminant block. The determinants are defined in terms of occupation numbers based on these orbitals.

Listing 20.5: Basic framework for a multideterminant determinantset XML block.

```
  <wavefunction id="psi0" target="e">
    <determinantset name="LCAOBSet" type="MolecularOrbital" transform="yes" source=
↪"ion0">
      <basisset name="LCAOBSet">
        <atomicBasisSet name="Gaussian-G2" angular="cartesian" type="Gaussian"␣
↪elementType="O" normalized="no">
        ...
        </atomicBasisSet>
        ...
      </basisset>
      <sposet basisset="LCAOBSet" name="spo-up" size="8">
        <occupation mode="ground"/>
        <coefficient size="40" id="updetC">
        ...
</coefficient>
      </sposet>
      <sposet basisset="LCAOBSet" name="spo-dn" size="8">
        <occupation mode="ground"/>
        <coefficient size="40" id="downdetC">
        ...
      </coefficient>
      </sposet>
      <multideterminant optimize="yes" spo_up="spo-up" spo_dn="spo-dn">
        <detlist size="97" type="CSF" nca="0" ncb="0" nea="4" neb="4" nstates="8"␣
↪cutoff="0.001">
          <csf id="CSFcoeff_0" exctLvl="0" coeff="0.984378" qchem_coeff="0.984378"␣
↪occ="22220000">
            <det id="csf_0-0" coeff="1" alpha="11110000" beta="11110000"/>
          </csf>
          ...
        </detlist>
      </multideterminant>
    </determinantset>
    <jastrow name="J2" type="Two-Body" function="Bspline" print="yes">
    ...
    </jastrow>
  </wavefunction>
```

There are various options in the multideterminant block that users should be aware of.

- cutoff: (IMPORTANT!) Only configurations with (absolute value) "qchem coeff" larger than this value will be read by QMCPACK.
- optimize: Turn on/off the optimization of linear CI coefficients.
- coeff: (in csf) Current coefficient of given configuration. Gets updated during wavefunction optimization.
- qchem coeff: (in csf) Original coefficient of given configuration from GAMESS calculation. This is used when applying a cutoff to the configurations read from the file. The cutoff is applied on this parameter and not on the optimized coefficient.
- nca and nab: Number of core orbitals for up/down electrons. A core orbital is an orbital that is doubly occupied in all determinant configurations, not to be confused with core electrons. These are not explicitly listed on the definition of configurations.
- nea and neb: Number of up/down active electrons (those being explicitly correlated).
- nstates: Number of correlated orbitals.
- size (in detlist): Contains the number of configurations in the list.

The remaining part of the determinantset block is the definition of Jastrow factor. Any number of these can be defined. *Listing 65* shows a sample Jastrow block including 1-, 2- and 3-body terms. This is the standard block produced by `convert4qmc` with the option -add3BodyJ (this particular example is for a water molecule). Optimization of individual radial functions can be turned on/off using the "optimize" parameter. It can be added to any coefficients block, even though it is currently not present in the J1 and J2 blocks.

Listing 20.6: Sample Jastrow XML block.

```
<jastrow name="J2" type="Two-Body" function="Bspline" print="yes">
      <correlation rcut="10" size="10" speciesA="u" speciesB="u">
        <coefficients id="uu" type="Array">0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</
↪coefficients>
      </correlation>
      <correlation rcut="10" size="10" speciesA="u" speciesB="d">
        <coefficients id="ud" type="Array">0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</
↪coefficients>
      </correlation>
    </jastrow>
    <jastrow name="J1" type="One-Body" function="Bspline" source="ion0" print="yes">
      <correlation rcut="10" size="10" cusp="0" elementType="O">
        <coefficients id="eO" type="Array">0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</
↪coefficients>
      </correlation>
      <correlation rcut="10" size="10" cusp="0" elementType="H">
        <coefficients id="eH" type="Array">0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</
↪coefficients>
      </correlation>
    </jastrow>
    <jastrow name="J3" type="eeI" function="polynomial" source="ion0" print="yes">
      <correlation ispecies="O" especies="u" isize="3" esize="3" rcut="10">
        <coefficients id="uuO" type="Array" optimize="yes">
        </coefficients>
      </correlation>
      <correlation ispecies="O" especies1="u" especies2="d" isize="3" esize="3" rcut=
↪"10">
        <coefficients id="udO" type="Array" optimize="yes">
        </coefficients>
      </correlation>
      <correlation ispecies="H" especies="u" isize="3" esize="3" rcut="10">
```

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```
        <coefficients id="uuH" type="Array" optimize="yes">
        </coefficients>
      </correlation>
      <correlation ispecies="H" especies1="u" especies2="d" isize="3" esize="3" rcut=
↪"10">
        <coefficients id="udH" type="Array" optimize="yes">
        </coefficients>
      </correlation>
      </jastrow>
```

This training assumes basic familiarity with the UNIX operating system. In particular, we use simple scripts written in "csh." In addition, we assume you have obtained all the necessary files and executables and that the training files are located at ${TRAINING TOP}.

The goal of this training is not only to familiarize you with the execution and options in QMCPACK but also to introduce you to important concepts in QMC calculations and many-body electronic structure calculations.

CHAPTER

TWENTYONE

LAB 4: CONDENSED MATTER CALCULATIONS

21.1 Topics covered in this lab

- Tiling DFT primitive cells into QMC supercells
- Reducing finite-size errors via extrapolation
- Reducing finite-size errors via averaging over twisted boundary conditions
- Using the B-spline mesh factor to reduce memory requirements
- Using a coarsely resolved vacuum buffer region to reduce memory requirements
- Calculating the DMC total energies of representative 2D and 3D extended systems

21.2 Lab directories and files

```
labs/lab4_condensed_matter/
├── Be-2at-setup.py           - DFT only for prim to conv cell
├── Be-2at-qmc.py             - QMC only for prim to conv cell
├── Be-16at-qmc.py            - DFT and QMC for prim to 16 atom cell
├── graphene-setup.py         - DFT and OPT for graphene
├── graphene-loop-mesh.py     - VMC scan over orbital bspline mesh factors
├── graphene-final.py         - DMC for final meshfactor
└── pseudopotentials          - pseudopotential directory
    ├── Be.ncpp                 - Be PP for Quantum ESPRESSO
    ├── Be.xml                  - Be PP for QMCPACK
    ├── C.BFD.upf               - C  PP for Quantum ESPRESSO
    └── C.BFD.xml               - C  PP for QMCPACK
```

The goal of this lab is to introduce you to the somewhat specialized problems involved in performing DMC calculations on condensed matter as opposed to the atoms and molecules that were the focus of the preceding labs. Calculations will be performed on two different systems. Firstly, we will perform a series of calculations on BCC beryllium, focusing on the necessary methodology to limit finite-size effects. Secondly, we will perform calculations on graphene as an example of a system where QMCPACK's capability to handle cases with mixed periodic and open boundary conditions is useful. This example will also focus on strategies to limit memory usage for such systems. All of the calculations performed in this lab will use the Nexus workflow management system, which vastly simplifies the process by automating the steps of generating trial wavefunctions and performing DMC calculations.

21.3 Preliminaries

For any DMC calculation, we must start with a trial wavefunction. As is typical for our calculations of condensed matter, we will produce this wavefunction using DFT. Specifically, we will use QE to generate a Slater determinant of SPOs. This is done as a three-step process. First, we calculate the converged charge density by performing a DFT calculation with a fine grid of k-points to fully sample the Brillouin zone. Next, a non-self- consistent calculation is performed at the specific k-points needed for the supercell and twists needed in the DMC calculation (more on this later). Finally, a wavefunction is converted from the binary representation used by QE to the portable hdf5 representation used by QMCPACK.

The choice of k-points necessary to generate the wavefunctions depends on both the supercell chosen for the DMC calculation and by the supercell twist vectors needed. Recall that the wavefunction in a plane-wave DFT calculation is written using Bloch's theorem as:

$$\Psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) \,, \tag{21.1}$$

where $\vec{k}$ is confined to the first Brillouin zone of the cell chosen and $u(\vec{r})$ is periodic in this simulation cell. A plane-wave DFT calculation stores the periodic part of the wavefunction as a linear combination of plane waves for each SPO at all k-points selected. The symmetry of the system allows us to generate an arbitrary supercell of the primitive cell as follows: Consider the set of primitive lattice vectors, $\{\mathbf{a}_1^p, \mathbf{a}_2^p, \mathbf{a}_3^p\}$. We may write these vectors in a matrix, $\mathbf{L}_p$, the rows of which are the primitive lattice vectors. Consider a nonsingular matrix of integers, $\mathbf{S}$. A corresponding set of supercell lattice vectors, $\{\mathbf{a}_1^s, \mathbf{a}_2^s, \mathbf{a}_3^s\}$, can be constructed by the matrix product

$$\mathbf{a}_i^s = S_{ij}\mathbf{a}_j^p] \,. \tag{21.2}$$

If the primitive cell contains N_p atoms, the supercell will then contain $N_s = |\det(\mathbf{S})|N_p$ atoms.

Now, the wavefunciton at any point in this new supercell can be related to the wavefunction in the primitive cell by finding the linear combination of primitive lattice vectors that maps this point back to the primitive cell:

$$\vec{r}' = \vec{r} + x\mathbf{a}_1^p + y\mathbf{a}_2^p + z\mathbf{a}_3^p = \vec{r} + \vec{T} \,, \tag{21.3}$$

where x, y, z are integers. Now the wavefunction in the supercell at point $\vec{r}'$ can be written in terms of the wavefunction in the primitive cell at $\vec{r}'$ as:

$$\Psi(\vec{r}) = \Psi(\vec{r}')e^{i\vec{T}\cdot\vec{k}} \,, \tag{21.4}$$

where $\vec{k}$ is confined to the first Brillouin zone of the primitive cell. We have also chosen the supercell twist vector, which places a constraint on the form of the wavefunction in the supercell. The combination of these two constraints allows us to identify family of N k-points in the primitive cell that satisfy the constraints. Thus, for a given supercell tiling matrix and twist angle, we can write the wavefunction everywhere in the supercell by knowing the wavefunction a N k-points in the primitive cell. This means that the memory necessary to store the wavefunction in a supercell is only linear in the size of the supercell rather than the quadratic cost if symmetry were neglected.

21.4 Total energy of BCC beryllium

When performing calculations of periodic solids with QMC, it is essential to work with a reasonable size supercell rather than the primitive cells that are common in mean field calculations. Specifically, all of the finite-size correction schemes discussed in the morning require that the exchange-correlation hole be considerably smaller than the periodic simulation cell. Additionally, finite-size effects are lessened as the distance between the electrons in the cell and their periodic images increases, so it is advantageous to generate supercells that are as spherical as possible to maximize this distance. However, a competing consideration is that when calculating total energies we often want to extrapolate the energy per particle to the thermodynamic limit by means of the following formula in three dimensions:

$$E_{\text{inf}} = C + E_N/N \,. \tag{21.5}$$

This formula derived assuming the shape of the supercells is consistent (more specifically that the periodic distances scale uniformly with system size), meaning we will need to do a uniform tiling, that is, $2 \times 2 \times 2$, $3 \times 3 \times 3$, etc. As a $3 \times 3 \times 3$ tiling is 27 times larger than the supercell and the practical limit of DMC is on the order of 200 atoms (depending on Z), sometimes it is advantageous to choose a less spherical supercell with fewer atoms rather than a more spherical one that is too expensive to tile.

In the case of a BCC crystal, it is possible to tile the one atom primitive cell to a cubic supercell only by doubling the number of electrons. This is the best possible combination of a small number of atoms that can be tiled and a regular box that maximizes the distance between periodic images. We will need to determine the tiling matrix S that generates this cubic supercell by solving the following equation for the coefficients of the S matrix:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{bmatrix} \cdot \begin{bmatrix} 0.5 & 0.5 & -0.5 \\ -0.5 & 0.5 & 0.5 \\ 0.5 & -0.5 & 0.5 \end{bmatrix} . \tag{21.6}$$

We will now use Nexus to generate the trial wavefunction for this BCC beryllium.

Fortunately, the Nexus will handle determination of the proper k-vectors given the tiling matrix. All that is needed is to place the tiling matrix in the `Be-2at-setup.py` file. Now the definition of the physical system is

```
bcc_Be = generate_physical_system(
    lattice    = 'cubic',
    cell       = 'primitive',
    centering  = 'I',
    atoms      = 'Be',
    constants  = 3.490,
    units      = 'A',
    net_charge = 0,
    net_spin   = 0,
    Be         = 2,
    tiling     = [[a,b,c],[d,e,f],[g,h,i]],
    kgrid      = kgrid,
    kshift     = (.5,.5,.5)
    )
```

where the tiling line should be replaced with the preceding row major tiling matrix. This script file will now perform a converged DFT calculation to generate the charge density in a directory called `bcc-beryllium/scf` and perform a non-self-consistend DFT calculation to generate SPOs in the directory `bcc-beryllium/nscf`. Fortunately, Nexus will calculate the required k-points needed to tile the wavefunction to the supercell, so all that is necessary is the granularity of the supercell twists and whether this grid is shifted from the origin. Once this is finished, it performs the conversion from pwscf's binary format to the hdf5 format used by QMCPACK. Finally, it will optimize the coefficients of 1-body and 2-body Jastrow factors in the supercell defined by the tiling matrix.

Run these calculations by executing the script `Be-2at-setup.py`. You will notice the small calculations required to generate the wavefunction of beryllium in a one-atom cell are rather inefficient to run on a high-performance computer such as vesta in terms of the time spent doing calculations versus time waiting on the scheduler and booting compute nodes. One of the benefits of the portable HDF format that is used by QMCPACK is that you can generate data like wavefunctions on a local workstation or other convenient resource and use high-performance clusters for the more expensive QMC calculations.

In this case, the wavefunction is generated in the directory `bcc-beryllium/nscf-2at_222/pwscf_ output` in a file called `pwscf.pwscf.h5`. For debugging purposes, it can be useful to verify that the contents of this file are what you expect. For instance, you can use the tool `h5ls` to check the geometry of the cell where the DFT calculations were performed or the number of k-points or electrons in the calculation. This is done with the command h5ls -d pwscf.pwscf.h5/supercell or h5ls -d pwscf.pwscf.h5/electrons.

In the course of running `Be-2at-setup.py`, you will get an error when attempting to perform the VMC and wavefunction optimization calculations. This is because the wavefunction has generated supercell twists of the form (+/- 1/4, +/- 1/4, +/- 1/4). In the case that the supercell twist contains only 0 or 1/2, it is possible to operate entirely with

real arithmetic. The executable that has been indicated in `Be-2at-setup.py` was compiled for this case. Note that where possible, the memory use is a factor of two less than the general case and the calculations are somewhat faster. However, it is often necessary to perform calculations away from these special twist angles to reduce finite-size effects. To fix this, delete the directory `bcc-beryllium/opt-2at`, change the line near the top of `Be-2at-setup.py` from

```
qmcpack    = '/soft/applications/qmcpack/Binaries/qmcpack'
```

to

```
qmcpack    = '/soft/applications/qmcpack/Binaries/qmcpack_comp'
```

and rerun the script.

When the optimization calculation has finished, check that everything has proceeded correctly by looking at the output in the `opt-2at` directory. Firstly, you can grep the output file for Delta to see if the cost function has indeed been decreasing during the optimization. You should find something like this:

```
OldCost: 4.8789147e-02 NewCost: 4.0695360e-02 Delta Cost:-8.0937871e-03
OldCost: 3.8507795e-02 NewCost: 3.8338486e-02 Delta Cost:-1.6930674e-04
OldCost: 4.1079105e-02 NewCost: 4.0898345e-02 Delta Cost:-1.8076319e-04
OldCost: 4.2681333e-02 NewCost: 4.2356598e-02 Delta Cost:-3.2473514e-04
OldCost: 3.9168577e-02 NewCost: 3.8552883e-02 Delta Cost:-6.1569350e-04
OldCost: 4.2176276e-02 NewCost: 4.2083371e-02 Delta Cost:-9.2903058e-05
OldCost: 4.3977361e-02 NewCost: 4.2865751e-02 Delta Cost:-1.11161830-03
OldCost: 4.1420944e-02 NewCost: 4.0779569e-02 Delta Cost:-6.4137501e-04
```

which shows that the starting wavefunction was fairly good and that most of the optimization occurred in the first step. Confirm this by using `qmca` to look at how the energy and variance changed over the course of the calculation with the command: `qmca -q ev -e 10 *.scalar.dat` executed in the `opt-2at directory`. You should get output like the following:

```
                  LocalEnergy              Variance              ratio
opt  series 0  -2.159139 +/- 0.001897   0.047343 +/- 0.000758   0.0219
opt  series 1  -2.163752 +/- 0.001305   0.039389 +/- 0.000666   0.0182
opt  series 2  -2.160913 +/- 0.001347   0.040879 +/- 0.000682   0.0189
opt  series 3  -2.162043 +/- 0.001223   0.041183 +/- 0.001250   0.0190
opt  series 4  -2.162441 +/- 0.000865   0.039597 +/- 0.000342   0.0183
opt  series 5  -2.161287 +/- 0.000732   0.039954 +/- 0.000498   0.0185
opt  series 6  -2.163458 +/- 0.000973   0.044431 +/- 0.003583   0.0205
opt  series 7  -2.163495 +/- 0.001027   0.040783 +/- 0.000413   0.0189
```

Now that the optimization has completed successfully, we can perform DMC calculations. The first goal of the calculations will be to try to eliminate the 1-body finite-size effects by twist averaging. The script `Be-2at-qmc.py` has the necessary input. Note that on line 42 two twist grids are specified, (2,2,2) and (3,3,3). Change the tiling matrix in this input file as in `Be-2at-qmc.py` and start the calculations. Note that this workflow takes advantage of QMCPACK's capability to group jobs. If you look in the directory `dmc-2at_222` at the job submission script (`dmc.qsub.in`), you will note that rather than operating on an XML input file, `qmcapp` is targeting a text file called `dmc.in`. This file is a simple text file that contains the names of the eight XML input files needed for this job, one for each twist. When operated in this mode, QMCPACK will use MPI groups to run multiple copies of itself within the same MPI context. This is often useful both in terms of organizing calculations and for taking advantage of the large job sizes that computer centers often encourage.

The DMC calculations in this case are designed to complete in a few minutes. When they have finished running, first look at the `scalar.dat` files corresponding to the DMC calculations at the various twists in `dmc-2at_222`. Using a command such as `qmca -q ev -e 32 *.s001.scalar.dat` (with a suitably chosen number of blocks for the equilibration), you will see that the DMC energy in each calculation is nearly identical within the statistical uncertainty of the calculations. In the case of a large supercell, this is often indicative of a situation where the Brillouin zone

is so small that the 1-body finite-size effects are nearly converged without any twist averaging. In this case, however, this is because of the symmetry of the system. For this cubic supercell, all of the twist angles chosen in this shifted $2 \times 2 \times 2$ grid are equivalent by symmetry. In the case where substantial resources are required to equilibrate the DMC calculations, it can be beneficial to avoid repeating such twists and instead simply weight them properly. In this case, however, where the equilibration is inexpensive, there is no benefit to adding such complexity as the calculations can simply be averaged together and the result is equivalent to performing a single longer calculation.

Using the command `qmc -a -q ev -e 16 *.s001.scalar.dat`, average the DMC energies in `dmc-2at_222 and dmc-2at_333` to see whether the 1-body finite-size effects are converged with a $3 \times 3 \times 3$ grid of twists. When using beryllium as a metal, the convergence is quite poor (0.025 Ha/Be or 0.7 eV/Be). If this were a production calculation it would be necessary to perform calculations on much larger grids of supercell twists to eliminate the 1-body finite-size effects.

In this case there are several other calculations that would warrant a high priority. Script `Be-16at-qmc.py` has been provided in which you can input the appropriate tiling matrix for a 16-atom cell and perform calculations to estimate the 2-body finite-size effects, which will also be quite large in the 2-atom calculations. This script will take approximately 30 minutes to run to completion, so depending on your interest, you can either run it or work to modify the scripts to address the other technical issues that would be necessary for a production calculation such as calculating the population bias or the time step error in the DMC calculations.

Another useful exercise would be to attempt to validate this PP by calculating the ionization potential and electron affinity of the isolated atom and compare it with the experimental values: IP = 9.3227 eV , EA = 2.4 eV.

21.5 Handling a 2D system: graphene

In this section we examine a calculation of an isolated sheet of graphene. Because graphene is a 2D system, we will take advantage of QMCPACK's capability to mix periodic and open boundary conditions to eliminate and spurious interaction of the sheet with its images in the z direction. Run the script `graphene-setup.py`, which will generate the wavefunction and optimize one and two body jastrow factors. In the script; notice line 160: bconds = 'ppn' in the generate_qmcpack function, which specifies this mix of open and periodic boundary conditions. Consequently, the atoms will need to be kept away from this open boundary in the z direction as the electronic wavefunction will not be defined outside of the simulation box in this direction. For this reason, all of the atom positions at the beginning of the file have z coordinates 7.5. At this point, run the script `graphene-setup.py`.

Aside from the change in boundary conditions, the main thing that distinguishes this kind of calculation from the previous beryllium example is the large amount of vacuum in the cell. Although this is a very small calculation designed to run quickly in the tutorial, in general a more converged calculation would quickly become memory limited on an architecture like BG/Q. When the initial wavefunction optimization has completed to your satisfaction, run the script `graphene-loop-mesh.py`. This examines within VMC an approach to reducing the memory required to store the wavefunction. In `graphene-loop-mesh.py`, the spacing between the B-spline points is varied uniformly. The mesh spacing is a prefactor to the linear spacing between the spline points, so the memory use goes as the cube of the meshfactor. When you run the calculations, examine the `.s000.scalar.dat` files with `qmca` to determine the lowest possible mesh spacing that preserves both the VMC energy and the variance.

Finally, edit the file `graphene-final.py`, which will perform two DMC calculations. In the first, (qmc1) replace the following lines:

```
meshfactor    = xxx,
precision     = '---',
```

with the values you have determined will perform the calculation with as small as possible wavefunction. Note that we can also use single precision arithmetic to store the wavefunction by specifying precision=`single.' When you run the script, compare the output of the two DMC calculations in terms of energy and variance. Also, see if you can calculate the fraction of memory that you were able to save by using a meshfactor other than 1 and single precision arithmetic.

21.6 Conclusion

Upon completion of this lab, you should be able to use Nexus to perform DMC calculations on periodic solids when provided with a PP. You should also be able to reduce the size of the wavefunction in a solid-state calculation in cases where memory is a limiting factor.

CHAPTER

TWENTYTWO

LAB 5: EXCITED STATE CALCULATIONS

22.1 Topics covered in this lab

- Tiling DFT primitive cells into optimal QMC supercells
- Fundamentals of between neutral and charged calculations
- Calculating quasiparticle excitation energies of condensed matter systems
- Calculating optical excitation energies of condensed matter systems

22.2 Lab directories and files

```
labs/lab5_excited_properties/
├── band.py           - Band structure calculation for Carbon Diamond
├── optical.py        - VMC optical gap calculation using the tiling matrix from band.
↪py
├── quasiparticle.py  - VMC quasiparticle gap calculation using the tiling matrix␣
↪from band.py
└── pseudopotentials      - pseudopotential directory
    ├── C.BFD.upf         - C PP for Quantum ESPRESSO
    └── C.BFD.xml         - C PP for QMCPACK
```

The goal of this lab is to perform neutral and charged excitation calculations in condensed matter systems using QMCPACK. Throughout this lab, a working knowledge of *Lab4 Condensed Matter Calculations* is assumed. First, we will introduce the concepts of neutral and charged excitations. We will briefly discuss these in relation to the specific experimental studies that must be used to benchmark DMC results. Secondly, we will perform charged (quasiparticle) and neutral (optical) excitations calculations on C-diamond.

22.3 Basics and excited state experiments

Although VMC and DMC methods are better suited for studying ground state properties of materials, they can still provide useful information regarding the excited states. Unlike the applications of band structure theory such as DFT and GW, it is more challenging to obtain the complete excitation spectra using DMC. However, it is relatively straightforward to calculate the band gap minimum of a condensed matter system using DMC.

We will briefly discuss the two main ways of obtaining the band gap minimum through experiments: photoemission and absorption studies. The energy required to remove an electron from a neutral system is called the IP (ionization potential), which is available from direct photoemission experiments. In contrast, the emission energy of a negatively charged system (or the energy required to convert a negatively charged system to a neutral system), known as electron

affinity (EA), is available from inverse photoemission experiments. Outlines of these experiments are shown in Fig. 22.1.

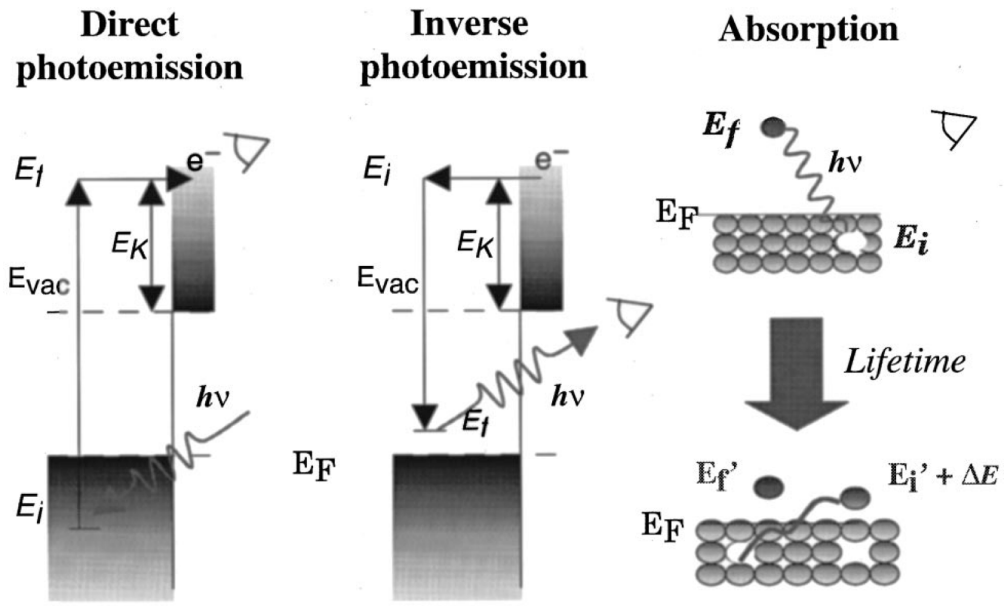


Fig. 22.1: Direct and inverse photoemission experiments involve charged excitations, whereas optical absorption experiments involve excitations that are just enough to be excited to the conduction band. From [[ORR02]]

Following the explanation in the previous paragraph and Fig. 22.1, the *quasiparticle* band gap of a material can be defined as:

$$E_g = EA - IP = (E_{N+1}^{CBM} - E_N^{K'}) - (E_N^{K'} - E_{N-1}^{VBM}) = E_{N+1}^{CBM} + E_{N-1}^{VBM} - 2 * E_N^{K'}, \tag{22.1}$$

where N is the number of electrons in the neutral system and E_N is the ground state energy of the neutral system. CBM and VBM stand for the conduction band minimum and valence band maximum, respectively. K' can formally be arbitrary at the infinite limit. However, in practical calculations, a supertwist that accommodates both CBM and VBM can be more efficient in terms of computational time and systematic finite-size error cancellation. In the literature, the quasiparticle gap is also called the electronic gap. The term electronic comes from the fact that in both photoemission experiments, it is assumed that the perturbed electron is not interacting with the sample.

Additionally, absorption experiments can be performed in which electrons are perturbed at relatively lower energies, just enough to be excited into the conduction band. In absorption experiments, electrons are perturbed at lower energies. Therefore, they are not completely free and the system is still considered neutral. Since a *quasihole* and *quasielectron* are formed simultaneously, a bound state is created, unlike the free electron in the quasiparticle gap as described previously. This process is also known as *optical* excitation, which is schematically shown in Fig. 22.1, under "Absorption." The optical gap can be formulated as follows:

$$E_g^{K_1 \to K_2} = E^{K_1 \to K_2} - E_0, \tag{22.2}$$

where $E^{K_1 \to K_2}$ is the energy of the system when a valence electron at wavevector K_1 is promoted to the conduction band at wavevector K_2. Therefore, the $E_g^{K_1 \to K_2}$ is called the optical gap for promoting an electron at K_1 to K_2. If both CBM and VBM are on the same k-vector then the material is called direct band gap since it can directly emit

photons without any external perturbation (phonons). However, if CBM and VBM share different k-vectors, then the photon-emitting electron has to transfer some of its momenta to the crystal lattice and then decay to the ground state. As this process involves an intermediate step, this property is called the indirect band gap. The difference between the optical and electronic band gaps is called the exciton binding energy. Exciton binding energy is very important for optoelectronic applications such as lasers. Since the recombination usually occurs between free holes and free electrons, a bound electron and hole state means that the spectrum of emission energies will be narrower. In the examples that follow, we will investigate the optical excitations of C-diamond.

22.4 Preparation for the excited state calculations

In this section, we will study the preparation steps to perform excited state calculations with QMC. Here, the most basic steps are listed in the implementation order:

1. Identify the high-symmetry k-points of the standardized primitive cell.
2. Perform DFT band structure calculation along high-symmetry paths.
3. Find a supertwist that includes all the k-points of interest.
4. Identify the indexing of k-points in the supertwist to be used in QMCPACK.

22.4.1 Identifying high-symmetry k-points

Primitive cell is the most basic, nonunique repeat unit of a crystal in real space. However, the translations of the repeat unit, the Bravais lattice is unique for each crystal and can be represented using discrete translation operations, R_n:

$$\mathbf{R_n} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}\ , \tag{22.3}$$

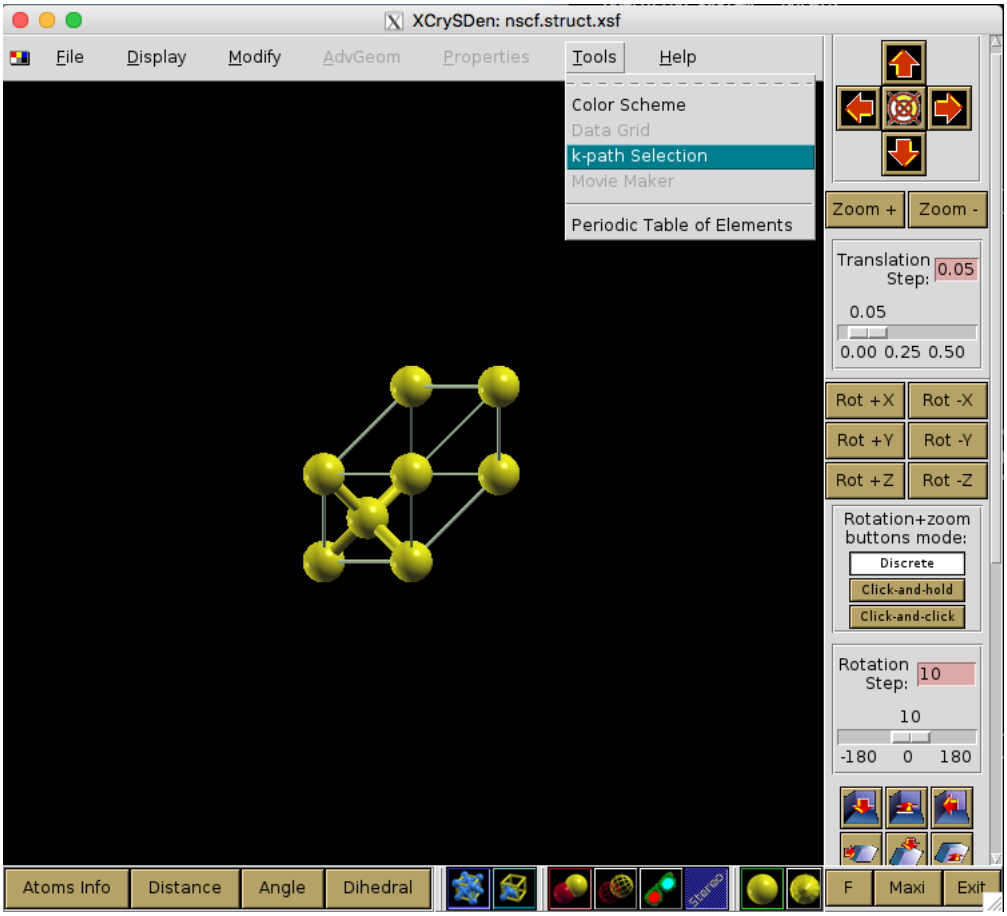
a_n are the real-space lattice vectors in three dimensions. Thanks to the periodicity of the Bravais lattice, a crystal can also be represented using periodic functions in the reciprocal space:

$$f(\mathbf{R_n} + \mathbf{r}) = \sum_m f_m e^{iG_m(\mathbf{R_n}+\mathbf{r})}, \tag{22.4}$$

where G_m are called as the reciprocal lattice vectors. (22.4) also satisfies the equality $G_m \cdot R_n = 2\pi N$. High-symmetry structures can be represented using a subspace of the BZ, which is called as the irreducible Brillouin Zone (iBZ). If we choose a series of paths of high-symmetry k-points that encapsulates the iBZ, we can determine the band gap and electronic structure of the material. For more discussion, please refer to any solid-state physics textbook.

There are multiple practical ways to find the high-symmetry k-point path. For example, pymatgen, [[ORJ+13]] XCRYSDEN [[Kok99]] or SeeK-path [[HPK+17]] can be used.

Fig. 22.2 shows the procedure for visualizing the Brillouin Zone using XCRYSDEN after the structure file is loaded. However, the primitive cell is not unique, and the actual shape of the BZ can depend on the structure used. In our example, we use the Python libraries of SeeK-path, using a wrapper written in Nexus.



SeeK-path includes routines to standardize primitive cells, which will be useful for our work.

SeeK-path can be installed easily using `pip`:

```
>pip install --user seekpath
```

In the `band.py` script, identification of high-symmetry k-points and band structure calculations are done within the workflow. In the script, where the `dia` PhysicalSystem object is used as the input structure, `dia2_structure` is the standardized primitive cell and `dia2_kpath` is the respective k-path around the iBZ. `dia2_kpath` has a dictionary of the k-path in various coordinate systems; please make sure you are using the right one.

```
from structure import get_primitive_cell, get_kpath
dia2_structure   = get_primitive_cell(structure=dia.structure)['structure']
dia2_kpath       = get_kpath(structure=dia2_structure)
```

22.4.2 DFT band structure calculation along high-symmetry paths

After the high-symmetry k-points are identified, band structure calculations can be performed in DFT. For an insulating structure, DFT can provide VBM and CBM wavevectors, which would be of interest to the DMC calculations. However, if available, CBM and VBM from DFT would need to be compared with the experiments. Basically, `band.py` will do the following:

1. Perform an SCF calculation in QE using a high-density reciprocal grid.
2. Identify the high-symmetry k-points on the iBZ and provide a k-path.

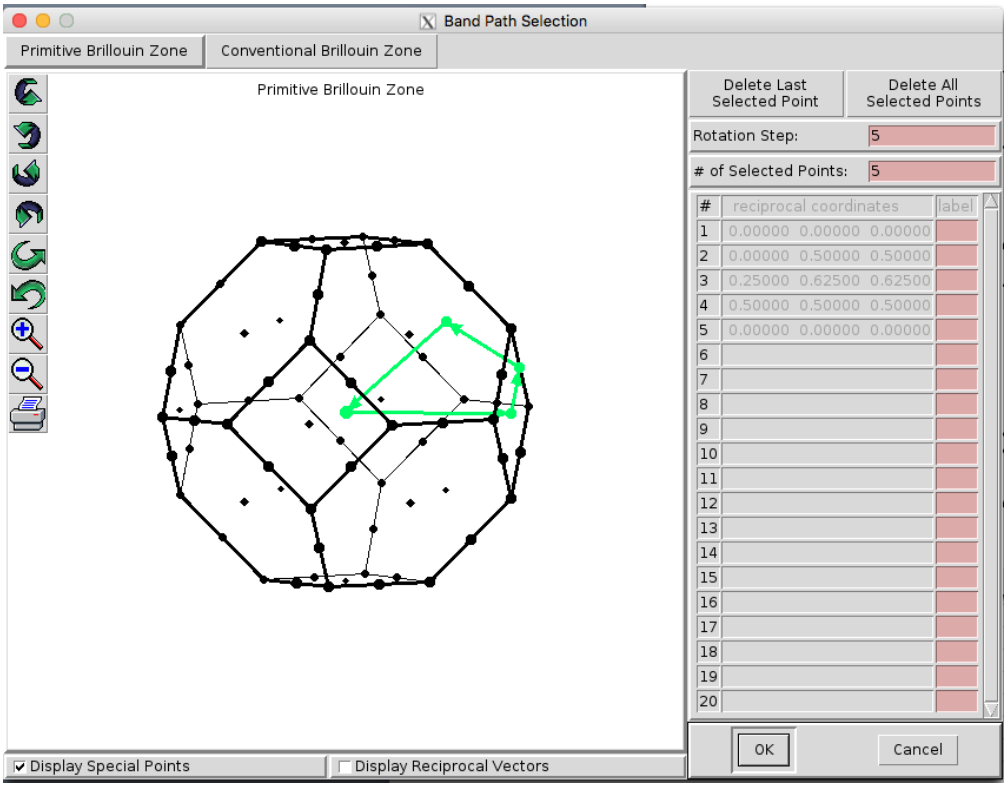


Fig. 22.2: Visualizing the Brillouin Zone using XCRYSDEN.

3. Perform a "band" calculation in QE, explicitly writing all the k-points on the path. (Make sure to add extra unoccupied bands.)
4. Plot the band structure curves and location of VBM/CBM if available.

In Fig. 22.3, C-diamond is shown to have an indirect band gap between the red and green dots (CBM and VBM, respectively). VBM is located at Γ. CBM is not located on a high-symmetry k-point in this case. Therefore, we can use the symbol Δ to denote the CBM wavevector in the rest of this document. In `band.py` script, once the band structure calculation is finished, you can use the following lines to get the exact location of VBM and CBM using

```
p = band.load_analyzer_image()
print "VBM:\n{0}".format(p.bands.vbm)
print "CBM:\n{0}".format(p.bands.cbm)
```

Output must be the following:

```
VBM:
  band_number      = 3
  energy           = 13.2874
  index            = 0
  kpoint_2pi_alat  = [0. 0. 0.]
  kpoint_rel       = [0. 0. 0.]
  pol              = up

CBM:
  band_number      = 4
  energy           = 17.1545
  index            = 51
```

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```
kpoint_2pi_alat = [0.         0.1095605 0.        ]
kpoint_rel      = [0.3695652 0.         0.3695652]
pol             = up
```

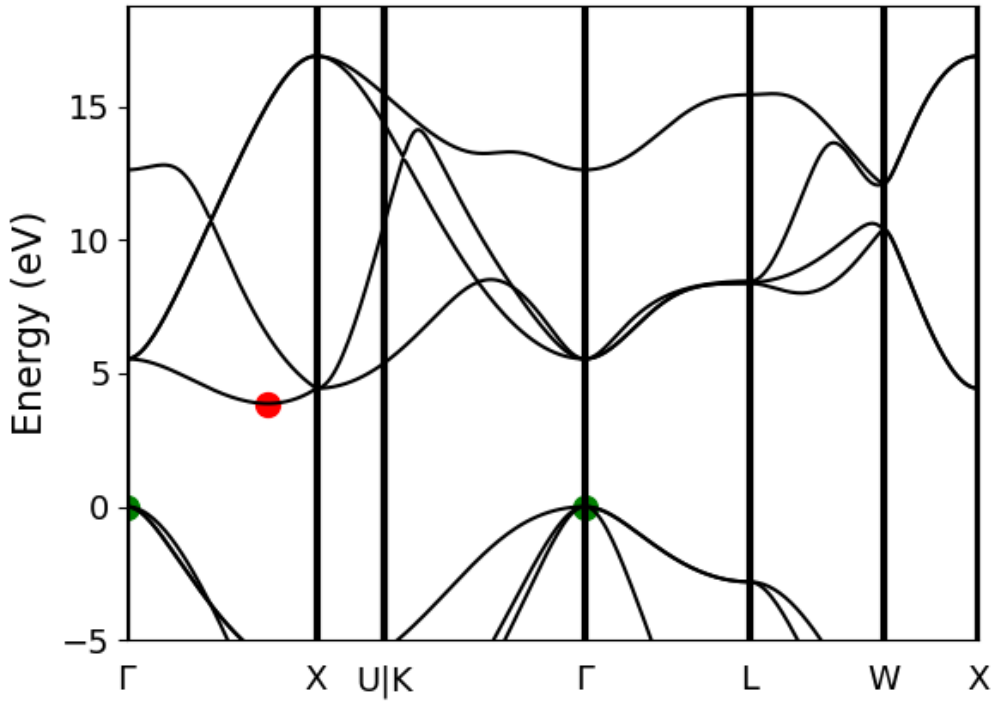

Fig. 22.3: Band structure calculation of C-diamond performed at the DFT-LDA level. CBMs are shown with red points, and the VBMs are shown with the green points, both at Γ. DFT-LDA calculations suggest that the material has an indirect band gap from $\Gamma \rightarrow \Delta$. However, $\Gamma \rightarrow \Gamma$ transition can also be investigated for more complete check.

