An Auxiliary-Field Quantum Monte Carlo Perspective on the Ground State of the Uniform Electron Gas: An Investigation with Spin-Restricted Hartree-Fock Trial Wavefunctions

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We assess the utility of spin-restricted Hartree-Fock (RHF) trial wavefunctions in performing phaseless auxiliary-field quantum Monte Carlo (ph-AFQMC) on the uniform electron gas (UEG) model. This particular combination, RHF+ph-AFQMC, was found to be highly accurate and efficient for systems containing up to 114 electrons in 2109 orbitals, particularly for \( r_s \leq 2.0 \). Compared to spin-restricted coupled-cluster (RCC) methods, we found that RHF+ph-AFQMC performs better than CC with singles, doubles, and triples (RCCSDT) and similarly to or slightly worse than CC with singles, doubles, triples, and quadruples (RCCSDTQ) for \( r_s \leq 3.0 \) in the 14-electron UEG model. With the 54-electron, we found RHF+ph-AFQMC to be nearly exact for \( r_s \leq 2.0 \) and pointed out potential biases in existing benchmarks. Encouraged by these, we performed RHF+ph-AFQMC on the 114-electron UEG model for \( r_s \leq 2.0 \) and provided new benchmark data for future method development. As the UEG models with \( r_s = 5.0 \) remain to be challenging for the RHF+ph-AFQMC, we emphasize the need for a better trial wavefunction for ph-AFQMC in simulating strongly correlated systems. With the 54-electron and 114-electron UEG models, we stress the potential utility of RHF+ph-AFQMC for simulating dense solids. LLNL-JRNL-772239-DRAFT

I. INTRODUCTION

Describing electron correlation in a scalable way that can handle hundreds of electrons is a grand challenge in quantum chemistry and condensed matter physics. State-of-the-art methods include coupled-cluster (CC) methods\(^1\)−\(^7\), density matrix renormalization group (DMRG) methods\(^8\),\(^9\), and quantum Monte Carlo (QMC) approaches\(^10\)−\(^12\). Each method exhibits different weaknesses and strengths and therefore they have been applied to solve a different class of problems in chemistry and condensed matter physics.

In this work, we will focus on a projector QMC method, namely, the auxiliary-field QMC (AFQMC) approach\(^11\),\(^13\). Projector Monte Carlo methods, while formally exact, typically impose a constraint in the imaginary time propagation in order to overcome the fermion sign problem and achieve a polynomial scaling algorithm. Both, diffusion Monte Carlo (DMC)\(^10\) and AFQMC enforce this constraint using a trial wavefunction, which can in principle be systematically improved towards the exact result. These constraints lead to the phaseless-AFQMC (ph-AFQMC) and fixed-node (FN-DMC) algorithms both of which scale like \( \mathcal{O}(N^3) - \mathcal{O}(N^4) \) with the number of electrons \( N \).

Although the formalism of DMC and AFQMC are very similar, there are some key differences between the two. First, AFQMC works in the second-quantized framework common to most quantum chemical methods, and introduces a finite basis set. Therefore, AFQMC energies need to be extrapolated to the complete basis set (CBS) limit in order to compare directly with experiments. This is in contrast with DMC which works in real space and directly in the CBS limit. Second, incorporating widely used Jastrow factors (JFs) into AFQMC is quite challenging. JFs are economical ways to incorporate residual electron correlation by enforcing cusp conditions either between electrons and nuclei or among electrons. Lastly, unlike FN-DMC, ph-AFQMC is not variational\(^14\).

Despite these issues, AFQMC offers a number of promising advantages precisely because it works directly in an orbital-based basis. In particular, all-electron, frozen core and non-local pseudopotential calculations can be performed with no additional approximations. Furthermore, as most quantum chemistry methods are performed with a finite basis set, many tricks used in quantum chemistry can be used to improve AFQMC as well. For instance, tensor hypercontraction approaches\(^15\)−\(^20\) have recently been employed to reduce the memory requirement of AFQMC\(^21\),\(^22\). Employing explicitly correlated basis functions (similar in spirit to JFs for DMC) should also be possible to reduce the basis set incompleteness error of AFQMC\(^23\). In addition to this, computing properties other than the total energy, which has historically been a challenge for projector QMC methods, can be more straightforwardly achieved in AFQMC\(^24\). Recent examples include one- and two-particle reduced density matrices\(^24\), imaginary time correlation functions\(^25\)−\(^27\) as well as forces\(^28\).

AFQMC has been successfully applied in recent years to a number of challenging problems in both quantum chemistry\(^29\)−\(^31\) and solid state physics\(^32\)−\(^36\). However, the broad applicability of the method is not as well understood as more traditional quantum chemistry approaches...
which have seen decades worth of sustained development and benchmarking. The primary limiting factor of AFQMC is the choice of trial wavefunction. Single-determinant trial wavefunctions from Hartree–Fock (HF) or density functional theory calculations have shown remarkable accuracy for a broad range of applications including the two-dimensional Hubbard model, dipole-bound anions and solid state applications, with total energies often approaching the accuracy of coupled cluster singles and doubles with perturbative triples CCSD(T). However, for more strongly correlated systems such as transition metal containing complexes single determinant trial wavefunctions are not sufficiently accurate and multi-determinant trial wavefunctions become necessary.

Often short determinantal expansions from complete active space self-consistent field (CASSCF) wavefunctions or non-orthogonal multi-Slater determinant trial wavefunction can help to restore the accuracy of the method. However, since multi-determinant wavefunctions scale exponentially with system size, this approach to improving the trial wavefunction is ultimately limited, particularly for large scale applications. The search for more economical and accurate trial wavefunctions for AFQMC (and also FN-DMC) is an active area of research and no single approach can achieve both polynomial scaling and broadly consistent accuracy at the same time.

Our goal is to assess the quality of HF trial wavefunctions for the Uniform Electron Gas (UEG) model. HF wavefunctions are the simplest possible reference states to perform subsequent correlation calculations in quantum chemistry. Often, artificial symmetry breaking caused by HF wavefunctions causes confusion in understanding electron correlation. For instance, with artificial symmetry breaking, subsequent correlation calculations become often ineffective. Therefore, one has to be cautious when choosing a proper HF state for correlation calculations. Nonetheless, HF is not only the simplest but also scalable to hundreds of electrons. With HF trials (which we name as HF+ph-AFQMC), AFQMC scales strictly as $O(N^3) - O(N^4)$ for a fixed statistical accuracy. Therefore, it is crucial to assess the accuracy of HF+ph-AFQMC and understand the scope of it in simulating large-scale chemical and solid-state systems. After all, the gold-standard quantum chemistry method, CCSD(T) is performed on top of HF states.

