

Final Report

Quantum Chemistry via Walks in Determinant Space

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I. INTRODUCTION

The main purpose of this Collaborative Research Team (CRT) was to improve upon the recently developed initiator full-configuration interaction quantum Monte Carlo (FCIQMC) method¹⁻⁵, with the goal of developing a highly accurate method for treating difficult chemical systems of interest to the DOE. Another related goal was to have cross-fertilization of ideas between FCIQMC and phaseless Auxilliary Field quantum Monte Carlo (AFQMC), developed by the Zhang-Krakauer group, since both methods employ walks in a space of determinants. The full configuration interaction (FCI) method is the most robust method for treating electronic correlations, but it is limited to a space of approximately 10^{10} determinants. In contrast the FCIQMC method can be used on a system with as many as 10^{108} determinants⁵, provided that the sign problem is not very severe, at the cost of introducing a systematically improvable “initiator” approximation and of course a statistical error. The FCIQMC method has a cost that is exponential in the system size (though with an exponent that is much smaller than that for FCI). Consequently, it was deemed very important to find ways to speed up the method to increase its range of applicability.

II. COMPLETED RESEARCH

A. Semistochastic Projection and Improved Trial Wave Functions

Semistochastic Quantum Monte Carlo Method⁶,

F. R. Petruzielo, A. A. Holmes, Hitesh J. Changlani, M. P. Nightingale and C. J. Umrigar

In collaboration with M. Peter Nightingale at the University of Rhode Island, we have made a very large improvement to the FCIQMC method⁶. Quantum Monte Carlo is nothing but a stochastic implementation of the power method for projecting onto the dominant state of a matrix or integral kernel. Recognizing this, the basic idea of our Semistochastic Quantum Monte Carlo (SQMC) method¹⁸ is identify a small subspace of say $10^3 - 10^6$ important determinants in which the projection is done deterministically. Only transitions for which both the initial and the final state are within the subspace are treated deterministically, the rest are treated stochastically. Since deterministic projection has no statistical error and no sign problem this results in a large gain in efficiency.

It is well known that improving the trial wave functions for calculating the mixed estimator for the energy results in a reduction in the statistical error. Accordingly we also developed a procedure for using multideterminantal trial wave functions (the original FCIQMC method uses just the Hartree-Fock determinant). The local energies required for calculating the mixed estimators are precomputed and so there is no increase in the computational time during the Monte Carlo part of the run.

Another important, though fairly obvious, improvement we made is to use real rather than integer weights for the walkers. These improvements were tested both for chemical systems and for the Hubbard model. They result in 3 orders of magnitude gain in the computational efficiency. Consequently we are able to redo, using SQMC, on a single core calculations that required a sizable parallel computer using the FCIQMC method.

These improvements have been adopted by the Alavi and Booth groups and all calculations they have performed recently have used them.

B. Improving the Basis-Size Error using the F12-Method

Spectroscopic accuracy directly from quantum chemistry:

Application to ground and excited states of beryllium dimer⁷,

Sandeep Sharma, Takeshi Yanai, George Booth, C. J. Umrigar and Garnet Kin-Lic Chan

The diffusion Monte Carlo (DMC) method has the advantage relative to FCIQMC or SQMC that it works directly in an infinite basis. In standard quantum chemistry methods it is becoming standard practice to employ so called F12 methods to enhance the convergence to the infinite basis limit. We worked with Sandeep Sharma (Princeton), Takeshi Yanai (Odazaki), Garnet Chan (Princeton) and George Booth (Cambridge) to use F12 methods to improve the basis set convergence of SQMC. This can be done in two ways, either as a post processing step or by employing integrals from a transformed Hamiltonian. We applied this method as well as the canonical transcorrelation approach with the density matrix renormalization group to the small but challenging Be₂ dimer.

C. Multideterminant wave functions in quantum Monte Carlo⁸,

Miguel A. Morales, J. McMinis, B. K. Clark, J. Kim and G. E. Scuseria

This paper reports on the performance of large scale multideterminant expansions in QMC when applied to the first row dimers and the 55 molecules of the G1 test set. It demonstrates the potential of this strategy for systematically reducing the fixed-node error in the wave function and for achieving chemical accuracy in energy predictions. When compared to traditional quantum chemistry methods like MP2, CCSD(T), and various DFT approximations, the QMC results show a marked improvement over all of them. Only the explicitly correlated CCSD(T) method with a large basis set produces more accurate results.

D. Constraint Release in AFQMC

An Auxiliary-Field Quantum Monte Carlo Study of the Chromium Dimer⁹,

Wirawan Purwanto, Shiwei Zhang and Henry Krakauer.

