Quantum Monte Carlo Method using Phase-Free Random Walks with Slater Determinants

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We develop a quantum Monte Carlo method for many fermions using random walks in the space of Slater determinants. An approximate approach is formulated with a trial wave function $|\Psi_T\rangle$ to control the phase problem. Using a plane-wave basis and nonlocal pseudopotentials, we apply the method to Be, Si, and P atoms and dimers, and to bulk Si supercells. Single-determinant wave functions from density functional theory calculations were used as $|\Psi_T\rangle$ with no additional optimization. The calculated binding energies of dimers and cohesive energy of bulk Si are in excellent agreement with experiments and are comparable to the best existing theoretical results.

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Quantum Monte Carlo (QMC) methods based on auxiliary fields (AF) are used in areas spanning condensed matter physics, nuclear physics, and quantum chemistry. These methods [1,2] allow essentially exact calculations of ground-state and finite-temperature equilibrium properties of interacting many-fermion systems. The required CPU time scales in principle as a power law with system size, and the methods have been applied to study a variety of problems including the Hubbard model, nuclear shell models, and molecular electronic structure. The central idea of these methods is to write the imaginary-time propagator of a many-body system with two-body interactions in terms of propagators for independent particles interacting with external AF. Averaging over different AF configurations is then performed by Monte Carlo (MC) techniques.

QMC methods with auxiliary fields have several appealing features. For example, they allow one to choose *any* one-particle basis suitable for the problem, and to fully take advantage of well-established techniques to treat independent particles. Given the remarkable development and success of the latter [3], it is clearly desirable to have a QMC method that can use exactly the same machinery and systematically include correlation effects by simply building stochastic ensembles of the independent-particle solutions. Vigorous attempts have been made from several fields to explore this possibility [4–7].

A significant hurdle exists, however: Except for special cases (e.g., Hubbard), the two-body interactions will require auxiliary fields that are *complex*. As a result, the single-particle orbitals become complex, and the MC averaging over AF configurations becomes an integration over complex variables in many dimensions. A phase problem thus occurs which ultimately defeats the algebraic scaling of MC and makes the method scale exponentially. This is analogous to but more severe than the fermion sign problem with real AF [8,9] or in real-space methods [10]. No satisfactory, general approach exists to control the phase problem. As a result, only small systems or special forms of interactions can be treated.

In this Letter, we address this problem. We develop a method for many fermions that allows the use of any one-particle basis. It projects out the ground state by random walks in the space of Slater determinants. The phase problem is eliminated with an approximation that relies on a trial wave function $|\Psi_T\rangle$. We apply the method to electronic systems using a plane-wave basis and nonlocal pseudopotentials, which can be implemented straightforwardly in this method. We calculate the binding energies of Be_2, Si_2, and P_2, and the cohesive energy of bulk Si using fcc supercells consisting of up to 54 atoms (216 electrons). This represents the first application of AF-based QMC to solids. Our results are in excellent agreement with experiments and are comparable to or better than the best existing theoretical results. Particularly worth noting is that our results were obtained with trial wave functions that are single determinants formed by orbitals from density functional theory (DFT) calculations [with the local density approximation (LDA)], with no additional parameters or optimization.

The Hamiltonian for a many-fermion system with two-body interactions can be written in any one-particle basis in the general form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^{N} T_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{i,j,k,l}^{N} V_{ijlk} c_i^\dagger c_j^\dagger c_k c_l, \quad (1)$$

where N is the size of the chosen one-particle basis, and $c_i^\dagger$ and c_i are the corresponding creation and annihilation operators. Both the one-body (T_{ij}) and two-body matrix elements (V_{ijlk}) are known.

To obtain the ground state $|\Psi_G\rangle$ of $\hat{H}$, QMC methods use the imaginary-time propagator $e^{-\tau\hat{H}}$ acting on a trial wave function $|\Psi_T\rangle$: $\lim_{n\to\infty}(e^{-\tau\hat{H}})^n|\Psi_T\rangle \propto |\Psi_G\rangle$. $|\Psi_T\rangle$ must not be orthogonal to $|\Psi_G\rangle$, and we will assume that it is of the form of a single determinant or a linear combination of determinants. The time step τ is chosen to

be small enough so that $\hat{H}_1$ and $\hat{H}_2$ in the propagator can be accurately separated with the Trotter decomposition.