22.4.3 DFT band structure calculation along high-symmetry paths

After the high-symmetry k-points are identified, band structure calculations can be performed in DFT. For an insulating structure, DFT can provide VBM and CBM wavevectors, which would be of interest to the DMC calculations. However, if available, CBM and VBM from DFT would need to be compared with the experiments. Basically, `band.py` will do the following:

1. Perform an SCF calculation in QE using a high-density reciprocal grid.
2. Identify the high-symmetry k-points on the iBZ and provide a k-path.
3. Perform a "band" calculation in QE, explicitly writing all the k-points on the path. (Make sure to add extra unoccupied bands.)
4. Plot the band structure curves and location of VBM/CBM if available.

In Fig. 22.3, C-diamond is shown to have an indirect band gap between the red and green dots (CBM and VBM, respectively). VBM is located at Γ. CBM is not located on a high-symmetry k-point in this case. Therefore, we can use the symbol Δ to denote the CBM wavevector in the rest of this document. In script, once the band structure calculation is finished, you can use the following lines to get the exact location of VBM and CBM using

```
p = band.load_analyzer_image()
print "VBM:\n{0}".format(p.bands.vbm)
print "CBM:\n{0}".format(p.bands.cbm)
```

Output must be the following:

```
VBM:
  band_number     = 3
  energy          = 13.2874
  index           = 0
  kpoint_2pi_alat = [0. 0. 0.]
  kpoint_rel      = [0. 0. 0.]
  pol             = up

CBM:
  band_number     = 4
  energy          = 17.1545
  index           = 51
  kpoint_2pi_alat = [0.        0.1095605 0.       ]
  kpoint_rel      = [0.3695652 0.        0.3695652]
  pol             = up
```

22.4.4 Finding a supertwist that includes all the k-points of interest

Using the VBM and CBM wavevectors defined in the previous section, we now construct the supertwist, which will hopefully contain both VBM and CBM. In Fig. 22.4, we provide a simple example using 2D rectangular lattice. Let us assume that we are interested in the indirect transition, $\Gamma \rightarrow X_1$. In Fig. 22.4 a, the first BZ of the primitive cell is shown as the square centered on Γ, which is drawn using dashed lines. Because of the periodicity of the lattice, this primitive cell BZ repeats itself with spacings equal to the reciprocal lattice vectors: (2π/a, 0) and (0, 2π/a) or (1,0) and (0,1) in crystal coordinates. We are interested in the first BZ, where X_1 is at (0,0.5). In Fig. 22.4 b, the first BZ of the 2×2 supercell is the smaller square, drawn using solid lines. In Fig. 22.4 c, the BZ of the 2×2 supercell also repeats in the space, similar to Fig. 22.4 a. Therefore, in the 2×2 supercell, X_1, X_2, and R are only the periodic images of Γ. The 2×2 supercell calculation can be performed in reciprocal space using a [2,2] tiling matrix. Therefore, individual k-points (twists) of the primitive cell are combined in the supercell calculation, which are then called as supertwists. In more complex primitive cells (hence BZ), more general criteria would be constructing a set of supercell reciprocal lattice vectors that contain the $\Gamma \rightarrow X_1$ (e.g., G_1 in Fig. 22.4) vector within their convex hull. Under this constraint, the Wigner-Seitz radius of the simulation cell can be maximized in an effort to reduce finite-size errors.

For the case of the indirect band gap in Diamond, several approximations might be needed to generate a supertwist that corresponds to a reasonable simulation cell. In the Diamond band gap, Δ is at . In your calculations, the Δ wavevector and the eigenvalues you find can be slightly different in value. The closest simple fraction to this number with the smallest denominator is 1/3. If we use $\Delta' = [1/3, 0., 1/3]$, we could use a $3 \times 1 \times 3$ supercell as the simple choice and include both Δ' and Γ in the same supertwist exactly. Near Δ, the LDA band curvature is very low and using Δ' can be a good approximation. We can compare the eigenvalues using their index numbers:

```
>>> print p.bands.up[51] ## CBM, $\Delta$ ##
  eigs            = [-3.2076  4.9221  7.5433  7.5433 17.1545 19.7598 28.3242 28.3242]
  index           = 51
  kpoint_2pi_alat = [0.        0.1095605 0.       ]
  kpoint_rel      = [0.3695652 0.        0.3695652]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
>>> print p.bands.up[46] ## $\Delta'$ ##
  eigs            = [-4.0953  6.1376  7.9247  7.9247 17.1972 20.6393 27.3653 27.3653]
```

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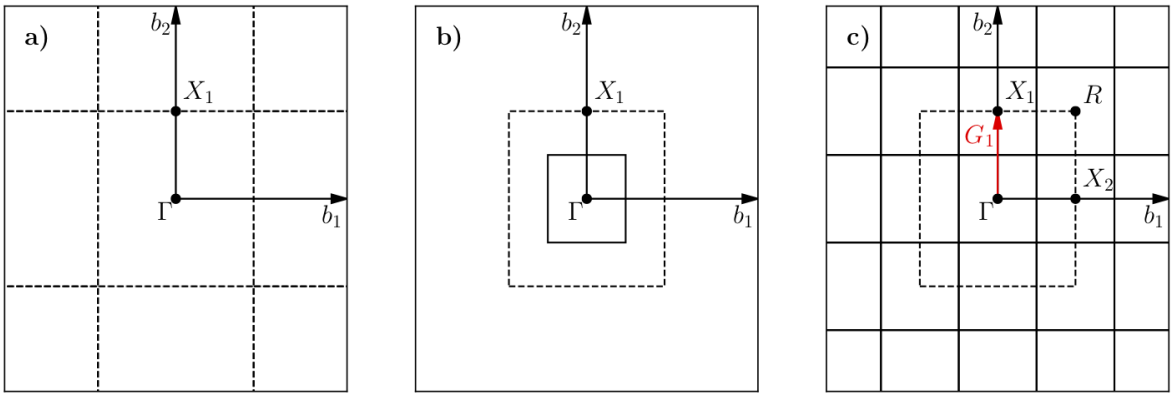

Fig. 22.4: a) First BZ of the primitive cell centered on Γ. Dashed lines indicate zone boundaries. b) First BZ of the 2×2 supercell inside the first BZ of the primitive cell. First BZ boundaries of the supercell are shown using solid lines. c) Periodic translations of the first BZ of the supercell showing that Γ and X_1 are periodic images of each other given the supercell BZ.

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```
  index           = 46
  kpoint_2pi_alat = [0.         0.0988193 0.        ]
  kpoint_rel      = [0.3333333 0.        0.3333333]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
```

This shows that the eigenvalues of the first unoccupied bands in Δ and Δ′ are 17.1545 and 17.1972 eV, respectively, meaning that according to LDA, a correction of nearly -40 meV is obtained. After electronic transitions between Γ and Δ′ are studied using DMC, the LDA correction can be applied to extrapolate the results to Γ and Δ transitions.

22.4.5 Identifying the indexing of k-points of interest in the supertwist

At this stage, we must have performed an *scf* calculation using a converged k-point grid and then an *nscf* calculation using the supertwist k-points given previously. We will be using the orbitals from neutral DFT calculations; therefore, we need to explicitly define the band and twist indexes of the excitations in QMCPACK (e.g., to define electron promotion). In C-diamond, we can give an example by finding the band and twist indexes of Γ and Δ′. For this end, a mock VMC calculation can be run and the `einspline.tile_300010003 .spin_0.tw_0.g0.bandinfo.dat` file read. The Einspline file prints out the eigenstates information from DFT calculations. Therefore, we can obtain the band and the state index from this file, which can later be used to define the electron promotion. You can see in the following an explanation of how the band and twist indexes are defined using a portion of the `einspline.tile_300010003.spin_0.tw_0.g0.bandinfo.dat` file. Spin_0 in the file name suggests that we are reading the spin-up eigenstates. Band, state, twistindex, and bandindex numbers all start from zero. We know we have 72 electrons in the simulation cell, with 36 of them spin-up polarized. Since the state number starts from zero, state number 35 must be occupied while state 36 should be unoccupied. States 35 and 36 have the same reciprocal crystal coordinates (K1,K2,K3) as Γ and Δ′, respectively. Therefore, an electron should be promoted from state number 35 to 36 to study the indirect band gap here.

```
#  Band State TwistIndex BandIndex Energy Kx Ky Kz K1 K2 K3 KmK
33 33 0  1     0.488302  0.0000  0.0000  0.0000 -0.0000 -0.0000 -0.0000      1
34 34 0  2     0.488302  0.0000  0.0000  0.0000 -0.0000 -0.0000 -0.0000      1
35 35 0  3     0.488302  0.0000  0.0000  0.0000 -0.0000 -0.0000 -0.0000      1
36 36 4  4     0.631985  0.0000 -0.6209  0.0000 -0.3333 -0.0000 -0.3333      1
```

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```
37 37 8  4     0.631985  0.0000 -1.2418  0.0000 -0.6667 -0.0000 -0.6667       1
38 38 0  4     0.691907  0.0000  0.0000  0.0000 -0.0000 -0.0000 -0.0000       1
```

However, we should always check whether this is really what we want. It can be seen that bands 33, 34, and 35 are degenerate (energy eigenvalues are listed in the 5th column), but they also have the same reciprocal coordinates in (K1,K2,K3). This is actually expected as one can see from Fig. 22.3, in the band diagram the band structure is threefold degenerate at Γ. Here, we can choose the state with the largest band index: (0,3). Following the (twistindex, bandindex) notation, we can say that Γ to Δ' transition can be defined as from (0,3) to (4,4).

Alternatively, we can also read the band and twist indexes using PwscfAnalyzer and determine the band/twist indexes on the go:

```
p = nscf.load_analyzer_image()
print 'band information'
print p.bands.up
print 'twist 0 k-point:',p.bands.up[0].kpoint_rel
print 'twist 4 k-point:',p.bands.up[4].kpoint_rel
print 'twist 0 band 3 eigenvalue:',p.bands.up[0].eigs[3]
print 'twist 4 band 4 eigenvalue:',p.bands.up[4].eigs[4]
```

Giving output:

```
0
  eigs            = [-8.0883 13.2874 13.2874 13.2874 18.8277 18.8277 18.8277 25.9151]
  index           = 0
  kpoint_2pi_alat = [0. 0. 0.]
  kpoint_rel      = [0. 0. 0.]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
1
  eigs            = [-5.0893  3.8761 10.9518 10.9518 21.5031 21.5031 21.5361 28.2574]
  index           = 1
  kpoint_2pi_alat = [-0.0494096  0.0494096  0.0494096]
  kpoint_rel      = [0.3333333 0.        0.       ]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
2
  eigs            = [-5.0893  3.8761 10.9518 10.9518 21.5031 21.5031 21.5361 28.2574]
  index           = 2
  kpoint_2pi_alat = [-0.0988193  0.0988193  0.0988193]
  kpoint_rel      = [0.6666667 0.        0.       ]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
3
  eigs            = [-5.0893  3.8761 10.9518 10.9518 21.5031 21.5031 21.5361 28.2574]
  index           = 3
  kpoint_2pi_alat = [ 0.0494096  0.0494096 -0.0494096]
  kpoint_rel      = [0.        0.        0.3333333]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
4
  eigs            = [-4.0954  6.1375  7.9247  7.9247 17.1972 20.6393 27.3652 27.3652]
  index           = 4
  kpoint_2pi_alat = [0.        0.0988193 0.       ]
  kpoint_rel      = [0.3333333 0.        0.3333333]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
```

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```
  pol             = up
5
  eigs            = [-0.6681  2.3791  3.7836  8.5596 19.3423 26.2181 26.6666 28.0506]
  index           = 5
  kpoint_2pi_alat = [-0.0494096  0.1482289  0.0494096]
  kpoint_rel      = [0.6666667 0.        0.3333333]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
6
  eigs            = [-5.0893  3.8761 10.9518 10.9518 21.5031 21.5031 21.5361 28.2574]
  index           = 6
  kpoint_2pi_alat = [ 0.0988193  0.0988193 -0.0988193]
  kpoint_rel      = [0.        0.        0.6666667]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
7
  eigs            = [-0.6681  2.3791  3.7836  8.5596 19.3423 26.2181 26.6666 28.0506]
  index           = 7
  kpoint_2pi_alat = [ 0.0494096  0.1482289 -0.0494096]
  kpoint_rel      = [0.3333333 0.        0.6666667]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up
8
  eigs            = [-4.0954  6.1375  7.9247  7.9247 17.1972 20.6393 27.3652 27.3652]
  index           = 8
  kpoint_2pi_alat = [0.        0.1976385 0.       ]
  kpoint_rel      = [0.6666667 0.        0.6666667]
  occs            = [1. 1. 1. 1. 0. 0. 0. 0.]
  pol             = up

twist 0 k-point: [0. 0. 0.]
twist 4 k-point: [0.3333333 0.        0.3333333]
twist 0 band 3 eigenvalue: 13.2874
twist 4 band 4 eigenvalue: 17.1972
```

22.5 Quasiparticle (electronic) gap calculations

In quasiparticle calculations, it is essential to work with reasonably large sized supercells to avoid spurious "1/N effects." Since quasiparticle calculations involve charged cells, large simulation cells ensure that the extra charge is diluted over the simulation cell. Coulombic interactions are conditionally convergent for neutral periodic systems, but they are divergent for the charged systems. A typical workflow for a quasiparticle calculation includes the following:

1. Run an SCF calculation in a neutral charged cell with QE using a high-density reciprocal grid.
2. Choose a tiling matrix that will at least approximately include VBM and CBM k-points.
3. Run 'nscf'/'p2q' calculations using the tiling matrix.
4. Run VMC/DMC calculations for the neutral and positively and negatively charged cells in QMCPACK.
5. Check the convergence of the quasiparticle gap with respect to the simulation cell size.

```
<particleset name="e" random="yes">
  <group name="u" size="36" mass="1.0"> ##Change size to 35
    <parameter name="charge"              >    -1                    </parameter>
    <parameter name="mass"                >    1.0                   </parameter>
```

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```
  </group>
...
...
<determinantset>
  <slaterdeterminant>
    <determinant id="updet" group="u" sposet="spo_u" size="36"> ##Change size to 35
      <occupation mode="ground" spindataset="0"/>
    </determinant>
    <determinant id="downdet" group="d" sposet="spo_d" size="36">
      <occupation mode="ground" spindataset="1"/>
    </determinant>
  </slaterdeterminant>
</determinantset>
```

Going back to (22.2), we can see that it is essential to include VBM and CBM wavevectors in the same twist for quasiparticle calculations as well. Therefore, the added electron will sit at CBM while the subtracted electron will be removed from VBM. However, for the charged cell calculations, we may need to make changes in the input files for the fourth step. Alternatively, in the quasiparticle.py file, the changes in the QMC input are shown for a negatively charged system:

```
qmc.input.simulation.qmcsystem.particlesets.e.groups.u.size +=1
(qmc.input.simulation.qmcsystem.wavefunction.determinantset
 .slaterdeterminant.determinants.updet.size += 1)
```

Here, the number of up electrons are increased by one (negatively charged system), and QMCPACK is instructed to read more one orbital in the up channel from the `.h5` file.

QE uses symmetry to reduce the number of k-points required for the calculation. Therefore, all symmetry tags in QE (`nosym`, `noinv`, and `nosym_evc`) must be set to false. An easy way to check whether this is the case is to see that all KmK values `einspline` files are equal to 1. Previously, the input for the neutral cell is given, while the changes are denoted as comments for the positively charged cell. Note that we have used `det_format = "old"` in the `vmc_+/-e.py` files.

22.6 Optical gap calculations

Routines for the optical gap calculations are very similar to the quasiparticle gap calculations. The first three items in the quasiparticle band gap calculations can be reused for the optical gap calculations. However, at the VMC/DMC level, the electronic transitions performed should be explicitly stated. Therefore, compared with the quasiparticle calculations, only item number 4 is different for optical gap calculations. Here, the modified input file is given for the $\Gamma \rightarrow \Delta'$ transition, which can be compared with the ground state input file in the previous section.

```
<determinantset>
  <slaterdeterminant>
    <determinant id="updet" group="u" sposet="spo_u" size="36">
      <occupation mode="excited" spindataset="0" format="band" pairs="1" >
        0 3 4 4
      </occupation>
    </determinant>
    <determinant id="downdet" group="d" sposet="spo_d" size="36">
      <occupation mode="ground" spindataset="1"/>
    </determinant>
  </slaterdeterminant>
</determinantset>
```

We have used the (twistindex, bandindex) notation in the annihilaion/creation order for the up-spin electrons. After resubmitting the batch job, in the output, you should be able to see the following lines in the `vmc.out` file:

```
Sorting the bands now:
  Occupying bands based on (ti,bi) data.
removing orbital 35
adding orbital 36
We will read 36 distinct orbitals.
There are 0 core states and 36 valence states.
```

And the `einspline.tile_300010003.spin_0.tw_0.g0.bandinfo.dat` file must be changed in the following way:

```
#  Band State TwistIndex BandIndex Energy Kx Ky Kz K1 K2 K3 KmK
33 33 0       1 0.499956      0.0000  0.0000 0.0000  0.0000 0.0000  0.0000 1
34 34 0       2 0.500126      0.0000  0.0000 0.0000  0.0000 0.0000  0.0000 1
35 35 4       4 0.637231      0.0000 -0.6209 0.0000 -0.3333 0.0000 -0.3333 1
36 36 0       3 0.502916      0.0000  0.0000 0.0000  0.0000 0.0000  0.0000 1
37 37 8       4 0.637231      0.0000 -1.2418 0.0000 -0.6667 0.0000 -0.6667 1
38 38 0       4 0.699993      0.0000  0.0000 0.0000  0.0000 0.0000  0.0000 1
```

Alternatively, the excitations within Nexus can be defined as shown in the `optical.py` file:

```
qmc = generate_qmcpack(
    ...
    excitation = ['up', '0 3 4 4'], # (ti, bi) notation
    #excitation = ['up', '-35 + 36'], # Orbital (state) index notation
    ...
    )
```

CHAPTER

TWENTYTHREE

AFQMC TUTORIALS

Below we will run through some full AFQMC workflow examples. The necessary scripts can be found in the `qmcpack/examples/afqmc` directory.

23.1 Example 1: Neon atom

In this example we will go through the basic steps necessary to generate AFQMC input from a pyscf scf calculation on a simple closed shell molecule (neon/aug-cc-pvdz).

The pyscf scf script is given below (scf.py in the current directory):

```
from pyscf import gto, scf, cc
from pyscf.cc import ccsd_t
import h5py

mol = gto.Mole()
mol.basis = 'aug-cc-pvdz'
mol.atom = (('Ne', 0,0,0),)
mol.verbose = 4
mol.build()

mf = scf.RHF(mol)
mf.chkfile = 'scf.chk'
ehf = mf.kernel()

ccsd = cc.CCSD(mf)
ecorr_ccsd = ccsd.kernel()[0]
ecorr_ccsdt = ccsd_t.kernel(ccsd, ccsd.ao2mo())
print("E(CCSD(T)) = {}".format(ehf+ecorr_ccsd+ecorr_ccsdt))
```

The most important point above is that we create a scf checkpoint file by specifying the *mf.chkfile* mol member variable. Note we will also compute the CCSD and CCSD(T) energies for comparison puposes since this system is trivially small.

We next run the pyscf calculation using

```
python scf.py > scf.out
```

which will yield a converged restricted Hartree–Fock total energy of -128.496349730541 Ha, a CCSD value of -128.7084878405062 Ha, and a CCSD(T) value of -128.711294157 Ha.

The next step is to generate the necessary qmcpack input from this scf calculation. To this we do (assuming afqmctools is in your PYTHONPATH):

```
/path/to/qmcpack/utils/afqmctools/bin/pyscf_to_afqmc.py -i scf.chk -o afqmc.h5 -t 1e-
↪5 -v
```

which will peform the necessary AO to MO transformation of the one and two electron integrals and perform a modified cholesky transormation of the two electron integrals. A full explanation of the various options available for *pyscf_to_afqmc.py* you can do

```
pyscf_to_afqmc.py -h
```

In the above example, *-i* designates the input pyscf checkpoint file, *-o* speficies the output filename to write the qmcpack hamiltonian/wavefunction to, *-t* specifies the convergence threshold for the Cholesky decomposition, *-v* increases verbosity. You can optionally pass the *-q/–qmcpack-input* to generate a qmcpack input file which is based on the hamiltonian and wavefunction generated. Greater control over input file generation can be achieved using the write_xml_input function provided with afqmctools. Run gen_input.py after the integrals/wavefunction have been generated to generate the input file *afqmc.xml*.

Running the above will generate one file: *afqmc.h5*. The plain text wavefunction files are deprecated and will be removed in later releases. The qmcpack input file *afqmc.xml* is a *skeleton* input file, meaning that it's created from the information in *hamil.h5* and is meant as a convenience, not as a guarantee that the convergeable parameters (timestep, walker number, bias bound etc. are converged or appropriate).

We will next run through the relevant sections of the input file *afqmc.xml* below:

```
<project id="qmc" series="0"/>
<random seed="7"/>

<AFQMCInfo name="info0">
    <parameter name="NMO">23</parameter>
    <parameter name="NAEA">5</parameter>
    <parameter name="NAEB">5</parameter>
</AFQMCInfo>
```

We first specify how to name the output file. We also have fixed the random number seed so that the results of this tutorial can be reproducible (if run on the same number of cores).

Next comes the system description, which is mostly a sanity check, as these parameters will be read from the hamiltonian file. They specify the number of single-particle orbitals in the basis set (*NMO*) and the number of alpha (*NAEA*) and beta (*NAEB*) electrons respectively.

Next we specify the Hamiltonian and wavefunction to use:

```
<Hamiltonian name="ham0" info="info0">
  <parameter name="filetype">hdf5</parameter>
  <parameter name="filename">afqmc.h5</parameter>
</Hamiltonian>

<Wavefunction name="wfn0" type="NOMSD" info="info0">
  <parameter name="filetype">hdf5</parameter>
  <parameter name="filename">afqmc.h5</parameter>
</Wavefunction>
```

The above should be enough for most calculations. A *NOMSD* (non-orthogonal multi-Slater determinant) wavefunction allows for a generalised wavefunction input in the form of a single (or multiple) matrix (matrices) of molecular orbital coefficients for the RHF calculation we perform here.

We next set the walker options:

```
<WalkerSet name="wset0" type="shared">
  <parameter name="walker_type">CLOSED</parameter>
</WalkerSet>
```

The important point here is that as we are using a RHF trial wavefunction we must specify that the *walker_type* is *CLOSED*. For a UHF trial wavefunction one would set this to *COLLINEAR*.

And now the propagator options:

```
<Propagator name="prop0" info="info0">
  <parameter name="hybrid">yes</parameter>
</Propagator>
```

In the above we specify that we will be using the hybrid approach for updating the walker weights. If you wish to use the local energy approximation you should set this flag to false.

Finally comes the execute block which controls how the simulation is run:

```
 <execute wset="wset0" ham="ham0" wfn="wfn0" prop="prop0" info="info0">
   <parameter name="ncores">1</parameter>
   <parameter name="timestep">0.01</parameter>
   <parameter name="nWalkers">10</parameter>
   <parameter name="blocks">100</parameter>
   <parameter name="steps">10</parameter>
</execute>
```

The time step (*timestep*), number of Monte Carlo samples (*blocks*`*`*steps*), and number of walkers (*nWalkers*) should be adjusted as appropriate. Note that *nWalkers* sets the number of walkers per *ncores*. For example, if we wanted to use 100 walkers we could run the above input file on 10 cores. If the problem size is very large we may want distribute the workload over more cores per walker, say 10. In this case we would require 100 cores to maintain the same number of walkers. Typically in this case you want to specify fewer walkers per core anyway.

We can now run the qmcpack simulation:

```
qmcpack afqmc.xml > qmcpack.out
```

Assuming the calculation finishes successfully, the very first thing you should do is check the information in *qmcpack.out* to see confirm no warnings were raised. The second thing you should check is that the energy of the starting determinant matches the Hartree–Fock energy you computed earlier from pyscf to within roughly the error threshold you specified when generating the Cholesky decomposition. This check is not very meaningful if using, say, DFT orbitals. However if this energy is crazy it's a good sign something went wrong with either the wavefunction or integral generation. Next you should inspect the *qmc.scalar.s000.dat* file which contains the mixed estimates for various quantities. This can be plotted using gnuplot. *EnergyEstim__nume_real* contains the block averaged values for the local energy, which should be the 7th column.

Assuming everything worked correctly we need to analyse the afqmc output using:

```
/path/to/qmcpack/nexus/bin/qmca -e num_skip -q el qmc.s000.scalar.dat
```

where *num_skip* is the number of blocks to skip for the equilibration stage. For a practical calculation you may want to use more walkers and run for longer to get meaningful statistics.

See the options for qmca for further information. Essentially we discarded the first 100 blocks as equilibaration and only computed the mixed estimate for the local energy internally called *EnergyEstim__nume_real*, which can be specified with *-q el*. We see that the ph-AFQMC energy agrees well with the CCSD(T) value. However, we probably did not run the simulation for long enough to really trust the error bars.

23.2 Example 2: Frozen Core

In this example we show how to perform a frozen core calculation, which only affects the integral generation step. We will use the the previous Neon example and freeze 2 core electrons. The following only currently works for RHF/ROHF trial wavefunctions.

```
mpirun -n 1 /path/to/qmcpack/utils/afqmctools/bin/pyscf_to_afqmc.py -i scf.chk -o␣
↪afqmc.h5 -t 1e-5 -v -c 8,22
```

Again, run gen_input.py to generate the input file *afqmc.xml*.

Comparing the above to the previous example we see that we have added the *-c* or *–cas* option followed by a comma separated list of the form N,M defining a (N,M) CAS space containing 8 electrons in 22 spatial orbitals (freezing the lowest MO).

The rest of the qmcpack process follows as before.

23.3 Example 3: UHF Trial

In this example we show how to use a unrestricted Hartree–Fock (UHF) style wavefunction to find the ph-AFQMC (triplet) ground state energy of the carbon atom (cc-pvtz). Again we first run the scf (scf.py) calculation followed by the integral generation script:

```
mpirun -n 1 /path/to/qmcpack/utils/afqmctools/bin/pyscf_to_afqmc.py -i scf.chk -o␣
↪afqmc.h5 -t 1e-5 -v -a
```

Note the new flag *-a*/*–ao* which tells the script to transform the integrals to an orthogonalised atomic orbital basis, rather that the more typical MO basis. This is necessary as qmcpack does not support spin dependent two electron integrals.

Running qmcpack as before should yield a mixed estimate for the energy of roughly: -37.78471 +/- 0.00014.

23.4 Example 4: NOMSD Trial

In this example we will show how to format trial different wavefunctions in such a way that qmcpack can read them.

Rather than use the *pyscf_to_afqmc.py*, script we will break up the process to allow for more flexibility and show what is going on under the hood.

The qmcpack input can be generated with the scf.py script. See the comments in scf.py for a breakdown of the steps involved.

Currently QMCPACK can deal with trial wavefunctions in two forms: Non-orthogonal multi slater determinant trial wavefunctions (NOMSD) and particle-hole style trial wavefunctions (PHMSD). The NOMSD trial wavefunctions are the most general form and expect Slater determinants in the form of M X N matrices of molecular orbital coefficients, where N is the number of electrons and M is the number of orbitals, along with a list of ci coefficients. Importantly the Slater determinants must be non-orthogonal.

23.5 Example 5: CASSCF Trial

In this example we will show how to format a casscf trial wavefunction.

Rather than use the *pyscf_to_afqmc.py*, script we will break up the process to allow for more flexibility and show what is going on under the hood.

The qmcpack input can be generated with the scf.py script followed by gen_input.py.

See the relevant code below for a breakdown of the steps involved.

The first step is to run a CASSCF calculation. Here we'll consider N:sub:2. This replicates the calculations from Al-Saidi et al J. Chem. Phys. 127, 144101 (2007). They find a CASSCF energy of -108.916484 Ha, and a ph-AFQMC energy of -109.1975(6) Ha with a 97 determinant CASSCF trial.

```
mol = gto.M(atom=[['N', (0,0,0)], ['N', (0,0,3.0)]],
            basis='cc-pvdz',
            unit='Bohr')
nalpha, nbeta = mol.nelec
rhf = scf.RHF(mol)
rhf.chkfile = 'scf.chk'
rhf.kernel()

M = 12
N = 6
nmo = rhf.mo_coeff.shape[-1]
mc = mcscf.CASSCF(rhf, M, N)
mc.chkfile = 'scf.chk'
mc.kernel()
```

Next we unpack the wavefunction

```
nalpha = 3
nbeta = 3
ci, occa, occb = zip(*fci.addons.large_ci(mc.ci, M, (nalpha,nbeta),
                     tol=tol, return_strs=False))
```

and sort the determinants by the magnitude of their weight:

```
ixs = numpy.argsort(numpy.abs(coeff))[::-1]
coeff = coeff[ixs]
occa = numpy.array(occa)[ixs]
occb = numpy.array(occb)[ixs]
```

Next we reinsert the frozen core as the AFQMC simulation is not run using an active space:

```
core = [i for i in range(mc.ncore)]
occa = [numpy.array(core + [o + mc.ncore for o in oa]) for oa in occa]
occb = [numpy.array(core + [o + mc.ncore for o in ob]) for ob in occb]
```

Next we need to generate the one- and two-electron integrals. Note that we need to use the CASSCF MO coefficients to rotate the integrals.

```
scf_data = load_from_pyscf_chk_mol('scf.chk', 'mcscf')
write_hamil_mol(scf_data, 'afqmc.h5', 1e-5, verbose=True)
```

Finally we can write the wavefunction to the QMCPACK format:

```
ci = numpy.array(ci, dtype=numpy.complex128)
uhf = True # UHF always true for CI expansions.
write_qmcpack_wfn('afqmc.h5', (ci, occa, occb), uhf, mol.nelec, nmo)
```

To generate the input file we again run `gen_input.py`. Note the `rediag` option which is necessary if the CI code used uses a different convention for ordering creation and annihilation operations when defining determinant strings.

23.6 Example 6: Back Propagation

Note: matplotlib is required to generate the figure in this example.

The basic estimators printed out in the qmcpack **.scalar.dat* files are *mixed* estimates. Unless the operator for which the mixed estimate is computed commutes with the Hamiltonian this result will generally be biased. To obtain pure estimates we can use back propagation as outlined in: *Motta & Zhang, JCTC 13, 5367 (2017)*. For this example we will look at computing the one-body energy of a methane molecule (see Fig. 2 of M&Z).

As before run scf.py and generate the integrals using *pyscf_to_afmqc.py*:

```
mpirun -n 1 /path/to/qmcpack/utils/afqmctools/bin/pyscf_to_afqmc.py -i scf.chk -o␣
↪afqmc.h5 -t 1e-5 -v
```

Note we are working in the MO basis. The input file is generated using *gen_input.py* and comparing to the previous examples we can now see the estimator block:

```
<Estimator name="back_propagation">
    <parameter name="naverages">4</parameter>
    <parameter name="block_size">2</parameter>
    <parameter name="ortho">1</parameter>
    <OneRDM />
    <parameter name="nsteps">200</parameter>
</Estimator>
```

Which will tell QMCPACK to compute the back propagated one-rdm. In the above we set *block_size* to be 2 meaning that we average the back propagated estimates into bins of length 2 in this case. This helps reduce the size of the hdf5 files. We also specify the option *nsteps*: We see that it is set to 200, meaning that we will back propagated the bra wavefunction in the estimator by 200*.01 = 2 a.u., where the timestep has been set to 0.01 a.u. Finally *naverages* allows us to split the full path into *naverages* chunks, so we will have averaged data at $\tau_{BP} = [0.5, 1.0, 1.5, 2.0]$ au. This allows us to monitor the convergence of the estimator with back propagation time.

Running QMCPACK as before we will notice that in addition to the *qmc.s000.scalar.dat* file we have generated a new file *qmc.s000.scalar.h5*. This file will contain the back propagated estimates, which, for the time being, means the back propagated one-particle reduced density matrix (1RDM), given as

$$P_{ij}^{\sigma} = \langle c_{i\sigma}^{\dagger} c_{j\sigma} \rangle$$

Before we analyse the output we should question why we chose a back propagation time of 2 au. The back propagation time represents yet another parameter which must be carefully converged.

In this example we will show how this is done. In this directory you will find a script *check_h1e_conv.py* which shows how to use various helper scripts provided in *afqmctools/analysis/average.py*. The most of important of which are:

```
from afqmctools.analysis.extraction import get_metadata
metadata = get_metadata(filename)
```

which returns a dict containing the RDM metadata,

```
from afqmctools.analysis.average import average_one_rdm
rdm_av, rdm_errs = average_one_rdm(f, name='back_propagated', eqlb=3, ix=2)
```

which computes the average of the 1RDM, where 'i' specifies the index for the length of back propagation time desired (e.g. $i = 2 \rightarrow \tau_{BP} = 1.5$ au). *eqlb* is the equilibration time, and here we skip 10 blocks of length 2 au.

```
from afqmctools.analysis.extraction import extract_observable
dm = extract_observable(filename,
                        estimator='back_propagated'
                        name='one_rdm',
                        ix=2)
```

which extracts the 1RDM for all blocks and finally,

```
from afqmctools.analysis.extraction import extract_observable
dm, weights = extract_observable(filename,
                                 estimator='back_propagated'
                                 name='one_rdm',
                                 ix=2,
                                 sample=index)
```

which extracts a single density matrix for block *index*.

Have a look through *check_h1e_conv.py* and run it. A plot should be produced which shows the back propagated AFQMC one-body energy as a function of back propagation time, which converges to a value of roughly -78.888(1). This system is sufficiently small to perform FCI on. How does ph-AFQMC compare? Why are the error bars getting bigger with back propagation time?

Finally, we should mention that the path restoration algorithm introduced in M&Z is also implemented and can be turned on using the *path_restoration* parameter in the Estimator block.

In QMCPACK path restoration restores both the cosine projection and phase along the back propagation path. In general it was found in M&Z that path restoration always produced better results than using the standard back propagation algorithm, and it is recommended that it is always used. Does path restoration affect the results for methane?

23.7 Example 7: 2x2x2 Diamond supercell

In this example we will show how to generate the AFQMC input from a pbc pyscf calculation for a 2x2x2 supercell of diamond using a RHF trial wavefunction.

Again the first step is to run a pyscf calculation using the scf.py script in this directory.

The first part of the pyscf calculation is straightforward. See pyscf/examples/pbc for more examples on how to set up Hartree–Fock and DFT simulations.

```
import h5py
import numpy
import sys
from pyscf.pbc import scf, dft, gto

cell = gto.Cell()
cell.verbose = 5
alat0 = 3.6
cell.a = (numpy.ones((3,3))-numpy.eye(3))*alat0 / 2.0
cell.atom = (('C',0,0,0), ('C',numpy.array([0.25,0.25,0.25])*alat0))
```

(continues on next page)

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```
cell.basis = 'gth-szv'
cell.pseudo = 'gth-pade'
cell.mesh = [28,28,28]
cell.build()
nk = [2,2,2]
kpts = cell.make_kpts(nk)

mf = scf.KRHF(cell, kpts=kpts)
mf.chkfile = 'scf.chk'
mf.kernel()
```

In addition to a standard pyscf calculation, we add the following lines:

```
from afqmctools.utils.linalg import get_ortho_ao
hcore = mf.get_hcore()
fock = (hcore + mf.get_veff())
X, nmo_per_kpt = get_ortho_ao(cell,kpts)
with h5py.File(mf.chkfile) as fh5:
  fh5['scf/hcore'] = hcore
  fh5['scf/fock'] = fock
  fh5['scf/orthoAORot'] = X
  fh5['scf/nmo_per_kpt'] = nmo_per_kpt
```

essentially, storing the fock matrix, core Hamiltonian and transformation matrix to the orthogonalised AO basis. This is currently required for running PBC AFQMC calculations.

Once the above (scf.py) script is run we will again use the *pyscf_to_afqmc.py* script to generate the necessary AFQMC input file.

```
mpirun -n 8 /path/to/qmcpack/utils/afqmctools/bin/pyscf_to_afqmc.py -i scf.chk -o␣
↪afqmc.h5 -t 1e-5 -v -a
```

Note that the commands necessary to generate the integrals are identical to those for the molecular calculations, except now we accelerate their calculation using MPI. Note that if the number of tasks > number of kpoints then the number of MPI tasks must be divisible by the number of kpoints.

Once this is done we will again find a Hamiltonian file and afqmc input xml file. Inspecting these you will notice that their structure is identical to the molecular calculations seen previously. This is because we have not exploited k-point symmetry and are writing the integrals in a supercell basis. In the next example we will show how exploiting k-point symmetry can be done explicitly, which leads to a faster and lower memory algorithm for AFQMC.

23.8 Example 8: 2x2x2 Diamond k-point symmetry

In this example we will show how to run an AFQMC simulation that exploits k-point symmetry which is much more efficient that running in the supercell way discussed in the previous example. We will again look at the same 2x2x2 cell of diamond. We assume you have run the scf calculation in the previous example.

Essentially all that changes in the integral generation step is that we pass the *-k/–kpoint* flag to *pyscf_to_afqmc.py*.

```
mpirun -n 8 /path/to/qmcpack/utils/afqmctools/bin/pyscf_to_afqmc.py -i ../07-diamond_
↪2x2x2_supercell/scf.chk -o afqmc.h5 -t 1e-5 -v -a -k
```

You will notice that now the Cholesky decomposition is done for each momentum transfer independently and the the form of the hamiltonian file has changed to be k-point dependent.

Apart from these changes, running the AFQMC simulation proceeds as before, however you should see a significant performance boost relative to the supercell simulations, particularly on GPU machines.

CHAPTER

TWENTYFOUR

ADDITIONAL TOOLS

QMCPACK provides a set of lightweight executables that address certain common problems in QMC workflow and analysis. These range from conversion utilities between different file formats and QMCPACK (e.g., `ppconvert` and `convert4qmc`), (qmc-extract-eshdf-kvectors) to postprocessing utilities (`trace-density` and `qmcfinitesize`) to many others. In this section, we cover the use cases, syntax, and features of all additional tools provided with QMCPACK.

24.1 Initialization

24.1.1 qmc-get-supercell

24.2 Postprocessing

24.2.1 qmca

`qmca` is a versatile tool to analyze and plot the raw data from QMCPACK `*.scalar.dat` files. It is a Python executable and part of the Nexus suite of tools. It can be found in `qmcpack/nexus/executables`. For details, see *Using the qmca tool to obtain total energies and related quantities*.

24.2.2 qmc-fit

`qmc-fit` is a curve fitting tool used to obtain statistical error bars on fitted parameters. It is useful for DMC time step extrapolation. For details, see *Using the qmc-fit tool for statistical time step extrapolation and curve fitting*.

24.2.3 qdens

`qdens` is a command line tool to produce density files from QMCPACK's `stat.h5` output files. For details, see *Using the qdens tool to obtain electron densities*.

24.2.4 qmcfinitesize

`qmcfinitesize` is a utility to compute many-body finite-size corrections to the energy. It is a C++ executable that is built alongside the QMCPACK executable. It can be found in `build/bin`.

24.3 Converters

24.3.1 convert4qmc

`Convert4qmc` allows conversion of orbitals and wavefunctions from quantum chemistry output files to QMCPACK XML and HDF5 input files. It is a small C++ executable that is built alongside the QMCPACK executable and can be found in `build/bin`.

To date, `convert4qmc` supports the following codes: GAMESS [[SBB+93]], PySCF [[SBB+18]] and QP2 [[GAG+19]] natively, and NWCHEM [[ApraBdJ+20]], TURBOMOLE [[FAH+14]], PSI4 [[TSP+12]], CFOUR 2.0beta [[MCH+20]], ORCA 3.X - 4.X [[Nee18]], DALTON2016 [[AAB+14]], MOLPRO [[WKK+12]], DIRAC [[DIR]], RMG [[RMG]], and QCHEM 4.X [[SGE+15]] through the molden2qmc converter (see *molden2qmc*).

General use

General use of `convert4qmc` can be prompted by running with no options:

```
>convert4qmc

Defaults : -gridtype log -first 1e-6 -last 100 -size 1001 -ci required -threshold 0.
↪01 -TargetState 0 -prefix sample

 convert [-gaussian|gamess|-orbitals|-dirac|-rmg]
 filename
[-nojastrow -hdf5 -prefix title -addCusp -production -NbImages NimageX NimageY␣
↪NimageZ]
[-psi_tag psi0 -ion_tag ion0 -gridtype log|log0|linear -first ri -last rf]
[-size npts -ci file.out -threshold cimin -TargetState state_number
-NaturalOrbitals NumToRead -optDetCoeffs]
Defaults : -gridtype log -first 1e-6 -last 100 -size 1001 -ci required
-threshold 0.01 -TargetState 0 -prefix sample
When the input format is missing, the  extension of filename is used to determine
the format
 *.Fchk -> gaussian; *.out -> gamess; *.h5 -> hdf5 format
```

As an example, to convert a GAMESS calculation using a single determinant, the following use is sufficient:

```
convert4qmc -gamess MyGamessOutput.out
```

By default, the converter will generate multiple files:

`convert4qmc` output:

output	file type	default	description
*.qmc.in-wfs.xml	XML	default	Main input file for QMCPACK
*.qmc.in-wfnoj.xml	XML	default	Main input file for QMCPACK
*.structure.xml	XML	default	File containing the structure of the system
*.wfj.xml	XML	default	Wavefunction file with 1-, 2-, and 3-body Jastrows
*.wfnoj.xml	XML	default	Wavefunction file with no Jastrows
*.orbs.h5	HDF5	with -hdf5	HDF5 file containing all wavefunction data

If no -prefix option is specified, the prefix is taken from the input file name. For instance, if the GAMESS output file is Mysim.out, the files generated by convert4qmc will use the prefix Mysim and output files will be Mysim.qmc.in-wfs.xml, Mysim.structure.xml, and so on.

- Files .in-wfs.xml and .in-wfnoj.xml

  These are the input files for QMCPACK. The geometry and the wavefunction are stored in external files *.structure.xml and *.wfj.xml (referenced from *.in-wfs.xml) or *.qmc.wfnoj.xml (referenced from *.qmc.in-wfnoj.xml). The Hamiltonian section is included, and the presence or lack of presence of an ECP is detected during the conversion. If use of an ECP is detected, a default ECP name is added (e.g., H.qmcpp.xml), and it is the responsibility of the user to modify the ECP name to match the one used to generate the wavefunction.

