

Nonlocal pseudopotentials and diffusion Monte Carlo

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(Received 6 March 1991; accepted 20 May 1991)

We have applied the technique of evaluating a nonlocal pseudopotential with a trial function to give an approximate, local many-body pseudopotential which was used in a valence-only diffusion Monte Carlo (DMC) calculation. The pair and triple correlation terms in the trial function have been carefully optimized to minimize the effect of the locality approximation. We discuss the accuracy and computational demands of the nonlocal pseudopotential evaluation for the DMC method. Calculations of Si, Sc, and Cu ionic and atomic states and the Si₂ dimer are reported. In most cases ~90% of the correlation energy was recovered at the variational level and excellent estimations of the ground state energies were obtained by the DMC simulations. The small statistical error allowed us to determine the quality of the assumed pseudopotentials by comparison of the DMC results with experimental values.

I. INTRODUCTION

Quantum Monte Carlo (QMC) methods¹ are one of the most promising candidates for determining accurate properties of highly correlated many-electron systems. Until ~5 years ago, QMC methods were applied only to relatively simple systems like liquid helium, the electron gas, solid hydrogen, and molecules with light atoms.^{2,3} Recently, there have been attempts to apply these methods to systems with heavier elements.⁴⁻⁷ Heavy atoms pose a special problem because the energy scale of the chemically inactive core electrons is orders of magnitude larger than that of the valence electrons. This makes it computationally expensive to obtain statistical errors small enough to extract the small valence energy differences from enormous total energies. Moreover the extra degrees of freedom of the core electrons impose additional computational burdens.^{1,3}

Even within single-body methods like local density-functional theory (LDFT) or Hartree-Fock (HF) the core electrons are often replaced by effective-core operators to speed up the calculations. The technique of *ab initio* norm-conserving pseudopotentials is one of the most appealing of such formulations. There exist several tables of pseudopotentials, either from LDFT or HF, and their qualitative properties, at least for some elements, are extensively tested in single-body methods.^{9,10} Unfortunately, the direct use of nonlocal pseudopotentials is possible only within the variational Monte Carlo (VMC) method because the nonlocal character of the effective core Hamiltonian is in direct con-

tradiction with the local character of the algorithms like diffusion Monte Carlo (DMC) and Green's function Monte Carlo which go beyond a variational treatment.¹ We will discuss this point later. To allow QMC calculations of heavier atoms, several new ideas, and methods for doing valence-only calculations have been proposed. For the purposes of briefly reviewing their main features we will divide them into the following three groups.

The first approach modifies the mass tensor of the valence electrons inside the core,⁴ replacing the full-core Hamiltonian with a pseudo-Hamiltonian. The pseudo-Hamiltonian has the great advantage that it is local by definition so that its use requires only a minor modification of the DMC method commonly used. Of the methods we will consider, it is the fastest, since the core degrees of freedom are completely absent and the elementary moves of the Monte Carlo are still simple. Very recently, the application of DMC to solid Si with several hundred electrons was successfully carried out with the pseudo-Hamiltonian.¹¹ Since the pseudo-Hamiltonian has three adjustable radial functions it can exactly reproduce the effect of a nonlocal operator in three angular momentum states, say, the *s*, *p*, and *d* channels. Unfortunately, this is not true in general: whenever there are large differences between the *s*, *p*, and *d* pseudopotentials one has to sacrifice accuracy in constructing the pseudo-Hamiltonian or even worse, it may not be possible to construct a pseudo-Hamiltonian at all¹² because the effective mass tensor of the electron must always be positive definite. Since, in addition, one has to satisfy norm conservation, the range of the pseudopotential differences among the various angular momenta is further constrained.^{12,13} In transition metals atoms, such as Cu, it would be necessary to include all of the electrons down to the Ne-like core for a total of 19 valence electrons to satisfy these constraints. Preliminary calculations with this

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pseudo-Hamiltonian gave very large energy fluctuations and resulting statistical errors were of the order of 1.0 eV as compared to 0.01 eV for a similar Si calculation.