The chromium dimer (Cr₂) presents an outstanding challenge for many-body electronic structure methods. Its complicated nature of binding, with a formal sextuple bond and an unusual potential energy curve, is emblematic of the competing tendencies and delicate balance found in many strongly correlated materials. We carried out a near-exact calculation of the potential energy curve (PEC) and ground state properties of Cr₂, using the auxiliary-field quantum Monte Carlo (AFQMC) method. Unconstrained, exact AFQMC calculations are first carried out for a medium-sized but realistic basis set. Elimination of the remaining finite-basis errors and extrapolation to the complete basis set (CBS) limit is then achieved with a combination of phaseless and exact AFQMC calculations. Final results for the PEC and spectroscopic constants are in excellent agreement with experiment.

E. Symmetry-projected Wave Functions in Quantum Monte Carlo Calculations¹⁰,

Hao Shi, Carlos A. Jiménez-Hoyos, R. Rodríguez-Guzmán, Gustavo E. Scuseria and Shiwei Zhang

We considered symmetry-projected Hartree–Fock trial wave functions in constrained-path Monte Carlo (CPMC) calculations. Previous CPMC calculations have mostly employed Hartree–Fock (HF) trial wave functions, restricted or unrestricted. The symmetry-projected HF approach results in a hierarchy of wave functions with increasing quality: the more symmetries that are broken and restored in a self-consistent manner, the higher the quality of the trial wave function. This hierarchy is approximately maintained in CPMC calculations: the accuracy in the energy increases and the statistical variance decreases when further symmetries are broken and restored. Significant improvement is achieved in CPMC with the best symmetry-projected trial wave functions over those from simple HF. We analyze and quantify the behavior using the two-dimensional repulsive Hubbard model as an example. In the sign-problem-free region, where CPMC can be made exact but a constraint is deliberately imposed here, spin-projected wave functions remove the constraint bias. Away from half-filling, spatial symmetry restoration in addition to that of the spin lead to highly accurate results from CPMC. Since the computational cost of symmetry-projected HF trial wave functions in CPMC can be made to scale algebraically with system size, this provides a potentially general approach for accurate calculations in many-fermion systems.

F. Symmetry in Auxiliary-Field Quantum Monte Carlo Calculations¹¹,

Hao Shi and Shiwei Zhang

We showed how symmetry properties can be used to greatly increase the accuracy and efficiency in auxiliary-field quantum Monte Carlo (AFQMC) calculations of electronic systems. With the Hubbard model as an example, we study symmetry preservation in two aspects of ground-state AFQMC calculations, the Hubbard–Stratonovich transformation and the form of the trial wave function. It is shown that significant improvement over state-of-the-art calculations can be achieved. In unconstrained calculations, the implementation of symmetry often leads to shorter convergence time and a substantial reduction of the sign problem, resulting in much smaller statistical errors. Moreover, certain excited states become possible to calculate which are otherwise beyond reach. In calculations with constraints, the use of symmetry can reduce the systematic error from the constraint. It also allows release-constraint calculations, leading to essentially exact results in many cases. Detailed comparisons are made with exact diagonalization results. Accurate ground-state energies are then presented for larger system sizes in the two-dimensional repulsive Hubbard model.

G. Introduction to the Variational and Diffusion Monte Carlo Methods¹²,

Julien Toulouse, Roland Assaraf and C. J. Umrigar

This paper gives a pedagogic introduction to VMC and DMC. An appendix gives a new and simpler approach to computing nonlinear functions of expectation values and their statistical uncertainties.

H. Observations on variational and projector Monte Carlo methods¹³,

C. J. Umrigar

This paper presents variational Monte Carlo (VMC) and various projector Monte Carlo (PMC) methods in a more unified way than is normally done. It points out various aspects of these algorithms that are not widely appreciated, particularly as regards to importance sampling as well as the sign problem. A proposal is presented for an exact PMC method in real space, i.e., a method that does not make a fixed-node or similar approximation and does not have a finite basis error. This method uses an approximate antisymmetrized projector and it is pointed out that with this projector the sign problem gets less severe and vanishes as the time step is increased. However, the time-step error prevents the use of very large time steps and the details of how best to sample from this projector remain to be worked out.

I. Efficient heat-bath sampling in Fock space¹⁴,

A. A. Holmes, Hitesh J. Changlani and C. J. Umrigar

FCIQMC/SQMC calculations have so far been done using proposal probabilities that are approximately uniform. Since the number of nonzero determinants connected to a given determinant scale as N^2M^2 , where N is the number of electrons and M the number of basis functions, this implies that the time step τ goes down as $1/(N^2M^2)$. Consequently the autocorrelation time becomes very large and the method becomes very inefficient as the number of electrons or the size of the basis is increased. Using the heat-bath method to sample moves with probability proportional to the absolute magnitude of the matrix elements is not an option because computing the matrix elements for all connected states is $\mathcal{O}(N^2M^2)$ and therefore prohibitively expensive. To overcome this problem, in this paper we present an approximate heat-bath algorithm that scales as $\mathcal{O}(N)$, which greatly improves the efficiency of the method for large N or M .

