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Full configuration interaction perspective on the homogeneous electron gas

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Highly accurate results for the homogeneous electron gas (HEG) have only been achieved to date within a diffusion Monte Carlo (DMC) framework. Here, we introduce a recently developed stochastic technique, full configuration interaction quantum Monte Carlo (FCIQMC), which samples the exact wave function expanded in plane-wave Slater determinants. Despite the introduction of a basis-set incompleteness error, we obtain a finite-basis energy, which is significantly and variationally lower than any previously published work for the 54-electron HEG at $r_s = 0.5$ a.u., in a Hilbert space of 10^{108} Slater determinants. At this value of r_s, as well as of 1.0 a.u., we remove the remaining basis-set incompleteness error by extrapolation, yielding results comparable to state-of-the-art DMC backflow energies. In doing so, we demonstrate that it is possible to yield highly accurate results with the FCIQMC method in periodic systems.

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The homogeneous electron gas (HEG), described by a simple model Hamiltonian, encapsulates many of the difficulties with modern electronic-structure theory. To date, the only truly successful *ab initio* methods to yield accurate ground-state energies at a range of densities have been quantum Monte Carlo techniques, in particular, diffusion Monte Carlo (DMC).[1–6] The most famous of these were the results of Ceperley and Alder from which the local density approximation (LDA) functionals of density functional theory were parametrized.[1,7] Diffusion Monte Carlo would be an exact technique but for the fixed-node approximation, which requires the nodes in the wave function due to fermionic exchange to be specified in advance by some trial wave function. In general, the fixed-node approximation lacks a method of being systematically improved to find the exact result. Attempts to go beyond the fixed-node approximation have been met with some success, however, complete elimination of this error has not been achieved.[1,2,4,6] In particular, the release node (RN) method is practical only in systems for which the bosonic ground state is close in energy to the fermionic one. In the HEG, this is only true at low density. At high densities, the RN-DMC is unstable, and fixed-node DMC with backflow corrections is the most viable option. This leaves open the question of the magnitude of the remaining fixed-node error.

Full configuration interaction (FCI) aims to find the wave function expressed as a linear combination of Slater determinants, formed from rearrangements of N electrons in an underlying one-electron basis of M spin orbitals.[8,9] This is equivalent to an exact diagonalization of this space. Since such a basis set of Slater determinants scales as $\binom{M}{N}^2$, benchmarks from FCI are extremely difficult to produce. There has been surprisingly little work undertaken with polynomially scaling high-accuracy quantum chemical techniques, even though it has recently been shown that finite systems ranging from as few as 54 electrons can begin to capture the physics of the three-dimensional (3D) HEG accurately.[10,11] In part, this might be due to the required size of the one-electron basis and that, on approaching the thermodynamic limit for metals, many approximate methods find divergent energies.[12] In contrast, truncated configuration interaction will tend toward zero correlation energy.

We present a first application of a new method, FCI quantum Monte Carlo (FCIQMC),[13–16] which stochastically samples the exact wave function providing the accuracy of exact diagonalization at a greatly reduced computational cost, to the high-density weakly correlated 54-electron HEG at $r_s = 0.5$ and 1.0 a.u. This is the regime in which backflow corrections to FN-DMC are the largest.[4,6]

Model. We seek to find the ground-state wave function and total energy of the N-electron HEG simulation-cell Hamiltonian

$$\hat{H} = \sum_{\alpha} -\frac{1}{2}\nabla_{\alpha}^2 + \sum_{\alpha\neq\beta}\frac{1}{2}\hat{v}_{\alpha\beta} + \frac{1}{2}N v_{\mathrm{M}}, \tag{1}$$

where the two-electron operator $\hat{v}_{\alpha\beta}$ is the Ewald interaction

$$\hat{v}_{\alpha\beta} = \frac{1}{\Omega}\sum_{\mathbf{q}} v_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{r}_{\alpha}-\mathbf{r}_{\beta})}, \quad v_{\mathbf{q}} = \begin{cases} \frac{4\pi}{\mathbf{q}^2}, & \mathbf{q}\neq\mathbf{0} \\ 0, & \mathbf{q}=\mathbf{0}. \end{cases} \tag{2}$$

v_{M} is the Madelung term, which represents contributions to the one-particle energy from interactions between a point charge and its own images and a neutralizing background,[10,17,18] and Ω is the real-space unit-cell volume.