```
  <?xml version="1.0"?>
<simulation>
  <!--

Example QMCPACK input file produced by convert4qmc

It is recommend to start with only the initial VMC block and adjust
parameters based on the measured energies, variance, and statistics.

-->
  <!--Name and Series number of the project.-->
  <project id="gms" series="0"/>
  <!--Link to the location of the Atomic Coordinates and the location of
      the Wavefunction.-->
  <include href="gms.structure.xml"/>
  <include href="gms.wfnoj.xml"/>
  <!--Hamiltonian of the system. Default ECP filenames are assumed.-->
  <hamiltonian name="h0" type="generic" target="e">
    <pairpot name="ElecElec" type="coulomb" source="e" target="e"
                                                physical="true"/>
    <pairpot name="IonIon" type="coulomb" source="ion0" target="ion0"/>
    <pairpot name="PseudoPot" type="pseudo" source="ion0" wavefunction="psi0"
                                                format="xml">
      <pseudo elementType="H" href="H.qmcpp.xml"/>
      <pseudo elementType="Li" href="Li.qmcpp.xml"/>
    </pairpot>
  </hamiltonian>

The ``qmc.in-wfnoj.xml`` file will have one VMC block with a
minimum number of blocks to reproduce the HF/DFT energy used to
```

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```
generate the trial wavefunction.

::

    <qmc method="vmc" move="pbyp" checkpoint="-1">
      <estimator name="LocalEnergy" hdf5="no"/>
      <parameter name="warmupSteps">100</parameter>
      <parameter name="blocks">20</parameter>
      <parameter name="steps">50</parameter>
      <parameter name="substeps">8</parameter>
      <parameter name="timestep">0.5</parameter>
      <parameter name="usedrift">no</parameter>
    </qmc>
  </simulation>
```

If the `qmc.in-wfj.xml` file is used, Jastrow optimization blocks followed by a VMC and DMC block are included. These blocks contain default values to allow the user to test the accuracy of a system; however, they need to be updated and optimized for each system. The initial values might only be suitable for a small molecule.

```
  <loop max="4">
    <qmc method="linear" move="pbyp" checkpoint="-1">
      <estimator name="LocalEnergy" hdf5="no"/>
      <parameter name="warmupSteps">100</parameter>
      <parameter name="blocks">20</parameter>
      <parameter name="timestep">0.5</parameter>
      <parameter name="walkers">1</parameter>
      <parameter name="samples">16000</parameter>
      <parameter name="substeps">4</parameter>
      <parameter name="usedrift">no</parameter>
      <parameter name="MinMethod">OneShiftOnly</parameter>
      <parameter name="minwalkers">0.0001</parameter>
    </qmc>
  </loop>
  <!--

Example follow-up VMC optimization using more samples for greater accuracy:

-->
  <loop max="10">
    <qmc method="linear" move="pbyp" checkpoint="-1">
      <estimator name="LocalEnergy" hdf5="no"/>
      <parameter name="warmupSteps">100</parameter>
      <parameter name="blocks">20</parameter>
      <parameter name="timestep">0.5</parameter>
      <parameter name="walkers">1</parameter>
      <parameter name="samples">64000</parameter>
      <parameter name="substeps">4</parameter>
      <parameter name="usedrift">no</parameter>
      <parameter name="MinMethod">OneShiftOnly</parameter>
      <parameter name="minwalkers">0.3</parameter>
    </qmc>
  </loop>
  <!--

Production VMC and DMC:
```

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```
Examine the results of the optimization before running these blocks.
For example, choose the best optimized jastrow from all obtained, put in the
wavefunction file, and do not reoptimize.

-->
  <qmc method="vmc" move="pbyp" checkpoint="-1">
    <estimator name="LocalEnergy" hdf5="no"/>
    <parameter name="warmupSteps">100</parameter>
    <parameter name="blocks">200</parameter>
    <parameter name="steps">50</parameter>
    <parameter name="substeps">8</parameter>
    <parameter name="timestep">0.5</parameter>
    <parameter name="usedrift">no</parameter>
    <!--Sample count should match targetwalker count for
      DMC. Will be obtained from all nodes.-->
    <parameter name="samples">16000</parameter>
  </qmc>
  <qmc method="dmc" move="pbyp" checkpoint="20">
    <estimator name="LocalEnergy" hdf5="no"/>
    <parameter name="targetwalkers">16000</parameter>
    <parameter name="reconfiguration">no</parameter>
    <parameter name="warmupSteps">100</parameter>
    <parameter name="timestep">0.005</parameter>
    <parameter name="steps">100</parameter>
    <parameter name="blocks">100</parameter>
    <parameter name="nonlocalmoves">yes</parameter>
  </qmc>
</simulation>
```

- File `.structure.xml`

  This file will be referenced from the main QMCPACK input. It contains the geometry of the system, position of the atoms, number of atoms, atomic types and charges, and number of electrons.

- Files `.wfj.xml` and `.wfnoj.xml`

  These files contain the basis set detail, orbital coefficients, and the 1-, 2-, and 3-body Jastrow (in the case of `.wfj.xml`). If the wavefunction is multideterminant, the expansion will be at the end of the file. We recommend using the option `-hdf5` when large molecules are studied to store the data more compactly in an HDF5 file.

- File `.orbs.h5` This file is generated only if the option `-hdf5` is added as follows:

```
convert4qmc -gamess MyGamessOutput.out -hdf5
```

  In this case, the `.wfj.xml` or `.wfnoj.xml` files will point to this HDF file. Information about the basis set, orbital coefficients, and the multideterminant expansion is put in this file and removed from the wavefunction files, making them smaller.

`convert4qmc` input type:

option name	description
`-orbitals`	Generic HDF5 input file. Mainly automatically generated from QP2, Pyscf and all codes in molden2qmc
`-gamess`	Gamess code
`-gaussian`	Gaussian code
`-dirac`	get spinors from DIRAC code
`-rmg`	RMG code

Command line options

`convert4qmc` command line options:

Option Name	Value	default	description
`-nojastrow`	•	•	Force no Jastrow. `qmc.in.wfj` will not be generated
`-hdf5`	•	•	Force the wf to be in HDF5 format
`-prefix`	string	•	All created files will have the name of the string
`-multidet`	string	•	HDF5 file containing a multideterminant expansion
`-addCusp`	•	•	Force to add orbital cusp correction (ONLY for all-electron)
`-production`	•	•	Generates specific blocks in the input
`-psi_tag`	string	psi0	Name of the electrons particles inside QMCPACK
`-ion_tag`	string	ion0	Name of the ion particles inside QMCPACK

- `-multidet`

  This option is to be used when a multideterminant expansion (mainly a CI expansion) is present in an HDF5 file. The trial wavefunction file will not display the full list of multideterminants and will add a path to the HDF5 file as follows (full example for the C2 molecule in qmcpack/tests/molecules/C2_pp).

```
<?xml version="1.0"?>
<qmcsystem>
  <wavefunction name="psi0" target="e">
    <determinantset type="MolecularOrbital" name="LCAOBSet" source="ion0"␣
↪transform="yes" href="C2.h5">
      <sposet basisset="LCAOBSet" name="spo-up" size="58">
        <occupation mode="ground"/>
        <coefficient size="58" spindataset="0"/>
      </sposet>
      <sposet basisset="LCAOBSet" name="spo-dn" size="58">
        <occupation mode="ground"/>
        <coefficient size="58" spindataset="0"/>
      </sposet>
      <multideterminant optimize="no" spo_up="spo-up" spo_dn="spo-dn">
        <detlist size="202" type="DETS" nca="0" ncb="0" nea="4" neb="4" nstates=
↪"58" cutoff="1e-20" href="C2.h5"/>
      </multideterminant>
    </determinantset>
```

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```
  </wavefunction>
</qmcsystem>
```

To generate such trial wavefunction, the converter has to be invoked as follows:

```
> convert4qmc -orbitals C2.h5 -multidet C2.h5
```

- `-nojastrow`

  This option generates only an input file, `*.qmc.in.wfnoj.xml`, containing no Jastrow optimization blocks and references a wavefunction file, `*.wfnoj.xml`, containing no Jastrow section.

- `-hdf5`

  This option generates the `*.orbs.h5` HDF5 file containing the basis set and the orbital coefficients. If the wavefunction contains a multideterminant expansion from QP2, it will also be stored in this file. This option minimizes the size of the `*.wfj.xml` file, which points to the HDF file, as in the following example:

```
 <?xml version="1.0"?>
<qmcsystem>
  <wavefunction name="psi0" target="e">
    <determinantset type="MolecularOrbital" name="LCAOBSet" source="ion0"
       transform="yes" href="test.orbs.h5">
      <slaterdeterminant>
        <determinant id="updet" size="39">
          <occupation mode="ground"/>
          <coefficient size="411" spindataset="0"/>
        </determinant>
        <determinant id="downdet" size="35">
          <occupation mode="ground"/>
          <coefficient size="411" spindataset="0"/>
        </determinant>
      </slaterdeterminant>
    </determinantset>
  </wavefunction>
</qmcsystem>
```

  Jastrow functions will be included if the option "-nojastrow" was not specified. Note that when initially optimization a wavefunction, we recommend temporarily removing/disabling the 3-body Jastrow.

- **-prefix**

  Sets the prefix for all output generated by `convert4qmc`. If not specified, `convert4qmc` will use the defaults for the following:

  - **Gamess** If the Gamess output file is named "**Name**.out" or "**Name**.output," all files generated by `convert4qmc` will carry **Name** as a prefix (i.e., **Name**.qmc.in.xml).
  - **Generic HDF5 input** If a generic HDF5 file is named "**Name**.H5," all files generated by `convert4qmc` will carry **Name** as a prefix (i.e., **Name**.qmc.in.xml).

- **-addCusp**

  This option is very important for all-electron (AE) calculations. In this case, orbitals have to be corrected for the electron-nuclear cusp. The cusp correction scheme follows the algorithm described by Ma et al. [[MTDN05]] When this option is present, the wavefunction file has a new set of tags:

```
qmcsystem>
 <wavefunction name="psi0" target="e">
```

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```
   <determinantset type="MolecularOrbital" name="LCAOBSet" source="ion0"
     transform="yes" cuspCorrection="yes">
     <basisset name="LCAOBSet">
```

The tag "cuspCorrection" in the `wfj.xml` (or `wfnoj.xml`) wavefunction file will force correction of the orbitals at the beginning of the run. In the "orbitals" section of the wavefunction file, a new tag "cuspInfo" will be added for orbitals spin-up and orbitals spin-down:

```
 <slaterdeterminant>
      <determinant id="updet" size="2"
          cuspInfo="../updet.cuspInfo.xml">
        <occupation mode="ground"/>
        <coefficient size="135" id="updetC">

<determinant id="downdet" size="2"
         cuspInfo="../downdet.cuspInfo.xml">
        <occupation mode="ground"/>
        <coefficient size="135" id="downdetC">
```

These tags will point to the files `updet.cuspInfo.xml` and `downdet.cuspInfo.xml`. By default, the converter assumes that the files are located in the relative path `../`. If the files are not present in the parent directory, QMCPACK will run the cusp correction algorithm to generate both files in the current run directory (not in `../`). If the files exist, then QMCPACK will apply the corrections to the orbitals.

Important notes:

The cusp correction implementations has been parallelized and performance improved. However, since the correction needs to be applied for every ion and then for every orbital on that ion, this operation can be costly (slow) for large systems. We recommend saving and reusing the computed cusp correction files `updet.cuspInfo.xml` and `downdet.cuspInfo.xml`, and transferring them between computer systems where relevant.

- **-psi_tag**

  QMCPACK builds the wavefunction as a named object. In the vast majority of cases, one wavefunction is simulated at a time, but there may be situations where we want to distinguish different parts of a wavefunction, or even use multiple wavefunctions. This option can change the name for these cases.

```
<wavefunction name="psi0" target="e">
```

- **-ion_tag**

  Although similar to **-psi_tag**, this is used for the type of ions.

```
<particleset name="ion0" size="2">
```

- **-production**

  Without this option, input files with standard optimization, VMC, and DMC blocks are generated. When the "-production" option is specified, an input file containing complex options that may be more suitable for large runs at HPC centers is generated. This option is for users who are already familiar with QMC and QMCPACK. We encourage feedback on the standard and production sample inputs.

The following options are specific to using MCSCF multideterminants from Gamess.

`convert4qmc` MCSCF arguments:

Option Name	Value	default	description
-ci	String	none	Name of the file containing the CI expansion
-threshold	double	1e-20	Cutoff of the weight of the determinants
-TargetState	int	none	?
-NaturalOrbitals	int	none	?
-optDetCoeffs	•	no	Enables the optimization of CI coefficients

- keyword **-ci** Path/name of the file containing the CI expansion in a Gamess Format.
- keyword **-threshold** The CI expansion contains coefficients (weights) for each determinant. This option sets the maximum coefficient to include in the QMC run. By default it is set to 1e-20 (meaning all determinants in an expansion are taken into account). At the same time, if the threshold is set to a different value, for example $1e-5$, any determinant with a weight $|weight| < 1e-5$ will be discarded and the determinant will not be considered.
- keyword **-TargetState** ?
- keyword **-NaturalOrbitals** ?
- keyword **-optDetCoeffs** This flag enables optimization of the CI expansion coefficients. By default, optimization of the coefficients is disabled during wavefunction optimization runs.

Examples and more thorough descriptions of these options can be found in the lab section of this manual: *Lab 3: Advanced molecular calculations*.

Grid options

These parameters control how the basis set is projected on a grid. The default parameters are chosen to be very efficient. Unless you have a very good reason, we do not recommend modifying them.

Tags			
keyword	**Value**	**default**	**description**
-gridtype	log|log0|linear	log	Grid type
-first	double	1e-6	First point of the grid
-last	double	100	Last point of the grid
-size	int	1001	Number of point in the grid

- **-gridtype** Grid type can be logarithmic, logarithmic base 10, or linear
- **-first** First value of the grid
- **-last** Last value of the grid
- **-size** Number of points in the grid between "first" and "last."

Supported codes

- **PySCF**

  PySCF [[SBB+18]] is an all-purpose quantum chemistry code that can run calculations from simple Hartree-Fock to DFT, MCSCF, and CCSD, and for both isolated systems and periodic boundary conditions. PySCF can be downloaded from https://github.com/sunqm/pyscf. Many examples and tutorials can be found on the PySCF website, and all types of single determinants calculations are compatible with , thanks to active support from the authors of PySCF. A few additional steps are necessary to generate an output readable by `convert4qmc`.

  This example shows how to run a Hartree-Fock calculation for the LiH dimer molecule from PySCF and convert the wavefunction for QMCPACK.

  - **Python path**

    PySCF is a Python-based code. A Python module named **PyscfToQmcpack** containing the function **savetoqmcpack** is provided by and is located at `qmcpack/src/QMCTools/PyscfToQmcpack.py`. To be accessible to the PySCF script, this path must be added to the PYTHONPATH environment variable. For the bash shell, this can be done as follows:

```
export PYTHONPATH=/PATH_TO_QMCPACK/qmcpack/src/QMCTools:\$PYTHONPATH
```

  - **PySCF Input File**

    Copy and paste the following code in a file named LiH.py.

```
#! /usr/bin/env python3
from pyscf import gto, scf, df
import numpy

cell = gto.M(
   atom ='''
Li 0.0 0.0 0.0
H  0.0 0.0 3.0139239778''',
   basis ='cc-pv5z',
   unit="bohr",
   spin=0,
   verbose = 5,
   cart=False,
)
mf = scf.ROHF(cell)
mf.kernel()

###SPECIFIC TO QMCPACK###
title='LiH'
from PyscfToQmcpack import savetoqmcpack

savetoqmcpack(cell,mf,title)
```

    The arguments to the function **savetoqmcpack** are:

    * **cell** This is the object returned from gto.M, containing the type of atoms, geometry, basisset, spin, etc.
    * **mf** This is an object representing the PySCF level of theory, in this example, ROHF. This object contains the orbital coefficients of the calculations.
    * **title** The name of the output file generated by PySCF. By default, the name of the generated file will be "default" if nothing is specified.

By adding the three lines below the "SPECIFIC TO QMCPACK" comment in the input file, the script will dump all the necessary data for QMCPACK into an HDF5 file using the value of "title" as an output name. PySCF is run as follows:

```
>python LiH.py
```

The generated HDF5 can be read by `convert4qmc` to generate the appropriate QMCPACK input files.

– **Generating input files**

As described in the previous section, generating input files for PySCF is as follows:

```
> convert4qmc -pyscf LiH.h5
```

The HDF5 file produced by "savetoqmcpack" contains the wavefunction in a form directly readable by QMCPACK. The wavefunction files from `convert4qmc` reference this HDF file as if the "-hdf5" option were specified (converting from PySCF implies the "-hdf5" option is always present).

Periodic boundary conditions with Gaussian orbitals from PySCF is fully supported for Gamma point and kpoints.

- **Quantum Package**

QP2 [[GAG+19]] is a quantum chemistry code developed by the LCPQ laboratory in Toulouse, France, and Argonne National Laboratory for the PBC version. It can be downloaded from https://github.com/QuantumPackage/qp2, and the tutorial within is quite extensive. The tutorial section of QP2 can guide you on how to install and run the code.

After a QP2 calculation, the data needed for `convert4qmc` can be generated through

```
qp_run save_for_qmcpack Myrun.ezfio
```

This command will generate an HDF5 file in the QMCPACK format named `QP2QMCPACK.h5` `convert4qmc` can read this file and generate the `*.structure.xml`, `*.wfj.xml` and other files needed to run QMCPACK. . For example:

```
convert4qmc -orbitals QP2QMCPACK.h5 -multidet QP2QMCPACK.h5 -prefix MySystem
```

The main reason to use QP2 is to access the CIPSI algorithm to generate a multideterminant wavefunction. CIPSI is the preferred choice for generating a selected CI trial wavefunction for QMCPACK. An example on how to use QP2 for Hartree-Fock and selected CI can be found in *CIPSI wavefunction interface* of this manual. The converter code is actively maintained and codeveloped by both QMCPACK and QP2 developers.

- **Using -hdf5 tag**

```
convert4qmc -gamess Myrun.out -hdf5
```

This option is only used/useful with the gamess code as it is the only code not providing an HDF5 output The result will create QMCPACK input files but will also store all key data in the HDF5 format.

- **Mixing orbitals and multideterminants**

Note that the `QP2QMCPACK.h5` combined with the tags `-orbitals` and `-multidet` allows the user to choose orbitals from a different code such as PYSCF and the multideterminant section from QP2. These two codes are fully compatible, and this route is also the only possible route for multideterminants for solids.

```
convert4qmc -orbitals MyPyscfrun.h5 -multidet QP2QMCPACK.h5
```

- **GAMESS**

  QMCPACK can use the output of GAMESS [[SBB+93]] for any type of single determinant calculation (HF or DFT) or multideterminant (MCSCF) calculation. A description with an example can be found in the Advanced Molecular Calculations Lab (*Lab 3: Advanced molecular calculations*).

- **DIRAC**

  QMCPACK can use the output of DIRAC to run spin-orbit calculations using single-particle spinor wave functions for single-determinant calculations (DFT or closed-shell Dirac HF) or multideterminant complete open-shell configuration interaction (COSCI) wavefunctions. In the case of COSCI, the desired ground or excited state can be requested with `-TargetState x`.

- **RMG**

  QMCPACK can use the HDF5 output of RMG DFT calculations. To generate this HDF5 output, set `write_qmcpack_restart = "true"` in the RMG input (file will be written to `Waves/wave.out.h5`). `convert4qmc` will read the data from this HDF5 file and generate `*.structure.xml`, `*.wf{j,noj}.xml`, and `*.qmc.in-wf{j,noj}.xml`. Pseudopotential files must be generated/moved manually by the user to `X.qmcpp.xml`, where `X` is the appropriate element symbol (PP filename/path can be changed in the Hamiltonian section of `*.qmc.in-wf{j,noj}.xml`).

```
convert4qmc -rmg wave.out.h5
```

24.3.2 pw2qmcpack.x

`pw2qmcpack.x` is an executable that converts PWSCF wavefunctions from the Quantum ESPRESSO (QE) package to QMCPACK readable HDF5 format. This utility is built alongside the QE postprocessing utilities. This utility is written in Fortran90 and is distributed as a patch of the QE source code. The patch, as well as automated QE download and patch scripts, can be found in `qmcpack/external_codes/quantum_espresso`. Once built, we recommend also build QMCPACK with the QE_BIN option pointing to the build pw.x and pw2qmcpack.x directory. This will enable workflow tests to be run.

pw2qmcpack can be used in serial in small systems and should be used in parallel with large systems for best performance. The K_POINT gamma optimization is not supported.

Listing 24.1: Sample `pw2qmcpack.x` input file `p2q.in`

```
&inputpp
  prefix      = 'bulk_silicon'
  outdir      = './'
  write_psir  = .false.
/
```

This example will cause `pw2qmcpack.x` to convert wavefunctions saved from PWSCF with the prefix "bulk_silicon." Perform the conversion via, for example:

```
mpirun -np 1 pw2qmcpack.x < p2q.in>& p2q.out
```

Because of the large plane-wave energy cutoffs in the pw.x calculation required by accurate PPs and the large system sizes of interest, one limitation of QE can be easily reached: that `wf_collect=.true.` results in problems of writing and loading correct plane-wave coefficients on disks by pw.x because of the 32 bit integer limits. Thus, `pw2qmcpack.x` fails to convert the orbitals for QMCPACK. Since the release of QE v5.3.0, the converter has been fully parallelized to overcome this limitation completely.

By setting `wf_collect=.false.` (by default `.false.` in v6.1 and before and `.true.` since v6.2), pw.x does not collect the whole wavefunction into individual files for each k-point but instead writes one smaller file for each

processor. By running `pw2qmcpack.x` in the same parallel setup (MPI tasks and k-pools) as the last scf/nscf calculation with pw.x, the orbitals distributed among processors will first be aggregated by the converter into individual temporal HDF5 files for each k-pool and then merged into the final file. In large calculations, users should benefit from a significant reduction of time in writing the wavefunction by pw.x thanks to avoiding the wavefunction collection.

pw2qmcpack has been included in the test suite of QMCPACK (see instructions about how to activate the tests in *Installing and patching Quantum ESPRESSO*). There are tests labeled "no-collect" running the pw.x with the setting `wf_collect=.false.` The input files are stored at `examples/solids/dft-inputs-polarized-no-collect`. The scf, nscf, and pw2qmcpack runs are performed on 16, 12, and 12 MPI tasks with 16, 2, and 2 k-pools respectively.

24.3.3 convertpw4qmc

Convertpw4qmc is an executable that reads xml from a plane wave based DFT code and produces a QMCPACK readable HDF5 format wavefunction. For the moment, this supports both QBox and Quantum Epresso

In order to save the wavefunction from QBox so that convertpw4qmc can work on it, one needs to add a line to the QBox input like

```
save -text -serial basename.sample
```

after the end of a converged dft calculation. This will write an ascii wavefunction file and will avoid QBox's optimized parallel IO (which is not currently supported).

After the wavefunction file is written (basename.sample in this case) one can use convertpw4qmc as follows:

```
convertpw4qmc basename.sample -o qmcpackWavefunction.h5
```

This reads the Qbox wavefunction and performs the Fourier transform before saving to a QMCPACK eshdf format wavefunction. Currently multiple k-points are supported, but due to difficulties with the qbox wavefunction file format, the single particle orbitals do not have their proper energies associated with them. This means that when tiling from a primitive cell to a supercell, the lowest n single particle orbitals from all necessary k-points will be used. This can be problematic in the case of a metal and this feature should be used with EXTREME caution.

In the case of Quantum ESPRESSO, QE must be compiled with HDF support. If this is the case, then an eshdf file can be generated by targeting the data-file-schema.xml file generated in the output of Quantum ESPRESSO. For example, if one is running a calculation with outdir = 'out' and prefix='Pt' then the converter can be invoked as:

```
convertpw4qmc out/Pt.save/data-file-schema.xml -o qmcpackWavefunction.h5
```

Note that this method is insensitive to parallelization options given to Quantum ESPRESSO. Additionally, it supports noncollinear magnetism and can be used to generate wavefunctions suitable for qmcpack calculations with spin-orbit coupling.

24.3.4 ppconvert

`ppconvert` is a utility to convert PPs between different commonly used formats. As with all operations on pseudopotentials, great care should be exercised when using this tool. The tool is not yet considered to be fully robust and converted potentials should be examined carefully. Please report any issues. Generally DFT-derived potentials should not be used with QMC. The main intended use for the converter is to convert potentials generated for QMC calculations into formats acceptable to DFT and quantum chemistry codes for trial wavefunction generation.

Currently it converts CASINO, FHI, UPF (generated by OPIUM), BFD, and GAMESS formats to several other formats including XML (QMCPACK) and UPF (QE). See all the formats via `ppconvert -h`.

For output formats requiring Kleinman-Bylander projectors, the atom will be solved with DFT if the projectors are not provided in the input formats. This requires providing reference states and often needs extra tuning for heavy elements. To avoid ghost states, the local channel can be changed via the `--local_channel` option. Ghost state considerations are similar to those of DFT calculations but could be worse if ghost states were not considered during the original PP construction. To make the self-consistent calculation converge, the density mixing parameter may need to be reduced via the `--density_mix` option. Note that the reference state should include only the valence electrons. One reference state should be included for each channel in the PP.

For example, for a sodium atom with a neon core, the reference state would be "1s(1)." `--s_ref` needs to include a 1s state, `--p_ref` needs to include a 2p state, `--d_ref` needs to include a 3d state, etc. If not specified, a corresponding state with zero occupation is added. If the reference state is chosen as the neon core, setting empty reference states "" is technically correct. In practice, reasonable reference states should be picked with care. For PP with semi-core electrons in the valence, the reference state can be long. For example, Ti PP has 12 valence electrons. When using the neutral atom state, `--s_ref`, `--p_ref`, and `--d_ref` are all set as "1s(2)2p(6)2s(2)3d(2)." When using an ionized state, the three reference states are all set as "1s(2)2p(6)2s(2)" or "1s(2)2p(6)2s(2)3d(0)."

Unfortunately, if the generated UPF file is used in QE, the calculation may be incorrect because of the presence of "ghost" states. Potentially these can be removed by adjusting the local channel (e.g., by setting `--local_channel 1`, which chooses the p channel as the local channel instead of d. For this reason, validation of UPF PPs is always required from the third row and is strongly encouraged in general. For example, check that the expected ionization potential and electron affinities are obtained for the atom and that dimer properties are consistent with those obtained by a quantum chemistry code or a plane-wave code that does not use the Kleinman-Bylander projectors.

24.3.5 molden2qmc

`molden2qmc` is a tool used to convert molden files into an HDF5 file with the QMCPACK format. Molden2qmc is a single program that can use multiple different quantum chemistry codes. It is python code developed by Vladimir Konjkov originally for the CASINO code but then extended to QMCPACK. This tool can be found at https://github.com/gjohnson3/molden2qmc.git.

Using molden2qmc

General use of `molden2qmc` can be prompted by running `molden2qmc.py` and entering the corresponding quantum chemistry code number and the molden file name:

```
number corresponding to the quantum chemistry code used to produce this MOLDEN file:
         0 -- TURBOMOLE
         1 -- PSI4
         2 -- CFOUR 2.0beta
         3 -- ORCA 3.X - 4.X
         4 -- DALTON2016
         5 -- MOLPRO
         6 -- NWCHEM
         7 -- QCHEM 4.X
```

Use the `--qmcpack` flag to create the file as an hdf5 file, suitable for QMCPACK. Without the `--qmcpack` flag, the file will become a gwfn file for CASINO. Example: `molden2qmc.py 5 n4.molden --qmcpack`.

24.4 Obtaining pseudopotentials

24.4.1 Pseudopotentiallibrary.org

An open website collecting community developed and tested pseudopotentials for QMC and other many-body calculations is being developed at https://pseudopotentiallibrary.org. This site includes potentials in QMCPACK format and an increasing range of electronic structure and quantum chemistry codes. We recommend using potentials from this site if available and suitable for your science application.

24.4.2 Opium

Opium is a pseudopotential generation code available from the website http://opium.sourceforge.net/. Opium can generate pseudopotentials with either Hartree-Fock or DFT methods. Once you have a useable pseudopotential param file (for example, Li.param), generate pseudopotentials for use in Quantum ESPRESSO with the upf format as follows:

This generates a UPF-formatted pseudopotential (`Li.upf`, in this case) for use in Quantum ESPRESSO. The pseudopotential conversion tool `ppconvert` can then convert UPF to FSAtom xml format for use in QMCPACK:

Listing 24.2: Convert UPF-formatted pseudopotential to FSAtom xml format

```
ppconvert --upf_pot Li.upf --xml Li.xml
```

24.4.3 Burkatzki-Filippi-Dolg

Burkatzki *et al.* developed a set of energy-consistent pseudopotenitals for use in QMC [[BFD07], [BFD08]], available at http://www.burkatzki.com/pseudos/index.2.html. To convert for use in QMCPACK, select a pseudopotential (choice of basis set is irrelevant to conversion) in GAMESS format and copy the ending (pseudopotential) lines beginning with(element symbol)-QMC GEN:

Listing 24.3: BFD Li pseudopotential in GAMESS format

```
Li-QMC GEN 2 1
3
1.00000000 1 5.41040609
5.41040609 3 2.70520138
-4.60151975 2 2.07005488
1
7.09172172 2 1.34319829
```

Save these lines to a file (here, named `Li.BFD.gamess`; the exact name may be anything as long as it is passed to `ppconvert` after –gamess_pot). Then, convert using `ppconvert` with the following:

Listing 24.4: Convert GAMESS-formatted pseudopotential to FSAtom xml format

```
ppconvert --gamess_pot Li.BFD.gamess --s_ref "2s(1)" --p_ref "2p(0)" --xml Li.BFD.xml
```

Listing 24.5: Convert GAMESS-formatted pseudopotential to Quantum ESPRESSO UPF format

```
ppconvert --gamess_pot Li.BFD.gamess --s_ref "2s(1)" --p_ref "2p(0)" --log_grid --upf␣
↪Li.BFD.upf
```

24.4.4 CASINO

The QMC code CASINO also makes available its pseudopotentials available at the website https://vallico.net/casinoqmc/pplib/. To use one in QMCPACK, select a pseudopotential and download its summary file (`summary.txt`), its tabulated form (`pp.data`), and (for ppconvert to construct the projectors to convert to Quantum ESPRESSO's UPF format) a CASINO atomic wavefunction for each angular momentum channel (`awfn.data_*`). Then, to convert using ppconvert, issue the following command:

Listing 24.6: Convert CASINO-formatted pseudopotential to Quantum ESPRESSO UPF format

```
ppconvert --casino_pot pp.data --casino_us awfn.data_s1_2S --casino_up awfn.data_p1_
↪2P --casino_ud awfn.data_d1_2D --upf Li.TN-DF.upf
```

QMCPACK can directly read in the CASINO-formated pseudopotential (`pp.data`), but four parameters found in the pseudopotential summary file must be specified in the pseudo element (`l-local`, `lmax`, `nrule`, `cutoff`)[see *Pseudopotentials* for details]:

Listing 24.7: XML syntax to use CASINO-formatted pseudopotentials in QMCPACK

```
<pairpot type="pseudo" name="PseudoPot" source="ion0" wavefunction="psi0" format="xml
↪">
   <pseudo elementType="Li" href="Li.pp.data" format="casino" l-local="s" lmax="2"␣
↪nrule="2" cutoff="2.19"/>
   <pseudo elementType="H" href="H.pp.data" format="casino" l-local="s" lmax="2"␣
↪nrule="2" cutoff="0.5"/>
</pairpot>
```

24.4.5 wftester

While not really a stand-alone application, wftester (short for "Wave Function Tester") is a helpful tool for testing pre-existing and experimental estimators and observables. It provides the user with derived quantities from the Hamiltonian and wave function, but evaluated at a small set of configurations.

The wftester is implemented as a QMCDriver, so one invokes QMCPACK in the normal manner with a correct input XML, the difference being the addition of an additional qmc input block. This is the main advantage of this tool–it allows testing of realistic systems and realistic combinations of observables. It can also be invoked before launching into optimization, VMC, or DMC runs, as it is a valid <qmc> block.

As an example, the following code generates a random walker configuration and compares the trial wave function ratio computed in two different ways:

Listing 24.8: The following executes the wavefunction ratio test in "wftester"

```
<qmc method="wftester">
  <parameter name="ratio">    yes    </parameter>
</qmc>
```

Here's a summary of some of the tests provided:

- Ratio Test. Invoked with

```
<parameter name="ratio">yes</parameter>
```

This computes the implemented wave function ratio associated with a single-particle move using two different methods.

- Clone Test. Invoked with

```
<parameter name="clone">yes</parameter>
```

This checks the cloning of TrialWaveFunction, ParticleSet, Hamiltonian, and Walkers.

- Elocal Test. Invoked with

```
<parameter name="printEloc">yes</parameter>
```

For an input electron configuration (can be random), print the value of TrialWaveFunction, LocalEnergy, and all local observables for this configuration.

- Derivative Test. Invoked with

```
<parameter name="ratio">deriv</parameter>}
```

Computes electron gradients, laplacians, and wave function parameter derivatives using implemented calls and compares them to finite-difference results.

- Ion Gradient Test. Invoked with

```
<parameter name="source">ion0</parameter>
```

Calls the implemented evaluateGradSource functions and compares them against finite-difference results.

- "Basic Test". Invoked with

```
<parameter name="basic">yes</parameter>
```

Performs ratio, gradient, and laplacian tests against finite-difference and direct computation of wave function values.

The output of the various tests will be to standard out or "wftest.000" after successful execution of qmcpack.

CHAPTER

TWENTYFIVE

EXTERNAL TOOLS

This chapter provides some information on using QMCPACK with external tools.

25.1 Sanitizer Libraries

Using CMake, set one of these flags for using the clang sanitizer libraries with or without lldb.

```
-DENABLE_SANITIZER  link with the GNU or Clang sanitizer library for asan, ubsan,␣
↪tsan or msan (default=none)
```

In general:

- address sanitizer (asan): catches most pointer-based errors and memory leaks (via lsan) by default.
- undefined behavior sanitizer (ubsan): low-overhead, catches undefined behavior accessing misaligned memory or signed or float to integer overflows.
- undefined behavior sanitizer (tsan): catches potential race conditions in threaded code.
- memory sanitizer (msan): catches using uninitialized memory errors, but is difficult to use without a full set of msan-instrumented libraries.

These set the basic flags required to build with either of these sanitizer libraries which are mutually exclusive. Depending on your system and linker, these may be incompatible with the "Release" build, so set `-DCMAKE_BUILD_TYPE=Debug` or `-DCMAKE_BUILD_TYPE=RelWithDebInfo`. They are tested on GitHub Actions CI using deterministic tests `ctest -L deterministic` (currently ubsan). See the following links for additional information on use, run time, and build options of the sanitizers: https://clang.llvm.org/docs/AddressSanitizer.html & https://clang.llvm.org/docs/MemorySanitizer.html.

25.2 Intel VTune

Intel's VTune profiler has an API that allows program control over collection (pause/resume) and can add information to the profile data (e.g., delineating tasks).

25.2.1 VTune API

If the variable `USE_VTUNE_API` is set, QMCPACK will check that the include file (`ittnotify.h`) and the library (`libittnotify.a`) can be found. To provide CMake with the VTune search paths, add `VTUNE_ROOT` which contains `include` and `lib64` sub-directories.

An example of options to be passed to CMake:

```
-DUSE_VTUNE_API=ON \
-DVTUNE_ROOT=/opt/intel/vtune_amplifier_xe
```

25.2.2 Timers as Tasks

To aid in connecting the timers in the code to the profile data, the start/stop of timers will be recorded as a task if `USE_VTUNE_TASKS` is set.

In addition to compiling with `USE_VTUNE_TASKS`, an option needs to be set at run time to collect the task API data. In the graphical user interface (GUI), select the checkbox labeled "Analyze user tasks" when setting up the analysis type. For the command line, set the `enable-user-tasks` knob to `true`. For example,

```
amplxe-cl -collect hotspots -knob enable-user-tasks=true ...
```

Collection with the timers set at "fine" can generate too much task data in the profile. Collection with the timers at "medium" collects a more reasonable amount of task data.

25.3 NVIDIA Tools Extensions

NVIDIA's Tools Extensions (NVTX) API enables programmers to annotate their source code when used with the NVIDIA profilers.

25.3.1 NVTX API

If the variable `USE_NVTX_API` is set, QMCPACK will add the library (`libnvToolsExt.so`) to the QMCPACK target. To add NVTX annotations to a function, it is necessary to include the `nvToolsExt.h` header file and then make the appropriate calls into the NVTX API. For more information about the NVTX API, see https://docs.nvidia.com/cuda/profiler-users-guide/index.html#nvtx. Any additional calls to the NVTX API should be guarded by the `USE_NVTX_API` compiler define.

25.4 Scitools Understand

Scitools Understand (https://scitools.com/) is a tool for static code analysis. The easiest configuration route is to use the JSON output from CMake, which the Understand project importer can read directly:

1. Configure QMCPACK by running CMake with `CMAKE_EXPORT_COMPILE_COMMANDS=ON`, for example:

   ```
   cmake -DCMAKE_C_COMPILER=clang -DCMAKE_CXX_COMPILER=clang++
   -DQMC_MPI=0 -DCMAKE_EXPORT_COMPILE_COMMANDS=ON ../qmcpack/
   ```

2. Run Understand and create a new C++ project. At the import files and settings dialog, import the `compile_commands.json` created by CMake in the build directory.

CHAPTER

TWENTYSIX

CONTRIBUTING TO THE MANUAL

This section briefly describes how to contribute to the manual and is primarily "by developers, for developers." This section should iterate until a consistent view on style/contents is reached.

Desirable:

- Use the following table templates when describing XML input.
- Unicode rules
  - Do not use characters for which well-established idioms exists, especially dashes, quotes, and apostrophes.
  - Use math mode markup instead of unicode characters for equations.
  - Be cautious of WYSIWYG word processors; cutting and pasting can pickup characters promoted to unicode by the program.
  - Take a look at your text multibyte expanded; that is open it in (emacs and 'esc-x toggle-enable-multibyte-characters')—see any unicode you did not intend?
- Newly added entries to a Bib file should be as complete as possible. Use a tool such as JabRef or Zotero that can automate creation of these entries from just a DOI.

Forbidden:

- Including images instead of text tables.
- Saving files in encodings other than UTF8. Some may report being ASCII encoded since they contain no unicode characters.

Missing sections (these are opinions, not decided priorities):

- Description of XML input in general. Discuss XML format, use of attributes and `<parameter/>` s in general, case sensitivity (input is generally case sensitive), and behavior of when unrecognized XML elements are encountered (they are generally ignored without notification).
- Overview of the input file in general, broad structure, and at least one full example that works in isolation.

Information currently missing for a complete reference specification:

- Noting how many instances of each child element are allowed. Examples: `simulation`–1 only, `method`–1 or more, `jastrow`–0 or more.

Table templates follow for describing XML elements in reference fashion. A number of examples can be found in, for example, *Hamiltonian and Observables*. Preliminary style is (please weigh in with opinions): typewriter text (`\texttt\{\}`) for XML elements, attributes, and parameter names; normal text for literal information in the datatype, values, and default columns; bold (`\textbf{}`) text if an attribute or parameter must take on a particular value (values column); italics (`\textit{}`) for descriptive (nonliteral) information in the values column (e.g., *anything*, *non-zero*); and required/optional attributes or parameters noted by `some_attr`^{r}/`some_attr`^{r} superscripts. Valid

datatypes are text, integer, real, Boolean, and arrays of each. Fixed length arrays can be noted, for example, by "real array(3)."

Template for a generic XML element:

`generic` element:

parent elements:	`parent1` `parent2`
child elements:	`child1` `child2` `child3`

attributes:

Name	Datatype	Values	Default	Description
`attr1`^{r}	text			
`attr2`^{r}	integer			
`attr3`^{r}	real			
`attr4`^{r}	boolean			
`attr5`^{r}	text array			
`attr6`^{r}	integer array			
`attr7`^{r}	real array			
`attr8`^{r}	boolean array			

parameters:

Name	Datatype	Values	Default	Description
`param1`^{r}	text			
`param2`^{r}	integer			
`param3`^{r}	real			
`param4`^{r}	boolean			
`param5`^{r}	text array			
`param6`^{r}	integer array			
`param7`^{r}	real array			
`param8`^{r}	boolean array			

body text: Long form description of body text format

"Factory" elements are XML elements that share a tag but whose contents change based on the value an attribute, or sometimes multiple attributes, take. The attribute(s) that determines the allowed content is subsequently referred to as the "type selector" (e.g., for `<estimator/>` elements, the type selector is usually the `type` attribute). These types of elements are frequently encountered as they correspond (sometimes loosely, sometimes literally) to polymorphic classes in QMCPACK that are built in "factories." This name is true to the underlying code but may be obscure to the general user (is there a better name to retain the general meaning?).

The following template should be provided each time a new "factory" type is encountered (such as `<estimator/>`). The table lists all types of possible elements (see "type options" in the template) and any attributes that are common to all possible related elements. Specific "derived" elements are then described one at a time with the previous template, noting the type selector in addition to the XML tag (e.g., "`estimator type=density` element").

Template for shared information about "factory" elements.

`generic` factory element:

parent elements:	`parent1` `parent2`
child elements:	`child1` `child2` `child3`
type selector	`some` attribute
type options	Selection 1
	Selection 2
	Selection 3
	...

shared attributes:

Name	Datatype	Values	Default	Description
`attr1`^{r}	text			
`attr2`^{r}	integer			
...				

CHAPTER

TWENTYSEVEN

UNIT TESTING

Unit testing is a standard software engineering practice to aid in ensuring a quality product. A good suite of unit tests provides confidence in refactoring and changing code, furnishes some documentation on how classes and functions are used, and can drive a more decoupled design.

If unit tests do not already exist for a section of code, you are encouraged to add them when modifying that section of code. New code additions should also include unit tests. When possible, fixes for specific bugs should also include a unit test that would have caught the bug.

27.1 Unit testing framework

The Catch framework is used for unit testing. See the project site for a tutorial and documentation: https://github.com/philsquared/Catch.

Catch consists solely of header files. It is distributed as a single include file about 400 KB in size. In QMCPACK, it is stored in `external_codes/catch`.

27.2 Unit test organization

The source for the unit tests is located in the `tests` directory under each directory in `src` (e.g., `src/QMCWavefunctions/tests`). All of the tests in each `tests` directory get compiled into an executable. After building the project, the individual unit test executables can be found in `build/tests/bin`. For example, the tests in `src/QMCWavefunctions/tests` are compiled into `build/tests/bin/test_wavefunction`.

All the unit test executables are collected under ctest with the `unit` label. When checking the whole code, it is useful to run through CMake (`cmake -L unit`). When working on an individual directory, it is useful to run the individual executable.

Some of the tests reference input files. The unit test CMake setup places those input files in particular locations under the `tests` directory (e.g., `tests/xml_test`). The individual test needs to be run from that directory to find the expected input files.

Command line options are available on the unit test executables. Some of the more useful ones are

- List command line options.
- List all the tests in the executable.

A test name can be given on the command line to execute just that test. This is useful when iterating on a particular test or when running in the debugger. Test names often contain spaces, so most command line environments require enclosing the test name in single or double quotes.

27.3 Example

The first example is one test from `src/Numerics/tests/test_grid_functor.cpp`.

Listing 27.1: Unit test example using Catch.