The action on a determinant of the propagator $e^{-\tau\hat{H}_1}$, which is the exponential of a one-body operator, simply yields another determinant. Any two-body operator can be written as a quadratic form of one-body operators: $\hat{H}_2 = -\frac{1}{2}\sum_\alpha \lambda_\alpha \hat{v}_\alpha^2$, where λ_α is a real number and $\hat{v}_\alpha$ is a one-body operator. Thus, the two-body propagator $e^{-\tau\hat{H}_2}$ can be expressed as an integral of one-body propagators of the same form as $e^{-\tau\hat{H}_1}$, via the Hubbard-Stratonovich (HS) transformation [11]:

$$e^{-\tau\hat{H}_2} = \prod_\alpha \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-(1/2)\sigma_\alpha^2} e^{\sqrt{\tau}\sigma_\alpha \sqrt{\lambda_\alpha}\hat{v}_\alpha} \, d\sigma_\alpha \right). \quad (2)$$

Introducing vector representations $\sigma \equiv \{\sigma_1, \sigma_2, \ldots\}$ and $\hat{\mathbf{v}} = \{\sqrt{\lambda_1}\,\hat{v}_1, \sqrt{\lambda_2}\,\hat{v}_2, \ldots\}$, we have the desired form

$$e^{-\tau\hat{H}} = \int P(\sigma) B(\sigma)\, d\sigma, \quad (3)$$

where $P(\sigma)$ is the normal distribution in Eq. (2), and

$$B(\sigma) \equiv e^{-\tau\hat{H}_1/2} e^{\sqrt{\tau}\sigma\cdot\hat{\mathbf{v}}} e^{-\tau\hat{H}_1/2} \quad (4)$$

is a one-body propagator.

The imaginary-time propagation thus requires evaluating the multidimensional integral in Eq. (3) over time slices n and the corresponding auxiliary fields. MC techniques are the only way to evaluate such integrals efficiently. We use a random walk approach [9]. In each step, a walker $|\phi\rangle$, which is a single Slater determinant, is propagated to a new position $|\phi'\rangle$: $|\phi'(\sigma)\rangle = B(\sigma)|\phi\rangle$, where σ is a random variable sampled from $P(\sigma)$. After a sufficient number of steps (iterations), the ensemble of random walkers is a MC representation of the ground-state wave function: $|\Psi_G\rangle \doteq \sum_{\phi'} |\phi'\rangle$.

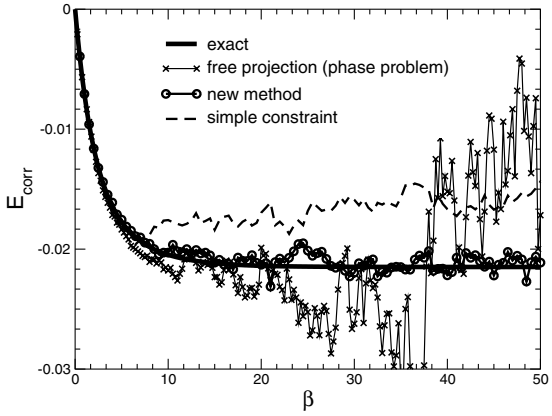

FIG. 1. Illustration of the phase problem and constraints to control it. The total correlation energy (in Ry) of an unpolarized two-electron Jellium system (interacting electrons with a uniform neutralizing background) is shown as a function of projection time $\beta = n\tau$, with $\tau = 0.01\ \mathrm{Ry}^{-1}$. Electrons are in a periodic cell, with density $r_s = 10$. The number of plane waves is $N = 19$. Simple generalization of the constraint that worked well for real determinants leads to poor results. The new method agrees well with exact diagonalization.