We use an expansion of the wave function in a Slater determinant basis

$$\Psi = \sum_{\mathbf{i}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle, \tag{3}$$

where each determinant is a normalized, antisymmetrized product of plane waves:

$$D_{\mathbf{i}} = \mathcal{A}[\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\ldots\psi_k(\mathbf{x}_N)], \tag{4}$$

$$\psi_j(\mathbf{x}) \equiv \psi_j(\mathbf{r},\sigma) = \sqrt{\frac{1}{\Omega}} e^{i\mathbf{k}_j\cdot\mathbf{r}}\delta_{\sigma_j,\sigma}. \tag{5}$$

The $\mathbf{i}$ index, which uniquely labels each determinant, is its normal-ordered string.[19] The wave vectors $\mathbf{k}$ are chosen to correspond to the reciprocal lattice vectors of a real-space cubic cell of length L:

$$\mathbf{k} = \frac{2\pi}{L}(n,m,l), \tag{6}$$

where n, m, and l are integers. The Hartree-Fock determinant is the determinant occupying N plane waves with the lowest

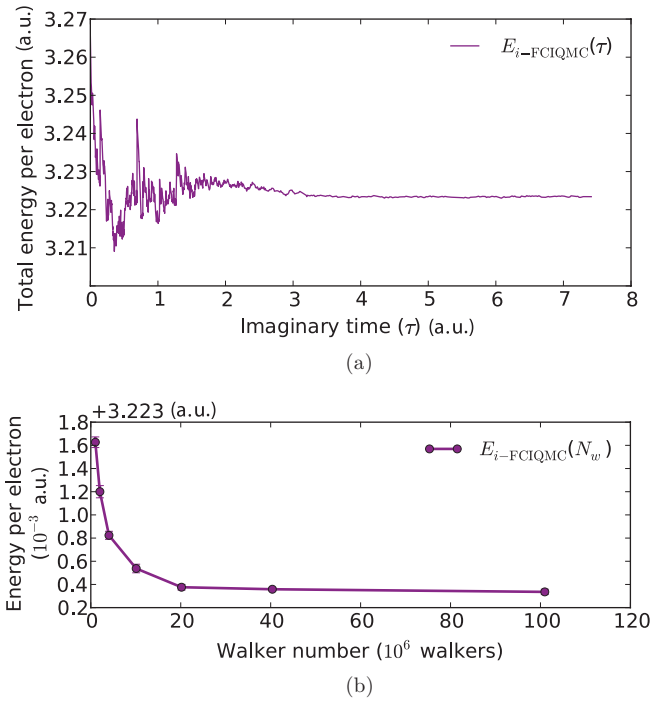

FIG. 1. (Color online) Plots showing calculation of the i-FCIQMC energy for $N = 54$, $M = 682$, $r_s = 0.5$ a.u. The result is reached in the limit of long time (iteration number) and large walker number N_w. (a) A typical i-FCIQMC run. At $\tau \simeq 3.8$ a.u., the shift S was allowed to vary to keep the walker number at an average of 20 million. From this point, an average was taken of the total energy. (b) i-FCIQMC calculations with $n_{\mathrm{add}} = 3$ are run at increasing N_w values, with the aim that the limit $N_w \to \infty$ is found by the simulation at maximum walker number.