In the context of this paper, the UEG model provides us with a simplified version of the full ab-initio Hamiltonian for a solid, essentially omitting the electron-ion interaction term and all of the material complications it entails. One can tune the magnitude of dynamic and static correlation at the Hamiltonian level using a single parameter (for a fixed number of electrons) through the dimensionless Wigner-Seitz radius $r_s$. This tunability allows for an unambiguous comparison between the strengths and weaknesses of various methods. Moreover, there exist a number of benchmark results both for intermediate system sizes within the reach of traditional quantum chemistry approaches, as well as results for much larger system sizes, and also results extrapolated to the thermodynamic limit.

Recently, the formally exact full configuration interaction quantum Monte Carlo method (FCIQMC) provided benchmark results for a range of densities for a 14- and 54-electron system. These FCIQMC studies also motivated recent coupled-cluster Monte Carlo studies on the 14-electron UEG model by Neufeld and Thom where they provided CCSD, CCSD and triples (CCSDT), CCSDT and quadruples (CCSDTQ) with spin-restricted HF (RHF) references results for a wide range of $r_s$ and basis sets. As the scope of truncated spin-restricted CC (RCC) approaches is relatively well understood, comparing HF+ph-AFQMC against these results will lead us to a better understanding of the scope of HF+ph-AFQMC.

This paper is organized as follows: (1) we briefly review the formalism of ph-AFQMC and the UEG model, (2) we analyze the basis set convergence of AFQMC in the 14-electron UEG model and compare its result against FCIQMC and CCMC, and (3) we study larger systems (54-electron and 114-electron) and discuss the AFQMC perspectives on simulating the ground state of solids.

## II. METHODS

In this section we briefly summarize the basics of the AFQMC method and the phaseless approximation which leads to the phaseless AFQMC algorithm (ph-AFQMC).

### A. AFQMC

#### 1. Free-Projection AFQMC

The zero-temperature AFQMC algorithm is a stochastic realization of power methods that target the lowest root of the Hamiltonian $\hat{H}$. The algorithm is based on the following identity:

$$\langle \Psi_0 | \Phi_0 \rangle = \lim_{\tau \to \infty} \exp \left( -\tau \hat{H} \right) \Phi_0 = \lim_{\tau \to \infty} \langle \Psi(\tau) | \Phi_0 \rangle = \langle \Psi_0 | \Phi_0 \rangle,$$

where $\langle \Psi_0 | \Phi_0 \rangle$ is the exact ground state and $\Phi_0$ is an initial starting wavefunction satisfying $\langle \Phi_0 | \Phi_0 \rangle \neq 0$. Although the initial wavefunction $\langle \Psi_0 | \Phi_0 \rangle$ can differ from the trial wavefunction $\langle \Psi_T | \Phi_T \rangle$, for the purpose of this work we will assume $\langle \Psi_0 | \Phi_0 \rangle = \langle \Phi_T | \Psi_T \rangle$ when using a RHF trial wavefunction. Eq. (1) is implemented stochastically by repeatedly applying a propagator, $\exp(-\Delta \tau \hat{H})$, to a set of random walkers until the ground state is reached.
walker is comprised of a Slater determinant, $|\psi_n(\tau)\rangle$, and a weight $w_n(\tau)$ such that the statistical representation of the wavefunction is given by $|\Psi(\tau)\rangle = \sum_n w_n(\tau)|\psi_n(\tau)\rangle$.

In order to practically realize the projection, we first split the Hamiltonian into one-body and two-body operators (i.e., $\hat{H} = \hat{H}_1 + \hat{H}_2$). For the two-body terms, we write them in the sum of squared operators,

$$\hat{H}_2 = -\frac{1}{2} \sum_{\alpha} \vec{v}_\alpha^2. \quad (2)$$

Then, we apply the Hubbard-Stratonovich\cite{Hubbard1963} transformation to rewrite the imaginary-time limit

$$\exp(-\Delta\tau \hat{H}) = \int dx p(x) \hat{B}(\Delta\tau, x), \quad (3)$$

where $p(x)$ is the standard normal distribution, $x$ is a vector of $N_\alpha$ auxiliary fields and $\hat{B}$ is defined as

$$\hat{B}(\Delta\tau, x) = e^{-\Delta\tau \hat{H}_1} e^{-\sqrt{\Delta\tau} \hat{x} \cdot \vec{v}} e^{-\Delta\tau \hat{H}_1}. \quad (4)$$

At each time step, each walker draws Gaussian random numbers to sample one instance of $x$ and provides a sample to the HS transformation in Eq. (3). The application of a one-body operator such as Eq. (4) to a Slater determinant yields yet another single Slater determinant\cite{Stratonovich1954,Hubbard1963}.

For a generic $ab$-initio Hamiltonian the propagators appearing in Eq. (4) will in general be complex and the weights of the walkers will acquire a phase that will be distributed uniformly in the complex plane in the long imaginary time limit\cite{Stratonovich1954}. This ‘phase problem’ is analogous to the notorious fermion sign problem encountered in DMC and has no known solution in general. The phase problem can be somewhat mitigated through mean-field subtraction\cite{DWave1993} (i.e., redefining $\vec{v}'_\alpha = \vec{v}_\alpha - \langle \vec{v}_\alpha \rangle_0$) in Eq. (4), but the statistics will be eventually swamped by the phase problem. Note that mean field subtraction is essentially identical to normal-ordering $\hat{v}_\alpha$ which ensures $\langle \hat{v}_\alpha | \Phi_0 \rangle = 0$ for all $\alpha$.