```
TEST_CASE("double_1d_grid_functor", "[numerics]")
{
  LinearGrid<double> grid;
  OneDimGridFunctor<double> f(&grid);

  grid.set(0.0, 1.0, 3);

  REQUIRE(grid.size() == 3);
  REQUIRE(grid.rmin() == 0.0);
  REQUIRE(grid.rmax() == 1.0);
  REQUIRE(grid.dh() == Approx(0.5));
  REQUIRE(grid.dr(1) == Approx(0.5));
}
```

The test function declaration is `TEST_CASE("double_1d_grid_functor","[numerics]")`. The first argument is the test name, and it must be unique in the test suite. The second argument is an optional list of tags. Each tag is a name surrounded by brackets (`"[tag1][tag2]"`). It can also be the empty string.

The `REQUIRE` macro accepts expressions with C++ comparison operators and records an error if the value of the expression is false.

Floating point numbers may have small differences due to roundoff, etc. The `Approx` class adds some tolerance to the comparison. Place it on either side of the comparison (e.g., `Approx(a) == 0.3` or `a = Approx(0.3)`). To adjust the tolerance, use the `epsilon` and `scale` methods to `Approx` (`REQUIRE(Approx(a).epsilon(0.001) = 0.3);`.

27.3.1 Expected output

When running the test executables individually, the output of a run with no failures should look like

```
===============================================================================
All tests passed (26 assertions in 4 test cases)
```

A test with failures will look like

```
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
test_numerics is a Catch v1.4.0 host application.
Run with -? for options

-------------------------------------------------------------------------------
double_1d_grid_functor
-------------------------------------------------------------------------------
/home/user/qmcpack/src/Numerics/tests/test_grid_functor.cpp:29
...............................................................................

/home/user/qmcpack/src/Numerics/tests/test_grid_functor.cpp:39: FAILED:
  REQUIRE( grid.dh() == Approx(0.6) )
with expansion:
  0.5 == Approx( 0.6 )
```

(continues on next page)

(continued from previous page)

```
===============================================================================
test cases:  4 |  3 passed | 1 failed
assertions: 25 | 24 passed | 1 failed
```

27.4 Adding tests

Three scenarios are covered here: adding a new test in an existing file, adding a new test file, and adding a new `test` directory.

27.4.1 Adding a test to existing file

Copy an existing test or from the example shown here. Be sure to change the test name.

27.4.2 Adding a test file

When adding a new test file, create a file in the test directory, or copy from an existing file. Add the file name to the `ADD_EXECUTABLE` in the `CMakeLists.txt` file in that directory.

One (and only one) file must define the `main` function for the test executable by defining `CATCH_CONFIG_MAIN` before including the Catch header. If more than one file defines this value, there will be linking errors about multiply defined values.

Some of the tests need to shut down MPI properly to avoid extraneous error messages. Those tests include `Message/catch_mpi_main.hpp` instead of defining `CATCH_CONFIG_MAIN`.

27.4.3 Adding a test directory

Copy the `CMakeLists.txt` file from an existing `tests` directory. Change the `SRC_DIR` name and the files in the `ADD_EXECUTABLES` line. The libraries to link in `TARGET_LINK_LIBRARIES` may need to be updated.

Add the new test directory to `src/CMakeLists.txt` in the `BUILD_UNIT_TESTS` section near the end.

27.5 Testing with random numbers

Many algorithms and parts of the code depend on random numbers, which makes validating the results difficult. One solution is to verify that certain properties hold for any random number. This approach is valuable at some levels of testing, but is unsatisfying at the unit test level.

The `Utilities` directory contains a "fake" random number generator that can be used for deterministic tests of these parts of the code. Currently it outputs a single, fixed value every time it is called, but it could be expanded to produce more varied, but still deterministic, sequences. See `src/QMCDrivers/test_vmc.cpp` for an example of using the fake random number generator.

CHAPTER

TWENTYEIGHT

INTEGRATION TESTS

Unlike unit tests requiring only a specific part of QMCPACK being built for testing, integration tests require the qmcpack executable. In this category, tests are made based on realistic simulations although the amount of statistics collected depends on sub-categories:

- Deterministic integration tests must be 100% reliable, quick to run, and always pass. They usually run one or a few walkers for a very few steps in a few seconds. They are used to rapidly identify changes as part of the continuous integration testing, to verify installations, and for development work.
- Short integration tests mostly run 16 walkers in a few hundred steps within a minutes. These are usually stochastic and should pass with very high reliability.
- Long integration tests mostly run 16 walkers in a few thousand steps within 10 minutes. These are usually stochastic and should pass with very high reliability.

To keep overall testing costs down, electron counts are usually kept small while still being large enough to comprehensively test the code e.g. 3-10. The complete test set except for the long tests has to be able to be run on a laptop or modest workstation in a reasonable amount of time.

28.1 Integration test organization

Integration tests are placed under directories such as `tests/heg`, `tests/solids` and `tests/molecules` from the top directory and one sub-directory for each simulation system. Each test source directory contains input XML files, orbital h5 files, pseudo-potential files and reference data (qmc_ref). These files may be shared by a few tests to minimize duplicated files. When cmake is invoked in the build directory, one directory per test is created and necessary files correspond to a given test are softlinked. It serves as a working directory when that test is being executed. To minimize the number file operation and make the cmake execution fast, there is limitation on file names used by tests. The filenames are given below and implemented in the COPY_DIRECTORY_USING_SYMLINK_LIMITED function in Cmake/macros.cmake.

```
qmc-ref/qmc_ref for reference data folder.
*.opt.xml/*.ncpp.xml/*.BFD.xml/*.ccECP.xml for pseudo-potential files.
*.py/*.sh for result checking helper scripts.
*.wfj.xml/*.wfnoj.xml/*.wfs.xml for standalone wavefunction input files.
*.structure.xml/*.ptcl.xml for standalone structure/particleset input files.
```

28.2 How to add a integration test

1. Generate reference data using a very long (many blocks >=2000) and possibly wide run (many nodes). This reduces both the error bar and the error bar of the error bar (10x samples than long test, 100x samples than short test). A folder named qmc-ref containing input.xml, scalar.dat and output file is required with the commit. The number of blocks should be about 200 to avoid large text files (a simple way to obtain these files is to repeat the reference run with 10x fewer blocks and 10x more steps).
2. Generate the short/long run input files. Use the reference error bar to appropriately estimate the error bar for the long and short tests. These error bars are sqrt(10+1) and sqrt(100+1) times larger than the very long reference. 10x grade is not a hard requirement but ref >= 10 long, long >= 10 short are required.
3. Short tests must be less than 20 sec VMC, 1 min OPT/DMC on a 16core Xeon processor. Long tests are preferably in the 5-10min range. For systems containing more than just a few electrons submitting only a long test may be appropriate.
4. Deterministic tests require a different approach: use of a fixed seed value, and for example, 3 blocks of 2 steps and a single walker. The intent of these tests is to exercise the code paths but keep the run short enough that the numerical deviations do not build up. Different reference data may be needed for mixed precision vs full precision runs.

28.2.1 Suggested procedure to add a test

1. Study some of the existing tests and their CMakeLists.txt configuration file to see what is required and the typical system sizes and run lengths used.
2. Perform a run ~30s in length on a 16 core machine (200 blocks min) using the CPU version of the code with 16 MPI and 1 thread per MPI. Decide if the resulting error bar is meaningful for a test. If so, short and long tests should be created. If not, possibly only a long test is appropriate.
3. Perform a reference run by increasing steps and blocks by 10x each (2000 blocks) and obtain reference mean and error bars. Long and short test error bars are then sqrt(100+1) and sqrt(10+1) of the reference.
4. Generate reference scalar data by redoing the reference run with 200 blocks and 100x steps. These data are should be committed in a qmc-ref directory with the test.
5. Create short (1x blocks, 1x steps) and long (1x blocks, 10x steps) input files (200 blocks each). Make one set of input files for CPU runs (walkers=1) and another for GPU runs (walkers=16).
6. Create CMakeLists.txt by following the example in other tests. CPU runs should include at least a 4 MPI, 4 thread test since this tests OpenMP, MPI, and any possible interactions between them. A GPU test should have 1 MPI and 16 threads.
7. Create a README file with information describing the tests and the reference data.
8. Check that the tests run properly with ctest on your local machine.
9. Submit a pull request with the final tests.

CHAPTER

TWENTYNINE

RUNNING QMCPACK ON DOCKER CONTAINERS

This guide will briefly cover running QMCPACK on your machine using a docker container. Docker containers are a portable way to achieve reproducibility across all developers and users. Two main uses:

1. Debugging CI related issues running on Docker containers that are not reproducible in other environments.
2. Ease the learning curve by providing a ready-to-go environment in a single container (binary available in DockerHub) to new community members.

29.1 Current Images

Docker containers are identified by *domain/image:tag* and stored using DockerHub. Currently available containers have pre-installed QMCPACK dependencies, see the Dockerfile file link for available dependencies on each image:

- **Linux containers**
  - williamfgc/qmcpack-ci:ubuntu20-openmpi: Dockerfile
  - williamfgc/qmcpack-ci:ubuntu20-clang-latest: Dockerfile

29.2 Running Docker Containers

1. **Install the Docker engine**: install the latest version of the Docker engine for your system. Please see the documentation for different Linux distros here.

   After installation run the following command to verify the Docker engine is properly installed. **Note**: restart your system if necessary.

   ```
   docker run hello-world
   ```

2. **Pull an image** (optional, see 3): once Docker is properly installed and running on your system, use the following command to download a QMCPACK image and tag:

   ```
   docker pull williamfgc/qmcpack-ci:ubuntu20-openmpi
   ```

3. **Run an image**: the *docker run* command will spin up a container with using the image we just downloaded from step 2. Alternatively, *docker run* will automatically fallback to pulling the image and tag from DockerHub (requires connection).

   For a quick and safe, non *sudo*, run:

   ```
   docker run -it williamfgc/qmcpack-ci:ubuntu20-openmpi /bin/bash
   ```

The above will run the container in interactive mode dropping the default *user* to */home/user* using the *bash* shell. If *sudo* access is needed (e.g. install a package *sudo apt-get install emacs*) the password for the default *user* is also *user*.

Run an image (for Development) *docker run* has a few extra options that can be used to run QMCPACK:

```
docker run -u $(id -u `stat -c "%U" .`):$(id -g `stat -c "%G" .`) -v <QMCPACK␣
↪Source Directory>:/home/user -it williamfgc/qmcpack-ci:ubuntu20-openmpi /bin/
↪bash
```

Flags used by *docker run* (Note: The flags -i and -t are combined above):

-u : For building we need write permissions, the current arguments will set your container user and group to match your host user and group (e.g. install additional packages, allocating shared volume permissions, etc.).

-v : Replace <*QMCPACK Source Directory*> with the direct path to your QMCPACK directory, this maps it to our landing directory and gives docker access to the files

-i : Specifies the image to use

-t : Allocate a pseudo-tty, allows an instance of bash to pass commands to it

As an example, if extra permissions are needed the container can be run with the *sudo* user (not recommended):

```
docker run -u root -v path/to/QMCPACK:home/user -it williamfgc/qmcpack-
↪ci:ubuntu20-openmpi /bin/bash
```

29.3 Build QMCPACK on Docker

The following steps just follow a regular QMCPACK build on any Linux environment

1. **Get QMCPACK**: use *https* as *ssh* requires extra authentication

- Option 1 (fresh build):

```
git clone https://github.com/QMCPACK/qmcpack.git
cd build
```

- Option 2 (for development):

```
cd build
```

  - Note: this assumes you have mapped your QMCPACK directory as outlined above, else traverse to your source directory, then the build folder inside.

2. **Configure**:

```
cmake -GNinja \
 -DCMAKE_BUILD_TYPE=RelWithDebInfo \
 -DCMAKE_C_COMPILER=mpicc -DCMAKE_CXX_COMPILER=mpicxx \
 -DQMC_COMPLEX=0 \
 ..
```

- Note: To reproduce the build in the Docker container used by GitHub Actions CI pipeline we provide an optimized build with debug symbols *-DCMAKE_BUILD_TYPE=RelWithDebInfo* , but users can select any other cmake build type(*Release* being default):

  - *Debug*

- *Release*
- *RelWithDebInfo*

3. **Build**:

```
ninja
```

3. **Test**:

```
ctest -VV -R deterministic-unit_test_wavefunction_trialwf
ctest -L deterministic
```

Caution: OpenMPI strongly advises against running as a *root* user, see docs

CHAPTER

THIRTY

QMCPACK DESIGN AND FEATURE DOCUMENTATION

This section contains information on the overall design of QMCPACK. Also included are detailed explanations/derivations of major features and algorithms present in the code.

30.1 QMCPACK design

TBD.

30.2 Feature: Optimized long-range breakup (Ewald)

Consider a group of particles interacting with long-range central potentials, $v^{\alpha\beta}(|r_i^\alpha - r_j^\beta|)$, where the Greek superscripts represent the particle species (e.g., $\alpha =$ electron, $\beta =$ proton), and Roman subscripts refer to particle number within a species. We can then write the total interaction energy for the system as

$$V = \sum_\alpha \left\{ \sum_{i<j} v^{\alpha\alpha}(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha|) + \sum_{\beta<\alpha} \sum_{i,j} v^{\alpha\beta}(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta|) \right\} \tag{30.1}$$

30.2.1 The long-range problem

Consider such a system in periodic boundary conditions in a cell defined by primitive lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. Let $\mathbf{L} \equiv n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ be a direct lattice vector. Then the interaction energy per cell for the periodic system is given by

$$\begin{aligned} V = \sum_{\mathbf{L}} \sum_\alpha \Bigg\{ & \overbrace{\sum_{i<j} v^{\alpha\alpha}(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha + \mathbf{L}|)}^{\text{homologous}} + \overbrace{\sum_{\beta<\alpha} \sum_{i,j} v^{\alpha\beta}(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta + \mathbf{L}|)}^{\text{heterologous}} \Bigg\} \\ & + \underbrace{\sum_{\mathbf{L}\neq\mathbf{0}} \sum_\alpha N^\alpha v^{\alpha\alpha}(|\mathbf{L}|)}_{\text{Madelung}} \ . \end{aligned} \tag{30.2}$$

where N^α is the number particles of species α. If the potentials $v^{\alpha\beta}(r)$ are indeed long-range, the summation over direct lattice vectors will not converge in this naive form. A solution to the problem was posited by Ewald. We break the central potentials into two pieces—a short-range and a long-range part defined by

$$v^{\alpha\beta}(r) = v_s^{\alpha\beta}(r) + v_l^{\alpha\beta}(r) \ . \tag{30.3}$$

We will perform the summation over images for the short-range part in real space, while performing the sum for the long-range part in reciprocal space. For simplicity, we choose $v_s^{\alpha\beta}(r)$ so that it is identically zero at the half-the-box length. This eliminates the need to sum over images in real space.

30.2.2 Reciprocal-space sums

Heterologous terms

We begin with (30.2), starting with the heterologous terms (i.e., the terms involving particles of different species). The short-range terms are trivial, so we neglect them here.

$$\text{heterologous} = \frac{1}{2}\sum_{\alpha\neq\beta}\sum_{i,j}\sum_{\mathbf{L}} v_l^{\alpha\beta}(\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta + \mathbf{L})\,. \tag{30.4}$$

We insert the resolution of unity in real space twice:

$$\begin{aligned}
\text{heterologous} = & \frac{1}{2}\sum_{\alpha\neq\beta}\int_{\text{cell}} d\mathbf{r}\, d\mathbf{r}' \sum_{i,j}\delta(\mathbf{r}_i^\alpha - \mathbf{r})\delta(\mathbf{r}_j^\beta - \mathbf{r}')\sum_{\mathbf{L}} v_l^{\alpha\beta}(|\mathbf{r}-\mathbf{r}'+\mathbf{L}|)\,, \\
= & \frac{1}{2\Omega^2}\sum_{\alpha\neq\beta}\int_{\text{cell}} d\mathbf{r}\, d\mathbf{r}' \sum_{\mathbf{k},\mathbf{k}',i,j} e^{i\mathbf{k}\cdot(\mathbf{r}_i^\alpha-\mathbf{r})}e^{i\mathbf{k}'\cdot(\mathbf{r}_j^\beta-\mathbf{r}')}\sum_{\mathbf{L}} v_l^{\alpha\beta}(|\mathbf{r}-\mathbf{r}'+\mathbf{L}|)\,, \\
= & \frac{1}{2\Omega^2}\sum_{\alpha\neq\beta}\int_{\text{cell}} d\mathbf{r}\, d\mathbf{r}' \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}'',i,j} e^{i\mathbf{k}\cdot(\mathbf{r}_i^\alpha-\mathbf{r})}e^{i\mathbf{k}'\cdot(\mathbf{r}_j^\beta-\mathbf{r}')}e^{i\mathbf{k}''\cdot(\mathbf{r}-\mathbf{r}')}v_{\mathbf{k}''}^{\alpha\beta}\,.
\end{aligned}$$

Here, the $\mathbf{k}$ summations are over reciprocal lattice vectors given by $\mathbf{k} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$, where

$$\begin{aligned}
\mathbf{b}_1 = & \quad 2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\,, \\
\mathbf{b}_2 = & \quad 2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\,, \\
\mathbf{b}_3 = & \quad 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\,.
\end{aligned}$$

We note that $\mathbf{k}\cdot\mathbf{L} = 2\pi(n_1m_1 + n_2m_2 + n_3m_3)$.

$$\begin{aligned}
v_{k''}^{\alpha\beta} = & \quad \frac{1}{\Omega}\int_{\text{cell}} d\mathbf{r}''\sum_{\mathbf{L}} e^{-i\mathbf{k}''\cdot(|\mathbf{r}''+\mathbf{L}|)}v^{\alpha\beta}(|\mathbf{r}''+\mathbf{L}|)\,, \\
= & \quad \frac{1}{\Omega}\int_{\text{all space}} d\tilde{\mathbf{r}}\, e^{-i\mathbf{k}''\cdot\tilde{\mathbf{r}}}v^{\alpha\beta}(\tilde{r})\,,
\end{aligned} \tag{30.5}$$

where Ω is the volume of the cell. Here we have used the fact that summing over all cells of the integral over the cell is equivalent to integrating over all space.

$$\text{hetero} = \frac{1}{2\Omega^2}\sum_{\alpha\neq\beta}\int_{\text{cell}} d\mathbf{r}\, d\mathbf{r}' \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}'',i,j} e^{i(\mathbf{k}\cdot\mathbf{r}_i^\alpha+\mathbf{k}'\cdot\mathbf{r}_j^\beta)}e^{i(\mathbf{k}''-\mathbf{k})\cdot\mathbf{r}}e^{-i(\mathbf{k}''+\mathbf{k}')\cdot\mathbf{r}'}v_{\mathbf{k}''}^{\alpha\beta}\,. \tag{30.6}$$

We have

$$\frac{1}{\Omega}\int d\mathbf{r}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = \delta_{\mathbf{k},\mathbf{k}'}\,. \tag{30.7}$$

Then, performing the integrations we have

$$\text{hetero} = \frac{1}{2}\sum_{\alpha\neq\beta}\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}'',i,j} e^{i(\mathbf{k}\cdot\mathbf{r}_i^\alpha+\mathbf{k}'\cdot\mathbf{r}_j^\beta)}\delta_{\mathbf{k},\mathbf{k}''}\delta_{-\mathbf{k}',\mathbf{k}''}v_{\mathbf{k}''}^{\alpha\beta}\,. \tag{30.8}$$

We now separate the summations, yielding

$$\text{hetero} = \frac{1}{2}\sum_{\alpha\neq\beta}\sum_{\mathbf{k},\mathbf{k}'}\underbrace{\left[\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i^\alpha}\right]}_{\rho_{\mathbf{k}}^\alpha}\underbrace{\left[\sum_j e^{i\mathbf{k}'\cdot\mathbf{r}_j^\beta}\right]}_{\rho_{\mathbf{k}'}^\beta}\delta_{\mathbf{k},\mathbf{k}''}\delta_{-\mathbf{k}',\mathbf{k}''}v_{\mathbf{k}''}^{\alpha\beta}\,. \tag{30.9}$$

Summing over $\mathbf{k}$ and $\mathbf{k}'$, we have

$$\text{hetero} = \frac{1}{2}\sum_{\alpha\neq\beta}\sum_{\mathbf{k}''}\rho_{\mathbf{k}''}^\alpha\,\rho_{-\mathbf{k}''}^\beta v_{k''}^{\alpha\beta}\,. \tag{30.10}$$

We can simplify the calculation a bit further by rearranging the sums over species:

$$\begin{aligned}\text{hetero} = &\frac{1}{2}\sum_{\alpha>\beta}\sum_{\mathbf{k}}\left(\rho_{\mathbf{k}}^\alpha\rho_{-\mathbf{k}}^\beta+\rho_{-\mathbf{k}}^\alpha\rho_{\mathbf{k}}^\beta\right)v_k^{\alpha\beta}\,,\\ = &\sum_{\alpha>\beta}\sum_{\mathbf{k}}\mathcal{R}e\left(\rho_{\mathbf{k}}^\alpha\rho_{-\mathbf{k}}^\beta\right)v_k^{\alpha\beta}.\end{aligned} \tag{30.11}$$

Homologous terms

We now consider the terms involving particles of the same species interacting with each other. The algebra is very similar to the preceding, with the slight difficulty of avoiding the self-interaction term.

$$\begin{aligned}\text{homologous} = &\sum_\alpha\sum_L\sum_{i<j}v_l^{\alpha\alpha}(|\mathbf{r}_i^\alpha-\mathbf{r}_j^\alpha+\mathbf{L}|)\,,\\ = &\frac{1}{2}\sum_\alpha\sum_L\sum_{i\neq j}v_l^{\alpha\alpha}(|\mathbf{r}_i^\alpha-\mathbf{r}_j^\alpha+\mathbf{L}|)\,.\end{aligned} \tag{30.12}$$

$$\begin{aligned}\text{homologous} = &\frac{1}{2}\sum_\alpha\sum_L\left[-N^\alpha v_l^{\alpha\alpha}(|\mathbf{L}|)+\sum_{i,j}v_l^{\alpha\alpha}(|\mathbf{r}_i^\alpha-\mathbf{r}_j^\alpha+\mathbf{L}|)\right]\,,\\ = &\frac{1}{2}\sum_\alpha\sum_{\mathbf{k}}\left(|\rho_k^\alpha|^2-N\right)v_k^{\alpha\alpha}\,.\end{aligned} \tag{30.13}$$

Madelung terms

Let us now consider the Madelung term for a single particle of species α. This term corresponds to the interaction of a particle with all of its periodic images.

$$\begin{aligned}v_M^\alpha = &\frac{1}{2}\sum_{\mathbf{L}\neq\mathbf{0}}v^{\alpha\alpha}(|\mathbf{L}|)\,,\\ = &\frac{1}{2}\left[-v_l^{\alpha\alpha}(0)+\sum_{\mathbf{L}}v^{\alpha\alpha}(|\mathbf{L}|)\right]\,,\\ = &\frac{1}{2}\left[-v_l^{\alpha\alpha}(0)+\sum_{\mathbf{k}}v_{\mathbf{k}}^{\alpha\alpha}\right]\,.\end{aligned} \tag{30.14}$$

$\mathbf{k} = 0$ terms

Thus far, we have neglected what happens at the special point $\mathbf{k} = \mathbf{0}$. For many long-range potentials, such as the Coulomb potential, $v_k^{\alpha\alpha}$ diverges for $k = 0$. However, we recognize that for a charge-neutral system, the divergent part of the terms cancel each other. If all the potential in the system were precisely Coulomb, the $\mathbf{k} = \mathbf{0}$ terms would cancel precisely, yielding zero. For systems involving PPs, however, it may be that the resulting term is finite, but nonzero. Consider the terms from $\mathbf{k} = \mathbf{0}$:

$$\begin{aligned} V_{k=0} = & \sum_{\alpha>\beta} N^\alpha N^\beta v_{k=0}^{\alpha\beta} + \frac{1}{2}\sum_\alpha \left(N^\alpha\right)^2 v_{k=0}^{\alpha\alpha} \,, \\ = & \frac{1}{2}\sum_{\alpha,\beta} N^\alpha N^\beta v_{k=0}^{\alpha\beta} \,. \end{aligned} \tag{30.15}$$

Next, we must compute $v_{k=0}^{\alpha\beta}$.

$$v_{k=0}^{\alpha\beta} = \frac{4\pi}{\Omega}\int_0^\infty dr\; r^2 v_l^{\alpha\beta}(r) \,. \tag{30.16}$$

We recognize that this integral will not converge because of the large-r behavior. However, we recognize that when we do the sum in (30.15), the large-r parts of the integrals will cancel precisely. Therefore, we define

$$\tilde{v}_{k=0}^{\alpha\beta} = \frac{4\pi}{\Omega}\int_0^{r_{\text{end}}} dr\; r^2 v_l^{\alpha\beta}(r) \,, \tag{30.17}$$

where r_{end} is some cutoff value after which the potential tails precisely cancel.

Neutralizing background terms

For systems with a net charge, such as the one-component plasma (jellium), we add a uniform background charge, which makes the system neutral. When we do this, we must add a term that comes from the interaction of the particle with the neutral background. It is a constant term, independent of the particle positions. In general, we have a compensating background for each species, which largely cancels out for neutral systems.

$$V_{\text{background}} = -\frac{1}{2}\sum_\alpha \left(N^\alpha\right)^2 v_{s\mathbf{0}}^{\alpha\alpha} - \sum_{\alpha>\beta} N_\alpha N_\beta v_{s\mathbf{0}}^{\alpha\beta} \,, \tag{30.18}$$

where $v_{s\mathbf{0}}^{\alpha\beta}$ is given by

$$\begin{aligned} v_{s\mathbf{0}}^{\alpha\beta} = & \frac{1}{\Omega}\int_0^{r_c} d^3r\; v_s^{\alpha\beta}(r) \,, \\ = & \frac{4\pi}{\Omega}\int_0^{r_c} r^2 v_s(r)\, dr \,. \end{aligned}$$

30.2.3 Combining terms

Here, we sum all of the terms we computed in the previous sections:

$$\begin{aligned}
V = & \sum_{\alpha>\beta}\left[\sum_{i,j} v_s(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta|) + \sum_{\mathbf{k}} \mathcal{R}e\left(\rho_{\mathbf{k}}^\alpha \rho_{-\mathbf{k}}^\beta\right) v_k^{\alpha\beta} - N^\alpha N^\beta v_{s\mathbf{0}}^{\alpha\beta}\right], \\
+ & \sum_{\alpha}\left[N^\alpha v_M^\alpha + \sum_{i>j} v_s(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha|) + \frac{1}{2}\sum_{\mathbf{k}}\left(|\rho_{\mathbf{k}}^\alpha|^2 - N\right) v_{\mathbf{k}}^{\alpha\alpha} - \frac{1}{2}\left(N_\alpha\right)^2 v_{s\mathbf{0}}^{\alpha\alpha}\right], \\
= & \sum_{\alpha>\beta}\left[\sum_{i,j} v_s(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta|) + \sum_{\mathbf{k}} \mathcal{R}e\left(\rho_{\mathbf{k}}^\alpha \rho_{-\mathbf{k}}^\beta\right) v_k^{\alpha\beta} - N^\alpha N^\beta v_{s\mathbf{0}}^{\alpha\beta} + \tilde{V}_{k=0}\right], \\
+ & \sum_{\alpha}\left[-\frac{N^\alpha v_l^{\alpha\alpha}(0)}{2} + \sum_{i>j} v_s(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha|) + \frac{1}{2}\sum_{\mathbf{k}}|\rho_{\mathbf{k}}^\alpha|^2 v_{\mathbf{k}}^{\alpha\alpha} - \frac{1}{2}\left(N_\alpha\right)^2 v_{s\mathbf{0}}^{\alpha\alpha} + \tilde{V}_{k=0}\right].
\end{aligned}$$

30.2.4 Computing the reciprocal potential

Now we return to (30.5). Without loss of generality, we define for convenience $\mathbf{k} = k\hat{\mathbf{z}}$.

$$v_k^{\alpha\beta} = \frac{2\pi}{\Omega}\int_0^\infty dr \int_{-1}^1 d\cos(\theta)\, r^2 e^{-ikr\cos(\theta)} v_l^{\alpha\beta}(r)\,. \tag{30.19}$$

We do the angular integral first. By inversion symmetry, the imaginary part of the integral vanishes, yielding

$$v_k^{\alpha\beta} = \frac{4\pi}{\Omega k}\int_0^\infty dr\, r\sin(kr) v_l^{\alpha\beta}(r)\,. \tag{30.20}$$

30.2.5 The Coulomb potential

For the case of the Coulomb potential, the preceding integral is not formally convergent if we do the integral naively. We may remedy the situation by including a convergence factor, $e^{-k_0 r}$. For a potential of the form $v^{\text{coul}}(r) = q_1 q_2/r$, this yields

$$\begin{aligned}
v_k^{\text{screened coul}} &= \frac{4\pi q_1 q_2}{\Omega k}\int_0^\infty dr\ \sin(kr) e^{-k_0 r}\,, \\
&= \frac{4\pi q_1 q_2}{\Omega(k^2 + k_0^2)}\,.
\end{aligned} \tag{30.21}$$

Allowing the convergence factor to tend to zero, we have

$$v_k^{\text{coul}} = \frac{4\pi q_1 q_2}{\Omega k^2}\,. \tag{30.22}$$

For more generalized potentials with a Coulomb tail, we cannot evaluate (30.20) numerically but must handle the coulomb part analytically. In this case, we have

$$v_k^{\alpha\beta} = \frac{4\pi}{\Omega}\left\{\frac{q_1 q_2}{k^2} + \int_0^\infty dr\, r\sin(kr)\left[v_l^{\alpha\beta}(r) - \frac{q_1 q_2}{r}\right]\right\}\,. \tag{30.23}$$

30.2.6 Efficient calculation methods

Fast computation of $\rho_{\mathbf{k}}$

We wish to quickly calculate the quantity

$$\rho_{\mathbf{k}}^{\alpha} \equiv \sum_i e^{i\mathbf{k}\cdot r_i^{\alpha}} \,. \tag{30.24}$$

First, we write

$$\begin{aligned} \mathbf{k} &= m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \,, \\ \mathbf{k}\cdot\mathbf{r}_i^{\alpha} &= m_1\mathbf{b}_1\cdot\mathbf{r}_i^{\alpha} + m_2\mathbf{b}_2\cdot\mathbf{r}_i^{\alpha} + m_3\mathbf{b}_3\cdot\mathbf{r}_i^{\alpha} \,, \\ e^{i\mathbf{k}\cdot r_i^{\alpha}} &= \underbrace{\left[e^{i\mathbf{b}_1\cdot\mathbf{r}_i^{\alpha}}\right]}_{C_1^{i\alpha}}{}^{m_1} \underbrace{\left[e^{i\mathbf{b}_2\cdot\mathbf{r}_i^{\alpha}}\right]}_{C_2^{i\alpha}}{}^{m_2} \underbrace{\left[e^{i\mathbf{b}_3\cdot\mathbf{r}_i^{\alpha}}\right]}_{C_3^{i\alpha}}{}^{m_3} \,. \end{aligned} \tag{30.25}$$

Now, we note that

$$^{m_1} = C_1^{i\alpha}[C^{i\alpha}]^{(m_1-1)} \,. \tag{30.26}$$

This allows us to recursively build up an array of the $C^{i\alpha}$s and then compute $\rho_{\mathbf{k}}$ for all $\mathbf{k}$-vectors by looping over all k-vectors, requiring only two complex multiplies per particle per $\mathbf{k}$.

Algorithm to quickly calculate $\rho_{\mathbf{k}}^{\alpha}$.

Create list of $\mathbf{k}$-vectors and corresponding (m_1, m_2, m_3) indices.
for all $\alpha \in$ species
  Zero out $\rho_{\mathbf{k}}^{\alpha}$
  for all $i \in$ particles **do**
    for $j \in [1 \cdots 3]$ **do**
      Compute $C_j^{i\alpha} \equiv e^{i\mathbf{b}_j\cdot\mathbf{r}_i^{\alpha}}$
      for $m \in [-m_{\max} \ldots m_{\max}]$ **do**
        Compute $[C_j^{i\alpha}]^m$ and store in array
      end for
    end for
    for all $(m_1, m_2, m_3) \in$ index list **do**
      Compute $e^{i\mathbf{k}\cdot r_i^{\alpha}} = [C_1^{i\alpha}]^{m_1}[C_2^{i\alpha}]^{m_2}[C_3^{i\alpha}]^{m_3}$ from array
    end for
  end for
end for

30.2.7 Gaussian charge screening breakup

This original approach to the short- and long-range breakup adds an opposite screening charge of Gaussian shape around each point charge. It then removes the charge in the long-range part of the potential. In this potential,

$$v_{\text{long}}(r) = \frac{q_1 q_2}{r}\text{erf}(\alpha r) \,, \tag{30.27}$$

where α is an adjustable parameter used to control how short ranged the potential should be. If the box size is L, a typical value for α might be $7/(Lq_1q_2)$. We should note that this form for the long-range potential should also work

for any general potential with a Coulomb tail (e.g., pseudo-Hamiltonian potentials. For this form of the long-range potential, we have in k-space

$$v_k = \frac{4\pi q_1 q_2 \exp\left[\frac{-k^2}{4\alpha^2}\right]}{\Omega k^2} \,. \tag{30.28}$$

30.2.8 Optimized breakup method

In this section, we undertake the task of choosing a long-range/short-range partitioning of the potential, which is optimal in that it minimizes the error for given real and k-space cutoffs r_c and k_c. Here, we slightly modify the method introduced by Natoli and Ceperley [[NC95]]. We choose $r_c = \frac{1}{2}\min\{L_i\}$ so that we require the nearest image in real-space summation. k_c is then chosen to satisfy our accuracy requirements.

Here we modify our notation slightly to accommodate details not previously required. We restrict our discussion to the interaction of two particle species (which may be the same), and drop our species indices. Thus, we are looking for short- and long-range potentials defined by

$$v(r) = v^s(r) + v^\ell(r) \,. \tag{30.29}$$

Define v_k^s and v_k^ℓ to be the respective Fourier transforms of the previous equation. The goal is to choose $v_s(r)$ such that its value and first two derivatives vanish at r_c, while making $v^\ell(r)$ as smooth as possible so that k-space components, v_k^ℓ, are very small for $k > k_c$. Here, we describe how to do this in an optimal way.

Define the periodic potential, V_p, as

$$V_p(\mathbf{r}) = \sum_l v(|\mathbf{r}+\mathbf{l}|), \tag{30.30}$$

where $\mathbf{r}$ is the displacement between the two particles and $\mathbf{l}$ is a lattice vector. Let us then define our approximation to this potential, V_a, as

$$V_a(\mathbf{r}) = v^s(r) + \sum_{|\mathbf{k}|<k_c} v_k^\ell e^{i\mathbf{k}\cdot\mathbf{r}} \,. \tag{30.31}$$

Now, we seek to minimize the RMS error over the cell,

$$\chi^2 = \frac{1}{\Omega}\int_\Omega d^3\mathbf{r}\ |V_p(\mathbf{r}) - V_a(\mathbf{r})|^2 \,. \tag{30.32}$$

We may write

$$V_p(\mathbf{r}) = \sum_{\mathbf{k}} v_k e^{i\mathbf{k}\cdot\mathbf{r}} \,, \tag{30.33}$$

where

$$v_k = \frac{1}{\Omega}\int d^3\mathbf{r}\ e^{-i\mathbf{k}\cdot\mathbf{r}} v(r) \,. \tag{30.34}$$

We now need a basis in which to represent the broken-up potential. We may choose to represent either $v^s(r)$ or $v^\ell(r)$ in a real-space basis. Natoli and Ceperley chose the former in their paper. We choose the latter for a number of reasons. First, singular potentials are difficult to represent in a linear basis unless the singularity is explicitly included. This requires a separate basis for each type of singularity. The short-range potential may have an arbitrary number of features for $r < r_c$ and still be a valid potential. By construction, however, we desire that $v^\ell(r)$ be smooth in real-space so that its Fourier transform falls off quickly with increasing k. We therefore expect that, in general, $v^\ell(r)$ should be well represented by fewer basis functions than $v^s(r)$. Therefore, we define

$$v^\ell(r) \equiv \begin{cases} \sum_{n=0}^{J-1} t_n h_n(r) & \text{for } r \le r_c \\ v(r) & \text{for } r > r_c. \end{cases} \,, \tag{30.35}$$

where the $h_n(r)$ are a set of J basis functions. We require that the two cases agree on the value and first two derivatives at r_c. We may then define

$$c_{nk} \equiv \frac{1}{\Omega}\int_0^{r_c} d^3\mathbf{r}\; e^{-i\mathbf{k}\cdot\mathbf{r}} h_n(r)\;. \tag{30.36}$$

Similarly, we define

$$x_k \equiv -\frac{1}{\Omega}\int_{r_c}^{\infty} d^3\mathbf{r}\; e^{-i\mathbf{k}\cdot\mathbf{r}} v(r)\;. \tag{30.37}$$

Therefore,

$$v_k^\ell = -x_k + \sum_{n=0}^{J-1} t_n c_{nk}\;. \tag{30.38}$$

Because $v^s(r)$ goes identically to zero at the box edge, inside the cell we may write

$$v^s(\mathbf{r}) = \sum_{\mathbf{k}} v_k^s e^{i\mathbf{k}\cdot\mathbf{r}}\;. \tag{30.39}$$

We then write

$$\chi^2 = \frac{1}{\Omega}\int_\Omega d^3\mathbf{r}\left|\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\left(v_k - v_k^s\right) - \sum_{|\mathbf{k}|\le k_c} v_k^\ell\right|^2\;. \tag{30.40}$$

We see that if we define

$$v^s(r) \equiv v(r) - v^\ell(r)\;. \tag{30.41}$$

Then

$$v_k^\ell + v_k^s = v_k\;, \tag{30.42}$$

which then cancels out all terms for $|\mathbf{k}| < k_c$. Then we have

$$\begin{aligned}
\chi^2 = &\quad \frac{1}{\Omega}\int_\Omega d^3\mathbf{r}\left|\sum_{|\mathbf{k}|>k_c} e^{i\mathbf{k}\cdot\mathbf{r}}\left(v_k - v_k^s\right)\right|^2\;,\\
= &\quad \frac{1}{\Omega}\int_\Omega d^3\mathbf{r}\left|\sum_{|\mathbf{k}|>k_c} e^{i\mathbf{k}\cdot\mathbf{r}} v_k^\ell\right|^2\;,\\
= &\quad \frac{1}{\Omega}\int_\Omega d^3\mathbf{r}\left|\sum_{|\mathbf{k}|>k_c} e^{i\mathbf{k}\cdot\mathbf{r}}\left(-x_k + \sum_{n=0}^{J-1} t_n c_{nk}\right)\right|^2\;.
\end{aligned} \tag{30.43}$$

We expand the summation,

$$\chi^2 = \frac{1}{\Omega}\int_\Omega d^3\mathbf{r}\sum_{\{|\mathbf{k}|,|\mathbf{k}'|\}>k_c} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\left(x_k - \sum_{n=0}^{J-1} t_n c_{nk}\right)\left(x_k - \sum_{m=0}^{J-1} t_m c_{mk'}\right)\;. \tag{30.44}$$

We take the derivative w.r.t. t_m:

$$\frac{\partial(\chi^2)}{\partial t_m} = \frac{2}{\Omega}\int_\Omega d^3\mathbf{r}\sum_{\{|\mathbf{k}|,|\mathbf{k}'|\}>k_c} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\left(x_k - \sum_{n=0}^{J-1} t_n c_{nk}\right) c_{mk'}\;. \tag{30.45}$$

We integrate w.r.t. $\mathbf{r}$, yielding a Kronecker δ.

$$\frac{\partial(\chi^2)}{\partial t_m} = 2 \sum_{\{|\mathbf{k}|,|\mathbf{k}'|\}>k_c} \delta_{\mathbf{k},\mathbf{k}'} \left(x_k - \sum_{n=0}^{J-1} t_n c_{nk} \right) c_{mk'} \ . \tag{30.46}$$

Summing over $\mathbf{k}'$ and equating the derivative to zero, we find the minimum of our error function is given by

$$\sum_{n=0}^{J-1} \sum_{|\mathbf{k}|>k_c} c_{mk} c_{nk} t_n = \sum_{|\mathbf{k}|>k_c} x_k c_{mk} \ , \tag{30.47}$$

which is equivalent in form to Equation 19 in [[NC95]], where we have x_k instead of V_k. Thus, we see that we can optimize the short- or long-range potential simply by choosing to use V_k or x_k in the preceding equation. We now define

$$\begin{aligned} A_{mn} &\equiv \sum_{|\mathbf{k}|>k_c} c_{mk} c_{nk} \ , \\ b_m &\equiv \sum_{|\mathbf{k}|>k_c} x_k c_{mk} \ . \end{aligned} \tag{30.48}$$

Thus, it becomes clear that our minimization equations can be cast in the canonical linear form

$$\mathbf{A}\mathbf{t} = \mathbf{b} \ . \tag{30.49}$$

Solution by SVD

In practice, we note that the matrix $\mathbf{A}$ frequently becomes singular in practice. For this reason, we use the singular value decomposition to solve for t_n. This factorization decomposes A as

$$\mathbf{A} = \mathbf{U}\mathbf{S}\mathbf{V}^T \ , \tag{30.50}$$

where $\mathbf{U}^T\mathbf{U} = \mathbf{V}^T\mathbf{V} = 1$ and $\mathbf{S}$ is diagonal. In this form, we have

$$\mathbf{t} = \sum_{i=0}^{J-1} \left(\frac{\mathbf{U}_{(i)} \cdot \mathbf{b}}{\mathbf{S}_{ii}} \right) \mathbf{V}_{(i)} \ , \tag{30.51}$$

where the parenthesized subscripts refer to columns. The advantage of this form is that if $\mathbf{S}_{ii}$ is zero or very near zero, the contribution of the i^{th} of $\mathbf{V}$ may be neglected since it represents a numerical instability and has little physical meaning. It represents the fact that the system cannot distinguish between two linear combinations of the basis functions. Using the SVD in this manner is guaranteed to be stable. This decomposition is available in LAPACK in the DGESVD subroutine.

Constraining Values

Often, we wish to constrain the value of t_n to have a fixed value to enforce a boundary condition, for example. To do this, we define

$$\mathbf{b}' \equiv \mathbf{b} - t_n \mathbf{A}_{(n)} \ . \tag{30.52}$$

We then define $\mathbf{A}^*$ as $\mathbf{A}$ with the n^{th} row and column removed and $\mathbf{b}^*$ as $\mathbf{b}'$ with the n^{th} element removed. Then we solve the reduced equation $\mathbf{A}^*\mathbf{t}^* = \mathbf{b}^*$ and finally insert t_n back into the appropriate place in $\mathbf{t}^*$ to recover the complete, constrained vector $\mathbf{t}$. This may be trivially generalized to an arbitrary number of constraints.

The LPQHI basis

The preceding discussion is general and independent of the basis used to represent $v^\ell(r)$. In this section, we introduce a convenient basis of localized interpolant functions, similar to those used for splines, which have a number of properties that are convenient for our purposes.

First, we divide the region from 0 to r_c into $M-1$ subregions, bounded above and below by points we term *knots*, defined by $r_j \equiv j\Delta$, where $\Delta \equiv r_c/(M-1)$. We then define compact basis elements, $h_{j\alpha}$, which span the region $[r_{j-1}, r_{j+1}]$, except for $j=0$ and $j=M$. For $j=0$, only the region $[r_0, r_1]$, while for $j=M$, only $[r_{M-1}, r_M]$. Thus, the index j identifies the knot the element is centered on, while α is an integer from 0 to 2 indicating one of three function shapes. The dual index can be mapped to the preceding single index by the relation $n = 3j+\alpha$. The basis functions are then defined as

$$h_{j\alpha}(r) = \begin{cases} \Delta^\alpha \sum_{n=0}^5 S_{\alpha n} \left(\frac{r-r_j}{\Delta}\right)^n, & r_j < r \le r_{j+1} \\ (-\Delta)^\alpha \sum_{n=0}^5 S_{\alpha n} \left(\frac{r_j-r}{\Delta}\right)^n, & r_{j-1} < r \le r_j \\ 0, & \text{otherwise}\,, \end{cases} \tag{30.53}$$

where the matrix $S_{\alpha n}$ is given by

$$S = \begin{bmatrix} 1 & 0 & 0 & -10 & 15 & -6 \\ 0 & 1 & 0 & -6 & 8 & -3 \\ 0 & 0 & \frac{1}{2} & -\frac{3}{2} & \frac{3}{2} & -\frac{1}{2} \end{bmatrix}\,. \tag{30.54}$$

Fig. 30.1 shows plots of these function shapes.

The basis functions have the property that at the left and right extremes (i.e., r_{j-1} and r_{j+1}) their values and first two derivatives are zero. At the center, r_j, we have the properties

$$\begin{aligned} h_{j0}(r_j) &= 1, h'_{j0}(r_j) = 0, \quad h''_{j0}(r_j) = 0\,, \\ h_{j1}(r_j) &= 0, h'_{j1}(r_j) = 1, \quad h''_{j1}(r_j) = 0\,, \\ h_{j2}(r_j) &= 0, h'_{j2}(r_j) = 0, \quad h''_{j2}(r_j) = 1\,. \end{aligned} \tag{30.55}$$

These properties allow the control of the value and first two derivatives of the represented function at any knot value simply by setting the coefficients of the basis functions centered around that knot. Used in combination with the method described in *Constraining Values*, boundary conditions can easily be enforced. In our case, we wish require that

$$h_{M0} = v(r_c), \;\; h_{M1} = v'(r_c), \;\; \text{and} \;\; h_{M2} = v''(r_c)\,. \tag{30.56}$$

This ensures that v^s and its first two derivatives vanish at r_c.

Fourier coefficients

We wish now to calculate the Fourier transforms of the basis functions, defined as

$$c_{j\alpha k} \equiv \frac{1}{\Omega}\int_0^{r_c} d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} h_{j\alpha}(r)\,. \tag{30.57}$$

We may then write,

$$c_{j\alpha k} = \begin{cases} \Delta^\alpha \sum_{n=0}^5 S_{\alpha n} D^+_{0kn}, & j=0 \\ \Delta^\alpha \sum_{n=0}^5 S_{\alpha n} (-1)^{\alpha+n} D^-_{Mkn}, & j=M \\ \Delta^\alpha \sum_{n=0}^5 S_{\alpha n} \left[D^+_{jkn} + (-1)^{\alpha+n} D^-_{jkn}\right] & \text{otherwise}\,, \end{cases} \tag{30.58}$$

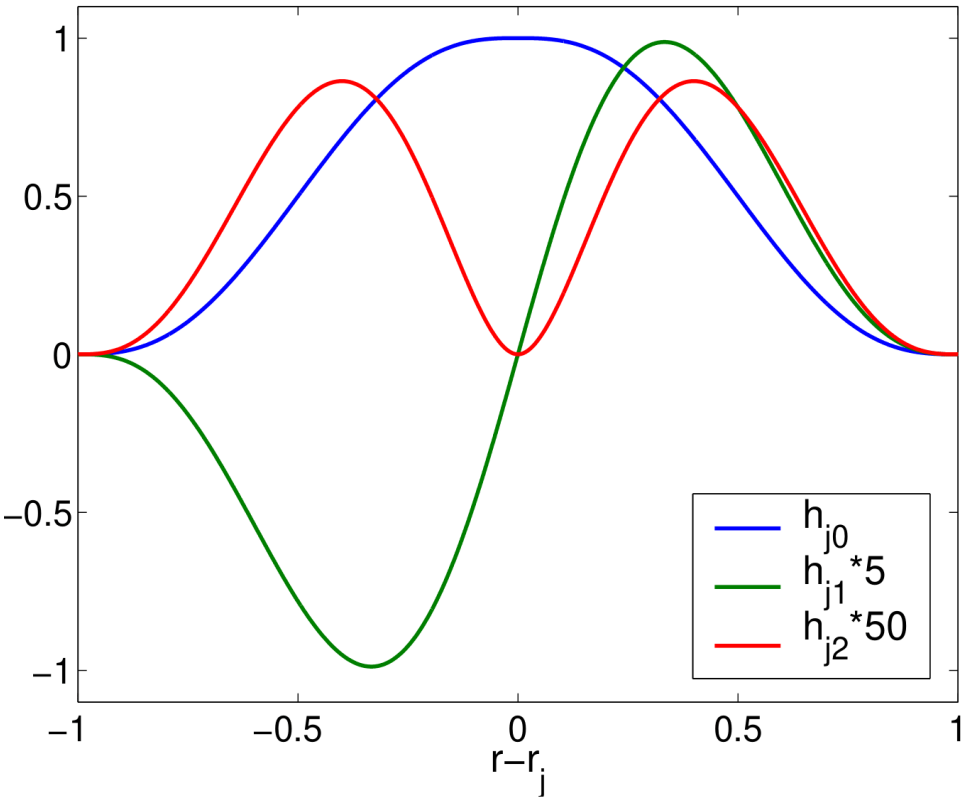

Fig. 30.1: Basis functions h_{j0}, h_{j1}, and h_{j2} are shown. We note that at the left and right extremes, the values and first two derivatives of the functions are zero; while at the center, h_{j0} has a value of 1, h_{j1} has a first derivative of 1, and h_{j2} has a second derivative of 1.

where

$$D^{\pm}_{jkn} \equiv \frac{1}{\Omega}\int_{r_j}^{r_{j\pm1}} d^3\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \left(\frac{r-r_j}{\Delta}\right)^n . \tag{30.59}$$

We then further make the definition that

$$D^{\pm}_{jkn} = \pm\frac{4\pi}{k\Omega}\left[\Delta \mathrm{Im}\left(E^{\pm}_{jk(n+1)}\right) + r_j \mathrm{Im}\left(E^{\pm}_{jkn}\right)\right] . \tag{30.60}$$

It can then be shown that

$$E^{\pm}_{jkn} = \begin{cases} -\frac{i}{k}e^{ikr_j}\left(e^{\pm ik\Delta}-1\right) & \text{if } n=0, \\ -\frac{i}{k}\left[(\pm1)^n e^{ik(r_j\pm\Delta)} - \frac{n}{\Delta}E^{\pm}_{jk(n-1)}\right] & \text{otherwise .} \end{cases} \tag{30.61}$$

Note that these equations correct typographical errors present in [[NC95]].

Enumerating k-points

We note that the summations over k, which are ubiquitous in this paper, require enumeration of the k-vectors. In particular, we should sum over all $|\mathbf{k}| > k_c$. In practice, we must limit our summation to some finite cutoff value $k_c < |\mathbf{k}| < k_{\text{max}}$, where k_{max} should be on the order of $3,000/L$, where L is the minimum box dimension. Enumerating these vectors in a naive fashion even for this finite cutoff would prove quite prohibitive, as it would require $\sim 10^9$ vectors.

Our first optimization comes in realizing that all quantities in this calculation require only $|\mathbf{k}|$ and not $\mathbf{k}$ itself. Thus, we may take advantage of the great degeneracy of $|\mathbf{k}|$. We create a list of (k, N) pairs, where N is the number of vectors with magnitude k. We make nested loops over n_1, n_2, and n_3, yielding $\mathbf{k} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$. If $|\mathbf{k}|$ is in the required range, we check to see whether there is already an entry with that magnitude on our list and increment the corresponding N if there is, or create a new entry if not. Doing so typically saves a factor of ~ 200 in storage and computation.

This reduction is not sufficient for large k_max since it requires that we still look over 10^9 entries. To further reduce costs, we may pick an intermediate cutoff, k_{cont}, above which we will approximate the degeneracy assuming a continuum of k-points. We stop our exact enumeration at k_{cont} and then add $\sim 1,000$ points, k_i, uniformly spaced between k_{cont} and k_{max}. We then approximate the degeneracy by

$$N_i = \frac{4\pi}{3}\frac{\left(k_b^3 - k_a^3\right)}{(2\pi)^3/\Omega} , \tag{30.62}$$

where $k_b = (k_i + k_{i+1})/2$ and $k_a = (k_i + k_{i-1})$. In doing so, we typically reduce our total number of k-points to sum more than $\sim 2,500$ from the 10^9 we had to start.

Calculating x_k's

The Coulomb potential

For $v(r) = \frac{1}{r}$, x_k is given by

$$x_k^{\text{coulomb}} = -\frac{4\pi}{\Omega k^2}\cos(kr_c) . \tag{30.63}$$

The $1/r^2$ potential

For $v(r) = \frac{1}{r^2}$, x_k is given by

$$x_k^{1/r^2} = \frac{4\pi}{\omega k}\left[\mathrm{Si}(kr_c) - \frac{\pi}{2}\right], \tag{30.64}$$

where the *sin integral*, $\mathrm{Si}(z)$, is given by

$$\mathrm{Si}(z) \equiv \int_0^z \frac{\sin\ t}{t} dt\,. \tag{30.65}$$

The $1/r^3$ potential

For $v(r) = \frac{1}{r^3}$, x_k is given by

$$x_k^{1/r^2} = \frac{4\pi}{\omega k}\left[\mathrm{Si}(kr_c) - \frac{\pi}{2}\right], \tag{30.66}$$

where the *cosine integral*, $\mathrm{Ci}(z)$, is given by

$$\mathrm{Ci}(z) \equiv -\int_z^\infty \frac{\cos t}{t} dt\,. \tag{30.67}$$

The $1/r^4$ potential

For $v(r) = \frac{1}{r^4}$, x_k is given by

$$x_k^{1/r^4} = -\frac{4\pi}{\Omega k}\left\{\frac{k\cos(kr_c)}{2r_c} + \frac{\sin(kr_c)}{2r_c^2} + \frac{k^2}{2}\left[\mathrm{Si}(kr_c) - \frac{\pi}{2}\right]\right\}. \tag{30.68}$$

30.3 Feature: Optimized long-range breakup (Ewald) 2

Given a lattice of vectors $\mathbf{L}$, its associated reciprocal lattice of vectors $\mathbf{k}$ and a function $\psi(\mathbf{r})$ periodic on the lattice we define its Fourier transform $\widetilde{\psi}(\mathbf{k})$ as

$$\widetilde{\psi}(\mathbf{k}) = \frac{1}{\Omega}\int_\Omega d\mathbf{r}\psi(\mathbf{r})e^{-i\mathbf{kr}}\,, \tag{30.69}$$

where we indicated both the cell domain and the cell volume by Ω. $\psi(\mathbf{r})$ can then be expressed as

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} \widetilde{\psi}(\mathbf{k})e^{i\mathbf{kr}}\,. \tag{30.70}$$

The potential generated by charges sitting on the lattice positions at a particular point $\mathbf{r}$ inside the cell is given by

$$V(\mathbf{r}) = \sum_{\mathbf{L}} v(|\mathbf{r}+\mathbf{L}|)\,, \tag{30.71}$$

and its Fourier transform can be explicitly written as a function of V or v

$$\widetilde{V}(\mathbf{k}) = \frac{1}{\Omega}\int_\Omega d\mathbf{r}V(\mathbf{r})e^{-i\mathbf{kr}} = \frac{1}{\Omega}\int_{\mathbb{R}^3} d\mathbf{r}v(\mathbf{r})e^{-i\mathbf{kr}}\,, \tag{30.72}$$

where $\mathbb{R}^3$ denotes the whole 3D space. We now want to find the best ("best" to be defined later) approximate potential of the form

$$V_a(\mathbf{r}) = \sum_{k \leq k_c} \widetilde{Y}(k) e^{i\mathbf{kr}} + W(r) \,, \tag{30.73}$$

where $W(r)$ has been chosen to go smoothly to 0 when $r = r_c$, being r_c lower or equal to the Wigner-Seitz radius of the cell. Note also the cutoff k_c on the momentum summation.

The best form of $\widetilde{Y}(k)$ and $W(r)$ is given by minimizing

$$\chi^2 = \frac{1}{\Omega} \int d\mathbf{r} \left(V(\mathbf{r}) - W(\mathbf{r}) - \sum_{k \leq k_c} \widetilde{Y}(k) e^{i\mathbf{kr}} \right)^2 \,, \tag{30.74}$$

or the reciprocal space equivalent

$$\chi^2 = \sum_{k \leq k_c} (\widetilde{V}(k) - \widetilde{W}(k) - \widetilde{Y}(k))^2 + \sum_{k > k_c} (\widetilde{V}(k) - \widetilde{W}(k))^2 \,. \tag{30.75}$$

(30.75) follows from (30.74) and the unitarity (norm conservation) of the Fourier transform.

This last condition is minimized by

$$\widetilde{Y}(k) = \widetilde{V}(k) - \widetilde{W}(k) \qquad \min_{\widetilde{W}(k)} \sum_{k > k_c} (\widetilde{V}(k) - \widetilde{W}(k))^2. \tag{30.76}$$

We now use a set of basis function $c_i(r)$ vanishing smoothly at r_c to expand $W(r)$; that is,

$$W(r) = \sum_i t_i c_i(r) \qquad \text{or} \qquad \widetilde{W}(k) = \sum_i t_i \widetilde{c}_i(k) \,. \tag{30.77}$$

Inserting the reciprocal space expansion of $\widetilde{W}$ in the second condition of (30.76) and minimizing with respect to t_i leads immediately to the linear system $\mathbf{At} = \mathbf{b}$ where

$$A_{ij} = \sum_{k > k_c} \widetilde{c}_i(k) \widetilde{c}_j(k) \qquad b_j = \sum_{k > k_c} V(k) \widetilde{c}_j(k) \,. \tag{30.78}$$

30.3.1 Basis functions

The basis functions are splines. We define a uniform grid with N_{knot} uniformly spaced knots at position $r_i = i \frac{r_c}{N_{\text{knot}}}$, where $i \in [0, N_{\text{knot}} - 1]$. On each knot we center $m + 1$ piecewise polynomials $c_{i\alpha}(r)$ with $\alpha \in [0, m]$, defined as

$$c_{i\alpha}(r) = \begin{cases} \Delta^\alpha \sum_{n=0}^{\mathcal{N}} S_{\alpha n} (\frac{r - r_i}{\Delta})^n & r_i < r \leq r_{i+1} \\ \Delta^{-\alpha} \sum_{n=0}^{\mathcal{N}} S_{\alpha n} (\frac{r_i - r}{\Delta})^n & r_{i-1} < r \leq r_i \\ 0 & |r - r_i| > \Delta \end{cases} . \tag{30.79}$$

These functions and their derivatives are, by construction, continuous and odd (even) (with respect to $r - r_i \to r_i - r$) when α is odd (even). We further ask them to satisfy

$$\begin{aligned} \frac{d^\beta}{dr^\beta} c_{i\alpha}(r) \bigg|_{r=r_i} &= \delta_{\alpha\beta} \quad \beta \in [0, m] \,, \\ \frac{d^\beta}{dr^\beta} c_{i\alpha}(r) \bigg|_{r=r_{i+1}} &= 0 \quad \beta \in [0, m] \,. \end{aligned} \tag{30.80}$$

(The parity of the functions guarantees that the second constraint is satisfied at r_{i-1} as well). These constraints have a simple interpretation: the basis functions and their first m derivatives are 0 on the boundary of the subinterval where

they are defined; the only function to have a nonzero β-th derivative in r_i is $c_{i\beta}$. These $2(m+1)$ constraints therefore impose $\mathcal{N} = 2m+1$. Inserting the definitions of (30.79) in the constraints of (30.80) leads to the set of $2(m+1)$ linear equation that fixes the value of $S_{\alpha n}$:

$$\begin{aligned} \Delta^{\alpha-\beta} S_{\alpha\beta}\beta! &= \delta_{\alpha\beta} \\ \Delta^{\alpha-\beta} \sum_{n=\beta}^{2m+1} S_{\alpha n} \frac{n!}{(n-\beta)!} &= 0\,. \end{aligned} \tag{30.81}$$

We can further simplify inserting the first of these equations into the second and write the linear system as

$$\sum_{n=m+1}^{2m+1} S_{\alpha n} \frac{n!}{(n-\beta)!} = \begin{cases} -\frac{1}{(\alpha-\beta)!} & \alpha \geq \beta \\ 0 & \alpha < \beta \end{cases}\,. \tag{30.82}$$

30.3.2 Fourier components of the basis functions in 3D

$k \neq 0$, non-Coulomb case

We now need to evaluate the Fourier transform $\widetilde{c}_{i\alpha}(k)$. Let us start by writing the definition

$$\widetilde{c}_{i\alpha}(k) = \frac{1}{\omega}\int_\Omega d\mathbf{r} e^{-i\mathbf{kr}} c_{i\alpha}(r)\,. \tag{30.83}$$

Because $c_{i\alpha}$ is different from zero only inside the spherical crown defined by $r_{i-1} < r < r_i$, we can conveniently compute the integral in spherical coordinates as

$$\widetilde{c}_{i\alpha}(k) = \Delta^\alpha \sum_{n=0}^{\mathcal{N}} S_{\alpha n}\left[D^+_{in}(k) + w_{\text{knot}}(-1)^{\alpha+n} D^-_{in}(k)\right]\,, \tag{30.84}$$

where we used the definition $w_{\text{knot}} = 1 - \delta_{i0}$ and

$$D^\pm_{in}(k) = \pm\frac{4\pi}{k\Omega}\text{Im}\left[\int_{r_i}^{r_i\pm\Delta} dr \left(\frac{r-r_i}{\Delta}\right)^n r e^{ikr}\right]\,, \tag{30.85}$$

obtained by integrating the angular part of the Fourier transform. Using the identity

$$\left(\frac{r-r_i}{\Delta}\right)^n r = \Delta\left(\frac{r-r_i}{\Delta}\right)^{n+1} + \left(\frac{r-r_i}{\Delta}\right)^n r_i \tag{30.86}$$

and the definition

$$E^\pm_{in}(k) = \int_{r_i}^{r_i\pm\Delta} dr \left(\frac{r-r_i}{\Delta}\right)^n e^{ikr}\,, \tag{30.87}$$

we rewrite Equation (30.85) as

$$D^\pm_{in}(k) = \pm\frac{4\pi}{k\Omega}\text{Im}\left[\Delta E^\pm_{i(n+1)}(k) + r_i E^\pm_{in}(k)\right]\,.$$

Finally, using integration by part, we can define $E^\pm_{in}$ recursively as

$$E^\pm_{in}(k) = \frac{1}{ik}\left[(\pm)^n e^{ik(r_i\pm\Delta)} - \frac{n}{\Delta}E^\pm_{i(n-1)}(k)\right]\,. \tag{30.88}$$

Starting from the $n=0$ term,

$$E^\pm_{i0}(k) = \frac{1}{ik}e^{ikr_i}\left(e^{\pm ik\Delta} - 1\right)\,. \tag{30.89}$$

$k \neq 0$, Coulomb case

To efficiently treat the Coulomb divergence at the origin, it is convenient to use a basis set $c_{i\alpha}^{\text{coul}}$ of the form

$$c_{i\alpha}^{\text{coul}} = \frac{c_{i\alpha}}{r} \,. \tag{30.90}$$

An equation identical to (30.85) holds but with the modified definition

$$D_{in}^{\pm}(k) = \pm \frac{4\pi}{k\Omega} \text{Im} \left[\int_{r_i}^{r_i \pm \Delta} dr \left(\frac{r - r_i}{\Delta} \right)^n e^{ikr} \right] \,, \tag{30.91}$$

which can be simply expressed using $E_{in}^{\pm}(k)$ as

$$D_{in}^{\pm}(k) = \pm \frac{4\pi}{k\Omega} \text{Im} \left[E_{in}^{\pm}(k) \right] \,. \tag{30.92}$$

$k = 0$ Coulomb and non-Coulomb case

The definitions of $D_{in}(k)$ given so far are clearly incompatible with the choice $k = 0$ (they involve division by k). For the non-Coulomb case, the starting definition is

$$D_{in}^{\pm}(0) = \pm \frac{4\pi}{\Omega} \int_{r_i}^{r_i \pm \Delta} r^2 \left(\frac{r - r_i}{\Delta} \right)^n dr \,. \tag{30.93}$$

Using the definition $I_n^{\pm} = (\pm)^{n+1}\Delta/(n+1)$, we can express this as

$$D_{in}^{\pm}(0) = \pm \frac{4\pi}{\Omega} \left[\Delta^2 I_{n+2}^{\pm} + 2r_i \Delta I_{n+1}^{\pm} + 2r_i^2 I_n^{\pm} \right] \,. \tag{30.94}$$

For the Coulomb case, we get

$$D_{in}^{\pm}(0) = \pm \frac{4\pi}{\Omega} \left(\Delta I_{n+1}^{\pm} + r_i I_n^{\pm} \right) \,. \tag{30.95}$$

30.3.3 Fourier components of the basis functions in 2D

(30.84) still holds provided we define

$$D_{in}^{\pm}(k) = \pm \frac{2\pi}{\Omega \Delta^n} \sum_{j=0}^{n} \binom{n}{j} (-r_i)^{n-j} \int_{r_i}^{r_i \pm \Delta} dr r^{j+1-C} J_0(kr) \,, \tag{30.96}$$

where $C = 1 (= 0)$ for the Coulomb(non-Coulomb) case. (30.96) is obtained using the integral definition of the zero order Bessel function of the first kind:

$$J_0(z) = \frac{1}{\pi} \int_0^{\pi} e^{iz\cos\theta} d\theta \,, \tag{30.97}$$

and the binomial expansion for $(r - r_i)^n$. The integrals can be computed recursively using the following identities:

$$\begin{aligned} &\int dz J_0(z) = \frac{z}{2} \left[\pi J_1(z) H_0(z) + J_0(z)(2 - \pi H_1(z)) \right] \,, \\ &\int dz z J_0(z) = z J_1(z) \,, \\ &\int dz z^n J_0(z) = z^n J_1(z) + (n-1) x^{n-1} J_0(z) - (n-1)^2 \int dz z^{n-2} J_0(z) \,. \end{aligned} \tag{30.98}$$

The bottom equation of (30.98) is obtained using the second equation in the same set, integration by part, and the identity $\int J_1(z) dz = -J_0(z)$. In the top equation, H_0 and H_1 are Struve functions.

30.3.4 Construction of the matrix elements

Using the previous equations, we can construct the matrix elements in (30.78) and proceed solving for t_i. It is sometimes desirable to put some constraints on the value of t_i. For example, when the Coulomb potential is concerned, we might want to set $t_0 = 1$. If the first g variable is constrained by $t_m = \gamma_m$ with $m = [1, g]$, we can simply redefine (30.78) as

$$\begin{aligned} A_{ij} &= \sum_{k>k_c} \widetilde{c}_i(k)\widetilde{c}_j(k) \quad i,j \notin [1,g]\,, \\ b_j &= \sum_{k>k_c} \left(\widetilde{V}(k) - \sum_{m=1}^{g} \gamma_m \widetilde{c}_m(k) \right) \widetilde{c}_j(k) \quad j \notin [1,g]\,. \end{aligned} \tag{30.99}$$

30.4 Feature: Cubic spline interpolation

We present the basic equations and algorithms necessary to construct and evaluate cubic interpolating splines in one, two, and three dimensions. Equations are provided for both natural and periodic boundary conditions.

30.4.1 One dimension

Let us consider the problem in which we have a function $y(x)$ specified at a discrete set of points x_i, such that $y(x_i) = y_i$. We wish to construct a piecewise cubic polynomial interpolating function, $f(x)$, which satisfies the following conditions:

- $f(x_i) = y_i$.
- $f'(x_i^-) = f'(x_i^+)$.
- $f''(x_i^-) = f''(x_i+)$.

Hermite interpolants

In our piecewise representation, we wish to store only the values y_i and first derivatives, y_i', of our function at each point x_i, which we call *knots*. Given this data, we wish to construct the piecewise cubic function to use between x_i and x_{i+1}, which satisfies the preceding conditions. In particular, we wish to find the unique cubic polynomial, $P(x)$, satisfying

$$\begin{aligned} P(x_i) &= y_i\,, \\ P(x_{i+1}) &= y_{i+1}\,, \\ P'(x_i) &= y_i'\,, \\ P'(x_{i+1}) &= y_{i+1}'\,. \end{aligned} \tag{30.100}$$

$$\begin{aligned} h_i &\equiv x_{i+1} - x_i\,, \\ t &\equiv \frac{x - x_i}{h_i}\,. \end{aligned} \tag{30.101}$$

We then define the basis functions,

$$\begin{aligned} p_1(t) &= (1+2t)(t-1)^2\,, \\ q_1(t) &= t(t-1)^2\,, \\ p_2(t) &= t^2(3-2t)\,, \\ q_2(t) &= t^2(t-1)\,. \end{aligned} \tag{30.102}$$

On the interval, $(x_i, x_{i+1}]$, we define the interpolating function

$$P(x) = y_i p_1(t) + y_{i+1} p_2(t) + h\left[y'_i q_1(t) + y'_{i+1} q_2(t)\right] \ . \tag{30.103}$$

It can be easily verified that $P(x)$ satisfies conditions of equations 1 through 3 of (30.100). It is now left to determine the proper values for the y'_i s such that the continuity conditions given previously are satisfied.

By construction, the value of the function and derivative will match at the knots; that is,

$$P(x_i^-) = P(x_i^+), \quad P'(x_i^-) = P'(x_i^+) \, .$$

Then we must now enforce only the second derivative continuity:

$$\begin{aligned} P''(x_i^-) &= P''(x_i^+) \, , \\ \frac{1}{h_{i-1}^2}\left[6y_{i-1} - 6y_i + h_{i-1}\left(2y'_{i-1} + 4y'_i\right)\right] &= \frac{1}{h_i^2}\left[-6y_i + 6y_{i+1} + h_i\left(-4y'_i - 2y'_{i+1}\right)\right] \ . \end{aligned}$$

Let us define

$$\begin{aligned} \lambda_i &\equiv \frac{h_i}{2(h_i + h_{i-1})} \, , \\ \mu_i &\equiv \frac{h_{i-1}}{2(h_i + h_{i-1})} = \frac{1}{2} - \lambda_i \, . \end{aligned} \tag{30.104}$$

Then we may rearrange

$$\lambda_i y'_{i-1} + y'_i + \mu_i y'_{i+1} = \underbrace{3\left[\lambda_i \frac{y_i - y_{i-1}}{h_{i-1}} + \mu_i \frac{y_{i+1} - y_i}{h_i}\right]}_{d_i} \ . \tag{30.105}$$

This equation holds for all $0 < i < (N-1)$, so we have a tridiagonal set of equations. The equations for $i = 0$ and $i = N-1$ depend on the boundary conditions we are using.

Periodic boundary conditions

For periodic boundary conditions, we have

$$\begin{array}{ccccccccccc} y'_0 & + & \mu_0 y'_1 & & & & \dots & & +\lambda_0 y'_{N-1} & = & d_0 \, , \\ \lambda_1 y'_0 & + & y'_1 & + & \mu_1 y'_2 & & \dots & & & = & d_1 \, , \\ & & \lambda_2 y'_1 & + & y'_2 + & \mu_2 y'_3 & \dots & & & = & d_2 \, , \\ & & & & \vdots & & & & & & \\ \mu_{N-1} y'_0 & & & & & +\lambda_{N-1} y'_{N-1} & & +y'_{N-2} & & = & d_3 \, . \end{array} \tag{30.106}$$

Or, in matrix form, we have

$$\begin{pmatrix} 1 & \mu_0 & 0 & 0 & \dots & 0 & \lambda_0 \\ \lambda_1 & 1 & \mu_1 & 0 & \dots & 0 & 0 \\ 0 & \lambda_2 & 1 & \mu_2 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \lambda_{N-3} & 1 & \mu_{N-3} & 0 \\ 0 & 0 & 0 & 0 & \lambda_{N-2} & 1 & \mu_{N-2} \\ \mu_{N-1} & 0 & 0 & 0 & 0 & \lambda_{N-1} & 1 \end{pmatrix} \begin{pmatrix} y'_0 \\ y'_1 \\ y'_2 \\ \vdots \\ y'_{N-3} \\ y'_{N-2} \\ y'_{N-1} \end{pmatrix} = \begin{pmatrix} d_0 \\ d_1 \\ d_2 \\ \vdots \\ d_{N-3} \\ d_{N-2} \\ d_{N-1} \end{pmatrix} . \tag{30.107}$$

The system is tridiagonal except for the two elements in the upper right and lower left corners. These terms complicate the solution a bit, although it can still be done in $\mathcal{O}(N)$ time. We first proceed down the rows, eliminating the the first non-zero term in each row by subtracting the appropriate multiple of the previous row. At the same time, we eliminate the first element in the last row, shifting the position of the first non-zero element to the right with each iteration. When we get to the final row, we will have the value for y'_{N-1}. We can then proceed back upward, backsubstituting values from the rows below to calculate all the derivatives.

Complete boundary conditions

If we specify the first derivatives of our function at the end points, we have what is known as *complete* boundary conditions. The equations in that case are trivial to solve:

$$\begin{pmatrix} 1 & 0 & 0 & 0 & \dots & 0 & 0 \\ \lambda_1 & 1 & \mu_1 & 0 & \dots & 0 & 0 \\ 0 & \lambda_2 & 1 & \mu_2 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \lambda_{N-3} & 1 & \mu_{N-3} & 0 \\ 0 & 0 & 0 & 0 & \lambda_{N-2} & 1 & \mu_{N-2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} y'_0 \\ y'_1 \\ y'_2 \\ \vdots \\ y'_{N-3} \\ y'_{N-2} \\ y'_{N-1} \end{pmatrix} = \begin{pmatrix} d_0 \\ d_1 \\ d_2 \\ \vdots \\ d_{N-3} \\ d_{N-2} \\ d_{N-1} \end{pmatrix} . \tag{30.108}$$

This system is completely tridiagonal, and we may solve trivially by performing row eliminations downward, then proceeding upward as before.

Natural boundary conditions

If we do not have information about the derivatives at the boundary conditions, we may construct a *natural spline*, which assumes the second derivatives are zero at the end points of our spline. In this case our system of equations is the following:

$$\begin{pmatrix} 1 & \frac{1}{2} & 0 & 0 & \dots & 0 & 0 \\ \lambda_1 & 1 & \mu_1 & 0 & \dots & 0 & 0 \\ 0 & \lambda_2 & 1 & \mu_2 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \lambda_{N-3} & 1 & \mu_{N-3} & 0 \\ 0 & 0 & 0 & 0 & \lambda_{N-2} & 1 & \mu_{N-2} \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 1 \end{pmatrix} \begin{pmatrix} y'_0 \\ y'_1 \\ y'_2 \\ \vdots \\ y'_{N-3} \\ y'_{N-2} \\ y'_{N-1} \end{pmatrix} = \begin{pmatrix} d_0 \\ d_1 \\ d_2 \\ \vdots \\ d_{N-3} \\ d_{N-2} \\ d_{N-1} \end{pmatrix} , \tag{30.109}$$

with

$$d_0 = \frac{3}{2}\frac{y_1 - y_1}{h_0} , \quad d_{N-1} = \frac{3}{2}\frac{y_{N-1} - y_{N-2}}{h_{N-1}} . \tag{30.110}$$

30.4.2 Bicubic splines

It is possible to extend the cubic spline interpolation method to functions of two variables, that is, $F(x, y)$. In this case, we have a rectangular mesh of points given by $F_{ij} \equiv F(x_i, y_j)$. In the case of 1D splines, we needed to store the value of the first derivative of the function at each point, in addition to the value. In the case of *bicubic splines*, we need to store four quantities for each mesh point:

$$\begin{aligned} F_{ij} &\equiv \quad F(x_i, y_i) , \\ F^x_{ij} &\equiv \quad \partial_x F(x_i, y_i) , \\ F^y_{ij} &\equiv \quad \partial_y F(x_i, y_i) , \\ F^{xy} &\equiv \partial_x \partial_y F(x_i, y_i) . \end{aligned} \tag{30.111}$$

Consider the point (x, y) at which we wish to interpolate F. We locate the rectangle that contains this point, such that $x_i <= x < x_{i+1}$ and $y_i <= x < y_{i+1}$. Let

$$\begin{aligned} h &\equiv x_{i+1} - x_i \,, \\ l &\equiv y_{i+1} - y_i \,, \\ u &\equiv \frac{x - x_i}{h} \,, \\ v &\equiv \frac{y - y_i}{l} \,. \end{aligned} \tag{30.112}$$

Then, we calculate the interpolated value as

$$F(x,y) = \begin{pmatrix} p_1(u) \\ p_2(u) \\ hq_1(u) \\ hq_2(u) \end{pmatrix}^T \begin{pmatrix} (*20c)F_{i,j} & F_{i+1,j} & F^y_{i,j} & F^y_{i,j+1} \\ F_{i+1,j} & F_{i+1,j+1} & F^y_{i+1,j} & F^y_{i+1,j+1} \\ F^x_{i,j} & F^x_{i,j+1} & F^{xy}_{i,j} & F^{xy}_{i,j+1} \\ F^x_{i+1,j} & F^x_{i+1,j+1} & F^{xy}_{i+1,j} & F^{xy}_{i+1,j+1} \end{pmatrix} \begin{pmatrix} p_1(v) \\ p_2(v) \\ kq_1(v) \\ kq_2(v) \end{pmatrix} \,. \tag{30.113}$$

Construction bicubic splines

We now address the issue of how to compute the derivatives that are needed for the interpolation. The algorithm is quite simple. For every x_i, we perform the tridiagonal solution as we did in the 1D splines to compute F^y_{ij}. Similarly, we perform a tridiagonal solve for every value of F^x_{ij}. Finally, to compute the cross-derivative we may *either* to the tridiagonal solve in the y direction of F^x_{ij}, *or* solve in the x direction for F^y_{ij} to obtain the cross-derivatives F^{xy}_{ij}. Hence, only minor modifications to the $1D$ interpolations are necessary.

30.4.3 Tricubic splines

Bicubic interpolation required two 4-component vectors and a 4×4 matrix. By extension, tricubic interpolation requires three 4-component vectors and a $4 \times 4 \times 4$ tensor. We summarize the forms of these vectors in the following:

$$\begin{aligned} h &\equiv x_{i+1} - x_i \,, \\ l &\equiv y_{i+1} - y_i \,, \\ m &\equiv z_{i+1} - z_i \,, \\ u &\equiv \frac{x - x_i}{h} \,, \\ v &\equiv \frac{y - y_i}{l} \,, \\ w &\equiv \frac{z - z_i}{m} \,. \end{aligned} \tag{30.114}$$

$$\begin{aligned} \vec{a} &= \begin{pmatrix} p_1(u) & p_2(u) & hq_1(u) & hq_2(u) \end{pmatrix}^T \,, \\ \vec{b} &= \begin{pmatrix} p_1(v) & p_2(v) & kq_1(v) & kq_2(v) \end{pmatrix}^T \,, \\ \vec{c} &= \begin{pmatrix} p_1(w) & p_2(w) & lq_1(w) & lq_2(w) \end{pmatrix}^T \,. \end{aligned} \tag{30.115}$$

$$\begin{pmatrix}
A_{000}=F_{i,j,k} & A_{001}=F_{i,j,k+1} & A_{002}=F^{z}_{i,j,k} & A_{003}=F^{z}_{i,j,k+1} \\
A_{010}=F_{i,j+1,k} & A_{011}=F_{i,j+1,k+1} & A_{012}=F^{z}_{i,j+1,k} & A_{013}=F^{z}_{i,j+1,k+1} \\
A_{020}=F^{y}_{i,j,k} & A_{021}=F^{y}_{i,j,k+1} & A_{022}=F^{yz}_{i,j,k} & A_{023}=F^{yz}_{i,j,k+1} \\
A_{030}=F^{y}_{i,j+1,k} & A_{031}=F^{y}_{i,j+1,k+1} & A_{032}=F^{yz}_{i,j+1,k} & A_{033}=F^{yz}_{i,j+1,k+1} \\
\\
A_{100}=F_{i+1,j,k} & A_{101}=F_{i+1,j,k+1} & A_{102}=F^{z}_{i+1,j,k} & A_{103}=F^{z}_{i+1,j,k+1} \\
A_{110}=F_{i+1,j+1,k} & A_{111}=F_{i+1,j+1,k+1} & A_{112}=F^{z}_{i+1,j+1,k} & A_{113}=F^{z}_{i+1,j+1,k+1} \\
A_{120}=F^{y}_{i+1,j,k} & A_{121}=F^{y}_{i+1,j,k+1} & A_{122}=F^{yz}_{i+1,j,k} & A_{123}=F^{yz}_{i+1,j,k+1} \\
A_{130}=F^{y}_{i+1,j+1,k} & A_{131}=F^{y}_{i+1,j+1,k+1} & A_{132}=F^{yz}_{i+1,j+1,k} & A_{133}=F^{yz}_{i+1,j+1,k+1} \\
\\
A_{200}=F^{x}_{i,j,k} & A_{201}=F^{x}_{i,j,k+1} & A_{202}=F^{xz}_{i,j,k} & A_{203}=F^{xz}_{i,j,k+1} \\
A_{210}=F^{x}_{i,j+1,k} & A_{211}=F^{x}_{i,j+1,k+1} & A_{212}=F^{xz}_{i,j+1,k} & A_{213}=F^{xz}_{i,j+1,k+1} \\
A_{220}=F^{xy}_{i,j,k} & A_{221}=F^{xy}_{i,j,k+1} & A_{222}=F^{xyz}_{i,j,k} & A_{223}=F^{xyz}_{i,j,k+1} \\
A_{230}=F^{xy}_{i,j+1,k} & A_{231}=F^{xy}_{i,j+1,k+1} & A_{232}=F^{xyz}_{i,j+1,k} & A_{233}=F^{xyz}_{i,j+1,k+1} \\
\\
A_{300}=F^{x}_{i+1,j,k} & A_{301}=F^{x}_{i+1,j,k+1} & A_{302}=F^{xz}_{i+1,j,k} & A_{303}=F^{xz}_{i+1,j,k+1} \\
A_{310}=F^{x}_{i+1,j+1,k} & A_{311}=F^{x}_{i+1,j+1,k+1} & A_{312}=F^{xz}_{i+1,j+1,k} & A_{313}=F^{xz}_{i+1,j+1,k+1} \\
A_{320}=F^{xy}_{i+1,j,k} & A_{321}=F^{xy}_{i+1,j,k+1} & A_{322}=F^{xyz}_{i+1,j,k} & A_{323}=F^{xyz}_{i+1,j,k+1} \\
A_{330}=F^{xy}_{i+1,j+1,k} & A_{331}=F^{xy}_{i+1,j+1,k+1} & A_{332}=F^{xyz}_{i+1,j+1,k} & A_{333}=F^{xyz}_{i+1,j+1,k+1}
\end{pmatrix} . \tag{30.116}$$

Now, we can write

$$F(x,y,z)=\sum_{i=0}^{3} a_i \sum_{j=0}^{3} b_j \sum_{k=0}^{3} c_k \, A_{i,j,k} \, . \tag{30.117}$$

The appropriate derivatives of F may be computed by a generalization of the previous method used for bicubic splines.

30.5 Feature: B-spline orbital tiling (band unfolding)

In continuum QMC simulations, it is necessary to evaluate the electronic orbitals of a system at real-space positions hundreds of millions of times. It has been found that if these orbitals are represented in a localized, B-spline basis, each evaluation takes a small, constant time that is independent of system size.

Unfortunately, the memory required for storing the B-spline grows with the second power of the system size. If we are studying perfect crystals, however, this can be reduced to linear scaling if we *tile* the primitive cell. In this approach, a supercell is constructed by tiling the primitive cell $N_1 \times N_2 \times N_3$ in the three lattice directions. The orbitals are then represented in real space only in the primitive cell and an $N_1 \times N_2 \times N_3$ k-point mesh. To evaluate an orbital at any point in the supercell, it is only necessary to wrap that point back into the primitive cell, evaluate the spline, and then multiply the phase factor, $e^{-i\mathbf{k}\cdot\mathbf{r}}$.

Here, we show that this approach can be generalized to a tiling constructed with a 3×3 nonsingular matrix of integers, of which the preceding approach is a special case. This generalization brings with it a number of advantages. The primary reason for performing supercell calculations in QMC is to reduce finite-size errors. These errors result from three sources: (1) the quantization of the crystal momentum, (2) the unphysical periodicity of the exchange-correlation (XC) hole of the electron, and (3) the kinetic-energy contribution from the periodicity of the long-range Jastrow correlation functions. The first source of error can be largely eliminated by twist averaging. If the simulation cell is large enough that XC hole does not "leak" out of the simulation cell, the second source can be eliminated either through use of the MPC interaction or the *a postiori* correction of Chiesa et al.

The satisfaction of the leakage requirement is controlled by whether the minimum distance, L_{min}, from one supercell image to the next is greater than the width of the XC hole. Therefore, given a choice, it is best to use a cell that is as nearly cubic as possible since this choice maximizes L_{min} for a given number of atoms. Most often, however, the primitive cell is not cubic. In these cases, if we wish to choose the optimal supercell to reduce finite-size effects, we cannot use the simple primitive tiling scheme. In the generalized scheme we present, it is possible to choose far

better supercells (from the standpoint of finite-size errors), while retaining the storage efficiency of the original tiling scheme.

30.5.1 The mathematics

Consider the set of primitive lattice vectors, $\{\mathbf{a}_1^{\mathrm{p}}, \mathbf{a}_2^{\mathrm{p}}, \mathbf{a}_3^{\mathrm{p}}\}$. We may write these vectors in a matrix, $\mathbf{L}_p$, whose rows are the primitive lattice vectors. Consider a nonsingular matrix of integers, $\mathbf{S}$. A corresponding set of supercell lattice vectors, $\{\mathbf{a}_1^{\mathrm{s}}, \mathbf{a}_2^{\mathrm{s}}, \mathbf{a}_3^{\mathrm{s}}\}$, can be constructed by the matrix product

$$\mathbf{a}_i^{\mathrm{s}} = S_{ij}\mathbf{a}_j^{\mathrm{p}} \,. \tag{30.118}$$

If the primitive cell contains N_p atoms, the supercell will then contain $N_s = |\det(\mathbf{S})|N_p$ atoms.

30.5.2 Example: FeO

As an example, consider the primitive cell for antiferromagnetic FeO (wustite) in the rocksalt structure. The primitive vectors, given in units of the lattice constant, are given by

$$\begin{aligned} \mathbf{a}_1^{\mathrm{p}} &= \frac{1}{2}\hat{\mathbf{x}} + \frac{1}{2}\hat{\mathbf{y}} + \hat{\mathbf{z}} \,, \\ \mathbf{a}_2^{\mathrm{p}} &= \frac{1}{2}\hat{\mathbf{x}} + \hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{z}} \,, \\ \mathbf{a}_3^{\mathrm{p}} &= \hat{\mathbf{x}} + \frac{1}{2}\hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{z}} \,. \end{aligned} \tag{30.119}$$

This primitive cell contains two iron atoms and two oxygen atoms. It is a very elongated cell with acute angles and, thus, has a short minimum distance between adjacent images.

The smallest cubic cell consistent with the AFM ordering can be constructed with the matrix

$$\mathbf{S} = \begin{bmatrix} -1 & -1 & 3 \\ -1 & 3 & -1 \\ 3 & -1 & -1 \end{bmatrix} . \tag{30.120}$$

This cell has $2|\det(\mathbf{S})| = 32$ iron atoms and 32 oxygen atoms. In this example, we may perform the simulation in the 32-iron supercell, while storing the orbitals only in the 2-iron primitive cell, for a savings of a factor of 16.

The k-point mesh

To be able to use the generalized tiling scheme, we need to have the appropriate number of bands to occupy in the supercell. This may be achieved by appropriately choosing the k-point mesh. In this section, we explain how these points are chosen.

For simplicity, let us assume that the supercell calculation will be performed at the Γ-point. We can easily lift this restriction later. The fact that supercell calculation is performed at Γ implies that the k-points used in the primitive-cell calculation must be $\mathbf{G}$-vectors of the superlattice. This still leaves us with an infinite set of vectors. We may reduce this set to a finite number by considering that the orbitals must form a linearly independent set. Orbitals with k-vectors $\mathbf{k}_1^p$ and $\mathbf{k}_2^p$ will differ by at most a constant factor of $\mathbf{k}_1^p - \mathbf{k}_2^p = \mathbf{G}^p$, where $\mathbf{G}^p$ is a reciprocal lattice vector of the primitive cell.

Combining these two considerations gives us a prescription for generating our k-point mesh. The mesh may be taken to be the set of k-point which are G-vectors of the superlattice, reside within the first Brillouin zone (FBZ) of the primitive lattice, whose members do not differ a G-vector of the primitive lattice. Upon constructing such a set, we find that the number of included k-points is equal to $|\det(\mathbf{S})|$, precisely the number we need. This can by considering

the fact that the supercell has a volume $|\det(\mathbf{S})|$ times that of the primitive cell. This implies that the volume of the supercell's FBZ is $|\det(\mathbf{S})|^{-1}$ times that of the primitive cell. Hence, $|\det(\mathbf{S})|$ G-vectors of the supercell will fit in the FBZ of the primitive cell. Removing duplicate k-vectors, which differ from another by a reciprocal lattice vector, avoids double-counting vectors that lie on zone faces.

Formulae

Let $\mathbf{A}$ be the matrix whose rows are the direct lattice vectors, $\{\mathbf{a}_i\}$. Then, let the matrix $\mathbf{B}$ be defined as $2\pi(\mathbf{A}^{-1})^\dagger$. Its rows are the primitive reciprocal lattice vectors. Let $\mathbf{A}_p$ and $\mathbf{A}_s$ represent the primitive and superlattice matrices, respectively, and similarly for their reciprocals. Then we have

$$\begin{aligned}
\mathbf{A}_s &= \mathbf{S}\mathbf{A}_p \,, \\
\mathbf{B}_s &= 2\pi \left[(\mathbf{S}\mathbf{A}_p)^{-1}\right]^\dagger \,, \\
&= 2\pi \left[\mathbf{A}_p^{-1}\mathbf{S}^{-1}\right]^\dagger \,, \\
&= 2\pi(\mathbf{S}^{-1})^\dagger(\mathbf{A}_p^{-1})^\dagger \,, \\
&= (\mathbf{S}^{-1})^\dagger\mathbf{B}_p \,.
\end{aligned} \tag{30.121}$$

Consider a k-vector, $\mathbf{k}$. It may alternatively be written in basis of reciprocal lattice vectors as $\mathbf{t}$.

$$\begin{aligned}
\mathbf{k} &= (\mathbf{t}^\dagger\mathbf{B})^\dagger \,, \\
&= \mathbf{B}^\dagger\mathbf{t} \,, \\
\mathbf{t} &= (\mathbf{B}^\dagger)^{-1}\mathbf{k} \,, \\
&= (\mathbf{B}^{-1})^\dagger\mathbf{k} \,, \\
&= \frac{\mathbf{A}\mathbf{k}}{2\pi} \,.
\end{aligned} \tag{30.122}$$

We may then express a twist vector of the primitive lattice, $\mathbf{t}_p$, in terms of the superlattice.

$$\begin{aligned}
\mathbf{t}_s &= \frac{\mathbf{A}_s\mathbf{k}}{2\pi} \,, \\
&= \frac{\mathbf{A}_s\mathbf{B}_p^\dagger\mathbf{t}_p}{2\pi} \,, \\
&= \frac{\mathbf{S}\mathbf{A}_p\mathbf{B}_p^\dagger\mathbf{t}_p}{2\pi} \,, \\
&= \frac{2\pi\mathbf{S}\mathbf{A}_p\mathbf{A}_p^{-1}\mathbf{t}_p}{2\pi} \,, \\
&= \mathbf{S}\mathbf{t}_p \,.
\end{aligned} \tag{30.123}$$

This gives the simple result that twist vectors transform in precisely the same way as direct lattice vectors.

30.6 Feature: Hybrid orbital representation

$$\phi(\mathbf{r}) = \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} Y_\ell^m(\hat{\Omega}) u_{\ell m}(r) \,, \tag{30.124}$$

where $u_{lm}(r)$ are complex radial functions represented in some radial basis (e.g., splines).

30.6.1 Real spherical harmonics

If $\phi(\mathbf{r})$ can be written as purely real, we can change the representation so that

$$\phi(\mathbf{r}) = \sum_{l=0}^{l_{\max}} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{\Omega}) \bar{u}_{lm}(r) \,, \tag{30.125}$$

where $\bar{Y}_\ell^m$ are the *real* spherical harmonics defined by

$$Y_{\ell m} = \begin{cases} Y_\ell^0 & \text{if } m = 0 \\ \frac{1}{2}\left(Y_\ell^m + (-1)^m Y_\ell^{-m}\right) = \mathrm{Re}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] & \text{if } m > 0 \\ \frac{1}{i2}\left(Y_\ell^{-m} - (-1)^m Y_\ell^m\right) = \mathrm{Im}\left[\mathrm{Y}_\ell^{-\mathrm{m}}\right] & \text{if } m < 0 \,. \end{cases} \tag{30.126}$$

We need then to relate $\bar{u}_{\ell m}$ to $u_{\ell m}$. We wish to express

$$\mathrm{Re}\left[\phi(\mathbf{r})\right] = \sum_{\ell=0}^{\ell_{\max}} \sum_{\mathrm{m}=-\ell}^{\ell} \mathrm{Re}\left[\mathrm{Y}_\ell^{\mathrm{m}}(\hat{\Omega}) \mathrm{u}_{\ell \mathrm{m}}(\mathrm{r})\right] \tag{30.127}$$

in terms of $\bar{u}_{\ell m}(r)$ and $Y_{\ell m}$.

$$\mathrm{Re}\left[\mathrm{Y}_\ell^{\mathrm{m}} \mathrm{u}_{\ell \mathrm{m}}\right] = \quad \mathrm{Re}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] \mathrm{Re}\left[\mathrm{u}_{\ell \mathrm{m}}\right] - \mathrm{Im}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] \mathrm{Im}\left[\mathrm{u}_{\ell \mathrm{m}}\right] \,. \tag{30.128}$$

For $m > 0$,

$$\mathrm{Re}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] = \mathrm{Y}_{\ell \mathrm{m}} \qquad \text{and} \qquad \mathrm{Im}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] = \mathrm{Y}_{\ell\, -\mathrm{m}} \,. \tag{30.129}$$

For $m < 0$,

$$\mathrm{Re}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] = (-1)^{\mathrm{m}} \mathrm{Y}_{\ell\, -\mathrm{m}} \qquad \text{and} \qquad \mathrm{Im}\left[\mathrm{Y}_\ell^{\mathrm{m}}\right] = -(-1)^{\mathrm{m}} \mathrm{Y}_{\ell \mathrm{m}} \,. \tag{30.130}$$

Then for $m > 0$,

$$\begin{aligned} \bar{u}_{\ell m} = &\quad \mathrm{Re}\left[\mathrm{u}_{\ell \mathrm{m}}\right] + (-1)^{\mathrm{m}} \mathrm{Re}\left[\mathrm{u}_{\ell\, -\mathrm{m}}\right] \,, \\ \bar{u}_{\ell\, -m} = &\quad -\mathrm{Im}\left[\mathrm{u}_{\ell \mathrm{m}}\right] + (-1)^{\mathrm{m}} \mathrm{Im}\left[\mathrm{u}_{\ell\, -\mathrm{m}}\right] \,. \end{aligned} \tag{30.131}$$

30.6.2 Projecting to atomic orbitals

Inside a muffin tin, orbitals are represented as products of spherical harmonics and 1D radial functions, primarily represented by splines. For a muffin tin centered at $\mathbf{I}$,

$$\phi_n(\mathbf{r}) = \sum_{\ell,m} Y_\ell^m(\mathbf{r} \hat{-} \mathbf{I}) u_{lm}\left(|\mathbf{r} - \mathbf{I}|\right) \,. \tag{30.132}$$

Let use consider the case that our original representation for $\phi(\mathbf{r})$ is of the form

$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c^n_{\mathbf{G}+\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \,. \tag{30.133}$$

Recall that

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell,m} i^\ell j_\ell(|\mathbf{r}||\mathbf{k}|) Y_\ell^m(\hat{\mathbf{k}}) \left[Y_\ell^m(\hat{\mathbf{r}})\right]^* \,. \tag{30.134}$$

Conjugating,

$$e^{-i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell,m} (-i)^\ell j_\ell(|\mathbf{r}||\mathbf{k}|) \left[Y_\ell^m(\hat{\mathbf{k}})\right]^* Y_\ell^m(\hat{\mathbf{r}}) \,. \tag{30.135}$$

Setting $\mathbf{k} \to -k$,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell,m} i^\ell j_\ell(|\mathbf{r}||\mathbf{k}|) \left[Y_\ell^m(\hat{\mathbf{k}})\right]^* Y_\ell^m(\hat{\mathbf{r}}) \,. \tag{30.136}$$

Then,

$$e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{I})} = 4\pi \sum_{\ell,m} i^\ell j_\ell(|\mathbf{r}-\mathbf{I}||\mathbf{k}|) \left[Y_\ell^m(\hat{\mathbf{k}})\right]^* Y_\ell^m(\mathbf{r} \hat{-} \mathbf{I}) \,. \tag{30.137}$$

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi e^{i\mathbf{k}\cdot\mathbf{I}} \sum_{\ell,m} i^\ell j_\ell(|\mathbf{r}-\mathbf{I}||\mathbf{k}|) \left[Y_\ell^m(\hat{\mathbf{k}})\right]^* Y_\ell^m(\mathbf{r} \hat{-} \mathbf{I}) \,. \tag{30.138}$$

Then

$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} 4\pi c^n_{\mathbf{G}+\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{I}} \sum_{\ell,m} i^\ell j_\ell(|\mathbf{G}+\mathbf{k}||\mathbf{r}-\mathbf{I}|) \left[Y_\ell^m(\mathbf{G} \hat{+} \mathbf{k})\right]^* Y_\ell^m(\mathbf{r} \hat{-} \mathbf{I}) \,. \tag{30.139}$$

Comparing with (30.132),

$$u^n_{\ell m}(r) = 4\pi i^\ell \sum_G c^n_{\mathbf{G}+\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{I}} j_\ell\left(|\mathbf{G}+\mathbf{k}|r|\right) \left[Y_\ell^m(\mathbf{G} \hat{+} \mathbf{k})\right]^* \,. \tag{30.140}$$

If we had adopted the opposite sign convention for Fourier transforms (as is unfortunately the case in wfconvert), we would have

$$u^n_{\ell m}(r) = 4\pi (-i)^\ell \sum_G c^n_{\mathbf{G}+\mathbf{k}} e^{-i(\mathbf{G}+\mathbf{k})\cdot\mathbf{I}} j_\ell\left(|\mathbf{G}+\mathbf{k}|r|\right) \left[Y_\ell^m(\mathbf{G} \hat{+} \mathbf{k})\right]^* \,. \tag{30.141}$$

30.7 Feature: Electron-electron-ion Jastrow factor

The general form of the 3-body Jastrow we describe here depends on the three interparticle distances, (r_{ij}, r_{iI}, r_{jI}).

$$J_3 = \sum_{I \in \text{ions}} \sum_{i,j \in \text{elecs}; i \neq j} U(r_{ij}, r_{iI}, r_{jI}) \,. \tag{30.142}$$

Note that we constrain the form of U such that $U(r_{ij}, r_{iI}, r_{jI}) = U(r_{ij}, r_{jI}, r_{iI})$ to preserve the particle symmetry of the wavefunction. We then compute the gradient as

$$\nabla_i J_3 = \sum_{I \in \text{ions}} \sum_{j \neq i} \left[\frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{ij}} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{iI}} \frac{\mathbf{r}_i - \mathbf{I}}{|\mathbf{r}_i - \mathbf{I}|} \right] \,. \tag{30.143}$$

To compute the Laplacian, we take

$$\begin{aligned} \nabla_i^2 J_3 = & \nabla_i \cdot (\nabla_i J_3) \,, \\ = & \sum_{I \in \text{ions}} \sum_{j \neq i} \left[\frac{\partial^2 U}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial U}{\partial r_{ij}} + 2 \frac{\partial^2 U}{\partial r_{ij} \partial r_{iI}} \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{iI}}{r_{ij} r_{iI}} + \frac{\partial^2 U}{\partial r_{iI}^2} + \frac{2}{r_{iI}} \frac{\partial U}{\partial r_{iI}} \right] \,. \end{aligned}$$

We now wish to compute the gradient of these terms w.r.t. the ion position, I.

$$\nabla_I J_3 = -\sum_{j \neq i} \left[\frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{iI}} \frac{\mathbf{r}_i - \mathbf{I}}{|\mathbf{r}_i - \mathbf{I}|} + \frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{jI}} \frac{\mathbf{r}_j - \mathbf{I}}{|\mathbf{r}_j - \mathbf{I}|} \right] \,. \tag{30.144}$$

For the gradient w.r.t. i of the gradient w.r.t. I, the result is a tensor:

$$\begin{aligned}
\nabla_I \nabla_i J_3 = \quad & \nabla_I \sum_{j\neq i} \left[\frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{ij}} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{iI}} \frac{\mathbf{r}_i - \mathbf{I}}{|\mathbf{r}_i - \mathbf{I}|} \right] , \\
= \quad & -\sum_{j\neq i} \left[\frac{\partial^2 U}{\partial r_{ij} r_{iI}} \hat{\mathbf{r}}_{ij} \otimes \hat{\mathbf{r}}_{iI} + \left(\frac{\partial^2 U}{\partial r_{iI}^2} - \frac{1}{r_{iI}} \frac{\partial U}{\partial r_{iI}} \right) \hat{\mathbf{r}}_{iI} \otimes \hat{\mathbf{r}}_{iI} + \right. \\
& \left. \frac{\partial^U}{\partial r_{ij} r_{jI}} \hat{\mathbf{r}}_{ij} \otimes \hat{\mathbf{r}}_{jI} + \frac{\partial^2 U}{\partial r_{iI} \partial r_{jI}} \hat{\mathbf{r}}_{iI} \otimes \hat{\mathbf{r}}_{jI} + \frac{1}{r_{iI}} \frac{\partial U}{\partial r_{iI}} \overleftrightarrow{\mathbf{1}} \right] .
\end{aligned}$$

$$\begin{aligned}
\nabla_I \nabla_i J_3 = \quad & \nabla_I \sum_{j\neq i} \left[\frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{ij}} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{\partial U(r_{ij}, r_{iI}, r_{jI})}{\partial r_{iI}} \frac{\mathbf{r}_i - \mathbf{I}}{|\mathbf{r}_i - \mathbf{I}|} \right] , \\
= \quad & \sum_{j\neq i} \left[-\frac{\partial^2 U}{\partial r_{ij} \partial r_{iI}} \hat{\mathbf{r}}_{ij} \otimes \hat{\mathbf{r}}_{iI} + \left(-\frac{\partial^2 U}{\partial r_{iI}^2} + \frac{1}{r_{iI}} \frac{\partial U}{\partial r_{iI}} \right) \hat{\mathbf{r}}_{iI} \otimes \hat{\mathbf{r}}_{iI} - \frac{1}{r_{iI}} \frac{\partial U}{\partial r_{iI}} \overleftrightarrow{\mathbf{1}} \right] .
\end{aligned}$$

For the Laplacian,

$$\begin{aligned}
\nabla_I \nabla_i^2 J_3 = \quad & \nabla_I \left[\nabla_i \cdot (\nabla_i J_3) \right] , \\
= \quad & \nabla_I \sum_{j\neq i} \left[\frac{\partial^2 U}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial U}{\partial r_{ij}} + 2 \frac{\partial^2 U}{\partial r_{ij} \partial r_{iI}} \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{iI}}{r_{ij} r_{iI}} + \frac{\partial^2 U}{\partial r_{iI}^2} + \frac{2}{r_{iI}} \frac{\partial U}{\partial r_{iI}} \right] , \\
= \quad & \sum_{j\neq i} \left[\frac{\partial^3 U}{\partial r_{iI} \partial^2 r_{ij}} + \frac{2}{r_{ij}} \frac{\partial^2 U}{\partial r_{iI} \partial r_{ij}} + 2 \left(\frac{\partial^3 U}{\partial r_{ij} \partial^2 r_{iI}} - \frac{1}{r_{iI}} \frac{\partial^2 U}{\partial r_{ij} \partial r_{iI}} \right) \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{iI}}{r_{ij} r_{iI}} + \frac{\partial^3 U}{\partial^3 r_{iI}} - \frac{2}{r_{iI}^2} \frac{\partial U}{\partial r_{iI}} + \frac{2}{r_{iI}} \frac{\partial^2 U}{\partial^2 r_{iI}} \right] \frac{\mathbf{I} - \mathbf{r}_i}{|\mathbf{I} - \mathbf{r}_i|} + \\
& \sum_{j\neq i} \left[\frac{\partial^3 U}{\partial r_{ij}^2 \partial r_{jI}} + \frac{2}{r_{ij}} \frac{\partial^2 U}{\partial r_{jI} \partial r_{ij}} + 2 \frac{\partial^3 U}{\partial r_{ij} \partial r_{iI} \partial r_{jI}} \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{iI}}{r_{ij} r_{iI}} + \frac{\partial^3 U}{\partial r_{iI}^2 \partial r_{jI}} + \frac{2}{r_{iI}} \frac{\partial^2 U}{\partial r_{iI} \partial r_{jI}} \right] \frac{\mathbf{I} - \mathbf{r}_j}{|\mathbf{r}_j - \mathbf{I}|} + \\
& \sum_{j\neq i} \left[-\frac{2}{r_{iI}} \frac{\partial^2 U}{\partial r_{ij} \partial r_{iI}} \right] \frac{\mathbf{r}_{ij}}{r_{ij}} .
\end{aligned}$$

30.8 Feature: Reciprocal-space Jastrow factors

30.8.1 Two-body Jastrow

$$J_2 = \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{i\neq j} a_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}_i - \mathbf{r}_j)} . \tag{30.145}$$

This may be rewritten as

$$\begin{aligned}
J_2 = \quad & \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{i\neq j} a_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}_i} e^{-i\mathbf{G}\cdot\mathbf{r}_j} , \\
= \quad & \sum_{\mathbf{G}\neq\mathbf{0}} a_{\mathbf{G}} \left\{ \underbrace{\left[\sum_i e^{i\mathbf{G}\cdot\mathbf{r}_i} \right]}_{\rho_{\mathbf{G}}} \underbrace{\left[\sum_j e^{-i\mathbf{G}\cdot\mathbf{r}_j} \right]}_{\rho_{-\mathbf{G}}} - 1 \right\} .
\end{aligned} \tag{30.146}$$

The -1 is just a constant term and may be subsumed into the $a_{\mathbf{G}}$ coefficient by a simple redefinition. This leaves a simple, but general, form:

$$J_2 = \sum_{\mathbf{G}\neq\mathbf{0}} a_{\mathbf{G}} \rho_{\mathbf{G}} \rho_{-\mathbf{G}} . \tag{30.147}$$

We may now further constrain this on physical grounds. First, we recognize that J_2 should be real. Since $\rho_{-\mathbf{G}} = \rho^*_{\mathbf{G}}$, it follows that $\rho_{\mathbf{G}}\rho_{-\mathbf{G}} = |\rho_{\mathbf{G}}|^2$ is real, so that $a_{\mathbf{G}}$ must be real. Furthermore, we group the $\mathbf{G}$'s into $(+\mathbf{G}, -\mathbf{G})$ pairs and sum over only the positive vectors to save time.

30.8.2 One-body Jastrow

The 1-body Jastrow has a similar form but depends on the displacement from the electrons to the ions in the system.

$$J_1 = \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{\alpha} \sum_{i\in\mathbf{I}^\alpha} \sum_{j\in\text{elec.}} b^\alpha_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{I}^\alpha_i - \mathbf{r}_j)} \,, \tag{30.148}$$

where α denotes the different ionic species. We may rewrite this in terms of $\rho^\alpha_{\mathbf{G}}$:

$$J_1 = \sum_{\mathbf{G}\neq\mathbf{0}} \left[\sum_{\alpha} b^\alpha_{\mathbf{G}} \rho^\alpha_{\mathbf{G}}\right] \rho_{-\mathbf{G}} \,, \tag{30.149}$$

where

$$\rho^\alpha_{\mathbf{G}} = \sum_{i\in\mathbf{I}^\alpha} e^{i\mathbf{G}\cdot\mathbf{I}^\alpha_i} \,. \tag{30.150}$$

We note that in the preceding equation, for a single configuration of the ions, the sum in brackets can be rewritten as a single constant. This implies that the per-species 1-body coefficients, $b^\alpha_{\mathbf{G}}$, are underdetermined for single configuration of the ions. In general, if we have N species, we need N linearly independent ion configurations to uniquely determine $b^\alpha_{\mathbf{G}}$. For this reason, we will drop the α superscript of $b_{\mathbf{G}}$ for now.

If we do desire to find a reciprocal space 1-body Jastrow that is transferable to systems with different ion positions and N ionic species, we must perform compute $b_{\mathbf{G}}$ for N different ion configurations. We may then construct N equations at each value of $\mathbf{G}$ to solve for the N unknown values, $b^\alpha_{\mathbf{G}}$.

In the 2-body case, $a_{\mathbf{G}}$ was constrained to be real by the fact that $\rho_{\mathbf{G}}\rho_{-\mathbf{G}}$ was real. However, in the 1-body case, there is no such guarantee about $\rho^\alpha_{\mathbf{G}}\rho_{\mathbf{G}}$. Therefore, in general, $b_{\mathbf{G}}$ may be complex.

30.8.3 Symmetry considerations

For a crystal, many of the $\mathbf{G}$-vectors will be equivalent by symmetry. It is useful then to divide the $\mathbf{G}$-vectors into symmetry-related groups and then require that they share a common coefficient. Two vectors, $\mathbf{G}$ and $\mathbf{G}'$, may be considered to be symmetry related if, for all α and β

$$\rho^\alpha_{\mathbf{G}}\rho^\beta_{-\mathbf{G}} = \rho^\alpha_{\mathbf{G}'}\rho^\beta_{-\mathbf{G}'} \,. \tag{30.151}$$

For the 1-body term, we may also omit from our list of $\mathbf{G}$-vectors those for which all species structure factors are zero. This is equivalent to saying that if we are tiling a primitive cell we should include only the $\mathbf{G}$-vectors of the primitive cell and not the supercell. Note that this is not the case for the 2-body term since the XC hole should not have the periodicity of the primitive cell.

30.8.4 Gradients and Laplacians

$$\begin{aligned}
\nabla_{\mathbf{r}_i} J_2 = &\sum_{\mathbf{G}\neq 0} a_{\mathbf{G}} \left[\left(\nabla_{\mathbf{r}_i}\rho_{\mathbf{G}}\right)\rho_{-\mathbf{G}} + \text{c.c.}\right] \,, \\
= &\sum_{\mathbf{G}\neq\mathbf{0}} 2\mathbf{G}a_{\mathbf{G}}\mathbf{Re}\left(ie^{i\mathbf{G}\cdot\mathbf{r}_i}\rho_{-\mathbf{G}}\right) \,, \\
= &\sum_{\mathbf{G}\neq\mathbf{0}} -2\mathbf{G}a_{\mathbf{G}}\mathbf{Im}\left(e^{i\mathbf{G}\cdot\mathbf{r}_i}\rho_{-\mathbf{G}}\right) \,.
\end{aligned} \tag{30.152}$$

The Laplacian is then given by

$$\begin{aligned}
\nabla^2 J_2 = & \sum_{\mathbf{G}\neq\mathbf{0}} a_{\mathbf{G}} \left[\left(\nabla^2 \rho_{\mathbf{G}}\right) \rho_{-\mathbf{G}} + \text{c.c.} + 2 \left(\nabla \rho_{\mathbf{G}}\right) \cdot \left(\nabla \rho_{-\mathbf{G}}\right) \right] , \\
= & \sum_{\mathbf{G}\neq\mathbf{0}} a_{\mathbf{G}} \left[-2G^2 \mathbf{Re}(e^{i\mathbf{G}\cdot\mathbf{r}_i} \rho_{-\mathbf{G}}) + 2 \left(i\mathbf{G} e^{i\mathbf{G}\cdot\mathbf{r}_i}\right) \cdot \left(-i\mathbf{G} e^{-i\mathbf{G}\cdot\mathbf{r}_i}\right) \right] , \\
= & 2 \sum_{\mathbf{G}\neq\mathbf{0}} G^2 a_{\mathbf{G}} \left[-\mathbf{Re} \left(e^{i\mathbf{G}\cdot\mathbf{r}_i} \rho_{-\mathbf{G}}\right) + 1 \right] .
\end{aligned} \tag{30.153}$$

CHAPTER

THIRTYONE

DEVELOPMENT GUIDE

The section gives guidance on how to extend the functionality of QMCPACK. Future examples will likely include topics such as the addition of a Jastrow function or a new QMC method.

31.1 QMCPACK coding standards

This chapter presents what we collectively have agreed are best practices for the code. This includes formatting style, naming conventions, documentation conventions, and certain prescriptions for C++ language use. At the moment only the formatting can be enforced in an objective fashion.

New development should follow these guidelines, and contributors are expected to adhere to them as they represent an integral part of our effort to continue QMCPACK as a world-class, sustainable QMC code. Although some of the source code has a ways to go to live up to these ideas, new code, even in old files, should follow the new conventions not the local conventions of the file whenever possible. Work on the code with continuous improvement in mind rather than a commitment to stasis.

The current workflow conventions for the project are described in the wiki on the GitHub repository. It will save you and all the maintainers considerable time if you read these and ask questions up front.

A PR should follow these standards before inclusion in the mainline. You can be sure of properly following the formatting conventions if you use clang-format. The mechanics of clang-format setup and use can be found at https://github.com/QMCPACK/qmcpack/wiki/Source-formatting.

The clang-format file found at `qmcpack/src/.clang-format` should be run over all code touched in a PR before a pull request is prepared. We also encourage developers to run clang-tidy with the `qmcpack/src/.clang-tidy` configuration over all new code.

As much as possible, try to break up refactoring, reformatting, feature, and bugs into separate, small PRs. Aim for something that would take a reviewer no more than an hour. In this way we can maintain a good collective development velocity.

31.2 Files

Each file should start with the header.