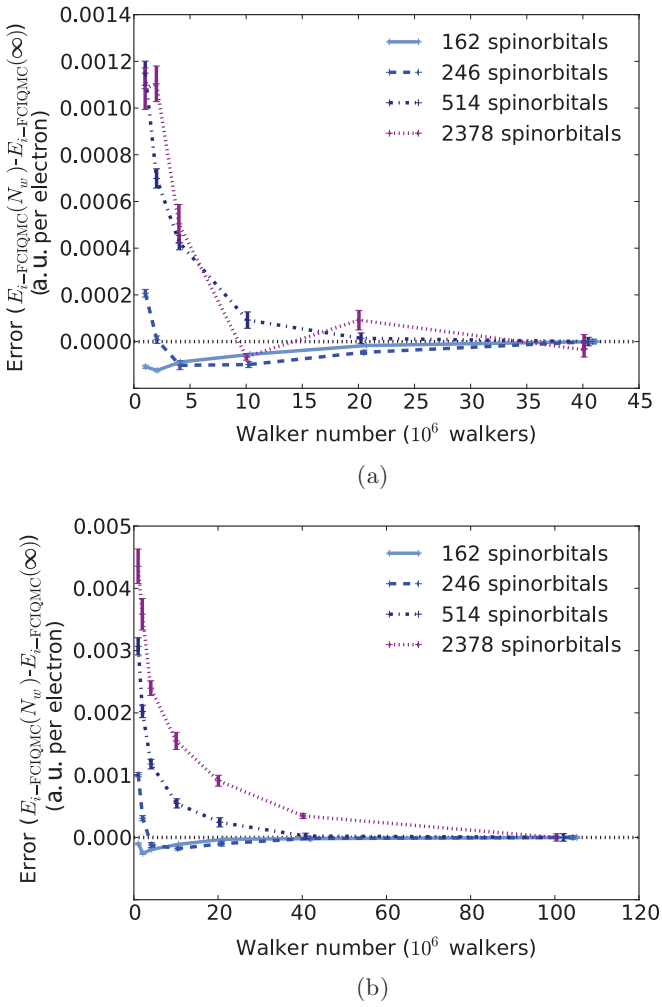

FIG. 2. (Color online) Convergence of initiator error for $N = 54$ is shown for a variety of basis sets for (a) $r_s = 0.5$ and (b) $r_s = 1.0$ a.u. The infinite N_w limit is estimated from approximately 40 million walkers and 100 million walkers for each r_s, respectively. Each line is labeled with the spin orbital number M and was calculated with $n_{\mathrm{add}} = 3$. As the basis-set size grows, so the size of space and the number of walkers required to sample the space accurately grows.

kinetic energy. The full basis set for our calculation is constructed of all Slater determinants that can be made from $M/2$ plane waves (M spin orbitals) forming a closed shell of orbitals in k space with a kinetic energy lower than an energy cutoff $\frac{1}{2}\mathbf{k}_c^2$. Plane waves are convenient because taking a single cutoff parameter to infinity makes the one-electron basis set complete. Moreover, plane waves are natural orbitals for the electron gas, implying that a FCI expansion is rapidly convergent in this basis.[20]

The determinant expansion given in Eq. (3) can be inserted into the imaginary-time Schrödinger equation, yielding a set of coupled equations for the determinant coefficients

$$-\frac{dC_{\mathbf{i}}}{d\tau} = (H_{\mathbf{ii}} - S)C_{\mathbf{i}} + \sum_{\mathbf{j}\neq\mathbf{i}} H_{\mathbf{ij}}C_{\mathbf{j}}. \tag{7}$$

Setting $dC_{\mathbf{i}}/d\tau = 0$ and solving for S by exact diagonalization yields the total energy for the problem in a given basis.

In a recently developed quantum Monte Carlo, termed full configuration interaction QMC,[13] Eq. (7) is regarded as a set of master equations governing the dynamics of the evolution of the determinant coefficients in imaginary time, with elements of $\mathbf{H}$ being nonunitary transition rates. These dynamics are simulated by introducing a population of N_w "walkers" distributed over the determinants, which are signed to represent the sign of the coefficients within the simulation $C_{\mathbf{i}} \propto \langle N_{\mathbf{i}}(\tau)\rangle$. The walker population is then allowed to evolve through discretized imaginary-time steps by spawning, death/cloning, and annihilation events according to Eq. (7) until a steady state is reached. The exact rules for this can be found in Ref. 13.

The parameter S, termed the shift, is a population control parameter, which can be updated self-consistently at equilibrium to oscillate around the total energy. However, throughout this work, the projected energy is used as a stochastic correlation energy estimator

$$E_{\mathrm{FCIQMC}} = \langle E(\tau)\rangle = \sum_{\mathbf{j}} \langle D_{\mathbf{j}}|H|D_{\mathbf{0}}\rangle \frac{\langle N_{\mathbf{j}}(\tau)\rangle}{\langle N_{\mathbf{0}}(\tau)\rangle}, \tag{8}$$

where $D_{\mathbf{0}}$ is taken as the Hartree-Fock determinant and the sum $\mathbf{j}$ need only be taken over the $\mathcal{O}(N^2M)$ doubly excited determinants of $D_{\mathbf{0}}$.