The one-body operators $\hat{\mathbf{v}}$ are generally complex, since the λ_α cannot all be made positive in Eq. (2) [12]. As a result, the orbitals in $|\phi\rangle$ will become complex as the projection proceeds, and the statistical fluctuations in the MC representation of $|\Psi_G\rangle$ increase exponentially with projection time $\beta \equiv n\tau$. This is the phase problem referred to earlier. It is of the same origin as the sign problem that occurs when $B(\sigma)$ is real. The phase problem is more severe, however, because for each $|\phi\rangle$, instead of a $+|\phi\rangle$ and $-|\phi\rangle$ symmetry [9], there is now an infinite set $\{e^{i\theta}|\phi\rangle\}$ [$\theta \in [0, 2\pi)$] from which the random walk cannot distinguish. At large β, the phase of each $|\phi\rangle$ becomes random, and the MC representation of $|\Psi_G\rangle$ becomes dominated by noise. This problem is generic, and the same analysis would apply if we had chosen, instead of the random walk, the standard AF QMC sampling approach [2]. In Fig. 1, the curve labeled "free projection" illustrates the phase problem.

Existing fixed-node-type approximations have often worked very well to control the sign/phase problem in real space [13,14] or in determinant space when the propagator is real [9]. The phase problem here is unique because not only do the determinants acquire overall phases, but the internal structures of their orbitals become complex. The real-space analogy would be to have walkers whose coordinates become complex. Straightforward generalization of existing approaches are thus ineffective. For example, similar to the constrained path approximation [9], we could impose the condition $\mathrm{Re}\langle\Psi_T|\phi\rangle > 0$. This does not work well, as shown in Fig. 1 ("simple constraint"). Several variants were tested and they gave similarly poor results [15].

To formulate a new method that can better separate the overall phase from the determinant, we first borrow from the idea of importance sampling [16], although our choice of the so-called importance function, $\langle\Psi_T|\phi\rangle$, is actually *complex*. We modify Eq. (3) to obtain the following new propagator for $|\phi\rangle$:

$$\int \langle\Psi_T|\phi'(\sigma - \bar{\sigma})\rangle P(\sigma - \bar{\sigma}) B(\sigma - \bar{\sigma}) \frac{1}{\langle\Psi_T|\phi\rangle} d\sigma, \quad (5)$$

where we have included a constant shift [5] $\bar{\sigma}$ in the integral in Eq. (3), which does not affect the equality. Equation (5) can be rewritten as

$$\int P(\sigma) W(\sigma, \phi) B(\sigma - \bar{\sigma})\, d\sigma, \quad (6)$$

where

$$W(\sigma, \phi) \equiv \frac{\langle\Psi_T|\phi'(\sigma - \bar{\sigma})\rangle}{\langle\Psi_T|\phi\rangle} e^{\sigma\cdot\bar{\sigma} - (\bar{\sigma}\cdot\bar{\sigma}/2)}. \quad (7)$$

The new propagator in Eq. (6) defines a new random walk. In each step a $\bar{\sigma}$ is determined for each walker $|\phi\rangle$, and the walker is propagated to $|\phi'\rangle$ by $B(\sigma - \bar{\sigma})$:

$$|\phi'(\sigma - \bar{\sigma})\rangle = e^{-\tau\hat{H}_1/2} e^{\sqrt{\tau}(\sigma-\bar{\sigma})\cdot\hat{\mathbf{v}}} e^{-\tau\hat{H}_1/2}|\phi\rangle, \quad (8)$$

where σ is again sampled from $P(\sigma)$. $W(\sigma, \phi)$ is a c number which can be accounted for by having every walker carry an overall weight factor and updating them according to $w_{\phi'} = W(\sigma, \phi) w_\phi$. Formally, the MC representation of $|\Psi_G\rangle$ in the new random walk is

$$|\Psi_G\rangle \doteq \sum_{\phi'} w_{\phi'} \frac{|\phi'\rangle}{\langle\Psi_T|\phi'\rangle}. \quad (9)$$

The optimal choice of $\bar{\sigma}$ is determined by minimizing the fluctuation of $W(\sigma, \phi)$ with respect to σ. This can be done by, for example, substituting Eq. (8) into Eq. (7) and setting $\partial \ln W/\partial\sigma = 0$. To $\mathcal{O}(\sqrt{\tau})$, we obtain

$$\bar{\sigma} = -\sqrt{\tau}\frac{\langle\Psi_T|\hat{\mathbf{v}}|\phi\rangle}{\langle\Psi_T|\phi\rangle}. \quad (10)$$