2. Phaseless AFQMC

It is possible to eliminate this phase problem entirely at the sake of introducing biases into the results using the so-called phaseless approximation\cite{Gustavsson2000}. This is achieved by first performing an importance sampling transformation to the propagator such that walkers now undergo the modified propagation:

$$w_n(\tau + \Delta\tau)|\psi_n(\tau + \Delta\tau)\rangle = \left[I(\mathbf{x}_n, \mathbf{x}_\bar{n}, \tau, \Delta\tau) \hat{B}(\Delta\tau, \mathbf{x}_n - \mathbf{x}_\bar{n})\right] w_n(\tau)|\psi_n(\tau)\rangle, \quad (5)$$

where the importance function (in hybrid form) is defined as

$$I(\mathbf{x}_n, \mathbf{x}_\bar{n}, \tau, \Delta\tau) = S_n(\tau, \Delta\tau) e^{\mathbf{x}_n \cdot \mathbf{x}_\bar{n} - \mathbf{x}_\bar{n} \cdot \mathbf{x}_n / 2}, \quad (6)$$

$S_n$ is the overlap ratio of the $n$-th walker

$$S_n(\tau, \Delta\tau) = \frac{\langle \Psi_T | \hat{B}(\Delta\tau, \mathbf{x}_n - \mathbf{x}_\bar{n}) | \psi_n(\tau) \rangle}{\langle \Psi_T | \psi_n(\tau) \rangle}, \quad (7)$$

and $\mathbf{x}_\bar{n}$ is an “optimal” force bias which is a shift to the Gaussian distribution, given as

$$\mathbf{x}_\bar{n}(\Delta\tau, \tau) = -\sqrt{\Delta\tau} \frac{\langle \Psi_T | \hat{v}' | \psi_n(\tau) \rangle}{\langle \Psi_T | \psi_n(\tau) \rangle}. \quad (8)$$

The phaseless approximation (ph) is then defined as a modification to this importance function

$$I_{ph}(\mathbf{x}_n, \mathbf{x}_\bar{n}, \tau, \Delta\tau) = |I(\mathbf{x}_n, \mathbf{x}_\bar{n}, \tau, \Delta\tau)| \times \max(0, \cos(\theta_n(\tau))) \quad (9)$$

where the phase $\theta_n(\tau)$ is given by

$$\theta_n(\tau) = \arg(S_n(\tau, \Delta\tau)). \quad (10)$$

The walker weights and Slater determinants are then updated as

$$w_n(\tau + \Delta\tau) = I_{ph}(\mathbf{x}_n, \mathbf{x}_\bar{n}, \tau, \Delta\tau) \times w_n(\tau) \quad (11)$$

$$|\psi_n(\tau + \Delta\tau)\rangle = \hat{B}(\Delta\tau, \mathbf{x}_n - \mathbf{x}_\bar{n}) |\psi_n(\tau)\rangle. \quad (12)$$

Evidently, the phaseless approximation ensures that the walker weights remain real and non-negative throughout the simulation and therefore removes the phase problem completely.

The mixed estimate for the local energy estimator can be computed with the generalized Green’s function (or one-particle reduced density matrix) $P$,

$$P_{pq} = \frac{\langle \Psi_T | \hat{a}_p^\dagger \hat{a}_q | \psi_n(\tau) \rangle}{\langle \Psi_T | \psi_n(\tau) \rangle} = (C_{\psi_n} C_{\Psi_T} C_{\psi_n})^{-1} C_{\Psi_T} \quad (13)$$

where $C_{\psi_n}$ is the occupied molecular orbital coefficient of $|\psi_n(\tau)\rangle$ and $C_{\Psi_T}$ the occupied molecular orbital coefficient of $|\Psi_T\rangle$. Once the simulation has equilibrated, we will have a statistical representation of the ground state wavefunction given by

$$|\Psi(\tau)\rangle = \sum_n w_n(\tau)|\psi_n(\tau)\rangle \quad (14)$$

from which we can compute the mixed estimator for the energy as

$$E(\tau) = \frac{\langle \Psi_T | \hat{H} | \Psi(\tau) \rangle}{\langle \Psi_T | \Psi(\tau) \rangle} = \frac{\sum_n w_n(\tau) \epsilon_n(\tau)}{\sum_n w_n(\tau)}, \quad (15)$$

where $\epsilon_n(\tau)$ is the local energy of a walker. We will see how the local energy evaluation is done specifically for the UEG model later.
3. Size-consistency of ph-AFQMC

Size-consistency is a property of a wavefunction for isolated systems $A$ and $B$ that asserts the product separability of a supersystem wavefunction ($\langle \Psi_{AB} | = | \Psi_A^B \rangle$) and also the additive separability of energy ($E_{AB} = E_A + E_B$). Configuration interaction (CI) based quantum chemistry methods are in general not size-consistent.\textsuperscript{72}

In particular, the only size-consistent CI methods are CI with singles (CIS) and FCI. On the other hand, single-reference CC methods are size-consistent as long as the form of wavefunction is parametrized by an exponential of the cluster operator. This is why CC methods are promising in terms of simulating solids because size-consistency is crucial to reliably obtain energy of large systems including solids.

We will show that ph-AFQMC is also size-consistent as long as the trial wavefunction is product separable. For isolated systems $A$ and $B$, the supersystem Hamiltonian separates into $\hat{H}_A$ and $\hat{H}_B$. Furthermore, these two operators commute since these systems are isolated. Therefore, the propagator is also product separable,

$$\exp(-\Delta \tau \hat{H}_{AB}) = \exp(-\Delta \tau \hat{H}_A) \exp(-\Delta \tau \hat{H}_B)$$

(16)

The HS transformation can be performed on $\exp(-\Delta \tau \hat{H}_A)$ and $\exp(-\Delta \tau \hat{H}_B)$ separately so that we have $\hat{B}_{AB} = \hat{B}_A \hat{B}_B$. This proves the size-consistency of free-projection AFQMC.

It can be also shown that the phaseless constraint is product separable. The overlap function in Eq. (7) can be written as

$$S_n^{AB} = \frac{\langle \Psi_A^B | \hat{B}_A | \psi_n^A \rangle \langle \psi_n^B | \hat{B}_B | \psi_n^B \rangle}{\langle \psi_n^A | \hat{S}_n^A | \psi_n^A \rangle \langle \psi_n^B | \hat{S}_n^B | \psi_n^B \rangle} = S_n^A S_n^B$$

(17)

where the only assumptions we are making are (1) the product separability of the trial wavefunction: $| \Psi_T^{AB} \rangle = | \Psi_T^A \rangle | \Psi_T^B \rangle$ and (2) the product separability of the Slater determinant of $n$-th walker: $| \psi_n^{AB} \rangle = | \psi_n^A \rangle | \psi_n^B \rangle$. The assumption (2) can be satisfied as long as we start from a product separable wavefunction since the propagator is product separable. With this overlap function, one can show that the importance function also obeys the product separability and therefore we conclude that ph-AFQMC is size-consistent.