Typically, the system is initially grown by setting S to some positive value and allowing evolution from a single

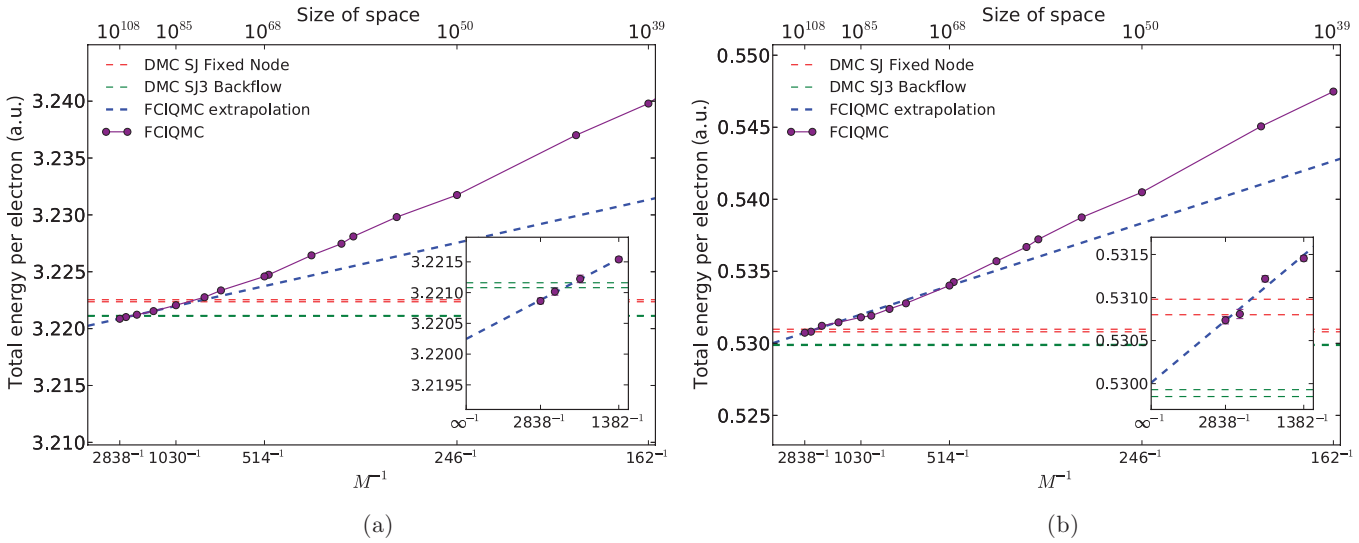

FIG. 3. (Color online) i-FCIQMC total energies for a basis of M spin orbitals for (a) $r_s = 0.5$ a.u. and (b) $r_s = 1.0$ a.u. Each basis set corresponds to a kinetic energy cutoff, with $M = 2838$ corresponding to 208 Ryd at (a) $r_s = 0.5$ a.u. and 52.1 Ryd at (b) $r_s = 1.0$ a.u. Each calculation used 40 million walkers for $r_s = 0.5$ a.u. and 100 million walkers for $r_s = 1.0$ a.u. The blue dashed line is an extrapolation to $M \to \infty$ based on the expected form $1/M$ using the data set with the largest number of walkers, shown with error bars in the inset. The DMC results, taken from Ríos *et al.* (Ref. 6), do not suffer from basis-set error and are shown as two horizontal lines representing the mean plus and minus one standard deviation. Almost identical backflow results can be found for $r_s = 1.0$ a.u. in a study by Kwon *et al.* (Ref. 4).

determinant to allow an unbiased evolution of the population. Only populations above a critical system-dependent size are able to converge to the FCI distribution, and this size scales linearly with the size of the Hilbert space.[13]

In order to alleviate this problem, an adaptation of this method has been developed, called initiator-FCIQMC (i-FCIQMC).[14–16] The determinant space is instantaneously divided into those determinants exceeding a population of n_{add} walkers, termed initiator determinants, and those that do not. When considering a determinant, the current population of which is zero, the sum in the second term of Eq. (7), the term describing net flux of walkers onto that determinant, is taken to be only over initiator determinants. This effectively introduces a survival of the fittest criterion for survival of newly spawned walkers. If a walker has been spawned from a determinant with an instantaneous population exceeding a parameter n_{add}, the child is allowed to survive. However, if the parent walker is a determinant with a population smaller or equal to n_{add}, then the child only survives if it has been spawned to a currently occupied determinant. This i-FCIQMC has been shown to dramatically accelerate the convergence of FCIQMC with respect to walker number. Note that in the large walker number limit, the i-FCIQMC tends to the FCIQMC algorithm, which itself converges rigourously to the FCI energy. Figure 1 illustrates an i-FCIQMC energy calculation in this way. Previous work has shown that the rapid convergence to this limit can be examined by finding correlation energies at increasing walker numbers Fig. 1(b).[16] As the basis set size grows, so the number of walkers required to recover the total energy to a given level of accuracy increases (Fig. 2).