Another approach proposed by Hammond *et al.*⁷ is based upon the plausible argument that large energy fluctuations from the core states are irrelevant for the valence properties. In this “damped-core” scheme the core degrees of freedom are sampled in a variational manner while the valence electrons are simulated by DMC. Energy fluctuations are suppressed but only to a certain extent. In addition, the number of degrees of freedom which has to be sampled is still not reduced resulting in a large overhead in calculations for heavy atoms. Finally there has not yet been an analysis of the transferability of this approach, i.e., what is the effect of the core approximations on energy differences.

In the third approach, which we apply in this paper, one starts with a conventional nonlocal pseudopotential but the nonlocal part is evaluated using an accurate trial function.^{5,6} This results in a local many-body pseudopotential which is amenable to DMC. Until now only two-electron and very recently three-electron¹⁴ systems have been simulated with this method so that accuracy for larger systems has not been tested. In particular, it has not been established that this technique would be reliable for many-fermion systems having large differences between the pseudopotentials in different angular momentum states. In addition, only uncorrelated determinantal trial functions were used in the evaluation of the term with nonlocal pseudopotentials.^{5,6} We remove this additional, unnecessary approximation. In this approach, there is no restriction on the pseudopotentials as there is with the pseudo-Hamiltonian, so that one can eliminate all but the valence electron shell thus reducing the energy fluctuations and the number of degrees of freedom to a minimum. Recently, VMC calculations of solid Si and C containing up to 54 atoms has been carried out with nonlocal pseudopotentials.⁸ The fixed-node DMC method is not much more difficult to apply once accurate trial functions are determined and DMC can remove much of the bias inherent in a strictly variational approach. On the other hand, this nonlocal DMC approach has the disadvantage relative to the pseudo-Hamiltonian approach that it is slower and introduces an additional nonvariational approximation (the calculated energy is not necessarily an upper bound). However, since the error of this approximation can be shown to be second order in the accuracy of the trial function, it can be controlled with careful optimization of the trial function on which the nonlocality is evaluated.

Yoshida and Iguchi¹⁵ also used the pseudopotentials for projecting out the core in DMC. In their approach the nonlocal terms were omitted from the valence Hamiltonian. The authors avoided the collapse of the electrons to the core by using the trial function built from orbitals which were orthogonal to the original core states and obtained reasonable results. But the valence wave function is not a ground state of the valence Hamiltonian without nonlocal terms and DMC simulations with more general trial functions (say, Bijl-Jastrow) would be problematic.

In this paper we apply the nonlocal DMC technique to

demonstrate its accuracy, feasibility, and possible practical limitations for many-fermion systems. Because of its general applicability, this approach offers a route to solve the challenging problems of the electronic structure of transition metal systems.

The organization of the paper is as follows. In the next section we give an outline of the method and attempt to understand the approximations involved in the calculation of the energy. Section III gives the form of the trial functions used and Sec. IV gives the evaluation of the energy terms with the nonlocal pseudopotential. We illustrate the performance of this technique on the Si, Sc, Cu ions and atoms and for the Si₂ dimer. Our results show that accurate trial functions can be constructed so that excellent estimations of the ground state energies can be found for a given pseudopotential. We compare our results to experiment and in some cases to the results of configurational interaction (CI) calculation, used here as an independent check.