B. Uniform Electron Gas

The Hamiltonian for the uniform electron gas (UEG) is given simply as the sum of the kinetic energy and electron-electron interaction operator (up to a constant):

$$\hat{H} = \hat{T} + \hat{V}_{ee} + E_M.$$

(18)

We will work with a basis of plane wave spin orbitals $\langle \mathbf{r} | G, \sigma_i = \frac{1}{L^{3/2}} e^{i \mathbf{G} \cdot \mathbf{r}} \delta_{\sigma, \sigma^i}$, where $L$ is the length of the simulation cell, $G_i = \frac{2\pi}{L} \mathbf{n}_i$ for $\mathbf{n}_i$, a vector of integers and $\sigma_i$ is a spin index (either $\alpha$ or $\beta$). We impose a kinetic energy cutoff $E_{cut}$ and work with a finite basis of $2M$ spin orbitals. In this basis the kinetic energy is written as

$$\hat{T} = \sum_G \frac{|G|^2}{2} a_G^\dagger a_G,$$

(19)

and the electron-electron interaction operator is given by

$$\hat{V}_{ee} = \frac{1}{2\Omega} \sum_{Q \neq 0, G_1, G_2} \frac{4\pi}{|Q|^2} G_{1+Q}^\dagger G_{2-Q}^\dagger G_{2-Q} G_{1+Q},$$

(20)

where $\Omega = L^3$ is the simulation cell volume, $Q$ is a momentum transfer vector that lives in an enlarged basis of size $4E_{cut}$ and we have dropped the subscript on $G$ for simplicity. Lastly, the Madelung energy $E_M$ is included to account for the self-interaction of the Ewald sum under periodic boundary conditions.\textsuperscript{73} For simplicity we use the formula proposed by Schoof and co-workers\textsuperscript{74}

$$E_M \approx -2.837297 \times \left( \frac{3}{4\pi} \right)^{1/3} N^{2/3} \pi^{-1},$$

(21)

where $N$ is the number of electrons in the simulation cell and $r_s = \left( \frac{3}{4\pi N} \right)^{1/3}$ is the dimensionless Wigner-Seitz radius.

The local energy $\epsilon_n(\tau)$ for the UEG then reads

$$\epsilon_n(\tau) = E_M + \sum_G \frac{|G|^2}{2} P_{GG} + \frac{1}{2\Omega} \sum_{G \neq 0, Q} \frac{4\pi}{|Q|^2} (\Gamma_Q - \Lambda_Q),$$

(22)

where the Coulomb two-body density matrix $\Gamma_Q$ is

$$\Gamma_Q = \left( \sum_{G_1} P_{G_1+Q,G_1} \right) \left( \sum_{G_2} P_{G_2-Q,G_2} \right)$$

(23)

and the exchange two-body density matrix $\Lambda_Q$ is

$$\Lambda_Q = \sum_{G_1,G_2} P_{G_1+Q,G_2} P_{G_2-Q,G_1}$$

(24)

The formation of $\Gamma_Q$ costs $O(M^2)$ whereas the formation of $\Lambda_Q$ takes $O(M^3)$ amount of work. Therefore, the evaluation of the exchange contribution is the bottleneck in the local energy evaluation. As noted in Ref. 39 the evaluation of the energy (and propagation) can be accelerated using fast Fourier transforms, however we did not use this optimization here.

The two-body Hamiltonian $\hat{V}_{ee}$ needs to be rewritten as a sum of squares to employ the AFQMC algorithm. It was shown in Ref. 39 that

$$\hat{V}_{ee} = \frac{1}{4} \sum_{Q=0} \left[ \hat{A}^2(Q) + \hat{B}^2(Q) \right],$$

(25)
where

\[
\hat{A}(Q) = \sqrt{\frac{2\pi}{\Omega|Q|^2}} \left( \hat{\rho}(Q) + \hat{\rho}^\dagger(Q) \right),
\]

and

\[
\hat{B}(Q) = i \sqrt{\frac{2\pi}{\Omega|Q|^2}} \left( \hat{\rho}(Q) - \hat{\rho}^\dagger(Q) \right),
\]

with the momentum transfer operator \( \hat{\rho} \) defined as

\[
\hat{\rho}(Q) = \sum_G \alpha^G_{G+Q} \alpha^G_{G} \Theta \left( E_{\text{cut}} - |G + Q|^2 \right),
\]

where \( \Theta \) is the Heaviside step function. The Hubbard-Stratonovich operators \( \hat{\nu} \) are now \( \hat{A}(Q) \) and \( \hat{B}(Q) \), and the rest of the AFQMC algorithm follows straightforwardly.

\[\text{C. Trial Wavefunctions}\]

In ph-AFQMC, the main source of error is the bias introduced by the phaseless constraint. The magnitude of this bias is heavily dependent on the quality of trial wavefunctions. Although there are advanced options available for these such as multideterminantal trials and self-consistently determined single-determinantal trials, we will employ a simple single determinant spin-restricted Hartree-Fock (RHF) trial wavefunction in most cases. In the UEG model, this is an \( M \times N \) matrix (where \( N \) is the number of electrons and \( M \) is the number of plane waves) with 1’s on the diagonal entries.

Typically, for strongly correlated systems it is useful to exploit essential symmetry breaking with HF wavefunctions. It is essential (as opposed to artificial) in the sense that the property of a single determinant wavefunction is qualitatively right without it. An attempt to exploit artificial symmetry breaking typically leads to either spin-unrestricted HF (UHF) or spin-generalized HF (GHF) which has a lower energy than RHF. The instability of RHF solutions is expected at all \( r_s \) values of the UEG model at the TDL as proven by Overhauser. As mentioned in Ref. 79, however, the R to U spin-symmetry breaking may not occur in the UEG model with a finite number of electrons. Instead, there is a critical Wigner-Seitz radius \( r_s^c \) below which no UHF solution exists. This is not surprising in the context of quantum chemistry since this is the same concept as “Coulson-Fischer points” in molecules.