```
//////////////////////////////////////////////////////////////////////////////////////
// This file is distributed under the University of Illinois/NCSA Open Source License.
// See LICENSE file in top directory for details.
//
// Copyright (c) 2021 QMCPACK developers
//
```

(continues on next page)

(continued from previous page)

```
// File developed by: Name, email, affiliation
//
// File created by: Name, email, affiliation
//////////////////////////////////////////////////////////////////////////////////////
```

If you make significant changes to an existing file, add yourself to the list of "developed by" authors.

31.2.1 File organization

Header files should be placed in the same directory as their implementations. Unit tests should be written for all new functionality. These tests should be placed in a `tests` subdirectory below the implementations.

31.2.2 File names

Each class should be defined in a separate file with the same name as the class name. Use separate `.cpp` implementation files whenever possible to aid in incremental compilation.

The filenames of tests are composed by the filename of the object tested and the prefix `test_`. The filenames of *fake* and *mock* objects used in tests are composed by the prefixes `fake_` and `mock_`, respectively, and the filename of the object that is imitated.

31.2.3 Header files

All header files should be self-contained (i.e., not dependent on following any other header when it is included). Nor should they include files that are not necessary for their use (i.e., headers needed only by the implementation). Implementation files should not include files only for the benefit of files they include.

There are many header files that currently violate this. Each header must use `#define` guards to prevent multiple inclusion. The symbol name of the `#define` guards should be `NAMESPACE(s)_CLASSNAME_H`.

31.2.4 Includes

Related header files should be included without any path. Header files from external projects and standard libraries should be includes using the `<iostream>` convention, while headers that are part of the QMCPACK project should be included using the `"our_header.h"` convention.

We are now using a new header file inclusion style following the modern CMake transition in QMCPACK, while the legacy code may still use the legacy style. Newly written code and refactored code should be transitioned to the new style.

New style for modern CMake

In QMCPACK, include paths are handled by modern CMake target dependency. Every top level folder is at least one target. For example, `src/Particle/CMakeLists.txt` defines *qmcparticle* target. It propagates include path `qmcpack/src/Particle` to compiling command lines in CMake via

```
TARGET_INCLUDE_DIRECTORIES(qmcparticle PUBLIC "${CMAKE_CURRENT_SOURCE_DIR}")
```

For this reason, the file `qmcpack/src/Particle/Lattice/ParticleBConds3DSoa.h` should be included as

```
#include "Lattice/ParticleBConds3DSoa.h"
```

If the compiled file is not part of the same target as *qmcparticle*, the target it belongs to should have a dependency on *qmcparticle*. For example, test source files under `qmcpack/src/Particle/tests` are not part of *qmcparticle* and thus requires the following additional CMake setting

```
TARGET_LINK_LIBRARIES(${UTEST_EXE} qmcparticle)
```

Legacy style

Header files should be included with the full path based on the `src` directory. For example, the file `qmcpack/src/QMCWaveFunctions/SPOSet.h` should be included as

```
#include "QMCWaveFunctions/SPOSet.h"
```

Even if the included file is located in the same directory as the including file, this rule should be obeyed.

Ordering

For readability, we suggest using the following standard order of includes:

1. related header
2. std C library headers
3. std C++ library headers
4. Other libraries' headers
5. QMCPACK headers

In each section the included files should be sorted in alphabetical order.

31.3 Naming

The balance between description and ease of implementation should be balanced such that the code remains self-documenting within a single terminal window. If an extremely short variable name is used, its scope must be shorter than ~ 40 lines. An exception is made for template parameters, which must be in all CAPS. Legacy code contains a great variety of hard to read code style, read this section and do not imitate existing code that violates it.

31.3.1 Namespace names

Namespace names should be one word, lowercase.

31.3.2 Type and class names

Type and class names should start with a capital letter and have a capital letter for each new word. Underscores (_) are not allowed. It's redundant to end these names with `Type` or `_t`.

:: \no using ValueMatrix_t = Matrix<Value>; using RealType = double;

31.3.3 Variable names

Variable names should not begin with a capital letter, which is reserved for type and class names. Underscores (_) should be used to separate words.

31.3.4 Class data members

Class private/protected data members names should follow the convention of variable names with a trailing underscore (_). The use of public member functions is discourage, rethink the need for it in the first place. Instead `get` and `set` functions are the preferred access method.

31.3.5 (Member) function names

Function names should start with a lowercase character and have a capital letter for each new word. The exception are the special cases for prefixed multiwalker (`mw_`) and flex (`flex_`) batched API functions. Coding convention should follow after those prefixes.

31.3.6 Template Parameters

Template parameters names should be in all caps with (_) separating words. It's redundant to end these names with `_TYPE`,

31.3.7 Lambda expressions

Named lambda expressions follow the naming convention for functions:

```
auto myWhatever = [](int i) { return i + 4; };
```

31.3.8 Macro names

Macro names should be all uppercase and can include underscores (_). The underscore is not allowed as first or last character.

31.3.9 Test case and test names

Test code files should be named as follows:

```
class DiracMatrix;
//leads to
test_dirac_matrix.cpp
//which contains test cases named
TEST_CASE("DiracMatrix_update_row","[wavefunction][fermion]")
```

where the test case covers the `updateRow` and `[wavefunction][fermion]` indicates the test belongs to the fermion wavefunction functionality.

31.4 Comments

31.4.1 Comment style

Use the `// Comment` syntax for actual comments.

Use

```
/** base class for Single-particle orbital sets
 *
 * SPOSet stands for S(ingle)P(article)O(rbital)Set which contains
 * a number of single-particle orbitals with capabilities of
 * evaluating \f$ \psi_j({\bf r}_i)\f$
 */
```

or

```
///index in the builder list of sposets
int builder_index;
```

31.4.2 Documentation

Doxygen will be used for source documentation. Doxygen commands should be used when appropriate guidance on this has been decided.

File docs

Do not put the file name after the `\file` Doxygen command. Doxygen will fill it in for the file the tag appears in.