II. NONLOCAL PSEUDOPOTENTIALS AND QMC METHODS

In this paper we will assume that there exists a valence Hamiltonian of the form

$$H_{\text{val}} = H_{\text{loc}} + W, \quad (1)$$

where H_{loc} includes the kinetic energy, local pseudopotential, and Coulomb interaction

$$H_{\text{loc}} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i,I} V_{\text{loc}}(r_{iI}) + \sum_{i<j} \frac{1}{r_{ij}} \quad (2)$$

and W is assumed to be nonlocal only in the angular directions⁸

$$W = \sum_{i,I} \sum_{l,m} v_l(r_{iI}) Y_{lm}(\Omega_{iI}) \int d\Omega'_{iI} Y_{lm}^*(\Omega'_{iI}), \quad (3)$$

where v_l is a radial pseudopotential, Y_{lm} is the spherical harmonic, I labels pseudo-ions, i, j refer to electrons, r_{iI} is the distance of the i th electron from the I th pseudo-ion, and Ω_{iI} denotes the corresponding angular variable. The summation over l in Eq. (3) is usually restricted over 2–4 lowest angular momenta.^{9,10}

The use of H_{val} in VMC is straightforward.⁸ Coordinates of N electrons are sampled from $|\Psi(R)|^2$, where $R = (r_1, \dots, r_N)$ denotes $3N$ spatial variables and $\Psi(R)$ is an antisymmetric trial function. The variational energy is defined as

$$E_V = \frac{\int \Psi^*(R) H_{\text{val}} \Psi(R) dR}{\int \Psi^*(R) \Psi(R) dR}. \quad (4)$$

The main complication resulting from the nonlocal Hamiltonian in a variational calculation is the necessity to perform an additional angular integration of the trial function for the operator, W which we will discuss in Sec. IV. This slows down the calculations but Fahy, Wang, and Louie⁸ have shown that simulations with hundreds of electrons are feasible.

However, there is a more fundamental complication with nonlocal potentials in the DMC method. The basis of the DMC method is the imaginary time Schrödinger equation in the integral form¹

$$\Phi(R, t + \tau) = \int G(R, R', t) \Phi(R', \tau) dR, \quad (5)$$

where $G(R, R', t)$ is the Green's function

$$G(R, R', t) = \langle R' | \exp[-t(H_{\text{val}} - E_T)] | R \rangle \quad (6)$$

and E_T is a trial energy. The solution of Eq. (5) at large t is proportional to the ground state wave function. In the DMC method, Eq. (5) is iterated many times using a number of walkers in $3N$ -dimensional space distributed according to $\Phi(R, t)$ and a short-time approximation³ to $G(R', R, t)$. One can avoid making the short-time approximation with the more complex, but very closely related Green's function Monte Carlo method.

The problem with the nonlocal Hamiltonians comes from the fact that, in general, the matrix $\langle R' | \exp(-tW) | R \rangle$ is not positive for arbitrary R, R' , and t . Consequently, the propagator cannot be interpreted as a probability density. This is similar to the problem of the fermion symmetry since the Green's function for fermions has negative pieces also. The problem of DMC simulations of fermions is overcome in two steps. First, a solution³ is found with the nodes constrained to be those of an antisymmetric trial function. This gives a positive Green's function and an upper bound to the exact fermion energy. Then a correction to the energy can be found by the release-node method¹⁶ for systems with relatively good trial functions. Although the fixed-node method is only approximate, it gets rid of most basis set and variational bias and usually gives 95%–99% of the correlation energy. Only the fixed-node method is useful for large (say more than 100 electrons) fermion systems, because the convergence of the release-node method slows down dramatically as the number of fermions increases.

The technique of evaluating the nonlocal part of the Hamiltonian by integrating over a trial function^{5,6} is analogous to the fixed-node way of getting rid of the negative parts of the fermion Green's function. Here we rederive the basic equations, show the character of the approximation, and analyze its impact on the calculated energy.