Instead of utilizing this essential symmetry breaking of the UEG model, we will use RHF trial wavefunctions for most AFQMC calculations and assess its performance. It will be interesting to see how much improvement one can achieve with UHF or GHF trial wavefunctions in the future.

\[\text{III. COMPUTATIONAL DETAILS}\]

Unless otherwise noted, the AFQMC calculations in this work were performed by a development version of QMCPACK\textsuperscript{81}. PAUXY\textsuperscript{82} was also used in the initial testing stages. Unless noted otherwise, AFQMC results below are obtained using QMCPACK. HANDE\textsuperscript{83,84} was used to cross-check our numbers for small systems that are not presented in this work. We used 0.005 a.u. for the time step \( \Delta \tau \) throughout the paper. This was found to be enough for systems we considered here. A total of 2880 walkers were used and the population bias from this was found to be negligible in the results reported here. The comb\textsuperscript{85} and pair branching\textsuperscript{86} population control algorithms are used in PAUXY and QMCPACK respectively. All calculations were performed with periodic boundary conditions; no twist averaging was performed.

\[\text{IV. RESULTS}\]

The UEG model has been explored by multiple methods at \( T = 0 \) and an extensive amount of benchmark data are already available. We compare our ph-AFQMC results against other methods and discuss whether the use of RHF trial wavefunction is reliable for \( r_s \leq 5.0 \).

It is expected that the quality of an RHF wavefunction degrades as \( r_s \) increases (approaching the atomic limit) since electrons tend to localize. \( r_s = 5.0 \) is a commonly investigated intermediate Wigner-Seitz radius so it will be interesting to see how ph-AFQMC performs without employing more sophisticated trial wavefunctions.

For simplicity, we will refer ph-AFQMC with an RHF trial wavefunction (RHF+ph-AFQMC) to as ph-AFQMC.

\[\text{A. The 14-Electron UEG Model}\]

We begin by studying the 14-electron UEG which was studied in detail by Shepherd and co-workers in Ref. 61. This small benchmark system is helpful as it is accessible to most quantum chemistry methods, whilst still exhibiting the typical challenges one faces when simulating real solids, namely basis set incompleteness error, and strong correlation (when \( r_s \) is large). In addition, it has of late emerged as a standard benchmark system for the UEG\textsuperscript{65}.

\[\text{1. Basis Set Convergence}\]

The basis set convergence of wavefunction based quantum chemistry methods for the UEG has been explored a number of times by various methods\textsuperscript{60,87,88} and we will only briefly comment on it here. For our purposes, it is sufficient to note that the convergence to the CBS limit is slowest at high densities (low \( r_s \)) and thus it is sufficient...
electron are more likely to coalesce). This is seen in Fig. 1 and Table I where on the order of 2000 PWs are necessary to converge the total energy to within 1 mHa in absolute energy (not per electron). Similar to previous studies we observe a more or less linear relationship between $E_c$ and $1/M$ for $M$ greater than 925.\textsuperscript{56,65} We point out that the use of transcorrelated approaches in AFQMC could greatly accelerate the convergence to the CBS limit.\textsuperscript{89}

FCIQMC with the initiator approximation ($i$-FCIQMC) is a formally exact approach as long as there is no initiator bias. Therefore, comparing ph-AFQMC with $i$-FCIQMC is a good way to assess the accuracy of ph-AFQMC. We see that ph-AFQMC agrees well with $i$-FCIQMC within the error bar up to $M = 179$ and it starts to deviate from $i$-FCIQMC beyond that. However, $i$-FCIQMC numbers for the larger $M$ values should be taken cautiously as it has been noted elsewhere that the bias from the initiator approximation was not completely removed\textsuperscript{65} and that the $i$-FCIQMC results for $r_s = 0.5$ may be too low by approximately $1\text{mE}_h$.

Comparing ph-AFQMC and CC methods is perhaps more relevant for the purpose of this paper. The UEG model $r_s = 0.5$ is relatively weakly correlated and thus CC methods on top of an RHF reference work very well. Neufeld and Thom found that for $r_s = 0.5$, CCSD is enough to converge the correlation energy with respect to the excitation levels.\textsuperscript{65} Therefore, the CCSDT numbers in Table I should be considered to be exact for a given basis set. As it is clear from Table I, the CCSD correlation energies are all above those of ph-AFQMC and ph-AFQMC agrees with CCSDT up to sub millihartree.

These results are particularly encouraging for the following reasons. This dense UEG model may be analogous to a weakly correlated molecular system, in the sense that for a finite number of electrons it is relatively well described by HF theory. In such a system, CCSDT (or CCSD(T)) should be more or less exact. Even if their absolute energies were not exact, the relative energies such as barrier heights and interaction energies should be close to exact. The results here suggest that ph-AFQMC is a potentially powerful tool to handle such weakly correlated systems. For the rest of this section, we will assess the accuracy of ph-AFQMC for higher $r_s$ where there can be a good mixture of weak and strong correlation. Furthermore, the quality of the RHF trial wavefunction will start to degrade so we will show how this affects ph-AFQMC.

$(M = 2109)$, we found that the ph-AFQMC energy is 15-16 mE$_h$ lower than RCCSD and is within the error bar of RCCSDT.

In Table II, we present the comparison of ph-AFQMC, $i$-FCIQMC, RCCSD, RCCSDT, and RCCSDTQ for selected basis sets. All of our ph-AFQMC is available in the Supporting Information. At $r_s = 1.0$, ph-AFQMC agrees with $i$-FCIQMC within the error bar of each result when $M = 1189$. Small basis set ($M = 179$) results suggest that from RCCSDT to RCCSDTQ only small correlation energy is gained. Therefore, we consider RCCSDT to be near-exact for larger basis sets. Near the CBS limit to converge the basis set error here. This slower convergence can be understood simply because the electron-electron cusp is more pronounced at high densities (the electron are more likely to coalesce).