In addition to the above, the following papers acknowledge support from the CMCSN grant: **Coupled cluster channels in the homogeneous electron gas**¹⁵, *J. J. Shepherd, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. 140, 124101 (2014).*

Range Separated Brueckner Coupled Cluster Doubles Theory¹⁶, *J. J. Shepherd, T. M.*

Henderson, and G. E. Scuseria, Phys. Rev. Lett. 112, 133002 (2014).

Analytic energy gradient for the projected Hartree-Fock method, R. Schutski¹⁷, C. A. Jimnez-Hoyos, and G. E. Scuseria, J. Chem. Phys. 140, 204101 (2014).

III. PROJECTS IN PROGRESS

There were some projects that started under the auspices of this grant, that are yet to be completed. These are listed next.

A. Calculations on solids

Miguel Morales is collaborating with the W&M group on the use of large multi-determinant trial wave functions for AFQMC calculations of solids. The FCIQMC/SQMC calculations of Morales serve as benchmarks to test the accuracy of the approximations employed in the AFQMC method, and at the same time generate accurate trial wave functions for use in AFQMC.

B. Heavy-atom systems

Morales is collaborating with the W&M group on extending the FCIQMC/SQMC and AFQMC methods to solids containing heavy elements. Both of these methods offer the possibility to incorporate frozen-core approximations as well as scalar relativistic and spin-orbit coupling, crucial for the correct description of heavy atom materials.

C. Organic chemistry applications

Graduate student Adam Holmes from Cornell spent the summer of 2013 visiting Miguel Morales at LLNL. The work involves the use of FCIQMC/SQMC calculations to study the interactions between water molecules, hydronium, hydroxide ions and hydroxyl radicals. These molecules play a very important role organic chemistry; in particular the hydroxyl group is the defining functional group in alcohols. The interactions between these molecules in solution define the mechanisms for proton transfer and transport in aqueous solutions. At the time of the visit, FCIQMC/SQMC was deemed too computationally expensive for these systems with the reasonably large basis sets needed for achieving sufficient accuracy because the time step goes down with increasing basis size. Consequently, we instead decided to first work on the approximate

heat-bath sampling algorithm described earlier, that allows the use of larger time steps. Now that this work has been successfully completed¹⁴ it may be worthwhile to try to compute these systems again.

IV. GROUP MEETINGS AND VISITS

In addition to the 5 funded members of the Computational Research Team (CRT) and our graduate students and postdocs, there are several affiliated members with whom we have had valuable discussions and in some cases have started collaborative research projects. These include M. Peter Nightingale at the University of Rhode Island, Garnet Chan at Princeton University, Ali Alavi at Cambridge University, George Booth at King's College, London, Bryan Clark at Illinois, Matthew Foulkes at Imperial College, London, Takeshi Yanai at Odazaki, Japan, Eric Neuscamman at Berkeley, and Francesco Pederiva and Alessandro Roggero in Trento, Italy.

Much of communication has been via Skype conference calls. In order to conserve funds, most of our meetings have been satellites of conferences that the CRT members attended, primarily the March Meeting of the APS and the Electronic Structure Workshops. In addition a meeting at Telluride Science Research Center also served such a dual purpose.

Besides these meetings, we have had several visits among collaborators. In December 2012 Miguel Morales visited Shiwei Zhang and Henry Krakauer. George Booth from Cambridge visited the Umrigar group at Cornell for 8 days from 3rd to 10th June, 2013. Adam Holmes spent the summer of 2013 working with Morales at LLNL. Alessandro Roggero, a graduate student of Francesco Pederiva in Trento, visited the Umrigar group for 2 weeks in April and May of 2014. Shiwei Zhang and Cyrus Umrigar visited Garnet Chan for a few days in Dec. 2014. Shiwei Zhang was invited to the inaugural meeting of the CMCSN CRT on DMFT of Andrew Millis and Garnet Chan (Columbia and Princeton).

V. STUDENTS AND POSTDOCS SUPPORTED BY GRANT

At Cornell, graduate student Adam Holmes is being fully supported by the CMCSN grant. In addition, graduate students Frank Petruzielo worked full-time and graduate student Hitesh Changlani worked half-time on CMCSN related projects for more than a year each, but were supported with other funds. They have both graduated; Petruzielo is working for the Boston Consulting Group, a leading management consulting company, and Changlani is a postdoc with David Ceperley at the University of Illinois.

At Rice University, James Shepherd, from the Alavi group at Cambridge, joined the Scuseria group as a postdoc in March 2013. He came from Ali Alavi's group in Cambridge, UK, with expertise in the FCIQMC method. Even before joining the Scuseria group recently, Shepherd traveled with funding from this grant to CMCSN group meetings at ES12 and at the APS March 2013 meeting. Shepherd is now doing a second postdoc at MIT.

At College of William and Mary, graduate student Hao Shi, was supported by the CMCSN grant.

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