Basis-set extrapolation. Although i-FCIQMC is able to produce exact results in a finite-basis set, these are only upper-bound estimates to the true ground-state energy. This error in the energy, termed the basis-set incompleteness error, is absent in DMC results, which do not have a substantial dependence on a basis set.[21]

Extrapolation of the correlation energy to the complete basis-set limit is performed regularly in molecular systems for which scaling laws have been investigated extensively.[22] In plane-wave systems, a $1/M$ extrapolation is used for the basis-set incompleteness error in methods employing the random phase approximation and second-order Møller-Plesset theory.[23,24] We note that analytic expressions can be derived with these methods for the HEG that also show a $1/M$ relationship. Figure 3 illustrates that by using this fit at high basis-set sizes, complete basis-set exact diagonalization energies can be obtained that compare well with most recent high-accuracy DMC results.[6]

Results and Conclusions. Results of i-FCIQMC calculations performed on the 54-electron gas, for basis sets containing between 162 and 2838 spin orbtials, are shown in Fig. 3 and Table I. In these calculations, Hilbert spaces ranging from 10^{39} to 10^{108} Slater determinants (Fig. 3) were sampled to produce high-accuracy energies for the HEG.

TABLE I. i-FCIQMC total energies for M spin orbitals. The error estimate for the finite-basis corresponds to stochastic error. The $M = \infty$ result is based on extrapolations shown in Fig. 3, from which the error estimate derives.

r_s (a.u.)	FCI $M = 2838$ (a.u. per electron)	FCI $M = \infty$ (a.u. per electron)
0.5	3.22086(2)	3.2202(2)
1.0	0.53073(4)	0.5300(3)

For $r_s = 0.5$ a.u., we obtain a variational finite-basis result that lies below the backflow DMC result. These are observed to be largely free of initiator error, although this error can not as yet be quantified if it is thought to be of the order 10^{-4} a.u. per electron [Fig. 2(a)]. Our extrapolated energy falls significantly below the lowest DMC result found to date, suggesting residual fixed-node error in the backflow DMC energies is of the same order as the backflow corrections themselves. This is a similar amount of energy lowering suggested by variance extrapolation.[4]

For $r_s = 1.0$ a.u., we obtain a finite-basis result that lies just below the fixed-node DMC result, with the extrapolated energy agreeing well with backflow DMC energies. This is in spite of having initiator error, which is below 10^{-3} a.u per electron [Fig. 2(b)], the largest source of error in these results. Nonetheless, these are thought to be upper-bound estimates of the exact energy due to the observed variationality of the initiator error in large basis sets (Fig. 2).

We observe that there is an increase in difficulty in converging the $r_s = 1.0$ a.u. result compared with the $r_s = 0.5$ a.u. result [Figs. 2(a) and 2(b)], which leaves a larger error remaining in the $r_s = 1.0$ a.u. result. We believe this is consistent with increased strength of correlation at lower-density electron gases. We suspect the growing difficulty of the FCIQMC method as r_s is increased, which DMC does not seem to suffer, is due to the use of a Jastrow factor, which aids in a compact wave-function representation compared with a purely multideterminantal expansion. We also note that our computational cost is $\mathcal{O}(10^5)$ core hours and, in comparison, that of modern DMC calculations is $\mathcal{O}(10^2)$.[25] Nonetheless, the strength in FCIQMC method is in its exactness and systematic improvability, and the ability to validate the accuracy of DMC results.

The significance of these results extends beyond the sheer size of the many-electron basis, which is being effectively sampled without error. The fact that the results can be taken as exact in principle within the designated basis set allows them to be used to benchmark other, more approximate, methods in this system. Our method can also easily be extended to examine other properties of the HEG, in particular, momentum distributions and Fermi-liquid parameters, which is the focus of many current studies.[2–6,11]

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