```
/** \file
 *  File level documentation
 */
```

Class docs

Every class should have a short description (in the header of the file) of what it is and what is does. Comments for public class member functions follow the same rules as general function comments. Comments for private members are allowed but are not mandatory.

Function docs

For function parameters whose type is non-const reference or pointer to non-const memory, it should be specified if they are input (In:), output (Out:) or input-output parameters (InOut:).

Example:

```
/** Updates foo and computes bar using in_1 .. in_5.
 * \param[in] in_3
 * \param[in] in_5
 * \param[in,out] foo
 * \param[out] bar
 */

//This is probably not what our clang-format would do
void computeFooBar(Type in_1, const Type& in_2, Type& in_3,
                   const Type* in_4, Type* in_5, Type& foo,
                   Type& bar);
```

Variable documentation

Name should be self-descriptive. If you need documentation consider renaming first.

31.4.3 Golden rule of comments

If you modify a piece of code, also adapt the comments that belong to it if necessary.

31.5 Formatting and “style”

Use the provided clang-format style in `src/.clang-format` to format `.h`, `.hpp`, `.cu`, and `.cpp` files. Many of the following rules will be applied to the code by clang-format, which should allow you to ignore most of them if you always run it on your modified code.

You should use clang-format support and the `.clangformat` file with your editor, use a Git precommit hook to run clang-format or run clang-format manually on every file you modify. However, if you see numerous formatting updates outside of the code you have modified, first commit the formatting changes in a separate PR.

31.5.1 Indentation

Indentation consists of two spaces. Do not use tabs in the code.

31.5.2 Line length

The length of each line of your code should be at most *120* characters.

31.5.3 Horizontal spacing

No trailing white spaces should be added to any line. Use no space before a comma (`,`) and a semicolon (`;`), and add a space after them if they are not at the end of a line.

31.5.4 Preprocessor directives

The preprocessor directives are not indented. The hash is the first character of the line.

31.5.5 Binary operators

The assignment operators should always have spaces around them.

31.5.6 Unary operators

Do not put any space between an unary operator and its argument.

31.5.7 Types

The `using` syntax is preferred to `typedef` for type aliases. If the actual type is not excessively long or complex, simply use it; renaming simple types makes code less understandable.

31.5.8 Pointers and references

Pointer or reference operators should go with the type. But understand the compiler reads them from right to left.

```
Type* var;
Type& var;

//Understand this is incompatible with multiple declarations
Type* var1, var2; // var1 is a pointer to Type but var2 is a Type.
```

31.5.9 Templates

The angle brackets of templates should not have any external or internal padding.

```
template<class C>
class Class1;

Class1<Class2<type1>> object;
```

31.5.10 Vertical spacing

Use empty lines when it helps to improve the readability of the code, but do not use too many. Do not use empty lines after a brace that opens a scope or before a brace that closes a scope. Each file should contain an empty line at the end of the file. Some editors add an empty line automatically, some do not.

31.5.11 Variable declarations and definitions

- Avoid declaring multiple variables in the same declaration, especially if they are not fundamental types:

```
int x, y;                          // Not recommended
Matrix a("my-matrix"), b(size);  // Not allowed

// Preferred
int x;
int y;
Matrix a("my-matrix");
Matrix b(10);
```

- Use the following order for keywords and modifiers in variable declarations:

```
// General type
[static] [const/constexpr] Type variable_name;

// Pointer
[static] [const] Type* [const] variable_name;

// Integer
// the int is not optional not all platforms support long, etc.
[static] [const/constexpr] [signedness] [size] int variable_name;

// Examples:
static const Matrix a(10);


const double* const d(3.14);
constexpr unsigned long l(42);
```

31.5.12 Function declarations and definitions

The return type should be on the same line as the function name. Parameters should also be on the same line unless they do not fit on it, in which case one parameter per line aligned with the first parameter should be used.

Also include the parameter names in the declaration of a function, that is,

```
// calculates a*b+c
double function(double a, double b, double c);

// avoid
double function(double, double, double);

// dont do this
double function(BigTemplatedSomething<double> a, BigTemplatedSomething<double> b,
                BigTemplatedSomething<double> c);

// do this
double function(BigTemplatedSomething<double> a,
                BigTemplatedSomething<double> b,
                BigTemplatedSomething<double> c);
```

31.5.13 Conditionals

Examples:

```
if (condition)
  statement;
else
  statement;

if (condition)
{
  statement;
}
else if (condition2)
{
  statement;
}
else
{
  statement;
}
```

31.5.14 Switch statement

Switch statements should always have a default case.

Example:

```
switch (var)
{
  case 0:
    statement1;
    statement2;
```

(continues on next page)

(continued from previous page)

```
    break;

  case 1:
    statement1;
    statement2;
    break;

  default:
    statement1;
    statement2;
}
```

31.5.15 Loops

Examples:

```
for (statement; condition; statement)
  statement;

for (statement; condition; statement)
{
  statement1;
  statement2;
}

while (condition)
  statement;

while (condition)
{
  statement1;
  statement2;
}

do
{
  statement;
}
while (condition);
```

31.5.16 Class format

`public`, `protected`, and `private` keywords are not indented.

Example:

```
class Foo : public Bar
{
public:
  Foo();
  explicit Foo(int var);

  void function();
  void emptyFunction() {}
```

(continues on next page)

(continued from previous page)

```
  void setVar(const int var)
  {
    var_ = var;
  }
  int getVar() const
  {
    return var_;
  }

private:
  bool privateFunction();

  int var_;
  int var2_;
};
```

Constructor initializer lists

Examples:

```
// When everything fits on one line:
Foo::Foo(int var) : var_(var)
{
  statement;
}

// If the signature and the initializer list do not
// fit on one line, the colon is indented by 4 spaces:
Foo::Foo(int var)
    : var_(var), var2_(var + 1)
{
  statement;
}

// If the initializer list occupies more lines,
// they are aligned in the following way:
Foo::Foo(int var)
    : some_var_(var),
      some_other_var_(var + 1)
{
  statement;
}

// No statements:
Foo::Foo(int var)
    : some_var_(var) {}
```

31.5.17 Namespace formatting

The content of namespaces is not indented. A comment should indicate when a namespace is closed. (clang-format will add these if absent). If nested namespaces are used, a comment with the full namespace is required after opening a set of namespaces or an inner namespace.

Examples:

```
namespace ns
{
void foo();
}  // ns
```

```
namespace ns1
{
namespace ns2
{
// ns1::ns2::
void foo();

namespace ns3
{
// ns1::ns2::ns3::
void bar();
}  // ns3
}  // ns2

namespace ns4
{
namespace ns5
{
// ns1::ns4::ns5::
void foo();
}  // ns5
}  // ns4
}  // ns1
```

31.6 QMCPACK C++ guidance

The guidance here, like any advice on how to program, should not be treated as a set of rules but rather the hard-won wisdom of many hours of suffering development. In the past, many rules were ignored, and the absolute worst results of that will affect whatever code you need to work with. Your PR should go much smoother if you do not ignore them.

31.6.1 Encapsulation

A class is not just a naming scheme for a set of variables and functions. It should provide a logical set of methods, could contain the state of a logical object, and might allow access to object data through a well-defined interface related variables, while preserving maximally ability to change internal implementation of the class.

Do not use `struct` as a way to avoid controlling access to the class. Only in rare cases where a class is a fully public data structure `struct` is this appropriate. Ignore (or fix one) the many examples of this in QMCPACK.

Do not use inheritance primarily as a means to break encapsulation. If your class could aggregate or compose another class, do that, and access it solely through its public interface. This will reduce dependencies.

31.6.2 Casting

In C++ source, avoid C style casts; they are difficult to search for and imprecise in function. An exception is made for controlling implicit conversion of simple numerical types.

Explicit C++ style casts make it clear what the safety of the cast is and what sort of conversion is expected to be possible.

```
int c = 2;
int d = 3;
double a;
a = (double)c / d;  // Ok

const class1 c1;
class2* c2;
c2 = (class2*)&c1; // NO
SPOSetAdvanced* spo_advanced = new SPOSetAdvanced();

SPOSet* spo = (SPOSet*)spo_advanced; // NO
SPOSet* spo = static_cast<SPOSet*>(spo_advanced); // OK if upcast, dangerous if␣
↪downcast
```

31.6.3 Pre-increment and pre-decrement

Use the pre-increment (pre-decrement) operator when a variable is incremented (decremented) and the value of the expression is not used. In particular, use the pre-increment (pre-decrement) operator for loop counters where i is not used:

```
for (int i = 0; i < N; ++i)
{
  doSomething();
}

for (int i = 0; i < N; i++)
{
  doSomething(i);
}
```

The post-increment and post-decrement operators create an unnecessary copy that the compiler cannot optimize away in the case of iterators or other classes with overloaded increment and decrement operators.

31.6.4 Alternative operator representations

Alternative representations of operators and other tokens such as `and`, `or`, and `not` instead of `&&`, `||`, and `!` are not allowed. For the reason of consistency, the far more common primary tokens should always be used.

31.6.5 Use of const

- Add the `const` qualifier to all function parameters that are not modified in the function body.
- For parameters passed by value, add only the keyword in the function definition.
- Member functions should be specified const whenever possible.

```
// Declaration
int computeFoo(int bar, const Matrix& m)

// Definition
int computeFoo(const int bar, const Matrix& m)
{
  int foo = 42;

  // Compute foo without changing bar or m.
  // ...

  return foo;
}

class MyClass
{
  int count_
  ...
  int getCount() const { return count_;}
}
```

31.6.6 Smart pointers

Use of smart pointers is being adopted to help make QMCPACK memory leak free. Prior to C++11, C++ uses C-style pointers. A C-style pointer can have several meanings and the ownership of a piece of help memory may not be clear. This leads to confusion and causes memory leaks if pointers are not managed properly. Since C++11, smart pointers were introduced to resolve this issue. In addition, it demands developers to think about the ownership and lifetime of declared pointer objects.

std::unique_ptr

A unique pointer is the unique owner of a piece of allocated memory. Pointers in per-walker data structure with distinct contents should be unique pointers. For example, every walker has a trial wavefunction object which contains an SPO object pointer. Because the SPO object has a vector to store SPO evaluation results, it cannot be shared between two trial wavefunction objects. For this reason the SPO object pointer should be an unique pointer.

In QMCPACK, most raw pointers can be directly replaced with `std::unique_ptr`. Corresponding use of `new` operator can be replaced with `std:make_unique`.

std::shared_ptr

A shared pointer is the shared owner of a piece of allocated memory. Moving a pointer ownership from one place to another should not use shared pointers but C++ move semantics. Shared contents between walkers may be candidates for shared pointers. For example, although the Jastrow factor object must be unique per walker, the pointer to the parameter data structure can be a shared pointer. During Jastrow optimization, any update to the parameter data managed by the shared pointer will be effective immediately in all the Jastrow objects. In another example, spline coefficients are managed by a shared pointer which achieves a single copy in memory shared by an SPOSet and all of its clones.

31.7 Particles and distance tables

31.7.1 ParticleSets

The `ParticleSet` class stores particle positions and attributes (charge, mass, etc).

The `R` member stores positions. For calculations, the `R` variable needs to be transferred to the structure-of-arrays (SoA) storage in `RSoA`. This is done by the `update` method. In the future the interface may change to use functions to set and retrieve positions so the SoA transformation of the particle data can happen automatically. For now, it is crucial to call `P.update()` to populate `RSoA` anytime `P.R` is changed. Otherwise, the distance tables associated with `R` will be uninitialized or out-of-date.

```
const SimulationCell sc;
ParticleSet elec(sc), ions(sc);
elec.setName("e");
ions.setName("ion0");

// initialize ions
ions.create({2});
ions.R[0] = {0.0, 0.0, 0.0};
ions.R[1] = {0.5, 0.5, 0.5};
ions.update(); // transfer to RSoA

// initialize elec
elec.create({1,1});
elec.R[0] = {0.0, 0.0, 0.0};
elec.R[1] = {0.0, 0.25, 0.0};
const int itab = elec.addTable(ions);
elec.update(); // update RSoA and distance tables

// d_table is an electron-ion distance table
const auto& d_table = elec.getDistTableAB(itab);
```

A particular distance table is retrieved with `getDistTable`. Use `addTable` to add a `ParticleSet` and return the index of the distance table. If the table already exists the index of the existing table will be returned.

The mass and charge of each particle is stored in `Mass` and `Z`. The flag, `SameMass`, indicates if all the particles have the same mass (true for electrons).

Groups

Particles can belong to different groups. For electrons, the groups are up and down spins. For ions, the groups are the atomic elements. The group type for each particle can be accessed through the `GroupID` member. The number of groups is returned from `groups()`. The total number particles is accessed with `getTotalNum()`. The number of particles in a group is `groupsize(int igroup)`. The particle indices for each group are found with `first(int igroup)` and `last(int igroup)`.

31.7.2 Distance tables

Distance tables store distances between particles. There are symmetric (AA) tables for distance between like particles (electron-electron or ion-ion) and asymmetric (AB) tables for distance between unlike particles (electron-ion)

The `Distances` and `Displacements` members contain the data. The indexing order is target index first, then source. For electron-ion tables, the sources are the ions and the targets are the electrons.

31.7.3 Looping over particles

Some sample code on how to loop over all the particles in an electron-ion distance table:

```
// d_table is an electron-ion distance table

for (int jat = 0; j < d_table.targets(); jat++) { // Loop over electrons
  for (int iat = 0; i < d_table.sources(); iat++) { // Loop over ions
     d_table.Distances[jat][iat];
  }
}
```

Interactions sometimes depend on the type of group of the particles. The code can loop over all particles and use `GroupID[idx]` to choose the interaction. Alternately, the code can loop over the number of groups and then loop from the first to last index for those groups. This method can attain higher performance by effectively hoisting tests for group ID out of the loop.

An example of the first approach is

```
// P is a ParticleSet

for (int iat = 0; iat < P.getTotalNum(); iat++) {
  int group_idx = P.GroupID[iat];
  // Code that depends on the group index
}
```

An example of the second approach is

```
// P is a ParticleSet
assert(P.IsGrouped == true); // ensure particles are grouped

for (int ig = 0; ig < P.groups(); ig++) { // loop over groups
  for (int iat = P.first(ig); iat < P.last(ig); iat++) { // loop over elements in␣
↪each group
     // Code that depends on group
  }
}
```

31.8 Wavefunction

A full `TrialWaveFunction` is formulated as a product of all the components. Each component derives from `WaveFunctionComponent`.

$$\psi = \prod_c \tilde{\psi}_c$$

QMCPACK doesn't directly use the product form but mostly uses the log of the wavefunction. It is a natural fit for QMC algorithms and offers a numerical advantage on computers. The log value grows linearly instead of exponentially, beyond the range of double precision, with respect to the electron counts in a Slater-Jastrow wave function.

The code contains an example of a wavefunction component for a Helium atom using a simple form and is described in *Helium Wavefunction Example*

31.8.1 Mathematical preliminaries

The wavefunction evaluation functions compute the log of the wavefunction, the gradient and the Laplacian of the log of the wavefunction. Expanded, the gradient and Laplacian are

$$\begin{aligned} \mathbf{G} &= \{\nabla_i \ln(\psi)\} = \left\{ \sum_c \nabla_i \ln(\tilde{\psi}_c) \right\}, \quad \tilde{\mathbf{G}} = \{\nabla_i \ln(\tilde{\psi})\} = \left\{ \frac{\nabla_i \tilde{\psi}}{\tilde{\psi}} \right\} \\ \mathbf{L} &= \{\nabla_i^2 \ln(\psi)\} = \left\{ \sum_c \nabla_i^2 \ln(\tilde{\psi}_c) \right\}, \quad \tilde{\mathbf{L}} = \{\nabla_i^2 \ln(\tilde{\psi})\} = \left\{ \frac{\nabla_i^2 \tilde{\psi}}{\tilde{\psi}} - \tilde{G}_i \cdot \tilde{G}_i \right\} \end{aligned} \tag{31.1}$$

where i is the electron index. In this separable form, each wavefunction component computes its $\tilde{\mathbf{G}}$ `WaveFunctionComponent::G` and $\tilde{\mathbf{L}}$ `WaveFunctionComponent::L`. The sum over components are stored in `TrialWaveFunction::G` and `TrialWaveFunction::L`. The $\frac{\nabla^2\psi}{\psi}$ needed by kinetic part of the local energy can be computed as

$$\frac{\nabla_i^2 \psi}{\psi} = \mathbf{L_i} + \mathbf{G}_i \cdot \mathbf{G}_i$$

see `QMCHamiltonians/BareKineticEnergy.h`.

31.8.2 Wavefunction evaluation

The process for creating a new wavefunction component class is to derive from WaveFunctionComponent and implement a number pure virtual functions. To start most of them can be empty.

The following four functions evaluate the wavefunction values and spatial derivatives:

`evaluateLog` Computes the log of the wavefunction and the gradient and Laplacian (of the log of the wavefunction) for all particles. The input is the`ParticleSet(P)` (of the electrons). The log of the wavefunction should be stored in the `LogValue` member variable, and used as the return value from the function. The gradient is stored in `G` and the Laplacian in `L`.

`ratio` Computes the wavefunction ratio (not the log) for a single particle move (ψ_{new}/ψ_{old}). The inputs are the `ParticleSet(P)` and the particle index (`iat`).

`evalGrad` Computes the gradient for a given particle. The inputs are the `ParticleSet(P)` and the particle index (`iat`).

`ratioGrad` Computes the wavefunction ratio and the gradient at the new position for a single particle move. The inputs are the `ParticleSet(P)` and the particle index (`iat`). The output gradient is in `grad_iat`;

The `updateBuffer` function needs to be implemented, but to start it can simply call `evaluateLog`.

The `put` function should be implemented to read parameter specifics from the input XML file.

31.8.3 Function use

For debugging it can be helpful to know the under what conditions the various routines are called.

The VMC and DMC loops initialize the walkers by calling `evaluateLog`. For all-electron moves, each timestep advance calls `evaluateLog`. If the `use_drift` parameter is no, then only the wavefunction value is used for sampling. The gradient and Laplacian are used for computing the local energy.

For particle-by-particle moves, each timestep advance

1. calls `evalGrad`
2. computes a trial move
3. calls `ratioGrad` for the wavefunction ratio and the gradient at the trial position. (If the `use_drift` parameter is no, the `ratio` function is called instead.)

The following example shows part of an input block for VMC with all-electron moves and drift.

```
<qmc method="vmc" target="e" move="alle">
  <parameter name="use_drift">yes</parameter>
</qmc>
```

31.8.4 Particle distances

The `ParticleSet` parameter in these functions refers to the electrons. The distance tables that store the inter-particle distances are stored as an array.

To get the electron-ion distances, add the ion `ParticleSet` using `addTable` and save the returned index. Use that index to get the ion-electron distance table.

```
const int ei_id = elecs.addTable(ions); // in the constructor only
const auto& ei_table = elecs.getDistTable(ei_id); // when consuming a distance table
```

Getting the electron-electron distances is very similar, just add the electron `ParticleSet` using `addTable`.

Only the lower triangle for the electron-electron table should be used. It is the only part of the distance table valid throughout the run. During particle-by-particle move, there are extra restrictions. When a move of electron iel is proposed, only the lower triangle parts [0,iel)[0,iel) [iel, Nelec)[iel, Nelec) and the row [iel][0:Nelec) are valid. In fact, the current implementation of distance based two and three body Jastrow factors in QMCPACK only needs the row [iel][0:Nelec).

In `ratioGrad`, the new distances are stored in the `Temp_r` and `Temp_dr` members of the distance tables.

31.8.5 Setup

A builder processes XML input, creates the wavefunction, and adds it to `targetPsi`. Builders derive from `WaveFunctionComponentBuilder`.

The new builder hooks into the XML processing in `WaveFunctionFactory.cpp` in the `build` function.

31.8.6 Caching values

The `acceptMove` and `restore` methods are called on accepted and rejected moves for the component to update cached values.

31.8.7 Threading

The `makeClone` function needs to be implemented to work correctly with OpenMP threading. There will be one copy of the component created for each thread. If there is no extra storage, calling the copy constructor will be sufficient. If there are cached values, the clone call may need to create space.

31.8.8 Parameter optimization

The `checkInVariables`, `checkOutVariables`, and `resetParameters` functions manage the variational parameters. Optimizable variables also need to be registered when the XML is processed.

Variational parameter derivatives are computed in the `evaluateDerivatives` function. It computes the derivatives of both the log of the wavefunction and kinetic energy with respect to optimizable parameters and adds the results to the corresponding output arrays.

The kinetic energy derivatives are computed as

$$\sum_i -\frac{1}{2m_i}(\partial_\alpha \mathbf{L}_i + 2\mathbf{G}_i \cdot \partial_\alpha \mathbf{G}_i)$$

with each `WaveFunctionComponent` contributing

$$-\frac{1}{2}\partial_\alpha \tilde{L} - G \cdot \partial_\alpha \tilde{G}$$

Right now $1/m$ factor is applied in `TrialWaveFunction`. This is a bug when the particle set doesn't hold equal mass particles.

31.8.9 Helium Wavefunction Example

The code contains an example of a wavefunction component for a Helium atom using STO orbitals and a Pade Jastrow.

to The wavefunction is

$$\psi = \frac{1}{\sqrt{\pi}} \exp(-Zr_1) \exp(-Zr_2) \exp(A/(1+Br_{12})) \tag{31.2}$$

where $Z = 2$ is the nuclear charge, $A = 1/2$ is the electron-electron cusp, and B is a variational parameter. The electron-ion distances are r_1 and r_2, and r_{12} is the electron-electron distance. The wavefunction is the same as the one expressed with built-in components in `examples/molecules/He/he_simple_opt.xml`.

The code is in `src/QMCWaveFunctions/ExampleHeComponent.cpp`. The builder is in `src/QMCWaveFunctions/ExampleHeBuilder.cpp`. The input file is in `examples/molecules/He/he_example_wf.xml`. A unit test compares results from the wavefunction evaluation functions for consistency in `src/QMCWaveFunctions/tests/test_example_he.cpp`.

The recommended approach for creating a new wavefunction component is to copy the example and the unit test. Implement the evaluation functions and ensure the unit test passes.

31.9 Linear Algebra

Like in many methods which solve the Schrödinger equation, linear algebra plays a critical role in QMC algorithms and thus is crucial to the performance of QMCPACK. There are a few components in QMCPACK use BLAS/LAPACK with their own characteristics.

31.9.1 Real space QMC

Single particle orbitals

Spline evaluation as commonly used in solid-state simulations does not use any dense linear algebra library calls. LCAO evaluation as commonly used in molecular calculations relies on BLAS2 GEMV to compute SPOs from a basis set.

Slater determinants

Slater determinants are calculated on $N \times N$ Slater matrices. N is the number of electrons for a given spin. In the actually implementation, operations on the inverse matrix of Slater matrix for each walker dominate the computation. To initialize it, DGETRF and DGETRI from LAPACK are called. The inverse matrix can be stored out of place. During random walking, inverse matrices are updated by either Sherman-Morrison rank-1 update or delayed update. Update algorithms heavily relies on BLAS. All the BLAS operations require S,C,D,Z cases.

Sherman-Morrison rank-1 update uses BLAS2 GEMV and GER on $N \times N$ matrices.

Delayed rank-K update uses

- BLAS1 SCOPY on N array.
- BLAS2 GEMV, GER on $k \times N$ and $k \times k$ matrices. k ranges from 1 to K when updates are delayed and accumulated.
- BLAS3 GEMM at the final update.
  - 'T', 'N', K, N, N
  - 'N', 'N', N, K, K
  - 'N', 'N', N, N, K

The optimal K depends on the hardware but it usually ranges from 32 to 256.

QMCPACK solves systems with a few to thousands of electrons. To make all the BLAS/LAPACK operation efficient on accelerators. Batching is needed and optimized for $N < 2000$. Non-batched functions needs to be optimized for $N > 500$. Note: 2000 and 500 are only rough estimates.

Wavefunction optimizer

to be added.

31.9.2 Auxiliary field QMC

The AFQMC implementation in QMCPACK relies heavily on linear algebra operations from BLAS/LAPACK. The performance of the code is netirely dependent on the performance of these libraries. See below for a detailed list of the main routines used from BLAS/LAPACK. Since the AFQMC code can work with both single and double precision builds, all 4 versions of these routines (S,C,D,Z) are generally needed, for this reason we omit the data type label.

- BLAS1: SCAL, COPY, DOT, AXPY
- BLAS2: GEMV, GER
- BLAS3: GEMM
- LAPACK: GETRF, GETRI, GELQF, UNGLQ, ORGLQ, GESVD, HEEVR, HEGVX

While the dimensions of the matrix operations will depend entirely on the details of the calculation, typical matrix dimensions range from the 100s, for small system sizes, to over 20000 for the largest calculations attempted so far. For builds with GPU accelerators, we make use of batched and strided implementations of these routines. Batched implementations of GEMM, GETRF, GETRI, GELQF and UNGLQ are particularly important for the performance of the GPU build on small to medium size problems. Batched implementations of DOT, AXPY and GEMV would also be quite useful, but they are not yet generally available. On GPU builds, the code uses batched implementations of these routines when available by default.

31.10 Slater-backflow wavefunction implementation details

For simplicity, consider N identical fermions of the same spin (e.g., up electrons) at spatial locations $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$. Then the Slater determinant can be written as

$$S = \det M \,, \tag{31.3}$$

where each entry in the determinant is an SPO evaluated at a particle position

$$M_{ij} = \phi_i(\mathbf{r}_j) \,. \tag{31.4}$$

When backflow transformation is applied to the determinant, the particle coordinates $\mathbf{r}_i$ that go into the SPOs are replaced by quasi-particle coordinates $\mathbf{x}_i$:

$$M_{ij} = \phi_i(\mathbf{x}_j) \,, \tag{31.5}$$

where

$$\mathbf{x}_i = \mathbf{r}_i + \sum_{j=1, j\neq i}^{N} \eta(r_{ij})(\mathbf{r}_i - \mathbf{r}_j) \,. \tag{31.6}$$

$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The integers i,j label the particle/quasi-particle. There is a one-to-one correspondence between the particles and the quasi-particles, which is simplest when $\eta = 0$.

31.10.1 Value

The evaluation of the Slater-backflow wavefunction is almost identical to that of a Slater wavefunction. The only difference is that the quasi-particle coordinates are used to evaluate the SPOs. The actual value of the determinant is stored during the inversion of the matrix M (`cgetrf`→`cgetri`). Suppose $M = LU$, then $S = \prod_{i=1}^{N} L_{ii}U_{ii}$.

```
// In DiracDeterminantWithBackflow::evaluateLog(P,G,L)
Phi->evaluate(BFTrans->QP, FirstIndex, LastIndex, psiM,dpsiM,grad_grad_psiM);
psiMinv = psiM;
LogValue=InvertWithLog(psiMinv.data(),NumPtcls,NumOrbitals
  ,WorkSpace.data(),Pivot.data(),PhaseValue);
```

QMCPACK represents the complex value of the wavefunction in polar coordinates $S = e^{U}e^{i\theta}$. Specifically, `LogValue` U and `PhaseValue` θ are handled separately. In the following, we will consider derivatives of the log value only.

31.10.2 Gradient

To evaluate particle gradient of the log value of the Slater-backflow wavefunction, we can use the $\log\det$ identity in (31.7). This identity maps the derivative of $\log\det M$ with respect to a real variable p to a trace over $M^{-1}dM$:

$$\frac{\partial}{\partial p}\log\det M = \mathrm{tr}\left(M^{-1}\frac{\partial M}{\partial p}\right). \tag{31.7}$$

Following Kwon, Ceperley, and Martin [[KCM93]], the particle gradient

$$G_i^{\alpha} \equiv \frac{\partial}{\partial r_i^{\alpha}}\log\det M = \sum_{j=1}^{N}\sum_{\beta=1}^{3} F_{jj}^{\beta}A_{jj}^{\alpha\beta}\,, \tag{31.8}$$

where the quasi-particle gradient matrix

$$A_{ij}^{\alpha\beta} \equiv \frac{\partial x_j^{\beta}}{\partial r_i^{\alpha}}\,, \tag{31.9}$$

and the intermediate matrix

$$F_{ij}^{\alpha} \equiv \sum_k M_{ik}^{-1}dM_{kj}^{\alpha}\,, \tag{31.10}$$

with the SPO derivatives (w.r. to quasi-particle coordinates)

$$dM_{ij}^{\alpha} \equiv \frac{\partial M_{ij}}{\partial x_j^{\alpha}}\,. \tag{31.11}$$

Notice that we have made the name change of $\phi \to M$ from the notations of ref. [[KCM93]]. This name change is intended to help the reader associate M with the QMCPACK variable `psiM`.

```
// In DiracDeterminantWithBackflow::evaluateLog(P,G,L)
for(int i=0; i<num; i++) // k in above formula
{
  for(int j=0; j<NumPtcls; j++)
  {
    for(int k=0; k<OHMMS_DIM; k++) // alpha in above formula
    {
      myG(i) += dot(BFTrans->Amat(i,FirstIndex+j),Fmat(j,j));
    }
  }
}
```

(31.8) is still relatively simple to understand. The A matrix maps changes in particle coordinates $d\mathbf{r}$ to changes in quasi-particle coordinates $d\mathbf{x}$. Dotting A into F propagates $d\mathbf{x}$ to dM. Thus $F \cdot A$ is the term inside the trace operator of (31.7). Finally, performing the trace completes the evaluation of the derivative.

31.10.3 Laplacian

The particle Laplacian is given in [[KCM93]] as

$$L_i \equiv \sum_\beta \frac{\partial^2}{\partial (r_i^\beta)^2} \log\det M = \sum_{j\alpha} B_{ij}^\alpha F_{jj}^\alpha - \sum_{jk}\sum_{\alpha\beta\gamma} A_{ij}^{\alpha\beta} A_{ik}^{\alpha\gamma} \times \left(F_{kj}^\alpha F_{jk}^\gamma - \delta_{jk} \sum_m M_{jm}^{-1} d2M_{mj}^{\beta\gamma} \right), \tag{31.12}$$

where the quasi-particle Laplacian matrix

$$B_{ij}^\alpha \equiv \sum_\beta \frac{\partial^2 x_j^\alpha}{\partial (r_i^\beta)^2}, \tag{31.13}$$

with the second derivatives of the single-particles orbitals being

$$d2M_{ij}^{\alpha\beta} \equiv \frac{\partial^2 M_{ij}}{\partial x_j^\alpha \partial x_j^\beta}. \tag{31.14}$$

Schematically, L_i has contributions from three terms of the form $BF, AAFF, and tr(AA, Md2M)$, respectively. $A, B, M, d2M$, and F can be calculated and stored before the calculations of L_i. The first BF term can be directly calculated in a loop over quasi-particle coordinates $j\alpha$.

```
// In DiracDeterminantWithBackflow::evaluateLog(P,G,L)
for(int j=0; j<NumPtcls; j++)
  for(int a=0; a<OHMMS_DIM; k++)
    myL(i) += BFTrans->Bmat_full(i,FirstIndex+j)[a]*Fmat(j,j)[a];
```

Notice that B_{ij}^α is stored in `Bmat_full`, NOT `Bmat`.

The remaining two terms both involve AA. Thus, it is best to define a temporary tensor AA:

$${}_iAA_{jk}^{\beta\gamma} \equiv \sum_\alpha A_{ij}^{\alpha\beta} A_{ij}^{\alpha\gamma}, \tag{31.15}$$

which we will overwrite for each particle i. Similarly, define FF:

$$FF_{jk}^{\alpha\gamma} \equiv F_{kj}^\alpha F_{jk}^\gamma, \tag{31.16}$$

which is simply the outer product of $F \otimes F$. Then the $AAFF$ term can be calculated by fully contracting AA with FF.

```
// In DiracDeterminantWithBackflow::evaluateLog(P,G,L)
for(int j=0; j<NumPtcls; j++)
  for(int k=0; k<NumPtcls; k++)
    for(int i=0; i<num; i++)
    {
      Tensor<RealType,OHMMS_DIM> AA = dot(transpose(BFTrans->Amat(i,FirstIndex+j)),
↪BFTrans->Amat(i,FirstIndex+k));
      HessType FF = outerProduct(Fmat(k,j),Fmat(j,k));
      myL(i) -= traceAtB(AA,FF);
    }
```

Finally, define the SPO derivative term:

$$Md2M_j^{\beta\gamma} \equiv \sum_m M_{jm}^{-1} d2M_{mj}^{\beta} \,, \tag{31.17}$$

then the last term is given by the contraction of $Md2M$ (`q_j`) with the diagonal of AA.

```
for(int j=0; j<NumPtcls; j++)
{
  HessType q_j;
  q_j=0.0;
  for(int k=0; k<NumPtcls; k++)
    q_j += psiMinv(j,k)*grad_grad_psiM(j,k);
  for(int i=0; i<num; i++)
  {
    Tensor<RealType,OHMMS_DIM> AA = dot(
      transpose(BFTrans->Amat(i,FirstIndex+j)),
      BFTrans->Amat(i,FirstIndex+j)
    );
    myL(i) += traceAtB(AA,q_j);
  }
}
```

31.10.4 Wavefunction parameter derivative

To use the robust linear optimization method of [[TU07]], the trial wavefunction needs to know its contributions to the overlap and hamiltonian matrices. In particular, we need derivatives of these matrices with respect to wavefunction parameters. As a consequence, the wavefunction ψ needs to be able to evaluate $\frac{\partial}{\partial p}\ln\psi$ and $\frac{\partial}{\partial p}\frac{\mathcal{H}\psi}{\psi}$, where p is a parameter.

When 2-body backflow is considered, a wavefunction parameter p enters the η function only (equation (31.6)). $\mathbf{r}$, ϕ, and M do not explicitly dependent on p. Derivative of the log value is almost identical to particle gradient. Namely, (31.8) applies upon the substitution $r_i^\alpha \to p$.

$$\frac{\partial}{\partial p}\ln\det M = \sum_{j=1}^{N}\sum_{\beta=1}^{3} F_{jj}^{\beta}\left({}_pC_j^{\beta}\right) \,, \tag{31.18}$$

where the quasi-particle derivatives are stored in `Cmat`

$${}_pC_i^{\alpha} \equiv \frac{\partial}{\partial p} x_i^{\alpha} \,. \tag{31.19}$$

The change in local kinetic energy is a lot more difficult to calculate

$$\frac{\partial T_{\text{local}}}{\partial p} = \frac{\partial}{\partial p}\left\{\left(\sum_{i=1}^{N}\frac{1}{2m_i}\nabla_i^2\right)\ln\det M\right\} = \sum_{i=1}^{N}\frac{1}{2m_i}\frac{\partial}{\partial p}L_i \,, \tag{31.20}$$

where L_i is the particle Laplacian defined in (31.12) To evaluate (31.20), we need to calculate parameter derivatives of all three terms defined in the Laplacian evaluation. Namely $(B)(F)$, $(AA)(FF)$, and $\mathrm{tr}(AA, Md2M)$, where we have put parentheses around previously identified data structures. After $\frac{\partial}{\partial p}$ hits, each of the three terms will split into two terms by the product rule. Each smaller term will contain a contraction of two data structures. Therefore, we will

need to calculate the parameter derivatives of each data structure defined in the Laplacian evaluation:

$$
\begin{aligned}
{}_pX_{ij}^{\alpha\beta} &\equiv \frac{\partial}{\partial p} A_{ij}^{\alpha\beta} \,, \\
{}_pY_{ij}^{\alpha} &\equiv \frac{\partial}{\partial p} B_{ij}^{\alpha} \,, \\
{}_pdF_{ij}^{\alpha} &\equiv \frac{\partial}{\partial p} F_{ij}^{\alpha} \,, \\
{}_{pi}AA'^{\beta\gamma}_{jk} &\equiv \frac{\partial}{\partial p} {}_iAA_{jk}^{\beta\gamma} \,, \\
{}_pFF'^{\alpha\gamma}_{jk} &\equiv \frac{\partial}{\partial p} FF_{jk}^{\alpha\gamma} \,, \\
{}_pMd2M'^{\beta\gamma}_{j} &\equiv \frac{\partial}{\partial p} Md2M_{j}^{\beta\gamma} \,.
\end{aligned}
\tag{31.21}
$$

X and Y are stored as `Xmat` and `Ymat_full` (NOT `Ymat`) in the code. dF is `dFa`. AA' is not fully stored; intermediate values are stored in `Aij_sum` and `a_j_sum`. FF' is calculated on the fly as $dF \otimes F + F \otimes dF$. $Md2M'$ is not stored; intermediate values are stored in `q_j_prime`.

31.11 Scalar estimator implementation

31.11.1 Introduction: Life of a specialized OperatorBase

Almost all observables in QMCPACK are implemented as specialized derived classes of the OperatorBase base class. Each observable is instantiated in HamiltonianFactory and added to QMCHamiltonian for tracking. QMCHamiltonian tracks two types of observables: main and auxiliary. Main observables contribute to the local energy. These observables are elements of the simulated Hamiltonian such as kinetic or potential energy. Auxiliary observables are expectation values of matrix elements that do not contribute to the local energy. These Hamiltonians do not affect the dynamics of the simulation. In the code, the main observables are labeled by "physical" flag; the auxiliary observables have"physical" set to false.

Initialization

When an `<estimator type="est_type" name="est_name" other_stuff="value"/>` tag is present in the `<hamiltonian/>` section, it is first read by HamiltonianFactory. In general, the `type` of the estimator will determine which specialization of OperatorBase should be instantiated, and a derived class with `myName="est_name"` will be constructed. Then, the put() method of this specific class will be called to read any other parameters in the `<estimator/>` XML node. Sometimes these parameters will instead be read by HamiltonianFactory because it can access more objects than OperatorBase.

Cloning

When `OpenMP` threads are spawned, the estimator will be cloned by the `CloneManager`, which is a parent class of many QMC drivers.