We start from the imaginary time Schrödinger equation

$$-\frac{\partial \Phi(R, t)}{\partial t} = (H_{\text{val}} - E_T) \Phi(R, t). \quad (7)$$

Multiplying this equation by the trial function $\Psi(R)$ and rearranging the terms one obtains

$$\begin{aligned} \frac{\partial f}{\partial t} = & \frac{1}{2} \sum_i \nabla_i^2 f - \sum_i \nabla_i \cdot (f \nabla_i \ln \Psi) \\ & - \left(\frac{(H_{\text{loc}} - E_T) \Psi}{\Psi} \right) f - \left(\frac{W\Phi}{\Phi} \right) f, \end{aligned} \quad (8)$$

where $f(R, t) = \Psi(R) \Phi(R, t)$. The first three terms in the right-hand side of Eq. (8) can be interpreted as a local diffusion, drifting and branching process.³ However, the last term of Eq. (8), the operation of the nonlocal potential onto the unknown wave function represents a nonlocal branching and we are forced to make a further approximation if we wish to keep the random walk local. We can rearrange it as

$$\begin{aligned} \frac{\partial f}{\partial t} = & \frac{1}{2} \sum_i \nabla_i^2 f - \sum_i \nabla_i \cdot (f \nabla_i \ln \Psi) \\ & - \left[\frac{(H_{\text{val}} - E_T) \Psi}{\Psi} \right] f - \epsilon(R) f, \end{aligned} \quad (9)$$

where

$$\epsilon(R) = \left(\frac{W\Phi}{\Phi} - \frac{W\Psi}{\Psi} \right). \quad (10)$$

The *locality approximation* consists of neglecting the term involving $\epsilon(R)$ so that Eq. (9) becomes formally identical to that one which is used for the cases with local potentials only³

$$\frac{\partial f}{\partial t} = \frac{1}{2} \sum_i \nabla_i^2 f - \sum_i \nabla_i \cdot (f \nabla_i \ln \Psi) - \left[\frac{(H_{\text{val}} - E_T) \Psi}{\Psi} \right] f. \quad (11)$$

The *local model potential* which represents the action of the pseudo-ion(s) on valence electrons is simply: $\sum_{i,l} V_{\text{loc}}(r_{il}) + W\Psi/\Psi$. Then we impose the fixed-node approximation so that f is a non-negative function everywhere. Standard DMC techniques can be used with this local model potential, the only difference being that it is truly many-body in character, not a pairwise additive function. A general discussion of the DMC method of solving Eq. (11) is given in Refs. 1 and 3.

The ground state energy is estimated in DMC in two ways.¹ First, the generational estimate is that value of E_T for which there exists a solution of Eq. (11). Practically this is determined by the value of the trial energy which gives a stable population of random walks. This generational estimate is equal to the mixed estimate of the energy

$$E_A = \frac{\int \Phi_A H_{\text{val}} \Psi dR}{\int \Phi_A \Psi dR}, \quad (12)$$

where Φ_A is determined by the stationary solution of Eq. (11)

$$\Phi_A(R) \propto \lim_{t \rightarrow \infty} f(R, t) / \Psi(R). \quad (13)$$

The energy, E_A and wave function, $\Phi_A(R)$ are approximate because of the neglect of the term with $\epsilon(R)$. Equation (11) becomes exact in the case when the trial function is equal to the exact solution, since as $\Psi \rightarrow \Phi_0$ then $\epsilon \rightarrow 0$, where Φ_0 is the exact stationary solution of Eq. (7). We now show that E_A converges quadratically to the exact value E_0 (corresponding to Φ_0) as $\Psi \rightarrow \Psi_0$. Let us split Ψ and Φ_A into components of Φ_0 parallel to and orthogonal to Φ_0 , supposing that Ψ and Φ_A are normalized,

$$\Psi(R) = \alpha_T \Phi_0(R) + \beta_T \delta_T(R), \quad (14)$$

$$\Phi_A(R) = \alpha_A \Phi_0(R) + \beta_A \delta_A(R), \quad (15)$$

where the constants $\alpha_A, \beta_T, \alpha_A, \beta_A$ fulfill the normalizing equations

$$\alpha_T^2 + \beta_T^2 = \alpha_A^2 + \beta_A^2 = 1 \quad (16)$$

and

$$\int \delta_T^2(R) dR = \int \delta_A^2(R) dR = 1, \quad (17)$$

$$\int \Phi_0(R) \delta_T(R) dR = \int \Phi_0(R) \delta_A(R) dR = 0. \quad (18)$$