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$M$ & ph-AFQMC & $i$-FCIQMC & RCCSDT \\
\hline
57 & -0.5173(1) & -0.5169(1) & N/A \\
93 & -0.5592(2) & -0.5589(1) & N/A \\
179 & -0.5794(2) & -0.5797(3) & -0.5796(4) \\
389 & -0.5884(2) & -0.5893(3) & N/A \\
925 & -0.5920(1) & -0.5936(3) & -0.5862(4) \\
1189 & -0.5921(2) & -0.5939(4) & N/A \\
1213 & -0.5926(8) & N/A & N/A \\
1419 & -0.5925(4) & N/A & -0.5872(1) \\
2109 & -0.5931(6) & N/A & -0.5875(1) \\
\hline
\end{tabular}
\caption{The correlation energy comparison between ph-AFQMC, $i$-FCIQMC, RCCSD, and RCCSDT for the 14-electron UEG model at $r_s = 0.5$. The $i$-FCIQMC numbers were taken from Ref. 60 and CC numbers were taken from Ref. 65. N/A means that the data is not available. These calculations were performed using the PAUXY package. Error bars were estimated using reblocking\textsuperscript{69} as implemented in the pyblock package.\textsuperscript{91}}
\end{table}
As shown in Table II, ph-AFQMC provides a lower correlation energy than even RCCSDTQ in the $M = 81$ basis set. This result highlights the utility of RHF+ph-AFQMC. Namely, it can provide quantitatively accurate results when the role of quadruples is not negligible and yet still small enough for the RHF trial wavefunction to behave well.

![Table II](image)

TABLE II. The correlation energy comparison between ph-AFQMC, i-FCIQMC, RCCSD, and RCCSDT for the 14-electron UEG model at $r_s = 1.0, 2.0, 3.0$ and $5.0$. The i-FCIQMC numbers were taken from ref. 61 and CC numbers were taken from ref. 65. N/A means that the data is not available.

Although at $r_s = 0.5, 1.0, 2.0$ ph-AFQMC provides more or less exact correlation energies, as the density is lowered further we find that the RHF trial wavefunction's performance degrades significantly. Not only does the ph-AFQMC correlation energy become above RCCSDTQ by about $2 \text{ m} E_h$ at $r_s = 3.0$, but the stability of the simulations suffers noticeably. Nevertheless, at $r_s = 3.0$ we observe that ph-AFQMC is comparable to RCCSDT and is able to reach the CBS limit reliably.

However, $r_s = 5.0$ is much more difficult to handle with an RHF trial wavefunction. This is typically evidenced by an increase in the number of rare event population fluctuation. These rare events are well understood, and arise due a divergent importance function which occurs when $\langle \Psi_T | \phi \rangle$ approaches zero. Although these rare events can be effectively controlled by the use of bounds on the local (and/or hybrid energy) they nevertheless signify a worsening in the quality of trial wavefunction for a fixed system size. To demonstrate this, in Fig. 2 we plot the convergence of the ph-AFQMC energy with projection time for a range of densities with $M = 93$ as well as an estimate for the overlap $\sum_n w_n |\langle \Psi_T | \phi_n \rangle| / \sum_n w_n$. We see from Fig. 2 (a) that as $r_s$ increases the projection time necessary to converge to the ground state increases as well as the frequency of rare events. This is correlated with a decrease in the magnitude in the overlap as is seen from Fig. 2 (b).

Indeed, at $r_s = 5.0$ we found that the ph-AFQMC energy did not converge monotonically with increasing basis set size past $M = 389$. Rather, the ph-AFQMC correlation energy decreases in magnitude with increasing basis set size. This signals a complete breakdown of the phaseless constraint with this trial wavefunction. We note that a similar effect can be observed in i-FCIQMC when the initiator error is not fully converged for increased basis set sizes, where one finds that the correlation energy begins to plateau as a function of basis set. This suggests that an improved trial wavefunction is necessary to attain sensible results for this system.

It is noteworthy to point out that this unusual behavior of ph-AFQMC energy with respect to the basis set size could indicate the “non-variational” failure of ph-AFQMC. ph-AFQMC is formally non-variational in the sense that a variational energy estimator of a given ph-AFQMC wavefunction can be above the mixed energy estimator in Eq. (15). Similarly, CC methods are also formally non-variational due to their projective nature. With an RHF reference, it has shown catastrophic non-variationality for strongly correlated systems. It is possible that RCCSD (and even RCCSDT) is also exhibiting non-variationality for this $r_s$ value. This can be confirmed with more sophisticated CC methods. The investigation of the non-variationality of ph-AFQMC and CC methods in the context of strong correlation will be an interesting subject for future study.

To investigate the ph-AFQMC results at $r_s = 5.0$ further, we explored the use of non-orthogonal multi-Slater determinant expansions (NOMSD) as trial wavefunctions generated using a version of the projected HartreeFock (PHF) algorithm developed by Scuseria and co-workers. Interested readers are referred to ref. 32 for further details. In Fig. 3, we find an initial rapid decrease in the error of the ph-AFQMC correlation energy and correspondingly a reduction in the ph-AFQMC statistical variance in the local energy estimator. This long tail in the convergence of the ph-AFQMC energy is indicative that the system is strongly correlated. We note that the FCI space for $M = 57$ contains on the order of $10^{16}$ determinants and therefore the improvement in the
Fig. 2. Panel (a) shows the convergence of the ph-AFQMC total energy to its equilibrated mean value ($\bar{E}$) as a function of projection time for a variety of values of $r_s$. Note that the data have been shifted and scaled by $r_s$ for clarity. Note the occurrence of spikes in the local energy increases with $r_s$. Here we bounded the local energy during propagation but not when printing the estimator to reveal the degradation in the results. Panel (b) plots the reduction in the magnitude in the overlap between the walkers and the trial wavefunction (see main text for definition) with decreasing $r_s$. The slower equilibration of the overlap compared to the local energy has been noted previously in Ref. 31.

Fig. 3. Panel (a) shows the behavior of the relative error in the ph-AFQMC correlation energy as a function of the number of determinants in the trial wavefunction expansion, $N_D$. The relative error is measured with respect to the i-FCIQMC value. Panel (b) shows the corresponding reduction in statistical variance defined as $\text{Var}(N_D=1)/\text{Var}(N_D)$.