With this choice we can simplify W by considering $\ln W$ again. Using Eqs. (7) and (8), we can expand $\ln W$ in τ, keeping terms up to $\mathcal{O}(\tau)$. As expected, the leading σ-dependent term, which is of $\mathcal{O}(\sqrt{\tau})$, vanishes and the only remaining term is proportional to σ^2. Noting that $\langle\sigma^2\rangle = 1$, we arrive at the following approximate expression by integrating over σ:

$$W(\sigma, \phi) \doteq \exp\left[-\tau\frac{\langle\Psi_T|\hat{H}|\phi\rangle}{\langle\Psi_T|\phi\rangle}\right] \equiv \exp[-\tau E_L(\phi)], \quad (11)$$

where the term E_L parallels the local energy in real-space QMC methods. Both E_L and the shift $\bar{\sigma}$ in Eq. (10) are independent of any overall phase factor of $|\phi\rangle$.

The weight of the walker in the new random walk is determined by E_L. In the limit of an exact $|\Psi_T\rangle$, E_L is a real constant, and the weight of each walker remains real. The so-called mixed estimate for the energy is phaseless:

$$E_G = \frac{\langle\Psi_T|\hat{H}|\Psi_G\rangle}{\langle\Psi_T|\Psi_G\rangle} \doteq \frac{\sum_{\phi'} w_{\phi'} E_L(\phi')}{\sum_{\phi'} w_{\phi'}}. \quad (12)$$

With a general $|\Psi_T\rangle$ which is not exact, a natural approximation is to replace E_L in Eqs. (11) and (12) by its real part, $\mathrm{Re}\, E_L$. We have thus obtained a phaseless formalism for the random walk, with real and positive weights in Eqs. (9) and (12).

The phase problem is still not completely eliminated, however. The random walk is "rotationally invariant" in the complex plane defined by $\langle\Psi_T|\phi\rangle$. That is, the overlaps of the walkers with the trial function evolve continuously during the random walk through a diffusionlike process. At large time, the walkers will populate the complex plane symmetrically, independent of their initial positions. This means that at the origin, where $\langle\Psi_T|\phi\rangle = 0$, there will be a finite density of walkers. Near the origin the local energy $E_L(\phi)$ diverges, which causes diverging fluctuations in the weights of walkers. Thus, although the phaseless formalism removes the explicit dependence on the phase of the determinant, the phase problem is still present because of the "two-dimensional" nature of the random walk in the complex plane. To break this rotational invariance, we make an additional approximation. We project the random walk to "one dimension" by multiplying the weight of each walker in each step by $\max\{0, \cos(\Delta\theta)\}$, where $\Delta\theta$ is the phase of $\langle\Psi_T|\phi'\rangle/\langle\Psi_T|\phi\rangle$. This *projection* ensures that the density of walkers vanishes at the origin. Note that, when $\hat{\mathbf{v}}$ is real, the projection has no effect as $\Delta\theta = 0$. [In fact, the shift in Eq. (10) is real in that case, and the method reduces to the constrained path Monte Carlo method [9].]

As Fig. 1 illustrates, the new method leads to a large improvement. The ground-state energy computed with Eq. (12) is approximate and is not variational. The systematic and statistical errors depend on $|\Psi_T\rangle$, vanishing when $|\Psi_T\rangle$ is exact. We apply the method to Be, Si, and P atoms and dimers, and to bulk Si supercells. The Be^{2+}, Si^{4+}, and P^{5+} ions are represented by LDA Kleinman-Bylander (KB) nonlocal pseudopotentials (V_{NL}) [17]. We use periodic boundary conditions and a plane-wave basis with a kinetic energy cutoff E_{cut}. Calculations involving $\hat{\mathbf{v}}$ and the local part of the pseudopotential are efficiently handled using fast Fourier transforms. The separable KB form of V_{NL} makes its application as efficient as in LDA codes [15]. Our $|\Psi_T\rangle$ is a single determinant of LDA orbitals generated using ABINIT [18].