```
// In CloneManager.cpp
#pragma omp parallel for shared(w,psi,ham)
for(int ip=1; ip<NumThreads; ++ip)
{
  wClones[ip]=new MCWalkerConfiguration(w);
```

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```
  psiClones[ip]=psi.makeClone(*wClones[ip]);
  hClones[ip]=ham.makeClone(*wClones[ip],*psiClones[ip]);
}
```

In the preceding snippet, `ham` is the reference to the estimator on the master thread. If the implemented estimator does not allocate memory for any array, then the default constructor should suffice for the `makeClone` method.

```
// In SpeciesKineticEnergy.cpp
OperatorBase* SpeciesKineticEnergy::makeClone(ParticleSet& qp, TrialWaveFunction& psi)
{
  return new SpeciesKineticEnergy(*this);
}
```

If memory is allocated during estimator construction (usually when parsing the XML node in the `put` method), then the `makeClone` method should perform the same initialization on each thread.

```
OperatorBase* LatticeDeviationEstimator::makeClone(ParticleSet& qp, TrialWaveFunction&
↪ psi)
{
  LatticeDeviationEstimator* myclone = new LatticeDeviationEstimator(qp,spset,tgroup,
↪sgroup);
  myclone->put(input_xml);
  return myclone;
}
```

Evaluate

After the observable class (derived class of OperatorBase) is constructed and prepared (by the put() method), it is ready to be used in a QMCDriver. A QMCDriver will call `H.auxHevaluate(W,thisWalker)` after every accepted move, where H is the QMCHamiltonian that holds all main and auxiliary Hamiltonian elements, W is a MCWalker-Configuration, and thisWalker is a pointer to the current walker being worked on. As shown in the following, this function goes through each auxiliary Hamiltonian element and evaluates it using the current walker configuration. Under the hood, observables are calculated and dumped to the main particle set's property list for later collection.

```
// In QMCHamiltonian.cpp
// This is more efficient.
// Only calculate auxH elements if moves are accepted.
void QMCHamiltonian::auxHevaluate(ParticleSet& P, Walker_t& ThisWalker)
{
#if !defined(REMOVE_TRACEMANAGER)
  collect_walker_traces(ThisWalker,P.current_step);
#endif
  for(int i=0; i<auxH.size(); ++i)
  {
    auxH[i]->setHistories(ThisWalker);
    RealType sink = auxH[i]->evaluate(P);
    auxH[i]->setObservables(Observables);
#if !defined(REMOVE_TRACEMANAGER)
    auxH[i]->collect_scalar_traces();
#endif
    auxH[i]->setParticlePropertyList(P.PropertyList,myIndex);
  }
}
```

For estimators that contribute to the local energy (main observables), the return value of evaluate() is used in accumulating the local energy. For auxiliary estimators, the return value is not used (`sink` local variable above); only the value of Value is recorded property lists by the setObservables() method as shown in the preceding code snippet. By default, the setObservables() method will transfer `auxH[i]->Value` to `P.PropertyList[auxH[i]->myIndex]`. The same property list is also kept by the particle set being moved by QMCDriver. This list is updated by `auxH[i]->setParticlePropertyList(P.PropertyList,myIndex)`, where myIndex is the starting index of space allocated to this specific auxiliary Hamiltonian in the property list kept by the target particle set P.

Collection

The actual statistics are collected within the QMCDriver, which owns an EstimatorManager object. This object (or a clone in the case of multithreading) will be registered with each mover it owns. For each mover (such as VMCUpdatePbyP derived from QMCUpdateBase), an accumulate() call is made, which by default, makes an accumulate(walkerset) call to the EstimatorManager it owns. Since each walker has a property set, EstimatorManager uses that local copy to calculate statistics. The EstimatorManager performs block averaging and file I/O.

31.11.2 Single scalar estimator implementation guide

Almost all of the defaults can be used for a single scalar observable. With any luck, only the put() and evaluate() methods need to be implemented. As an example, this section presents a step-by-step guide for implementing a verb|SpeciesKineticEnergy| estimator that calculates the kinetic energy of a specific species instead of the entire particle set. For example, a possible input to this estimator can be:

`<estimator type="specieskinetic" name="ukinetic" group="u"/>`

`<estimator type="specieskinetic" name="dkinetic" group="d"/>`.

This should create two extra columns in the `scalar.dat` file that contains the kinetic energy of the up and down electrons in two separate columns. If the estimator is properly implemented, then the sum of these two columns should be equal to the default `Kinetic` column.

Barebone

The first step is to create a barebone class structure for this simple scalar estimator. The goal is to be able to instantiate this scalar estimator with an XML node and have it print out a column of zeros in the `scalar.dat` file.

To achieve this, first create a header file "SpeciesKineticEnergy.h" in the QMCHamiltonians folder, with only the required functions declared as follows:

```
// In SpeciesKineticEnergy.h
#ifndef QMCPLUSPLUS_SPECIESKINETICENERGY_H
#define QMCPLUSPLUS_SPECIESKINETICENERGY_H

#include <Particle/WalkerSetRef.h>
#include <QMCHamiltonians/OperatorBase.h>

namespace qmcplusplus
{

class SpeciesKineticEnergy: public OperatorBase
{
public:

  SpeciesKineticEnergy(ParticleSet& P):tpset(P){ };
```

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```
  bool put(xmlNodePtr cur);          // read input xml node, required
  bool get(std::ostream& os) const; // class description, required

  Return_t evaluate(ParticleSet& P);
  inline Return_t evaluate(ParticleSet& P, std::vector<NonLocalData>& Txy)
  { // delegate responsity inline for speed
    return evaluate(P);
  }

  // pure virtual functions require overrider
  void resetTargetParticleSet(ParticleSet& P) { }                          // required
  OperatorBase* makeClone(ParticleSet& qp, TrialWaveFunction& psi); // required

private:
  ParticleSet& tpset;

}; // SpeciesKineticEnergy

} // namespace qmcplusplus
#endif
```

Notice that a local reference `tpset` to the target particle set `P` is saved in the constructor. The target particle set carries much information useful for calculating observables. Next, make "SpeciesKineticEnergy.cpp," and make vacuous definitions.

```
// In SpeciesKineticEnergy.cpp
#include <QMCHamiltonians/SpeciesKineticEnergy.h>
namespace qmcplusplus
{

bool SpeciesKineticEnergy::put(xmlNodePtr cur)
{
  return true;
}

bool SpeciesKineticEnergy::get(std::ostream& os) const
{
  return true;
}

SpeciesKineticEnergy::Return_t SpeciesKineticEnergy::evaluate(ParticleSet& P)
{
  Value = 0.0;
  return Value;
}

OperatorBase* SpeciesKineticEnergy::makeClone(ParticleSet& qp, TrialWaveFunction& psi)
{
  // no local array allocated, default constructor should be enough
  return new SpeciesKineticEnergy(*this);
}

} // namespace qmcplusplus
```

Now, head over to HamiltonianFactory and instantiate this observable if an XML node is found requesting it. Look for "gofr" in HamiltonianFactory.cpp, for example, and follow the if block.

```
// In HamiltonianFactory.cpp
#include <QMCHamiltonians/SpeciesKineticEnergy.h>
else if(potType =="specieskinetic")
{
  SpeciesKineticEnergy* apot = new SpeciesKineticEnergy(*target_particle_set);
  apot->put(cur);
  targetH->addOperator(apot,potName,false);
}
```

The last argument of addOperator() (i.e., the `false` flag) is **crucial**. This tells QMCPACK that the observable we implemented is not a physical Hamiltonian; thus, it will not contribute to the local energy. Changes to the local energy will alter the dynamics of the simulation. Finally, add "SpeciesKineticEnergy.cpp" to HAMSRCS in "CMakeLists.txt" located in the QMCHamiltonians folder. Now, recompile QMCPACK and run it on an input that requests `<estimator type="specieskinetic" name="ukinetic"/>` in the `hamiltonian` block. A column of zeros should appear in the `scalar.dat` file under the name "ukinetic."

Evaluate

The evaluate() method is where we perform the calculation of the desired observable. In a first iteration, we will simply hard-code the name and mass of the particles.

```
// In SpeciesKineticEnergy.cpp
#include <QMCHamiltonians/BareKineticEnergy.h> // laplaician() defined here
SpeciesKineticEnergy::Return_t SpeciesKineticEnergy::evaluate(ParticleSet& P)
{
  std::string group="u";
  RealType minus_over_2m = -0.5;

  SpeciesSet& tspecies(P.getSpeciesSet());

  Value = 0.0;
  for (int iat=0; iat<P.getTotalNum(); iat++)
  {
    if (tspecies.speciesName[ P.GroupID(iat) ] == group)
    {
      Value += minus_over_2m*laplacian(P.G[iat],P.L[iat]);
    }
  }
  return Value;

  // Kinetic column has:
  // Value = -0.5*( Dot(P.G,P.G) + Sum(P.L) );
}
```

Voila—you should now be able to compile QMCPACK, rerun, and see that the values in the "ukinetic" column are no longer zero. Now, the only task left to make this basic observable complete is to read in the extra parameters instead of hard-coding them.

Parse extra input

The preferred method to parse extra input parameters in the XML node is to implement the put() function of our specific observable. Suppose we wish to read in a single string that tells us whether to record the kinetic energy of the up electron (group="u") or the down electron (group="d"). This is easily achievable using the OhmmsAttributeSet class,

```
// In SpeciesKineticEnergy.cpp
#include <OhmmsData/AttributeSet.h>
bool SpeciesKineticEnergy::put(xmlNodePtr cur)
{
  // read in extra parameter "group"
  OhmmsAttributeSet attrib;
  attrib.add(group,"group");
  attrib.put(cur);

  // save mass of specified group of particles
  SpeciesSet& tspecies(tpset.getSpeciesSet());
  int group_id  = tspecies.findSpecies(group);
  int massind   = tspecies.getAttribute("mass");
  minus_over_2m = -1./(2.*tspecies(massind,group_id));

  return true;
}
```

where we may keep "group" and "minus_over_2m" as local variables to our specific class.

```
// In SpeciesKineticEnergy.h
private:
  ParticleSet& tpset;
  std::string  group;
  RealType minus_over_2m;
```

Notice that the previous operations are made possible by the saved reference to the target particle set. Last but not least, compile and run a full example (i.e., a short DMC calculation) with the following XML nodes in your input:

```
<estimator type="specieskinetic" name="ukinetic" group="u"/>
```

```
<estimator type="specieskinetic" name="dkinetic" group="d"/>
```

Make sure the sum of the "ukinetic" and "dkinetic" columns is **exactly** the same as the Kinetic columns at **every block**.

For easy reference, a summary of the complete list of changes follows:

```
// In HamiltonianFactory.cpp
#include "QMCHamiltonians/SpeciesKineticEnergy.h"
else if(potType =="specieskinetic")
{
      SpeciesKineticEnergy* apot = new SpeciesKineticEnergy(*targetPtcl);
      apot->put(cur);
      targetH->addOperator(apot,potName,false);
}
```

```
// In SpeciesKineticEnergy.h
#include <Particle/WalkerSetRef.h>
#include <QMCHamiltonians/OperatorBase.h>
```

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```
namespace qmcplusplus
{

class SpeciesKineticEnergy: public OperatorBase
{
public:

  SpeciesKineticEnergy(ParticleSet& P):tpset(P){ };

  // xml node is read by HamiltonianFactory, eg. the sum of following should be␣
↪equivalent to Kinetic
  // <estimator name="ukinetic" type="specieskinetic" target="e" group="u"/>
  // <estimator name="dkinetic" type="specieskinetic" target="e" group="d"/>
  bool put(xmlNodePtr cur);         // read input xml node, required
  bool get(std::ostream& os) const; // class description, required

  Return_t evaluate(ParticleSet& P);
  inline Return_t evaluate(ParticleSet& P, std::vector<NonLocalData>& Txy)
  { // delegate responsity inline for speed
    return evaluate(P);
  }

  // pure virtual functions require overrider
  void resetTargetParticleSet(ParticleSet& P) { }                          // required
  OperatorBase* makeClone(ParticleSet& qp, TrialWaveFunction& psi); // required

private:
  ParticleSet&       tpset; // reference to target particle set
  std::string        group; // name of species to track
  RealType   minus_over_2m; // mass of the species !! assume same mass
  // for multiple species, simply initialize multiple estimators

}; // SpeciesKineticEnergy

} // namespace qmcplusplus
#endif
```

```
// In SpeciesKineticEnergy.cpp
#include <QMCHamiltonians/SpeciesKineticEnergy.h>
#include <QMCHamiltonians/BareKineticEnergy.h> // laplaician() defined here
#include <OhmmsData/AttributeSet.h>

namespace qmcplusplus
{

bool SpeciesKineticEnergy::put(xmlNodePtr cur)
{
  // read in extra parameter "group"
  OhmmsAttributeSet attrib;
  attrib.add(group,"group");
  attrib.put(cur);

  // save mass of specified group of particles
  int group_id  = tspecies.findSpecies(group);
  int massind   = tspecies.getAttribute("mass");
  minus_over_2m = -1./(2.*tspecies(massind,group_id));
```

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```
  return true;
}

bool SpeciesKineticEnergy::get(std::ostream& os) const
{ // class description
  os << "SpeciesKineticEnergy: " << myName << " for species " << group;
  return true;
}

SpeciesKineticEnergy::Return_t SpeciesKineticEnergy::evaluate(ParticleSet& P)
{
  Value = 0.0;
  for (int iat=0; iat<P.getTotalNum(); iat++)
  {
    if (tspecies.speciesName[ P.GroupID(iat) ] == group)
    {
      Value += minus_over_2m*laplacian(P.G[iat],P.L[iat]);
    }
  }
  return Value;
}

OperatorBase* SpeciesKineticEnergy::makeClone(ParticleSet& qp, TrialWaveFunction& psi)
{ //default constructor
  return new SpeciesKineticEnergy(*this);
}

} // namespace qmcplusplus
```

31.11.3 Multiple scalars

It is fairly straightforward to create more than one column in the `scalar.dat` file with a single observable class. For example, if we want a single SpeciesKineticEnergy estimator to simultaneously record the kinetic energies of all species in the target particle set, we only have to write two new methods: addObservables() and setObservables(), then tweak the behavior of evaluate(). First, we will have to override the default behavior of addObservables() to make room for more than one column in the `scalar.dat` file as follows,

```
// In SpeciesKineticEnergy.cpp
void SpeciesKineticEnergy::addObservables(PropertySetType& plist, BufferType&␣
↪collectables)
{
  myIndex = plist.size();
  for (int ispec=0; ispec<num_species; ispec++)
  { // make columns named "$myName_u", "$myName_d" etc.
    plist.add(myName + "_" + species_names[ispec]);
  }
}
```

where “num_species” and “species_name” can be local variables initialized in the constructor. We should also initialize some local arrays to hold temporary data.

```
// In SpeciesKineticEnergy.h
private:
```

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```
  int num_species;
  std::vector<std::string> species_names;
  std::vector<RealType> species_kinetic,vec_minus_over_2m;

// In SpeciesKineticEnergy.cpp
SpeciesKineticEnergy::SpeciesKineticEnergy(ParticleSet& P):tpset(P)
{
  SpeciesSet& tspecies(P.getSpeciesSet());
  int massind = tspecies.getAttribute("mass");

  num_species = tspecies.size();
  species_kinetic.resize(num_species);
  vec_minus_over_2m.resize(num_species);
  species_names.resize(num_species);
  for (int ispec=0; ispec<num_species; ispec++)
  {
    species_names[ispec] = tspecies.speciesName[ispec];
    vec_minus_over_2m[ispec] = -1./(2.*tspecies(massind,ispec));
  }
}
```

Next, we need to override the default behavior of `setObservables()` to transfer multiple values to the property list kept by the main particle set, which eventually goes into the `scalar.dat` file.

```
// In SpeciesKineticEnergy.cpp
void SpeciesKineticEnergy::setObservables(PropertySetType& plist)
{ // slots in plist must be allocated by addObservables() first
  copy(species_kinetic.begin(),species_kinetic.end(),plist.begin()+myIndex);
}
```

Finally, we need to change the behavior of evaluate() to fill the local vector “species_kinetic” with appropriate observable values.

```
SpeciesKineticEnergy::Return_t SpeciesKineticEnergy::evaluate(ParticleSet& P)
{
  std::fill(species_kinetic.begin(),species_kinetic.end(),0.0);

  for (int iat=0; iat<P.getTotalNum(); iat++)
  {
    int ispec = P.GroupID(iat);
    species_kinetic[ispec] += vec_minus_over_2m[ispec]*laplacian(P.G[iat],P.L[iat]);
  }

  Value = 0.0; // Value is no longer used
  return Value;
}
```

That’s it! The SpeciesKineticEnergy estimator no longer needs the “group” input and will automatically output the kinetic energy of every species in the target particle set in multiple columns. You should now be able to run with `<estimator type="specieskinetic" name="skinetic"/>` and check that the sum of all columns that start with “skinetic” is equal to the default “Kinetic” column.

31.11.4 HDF5 output

If we desire an observable that will output hundreds of scalars per simulation step (e.g., SkEstimator), then it is preferred to output to the `stat.h5` file instead of the `scalar.dat` file for better organization. A large chunk of data to be registered in the `stat.h5` file is called a "Collectable" in QMCPACK. In particular, if a OperatorBase object is initialized with `UpdateMode.set(COLLECTABLE,1)`, then the "Collectables" object carried by the main particle set will be processed and written to the `stat.h5` file, where "UpdateMode" is a bit set (i.e., a collection of flags) with the following enumeration:

```
// In OperatorBase.h
///enum for UpdateMode
enum {PRIMARY=0,
  OPTIMIZABLE=1,
  RATIOUPDATE=2,
  PHYSICAL=3,
  COLLECTABLE=4,
  NONLOCAL=5,
  VIRTUALMOVES=6
};
```

As a simple example, to put the two columns we produced in the previous section into the `stat.h5` file, we will first need to declare that our observable uses "Collectables."

```
// In constructor add:
hdf5_out = true;
UpdateMode.set(COLLECTABLE,1);
```

Then make some room in the "Collectables" object carried by the target particle set.

```
// In addObservables(PropertySetType& plist, BufferType& collectables) add:
if (hdf5_out)
{
  h5_index = collectables.size();
  std::vector<RealType> tmp(num_species);
  collectables.add(tmp.begin(),tmp.end());
}
```

Next, make some room in the `stat.h5` file by overriding the registerCollectables() method.

```
// In SpeciesKineticEnergy.cpp
void SpeciesKineticEnergy::registerCollectables(std::vector<observable_helper>&␣
↪h5desc, hid_t gid) const
{
  if (hdf5_out)
  {
    std::vector<int> ndim(1,num_species);
    observable_helper h5o(myName);
    h5o.set_dimensions(ndim,h5_index);
    h5o.open(gid);
    h5desc.push_back(h5o);
  }
}
```

Finally, edit evaluate() to use the space in the "Collectables" object.

```
// In SpeciesKineticEnergy.cpp
SpeciesKineticEnergy::Return_t SpeciesKineticEnergy::evaluate(ParticleSet& P)
```

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```
{
  RealType wgt = tWalker->Weight; // MUST explicitly use DMC weights in Collectables!
  std::fill(species_kinetic.begin(),species_kinetic.end(),0.0);

  for (int iat=0; iat<P.getTotalNum(); iat++)
  {
    int ispec = P.GroupID(iat);
    species_kinetic[ispec] += vec_minus_over_2m[ispec]*laplacian(P.G[iat],P.L[iat]);
    P.Collectables[h5_index + ispec] += vec_minus_over_2m[ispec]*laplacian(P.G[iat],P.
↪L[iat])*wgt;
  }

  Value = 0.0; // Value is no longer used
  return Value;
}
```

There should now be a new entry in the `stat.h5` file containing the same columns of data as the `stat.h5` file. After this check, we should clean up the code by

- making "hdf5_out" and input flag by editing the put() method and
- disabling output to `scalar.dat` when the "hdf5_out" flag is on.

31.12 Estimator output

31.12.1 Estimator definition

For simplicity, consider a local property $O(\mathbf{R})$, where $\mathbf{R}$ is the collection of all particle coordinates. An *estimator* for $O(\mathbf{R})$ is a weighted average over walkers:

$$E[O] = \left(\sum_{i=1}^{N_{walker}^{tot}} w_i O(\mathbf{R_i}) \right) / \left(\sum_{i=1}^{N_{walker}^{tot}} w_i \right) . \tag{31.22}$$

N_{walker}^{tot} is the total number of walkers collected in the entire simulation. Notice that N_{walker}^{tot} is typically far larger than the number of walkers held in memory at any given simulation step. w_i is the weight of walker i.

In a VMC simulation, the weight of every walker is 1.0. Further, the number of walkers is constant at each step. Therefore, (31.22) simplifies to

$$E_{VMC}[O] = \frac{1}{N_{step} N_{walker}^{ensemble}} \sum_{s,e} O(\mathbf{R_{s,e}}) . \tag{31.23}$$

Each walker $\mathbf{R_{s,e}}$ is labeled by *step index* s and *ensemble index* e.

In a DMC simulation, the weight of each walker is different and may change from step to step. Further, the ensemble size varies from step to step. Therefore, (31.22) simplifies to

$$E_{DMC}[O] = \frac{1}{N_{step}} \sum_{s} \left\{ \left(\sum_{e} w_{s,e} O(\mathbf{R_{s,e}}) \right) / \left(\sum_{e} w_{s,e} \right) \right\} . \tag{31.24}$$

We will refer to the average in the $\{\}$ as *ensemble average* and to the remaining averages as *block average*. The process of calculating $O(\mathbf{R})$ is *evaluate*.

31.12.2 Class relations

A large number of classes are involved in the estimator collection process. They often have misleading class or method names. Check out the document gotchas in the following list:

1. `EstimatorManager` is an unused copy of `EstimatorManagerBase`. `EstimatorManagerBase` is the class used in the QMC drivers. (PR #371 explains this.)
2. `EstimatorManagerBase::Estimators` is completely different from `QMCDriver::Estimators`, which is subtly different from `OperatorBase::Estimators`. The first is a list of pointers to `ScalarEstimatorBase`. The second is the master estimator (one per MPI group). The third is the slave estimator that exists one per OpenMP thread.
3. `QMCHamiltonian` is NOT a parent class of `OperatorBase`. Instead, `QMCHamiltonian` owns two lists of `OperatorBase` named `H` and `auxH`.
4. `QMCDriver::H` is NOT the same as `QMCHamiltonian::H`. The first is a pointer to a `QMCHamiltonian`. `QMCHamiltonian::H` is a list.
5. `EstimatorManager::stopBlock(std::vector)` is completely different from `EstimatorManager:: stopBlock(RealType)`, which is the same as `stopBlock(RealType, true)` but that is subtly different from `stopBlock(RealType, false)`. The first three methods are intended to be called by the master estimator, which exists one per MPI group. The last method is intended to be called by the slave estimator, which exists one per OpenMP thread.

31.12.3 Estimator output stages

Estimators take four conceptual stages to propagate to the output files: evaluate, load ensemble, unload ensemble, and collect. They are easier to understand in reverse order.

Collect stage

File output is performed by the master `EstimatorManager` owned by `QMCDriver`. The first 8+ entries in `EstimatorManagerBase::AverageCache` will be written to `scalar.dat`. The remaining entries in `AverageCache` will be written to `stat.h5`. File writing is triggered by `EstimatorManagerBase ::collectBlockAverages` inside `EstimatorManagerBase::stopBlock`.

```
// In EstimatorManagerBase.cpp::collectBlockAverages
  if(Archive)
  {
    *Archive << std::setw(10) << RecordCount;
    int maxobjs=std::min(BlockAverages.size(),max4ascii);
    for(int j=0; j<maxobjs; j++)
      *Archive << std::setw(FieldWidth) << AverageCache[j];
    for(int j=0; j<PropertyCache.size(); j++)
      *Archive << std::setw(FieldWidth) << PropertyCache[j];
    *Archive << std::endl;
    for(int o=0; o<h5desc.size(); ++o)
      h5desc[o]->write(AverageCache.data(),SquaredAverageCache.data());
    H5Fflush(h_file,H5F_SCOPE_LOCAL);
  }
```

`EstimatorManagerBase::collectBlockAverages` is triggered from the master-thread estimator via either `stopBlock(std::vector)` or `stopBlock(RealType, true)`. Notice that file writing is NOT triggered by the slave-thread estimator method `stopBlock(RealType, false)`.

```
// In EstimatorManagerBase.cpp
void EstimatorManagerBase::stopBlock(RealType accept, bool collectall)
{
  //take block averages and update properties per block
  PropertyCache[weightInd]=BlockWeight;
  PropertyCache[cpuInd] = MyTimer.elapsed();
  PropertyCache[acceptInd] = accept;
  for(int i=0; i<Estimators.size(); i++)
    Estimators[i]->takeBlockAverage(AverageCache.begin(),SquaredAverageCache.begin());
  if(Collectables)
  {
    Collectables->takeBlockAverage(AverageCache.begin(),SquaredAverageCache.begin());
  }
  if(collectall)
    collectBlockAverages(1);
}
```

```
// In ScalarEstimatorBase.h
template<typename IT>
inline void takeBlockAverage(IT first, IT first_sq)
{
  first += FirstIndex;
  first_sq += FirstIndex;
  for(int i=0; i<scalars.size(); i++)
  {
    *first++ = scalars[i].mean();
    *first_sq++ = scalars[i].mean2();
    scalars_saved[i]=scalars[i]; //save current block
    scalars[i].clear();
  }
}
```

At the collect stage, `calarEstimatorBase::scalars` must be populated with ensemble-averaged data. Two derived classes of `ScalarEstimatorBase` are crucial: `LocalEnergyEstimator` will carry `Properties`, where as `CollectablesEstimator` will carry `Collectables`.

Unload ensemble stage

`LocalEnergyEstimator::scalars` are populated by `ScalarEstimatorBase::accumulate`, whereas `CollectablesEstimator::scalars` are populated by `CollectablesEstimator::accumulate_all`. Both accumulate methods are triggered by `EstimatorManagerBase::accumulate`. One confusing aspect about the unload stage is that `EstimatorManagerBase::accumulate` has a master and a slave call signature. A slave estimator such as `QMCUpdateBase::Estimators` should unload a subset of walkers. Thus, the slave estimator should call `accumulate(W,it,it_end)`. However, the master estimator, such as `SimpleFixedNodeBranch::myEstimator`, should unload data from the entire walker ensemble. This is achieved by calling `accumulate(W)`.

```
void EstimatorManagerBase::accumulate(MCWalkerConfiguration& W)
{ // intended to be called by master estimator only
  BlockWeight += W.getActiveWalkers();
  RealType norm=1.0/W.getGlobalNumWalkers();
  for(int i=0; i< Estimators.size(); i++)
    Estimators[i]->accumulate(W,W.begin(),W.end(),norm);
  if(Collectables)//collectables are normalized by QMC drivers
```

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```
    Collectables->accumulate_all(W.Collectables,1.0);
}
```

```
void EstimatorManagerBase::accumulate(MCWalkerConfiguration& W
 , MCWalkerConfiguration::iterator it
 , MCWalkerConfiguration::iterator it_end)
{ // intended to be called slaveEstimator only
  BlockWeight += it_end-it;
  RealType norm=1.0/W.getGlobalNumWalkers();
  for(int i=0; i< Estimators.size(); i++)
    Estimators[i]->accumulate(W,it,it_end,norm);
  if(Collectables)
    Collectables->accumulate_all(W.Collectables,1.0);
}
```

```
// In LocalEnergyEstimator.h
inline void accumulate(const Walker_t& awalker, RealType wgt)
{ // ensemble average W.Properties
  // expect ePtr to be W.Properties; expect wgt = 1/GlobalNumberOfWalkers
  const RealType* restrict ePtr = awalker.getPropertyBase();
  RealType wwght= wgt* awalker.Weight;
  scalars[0](ePtr[WP::LOCALENERGY],wwght);
  scalars[1](ePtr[WP::LOCALENERGY]*ePtr[WP::LOCALENERGY],wwght);
  scalars[2](ePtr[LOCALPOTENTIAL],wwght);
  for(int target=3, source=FirstHamiltonian; target<scalars.size(); ++target,␣
↪++source)
    scalars[target](ePtr[source],wwght);
}
```

```
// In CollectablesEstimator.h
inline void accumulate_all(const MCWalkerConfiguration::Buffer_t& data, RealType wgt)
{ // ensemble average W.Collectables
  // expect data to be W.Collectables; expect wgt = 1.0
  for(int i=0; i<data.size(); ++i)
    scalars[i](data[i], wgt);
}
```

At the unload ensemble stage, the data structures `Properties` and `Collectables` must be populated by appropriately normalized values so that the ensemble average can be correctly taken. `QMCDriver` is responsible for the correct loading of data onto the walker ensemble.

Load ensemble stage

`Properties` in the MC ensemble of walkers `QMCDriver::W` is populated by `QMCHamiltonian::saveProperties`. The master `QMCHamiltonian::LocalEnergy`, `::KineticEnergy`, and `::Observables` must be properly populated at the end of the evaluate stage.

```
// In QMCHamiltonian.h
  template<class IT>
  inline
  void saveProperty(IT first)
  { // expect first to be W.Properties
```

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```
    first[LOCALPOTENTIAL]= LocalEnergy-KineticEnergy;
    copy(Observables.begin(),Observables.end(),first+myIndex);
  }
```

`Collectables`'s load stage is combined with its evaluate stage.

Evaluate stage

The master `QMCHamiltonian::Observables` is populated by slave `OperatorBase::setObservables`. However, the call signature must be `OperatorBase::setObservables(QMCHamiltonian::Observables)`. This call signature is enforced by `QMCHamiltonian::evaluate` and `QMCHamiltonian::auxHevaluate`.

```
// In QMCHamiltonian.cpp
QMCHamiltonian::Return_t
QMCHamiltonian::evaluate(ParticleSet& P)
{
  LocalEnergy = 0.0;
  for(int i=0; i<H.size(); ++i)
  {
    myTimers[i]->start();
    LocalEnergy += H[i]->evaluate(P);
    H[i]->setObservables(Observables);
#if !defined(REMOVE_TRACEMANAGER)
    H[i]->collect_scalar_traces();
#endif
    myTimers[i]->stop();
    H[i]->setParticlePropertyList(P.PropertyList,myIndex);
  }
  KineticEnergy=H[0]->Value;
  P.PropertyList[WP::LOCALENERGY]=LocalEnergy;
  P.PropertyList[LOCALPOTENTIAL]=LocalEnergy-KineticEnergy;
  // auxHevaluate(P);
  return LocalEnergy;
}
```

```
// In QMCHamiltonian.cpp
void QMCHamiltonian::auxHevaluate(ParticleSet& P, Walker_t& ThisWalker)
{
#if !defined(REMOVE_TRACEMANAGER)
  collect_walker_traces(ThisWalker,P.current_step);
#endif
  for(int i=0; i<auxH.size(); ++i)
  {
    auxH[i]->setHistories(ThisWalker);
    RealType sink = auxH[i]->evaluate(P);
    auxH[i]->setObservables(Observables);
#if !defined(REMOVE_TRACEMANAGER)
    auxH[i]->collect_scalar_traces();
#endif
    auxH[i]->setParticlePropertyList(P.PropertyList,myIndex);
```

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```
  }
}
```

31.12.4 Estimator use cases

VMCSingleOMP pseudo code

```
bool VMCSingleOMP::run()
{
  masterEstimator->start(nBlocks);
  for (int ip=0; ip<NumThreads; ++ip)
    Movers[ip]->startRun(nBlocks,false);  // slaveEstimator->start(blocks, record)

  do // block
  {
    #pragma omp parallel
    {
      Movers[ip]->startBlock(nSteps);  // slaveEstimator->startBlock(steps)
      RealType cnorm = 1.0/static_cast<RealType>(wPerNode[ip+1]-wPerNode[ip]);
      do // step
      {
        wClones[ip]->resetCollectables();
        Movers[ip]->advanceWalkers(wit, wit_end, recompute);
        wClones[ip]->Collectables *= cnorm;
        Movers[ip]->accumulate(wit, wit_end);
      } // end step
      Movers[ip]->stopBlock(false);  // slaveEstimator->stopBlock(acc, false)
    } // end omp
    masterEstimator->stopBlock(estimatorClones);  // write files
  } // end block
  masterEstimator->stop(estimatorClones);
}
```

DMCOMP pseudo code

```
bool DMCOMP::run()
{
  masterEstimator->setCollectionMode(true);

  masterEstimator->start(nBlocks);
  for(int ip=0; ip<NumThreads; ip++)
    Movers[ip]->startRun(nBlocks,false);  // slaveEstimator->start(blocks, record)

  do // block
  {
    masterEstimator->startBlock(nSteps);
    for(int ip=0; ip<NumThreads; ip++)
      Movers[ip]->startBlock(nSteps);  // slaveEstimator->startBlock(steps)

    do // step
    {
      #pragma omp parallel
```

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```
      {
      wClones[ip]->resetCollectables();
      // advanceWalkers
      } // end omp

      //branchEngine->branch
      { // In WalkerControlMPI.cpp::branch
      wgt_inv=WalkerController->NumContexts/WalkerController->EnsembleProperty.Weight;
      walkers.Collectables *= wgt_inv;
      slaveEstimator->accumulate(walkers);
      }
      masterEstimator->stopBlock(acc)  // write files
    }  // end for step
  }  // end for block

  masterEstimator->stop();
}
```

31.12.5 Summary

Two ensemble-level data structures, `ParticleSet::Properties` and `::Collectables`, serve as intermediaries between evaluate classes and output classes to `scalar.dat` and `stat.h5`. `Properties` appears in both `scalar.dat` and `stat.h5`, whereas `Collectables` appears only in `stat.h5`. `Properties` is overwritten by `QMCHamiltonian::Observables` at the end of each step. `QMCHamiltonian::Observables` is filled upon call to `QMCHamiltonian::evaluate` and `::auxHevaluate`. `Collectables` is zeroed at the beginning of each step and accumulated upon call to `::auxHevaluate`.

Data are output to `scalar.dat` in four stages: evaluate, load, unload, and collect. In the evaluate stage, `QMCHamiltonian::Observables` is populated by a list of `OperatorBase`. In the load stage, `QMCHamiltonian::Observables` is transferred to `Properties` by `QMCDriver`. In the unload stage, `Properties` is copied to `LocalEnergyEstimator::scalars`. In the collect stage, `LocalEnergyEstimator::scalars` is block-averaged to `EstimatorManagerBase::AverageCache` and dumped to file. For `Collectables`, the evaluate and load stages are combined in a call to `QMCHamiltonian::auxHevaluate`. In the unload stage, `Collectables` is copied to `CollectablesEstimator::scalars`. In the collect stage, `CollectablesEstimator::scalars` is block-averaged to `EstimatorManagerBase::AverageCache` and dumped to file.

31.12.6 Appendix: dmc.dat

There is an additional data structure, `ParticleSet::EnsembleProperty`, that is managed by `WalkerControlBase::EnsembleProperty` and directly dumped to `dmc.dat` via its own averaging procedure. `dmc.dat` is written by `WalkerControlBase::measureProperties`, which is called by `WalkerControlBase::branch`, which is called by `SimpleFixedNodeBranch::branch`, for example.

CHAPTER

THIRTYTWO

APPENDICES

32.1 Appendix A: Derivation of twist averaging efficiency

In this appendix we derive the relative statistical efficiency of twist averaging with an irreducible (weighted) set of k-points versus using uniform weights over an unreduced set of k-points (e.g., a full Monkhorst-Pack mesh).

Consider the weighted average of a set of statistical variables $\{x_m\}$ with weights $\{w_m\}$:

$$x_{TA} = \frac{\sum_m w_m x_m}{\sum_m w_m} \,. \tag{32.1}$$

If produced by a finite QMC run at a set of twist angles/k-points $\{k_m\}$, each variable mean $\langle x_m \rangle$ has a statistical error bar σ_m, and we can also obtain the statistical error bar of the mean of the twist-averaged quantity $\langle x_{TA} \rangle$:

$$\sigma_{TA} = \frac{\left(\sum_m w_m^2 \sigma_m^2\right)^{1/2}}{\sum_m w_m} \,. \tag{32.2}$$

The error bar of each individual twist σ_m is related to the autocorrelation time κ_m, intrinsic variance v_m, and the number of postequilibration MC steps N_{step} in the following way:

$$\sigma_m^2 = \frac{\kappa_m v_m}{N_{step}} \,. \tag{32.3}$$

In the setting of twist averaging, the autocorrelation time and variance for different twist angles are often very similar across twists, and we have

$$\sigma_m^2 = \sigma^2 = \frac{\kappa v}{N_{step}} \,. \tag{32.4}$$

If we define the total weight as W, that is, $W \equiv \sum_{m=1}^{M} w_m$, for the weighted case with M irreducible twists, the error bar is

$$\sigma_{TA}^{weighted} = \frac{\left(\sum_{m=1}^{M} w_m^2\right)^{1/2}}{W} \sigma \,. \tag{32.5}$$

For uniform weighting with $w_m = 1$, the number of twists is W and we have

$$\sigma_{TA}^{uniform} = \frac{1}{\sqrt{W}} \sigma \,. \tag{32.6}$$

We are interested in comparing the efficiency of choosing weights uniformly or based on the irreducible multiplicity of each twist angle for a given target error bar σ_{target}. The number of MC steps required to reach this target for uniform weighting is

$$N_{step}^{uniform} = \frac{1}{W} \frac{\kappa v}{\sigma_{target}^2} \,, \tag{32.7}$$

while for nonuniform weighting we have

$$\begin{aligned} N_{step}^{weighted} &= \frac{\sum_{m=1}^{M} w_m^2}{W^2} \frac{\kappa v}{\sigma_{target}^2} , \\ &= \frac{\sum_{m=1}^{M} w_m^2}{W} N_{step}^{uniform} . \end{aligned}$$

The MC efficiency is defined as

$$\xi = \frac{1}{\sigma^2 t} , \tag{32.8}$$

where σ is the error bar and t is the total CPU time required for the MC run.

The main advantage made possible by irreducible twist weighting is to reduce the equilibration time overhead by having fewer twists and, hence, fewer MC runs to equilibrate. In the context of twist averaging, the total CPU time for a run can be considered to be

$$t = N_{twist}(N_{eq} + N_{step}) t_{step} , \tag{32.9}$$

where N_{twist} is the number of twists, N_{eq} is the number of MC steps required to reach equilibrium, N_{step} is the number of MC steps included in the statistical averaging as before, and t_{step} is the wall clock time required to complete a single MC step. For uniform weighting $N_{twist} = W$; while for irreducible weighting $N_{twist} = M$.

We can now calculate the relative efficiency (η) of irreducible vs. uniform twist weighting with the aim of obtaining a target error bar σ_{target}:

$$\begin{aligned} \eta &= \frac{\xi_{TA}^{weighted}}{\xi_{TA}^{uniform}} , \\ &= \frac{\sigma_{target}^2 t_{TA}^{uniform}}{\sigma_{target}^2 t_{TA}^{weighted}} , \\ &= \frac{W(N_{eq} + N_{step}^{uniform})}{M(N_{eq} + N_{step}^{weighted})} , \\ &= \frac{W(N_{eq} + N_{step}^{uniform})}{M(N_{eq} + \frac{\sum_{m=1}^{M} w_m^2}{W} N_{step}^{uniform})} , \\ &= \frac{W}{M} \frac{1+f}{1 + \frac{\sum_{m=1}^{M} w_m^2}{W} f} . \end{aligned}$$

In this last expression, f is the ratio of the number of usable MC steps to the number that must be discarded during equilibration ($f = N_{step}^{uniform}/N_{eq}$); and as before, $W = \sum_m w_m$, which is the number of twist angles in the uniform weighting case. It is important to recall that $N_{step}^{uniform}$ in f is defined relative to uniform weighting and is the number of MC steps required to reach a target accuracy in the case of uniform twist weights.

The formula for η in the preceding can be easily changed with the help of (32.8) to reflect the number of MC steps obtained in an irreducibly weighted run instead. A good exercise is to consider runs that have already completed with either uniform or irreducible weighting and calculate the expected efficiency change had the opposite type of weighting been used.

The break even point ($\eta = 1$) can be found at a usable step fraction of

$$f = \frac{W - M}{M \frac{\sum_{m=1}^{M} w_m^2}{W} - W} . \tag{32.10}$$

The relative efficiency (η) is useful to consider in view of certain scenarios. An important case is where the number of required sampling steps is no larger than the number of equilibration steps (i.e., $f \approx 1$). For a very simple case

with eight uniform twists with irreducible multiplicities of $w_m \in \{1, 3, 3, 1\}$ ($W = 8$, $M = 4$), the relative efficiency of irreducible vs. uniform weighting is $\eta = \frac{8}{4}\frac{2}{1+20/8} \approx 1.14$. In this case, irreducible weighting is about 14% more efficient than uniform weighting.

Another interesting case is one in which the number of sampling steps you can reach with uniform twists before wall clock time runs out is small relative to the number of equilibration steps ($f \to 0$). In this limit, $\eta \approx W/M$. For our eight-uniform-twist example, this would result in a relative efficiency of $\eta = 8/4 = 2$, making irreducible weighting twice as efficient.

A final case of interest is one in which the equilibration time is short relative to the available sampling time ($f \to \infty$), giving $\eta \approx W^2/(M\sum_{m=1}^{M} w_m^2)$. Again, for our simple example we find $\eta = 8^2/(4 \times 20) \approx 0.8$, with uniform weighting being 25% more efficient than irreducible weighting. For this example, the crossover point for irreducible weighting being more efficient than uniform weighting is $f < 2$, that is, when the available sampling period is less than twice the length of the equilibration period. The expected efficiency ratio and crossover point should be checked for the particular case under consideration to inform the choice between twist averaging methods.

```
QMCPACK website: http://www.qmcpack.org

Releases & source code: https://github.com/QMCPACK

Google Group: https://groups.google.com/forum/#!forum/qmcpack
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