Table III. Comparison between ph-AFQMC correlation energies using a RHF and ten determinant NOMSD trial wavefunction at $r_s=5.0$. i-FCIQMC energies were taken from Ref. 61. ph-AFQMC calculations were performed using the development version of QMCPACK. Note that the $M=389$ RHF+ph-AFQMC energy is above the $M=179$ RHF+ph-AFQMC energy in Table II and this is an artifact of the breakdown of the RHF trial wavefunction.

B. Larger Supercells

As explained in Section II A 3, ph-AFQMC is size-consistent and thus can reliably reach the TDL using larger super cells along combined with finite size corrections and twist averaging. As the total energy of the UEG model in the TDL is already well understood for solid state densities, here we instead just study finite-sized UEG models and compare with other available methods when applicable.

Following the sequence of “magic numbers” in the UEG model, we study larger supercells (54 electrons and 114 electrons) with ph-AFQMC for $r_s=0.5, 1.0, 2.0$. In the 14-electron UEG model, we obtained energies with error bars of the order of 1 m$E_h$. This is important for molecular applications where we aim for energy differences between two finite systems. On the other hand, the cost of achieving the same statistical error for larger systems adds an extra $O(N)$ to the computational cost of ph-AFQMC. This extra cost for sampling may be avoided...
by the correlated sampling technique\textsuperscript{105,106}, but here we instead compare the total energy per electron. This metric is well-suited for ab-initio solids (or extended systems) in general.

High-quality DMC numbers are available for the 54-electron UEG model and we compare ph-AFQMC against this. For the 114-electron UEG model, there are only variational MC (VMC) results available so we will compare against these.

1. The 54-Electron UEG Model

We found that from $M = 1419$ to $M = 2109$ the change in $E_{\text{tot}}/N$ at $r_s = 0.5$ is only of the order of 0.1 $mE_h$. We therefore do not perform the CBS extrapolation for the comparison between ph-AFQMC and DMC. The reported ph-AFQMC numbers are obtained from $M = 1419$ which enables a direct comparison between ph-AFQMC and $i$-FCIQMC at $r_s = 0.5$ and $r_s = 1.0$. The ph-AFQMC results for $M = 2109$ at $r_s = 0.5, 1.0, 2.0$ are available in the Supplementary Materials.

In Table IV, we summarize the comparison between ph-AFQMC, $i$-FCIQMC, and DMC for the 54-electron UEG model. At $r_s = 0.5$, ph-AFQMC and $i$-FCIQMC agree with each other within the error bar. Shepherd and co-workers found that the DMC-BF energy is somewhat higher than $i$-FCIQMC and suggested that the fixed-node error with the backflow (BF) trial wavefunction may not be small. Indeed, we reach the same conclusion with ph-AFQMC. As explained in Section I, the difference between DMC and AFQMC is mainly the discretization (or basis set) we work with. It is interesting that the fixed-node error in FN-DMC can be non-negligible even with more sophisticated trial wavefunctions such as Slater-Jastrow (SJ) and BF. It is encouraging that we can achieve near-exact accuracy with ph-AFQMC at $r_s = 0.5$ with this simplest possible RHF trial wavefunction.

At $r_s = 1.0$, we observe that ph-AFQMC performs better than $i$-FCIQMC and is in agreement with FN-DMC-BF up to 0.2 $mE_h$. In fact, the ph-AFQMC energy is lower than that of FN-DMC-BF, which may indicate non-negligible fixed-node errors even in FN-DMC-BF. In the $M = 2109$ basis set, the difference becomes 0.3 $mE_h$ as shown in the Supplementary Materials. In this case, $i$-FCIQMC suffers from the initiator bias and results into about 1 $mE_h$ above the FN-DMC-BF energy. The performance of ph-AFQMC is better than FN-DMC-BF by 1 $mE_h$/e similarly to the $r_s = 0.5$ case.

No $i$-FCIQMC results at $r_s = 2.0$ due to the severity of the sign problem so we instead must compare only to FN-DMC. We find that the ph-AFQMC energy is 1.1 $mE_h$/e below the FN-DMC-SJ energy and 0.3 $mE_h$/e below the FN-DMC-BF energy. With a larger basis set $M = 2109$, the ph-AFQMC energy lies 0.4 $mE_h$/e below the FN-DMC-BF energy as shown in the Supplementary Materials.

Further increasing $r_s$ to 5.0, we observe that ph-AFQMC is no longer comparable to FN-DMC-SJ and FN-DMC-BF as expected. It should be noted that despite the severe sign problem at $r_s = 5.0$ ph-AFQMC is still able to provide an answer with good statistics owing to the phaseless approximation (though the correlation energy error is significant).

In summary, for the 54-electron UEG model at $r_s = 0.5, 1.0, 2.0$, we observe that ph-AFQMC can obtain nearly exact $E_{\text{tot}}/N$. In particular, its accuracy is comparable to other state-of-the-art methods such as $i$-FCIQMC and FN-DMC-BF. The general conclusions are similar to the 14-electron UEG model: ph-AFQMC is particularly well-suited for $r_s$ values smaller than 5 where there exists moderate strong correlation. It is encouraging that ph-AFQMC achieved these highly accurate results using the simplest trial wavefunction, RHF.

2. The 114-Electron UEG Model

Encouraged by the near-exact accuracy of ph-AFQMC for low $r_s$ values in the 14- and 54-electron UEG models, we used ph-AFQMC to provide benchmark numbers for the 114-electron UEG model for future method development. The 114-electron UEG model has been relatively less explored. For determinant-based algorithms like $i$-FCIQMC the sign problem is likely to preclude its application except for very high densities. On the other hand, for ph-AFQMC this does not pose a significant challenge especially when considering $r_s \leq 2.0$.

At $r_s = 0.5$, the total energy per electron changes by 0.5 $mE_h/e$ when increasing $M$ from 1419 to 2109. For higher $r_s$ values, we expect this energy change to be smaller. We will present the ph-AFQMC energies at $r_s = 0.5, 1.0, 2.0$ all obtained with $M = 2109$. We expect that our ph-AFQMC energies reported here have the basis set incompleteness error of the order of 0.5 $mE_h/e$ per electron. Therefore, the numbers reported here may be considered as an upper bound to the ph-AFQMC energies at the CBS limit.