In the atom and dimer calculations, periodic cells of size $15 \times 15 \times 20$, $19 \times 19 \times 19$, and $14 \times 14 \times 18$ (in a_B^3) were used for Be, Si, and P, respectively, with corresponding E_{cut} of 25, 12.25, and 36 (in Ry) (12 875 plane waves for P and P_2). The cell size and E_{cut} were chosen such that the resulting errors, systematically analyzed with LDA, were much smaller than the expected QMC statistical errors. The LDA estimates were then confirmed with QMC calculations for selected cases. Table I shows dimer binding energies. Be_2 is challenging because of the small binding energy and near $2s$ and $2p$ degeneracies. A recent pseudopotential AF QMC calculation gave 0.0(2) eV [19], while diffusion Monte Carlo (DMC) with multideterminant trial wave functions gave 0.05(3) eV [20]. P_2 is a difficult case for DMC. With single-determinant (times Jastrow) trial wave functions, pseudopotential fixed-node DMC gave 4.68(1) eV; multideterminant trial wave functions improved the binding energy by about 0.15 eV [21]. These are thus stringent

TABLE I. Binding energies of Be_2, Si_2, and P_2. The molecules were calculated at the experimental equilibrium bond lengths of 4.63, 4.24, and 3.58 (in a_B), respectively. Energies are in eV. Statistical errors are in the last digits and in parentheses.

	Be_2	Si_2	P_2
LDA	0.53	3.879	5.97
QMC	0.07(2)	3.12(8)	5.09(10)
Experiment	0.11(1)	3.21(13)	5.03(2)

TABLE II. Cohesive energy of bulk Si. Calculations are done for fcc supercells with 2, 16, and 54 atoms, at $a_{\text{exp}} = 5.43$ Å. QMC at ∞ is from 54 atoms and includes two finite-size corrections: (i) an independent-particle correction of 0.311 eV from LDA and (ii) an additional Coulomb correction of -0.174 eV from Ref. [23,24]. A zero-point energy correction of -0.061 eV was also added to the calculated results at ∞. Energies are in eV/atom. Statistical errors are in parentheses.

	2	16	54	∞
LDA	-3.962	3.836	4.836	5.086
QMC	$-1.95(5)$	3.79(4)	4.51(3)	4.59(3)
Experiment				4.62(8)

tests. Our results are comparable to or better than the best existing QMC results, and are in good agreement with experimental values (from [19,21,22], and references therein).

Bulk Si results using fcc supercells with 2, 16, 54 atoms (5209 plane waves) are shown in Table II. Our calculation for 54 atoms took several days on 20 Compaq Alpha 667 MHz processors. For the bulk cohesive energy, we first included a correction for the independent-particle finite-size error from the LDA results. We then corrected for the remaining Coulomb finite-size error [25] using the results of Kent *et al.* [23]. Our result is again in excellent agreement with the experimental value (from Ref. [13]). It also compares very well with the result of a recent fixed-node DMC calculation [26], which also used a 54-atom supercell and gave 4.63(2) eV per atom after similar finite-size and zero-point energy corrections.

Our method provides a general framework for treating two-body interactions that can be useful in two complementary approaches to many-fermion systems. For *ab initio* calculations, it provides a QMC approach that can be implemented using the same machinery as in traditional independent-particle methods. For model Hamiltonians, where AF-based QMC has been a major tool, it allows interactions beyond the simple Hubbard type, so more realistic models can be studied. Here we have demonstrated the former. Our approach eliminated the problem with nonlocal pseudopotentials, which in standard real-space DMC has required, in addition to fixed-node, a localization approximation [27] that depends on not just the nodes but the overall quality of $|\Psi_T\rangle$. This has increased the demand on the accuracy of $|\Psi_T\rangle$, and a large number of variational parameters have often been needed [13]. Without an exact solution to the sign/phase problem, reducing the reliance on trial wave functions is clearly of key importance to increasing the predictive power of QMC. Our test results, given the simplicity of $|\Psi_T\rangle$, are therefore especially encouraging.

In conclusion, we have described a method for ground-state QMC calculations that allows the use of any one-particle basis. The method is general and applies to any Hamiltonian of the form in Eq. (1). It provides an approximate way to control the phase problem in all AF-based QMC methods, while allowing many of their advantages to be retained that lead to their applications spanning several areas. We have shown that the method can give accurate results for systems from an atom to a large supercell, using a simple trial wave function.

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