The ph-AFQMC results are presented in Table V. The only data available in literature is $r_s = 1.0$ with a VMC approach with a Slater-Jastrow wavefunction. The VMC

| $r_s$ | ph-AFQMC | $i$-FCIQMC | FN-DMC-SJ | FN-DMC-BF |
|-------|----------|-------------|------------|------------|
| 0.5   | 3.22087(2) | 3.22086(2) | 3.22245(9) | 3.22112(4) |
| 1     | 0.52967(2) | 0.53073(4) | 0.53089(9) | 0.52989(4) |
| 2     | -0.01429(3) | N/A         | -0.01311(2) | -0.013966(9) |
| 5     | -0.07589(5) | N/A         | -0.078649(7) | -0.079036(3) |

TABLE IV. The total energy per electron ($E_h/e$) comparison between ph-AFQMC, $i$-FCIQMC, FN-DMC with a Slater-Jastrow (SJ) trial wavefunction, and DMC with a backflow (BF) trial wavefunction for the 54-electron UEG model at $r_s = 0.5, 1.0, 2.0, 5.0$. Both ph-AFQMC and $i$-FCIQMC numbers are obtained from $M = 1419$. The $i$-FCIQMC numbers were taken from Ref. 107. N/A means that the data is not available.
TABLE V. The total energy per electron \( \langle E_h^r/e \rangle \) of ph-AFQMC for the 114-electron UEG model at \( r_s = 0.5, 1.0, 2.0 \). All results were obtained with \( M = 2109 \). The VMC (Slater-Jastrow) energy at \( r_s = 1.0 \) is 0.60395(25) \( E_h^r/e \).

| \( r_s \) | ph-AFQMC |
|------|----------|
| 0.5  | 3.484538(8) |
| 1.0  | 0.598776(6) |
| 2.0  | 0.00487(6) |

energy is 0.60395(25) \( E_h^r/e \) which is at least 5 \( mE_h^r/e \) higher than our ph-AFQMC energies. Comparing ph-AFQMC energies in Table IV and Table V, we note that the finite-size effect is still very large. Namely, the energy per electron is far from the convergence with respect to the system size. It will be interesting to investigate finite-size effects with ph-AFQMC in more realistic systems in the future. Although further comparisons are not possible due to the lack of benchmark data, we believe that the ph-AFQMC numbers in Table V are close to the exact energies and the correlation energy error is smaller than 1 \( mE_h^r/e \) per electron given the results for the 54-electron model.

V. CONCLUSIONS

In this paper, we examined the performance of phaseless auxiliary-field quantum Monte Carlo (ph-AFQMC) with the spin-restricted Hartree-Fock (RHF) trial wavefunction (i.e., RHF+ph-AFQMC) on the uniform electron gas (UEG) problem. We considered the 14-electron, 54-electron, and 114-electron UEG model. Through these studies, we found the following conclusions:

1. In the 14-electron case, we compared RHF+ph-AFQMC with spin-restricted coupled-cluster (RCC) methods. Compared to RCC with singles and doubles (RCCSD) and CC with singles, doubles, and triples (RCCSDT), RHF+ph-AFQMC performs better than RCCSDT and similarly to or slightly worse than RCCSDTQ for \( r_s \leq 3.0 \).

2. For the 14-electron problem at \( r_s = 5.0 \) where CCSDT is inadequate, RHF+ph-AFQMC exhibits rare fluctuations in the energy estimator, which makes the phaseless approximation difficult to use. We found that using a small multi-determinant trial wavefunction is effective in stabilizing the simulations but still ineffective in obtaining highly accuracy results in such cases.

3. In the case of the 54-electron UEG model, the comparison with initiator full configuration interaction QMC (\( \iFCIQMC \)) and fixed-node diffusion MC (FN-DMC) suggested that RHF+ph-AFQMC is a promising tool for simulating dense solids. RHF+ph-AFQMC confirmed that the fixed-node error in FN-DMC for \( r_s = 0.5 \) as noted before in an \( \iFCIQMC \) study. Moreover, RHF+ph-AFQMC revealed that the initiator bias in \( \iFCIQMC \) for \( r_s = 1.0 \) is large (about 1 \( mE_h^r \) per electron) and the fixed-node error in FN-DMC with a back flow trial wavefunction (FN-DMC-BF) may not be negligible (0.3 \( mE_h^r \) per electron). A similar trend was observed in the case of \( r_s = 2.0 \). Lastly, \( r_s = 5.0 \) was found to be challenging for RHF+ph-AFQMC to tackle and the ph-AFQMC correlation energy was simply inadequate compared to FN-DMC-BF for this case. Overall, RHF+ph-AFQMC was found to be as accurate as or potentially more accurate than FN-DMC-BF wavefunction for \( r_s \) up to 2.0.

4. We produced RHF+ph-AFQMC energies of the 114-electron problem for \( r_s \leq 2.0 \) where not many benchmark data are available. Given its performance for the 54-electron case, we expect the RHF+ph-AFQMC correlation energy error to be less than 1 \( mE_h^r \) per electron.

It is the central message of this paper that even with the simplest trial wavefunction (RHF) ph-AFQMC is a powerful tool for simulating molecules and solids where there is no noticeable strong correlation between electrons. In particular, its scope lies between CCSD and CCSDT. Given its low scaling (\( \mathcal{O}(3^N) - \mathcal{O}(4^N) \)), RHF+ph-AFQMC remains a promising tool.

The future study should include a more extensive benchmark of RHF+ph-AFQMC on more chemically relevant systems such as the W4-11\(^{109}\) set as well as designing a better and yet compact trial wavefunctions for AFQMC. Using dynamically correlated orbitals such as those from orbital-optimized Møller-Plesset perturbation theory can be an economical way to go beyond HF trial wavefunctions.\(^{49,110,111}\) Some essential symmetry breaking in the HF trial wavefunction can potentially improve the performance of ph-AFQMC greatly such as using complex, restricted HF orbitals.\(^{112,113}\) Lastly, the finite-temperature extension of ph-AFQMC has been well established.\(^{114-116}\) The assessment of ph-AFQMC for the warm dense UEG model\(^{117}\), which has been the subject of intense research of late\(^{74,118-121}\) is currently work in progress.

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