As soon as Ψ is reasonably close to Φ_0 , then Φ_A will be close to the exact solution and we expect that $|\beta_A| \ll |\beta_T|$. Now, by the substitution of Eqs. (14) and (15) to Eq. (12), one finds that the energy difference $E_A - E_0$ can be expressed in the form

$$E_A - E_0 = \beta_T \beta_A \frac{\langle \delta_T | H_{\text{val}} - E_0 | \delta_A \rangle}{\langle \Psi | \Phi_A \rangle}. \quad (19)$$

This shows that the convergence is quadratic. Unfortunately, it is not generally true that E_A is an upper bound to E_0 , but E_A must be less than the variational energy, E_V .

The fixed-node approximation and the locality approximation are intimately connected. In fact, if the fixed-node approximation is not made, the model potential will cause large, possibly unbounded fluctuations in the random walks, so that release-node calculations¹⁶ are problematical within the present formalism. One can see this as follows. The approximate eigenfunction, Φ_A is a solution to the Schrödinger equation with the Hamiltonian $H_{\text{loc}} + W\Psi/\Psi$. If the trial function Ψ has nodes, as it must for more than two electrons, then the model potential $\sum_{i,j} V_{\text{loc}}(r_{ij}) + W\Psi/\Psi$ will generally diverge at those places. Near a point on the nodal surface one can separate the coordinates into the normal direction (which we will denote by x) and all the other irrelevant $(3N-1)$ parallel directions. The model potential in the normal direction will have the form $U_0/x + U_1$, where U_0 and U_1 are some constants. By applying the fixed-node boundary conditions we are demanding that the solutions vanish linearly near the nodal surface, which yields stable random walks. It will be very difficult to use this Hamiltonian to determine eigenfunctions with different nodal surfaces because then the wave function no longer vanishes at the place where the model potential diverges. In fermion release-node calculations, one must use a symmetric function to guide the random walks and then use an antisymmetric trial function to project out the fermi component.¹⁶ To perform a release-node calculation with this model potential, one would need to first smooth out the divergence of the model potential. For nonlocal Hamiltonians, in order to completely avoid either the locality approximation or the fixed-node approximation, one is forced to deal with nonlocal random walks, where electrons can instantaneously "hop" from one angle in the core to another angle. This is likely to be a very noisy procedure because random walks carrying positive and negative signs would almost completely cancel.

One might expect that the locality approximation would be more serious than the fixed-node approximation since in the latter case the trial function has to correctly divide the configuration space into a positive and negative region or equivalently specify the nodal surface, a $(3N-1)$ -dimensional object. Mean field solutions coming from HF or LDFT give usually quite reasonable nodes. The locality approximation requires, in addition, that the "error" term $\epsilon(R)$ be small everywhere which means that $\Psi(R)$ has to be close to the true solution on some subspace of the $3N$ -dimensional space. This subspace consists of all regions of configura-

tion space where at least one electron is in the core of an atom (the core is defined as the radial extent of the nonlocal potential). However we note that the magnitude of the locality approximation is proportional to the strength of the nonlocal potential alone and can be minimized by choosing pseudopotentials which minimize the nonlocal part of the potential. In any case, the precision of the trial function, particularly in the core region, is crucial for the success of this method. But, in general, the wave function in the core region is determined by atomic effects which can be accurately calculated.

Since the local model potential is no longer a pair potential, but a many-body function, it might also be thought that it would be more difficult to write down accurate trial functions and, as a consequence, the statistical variance would be much larger than in the case of the pair potential. But the original pseudopotentials have been constructed with an aim to keep the valence wave functions unaltered and smooth and our results show that it is no more difficult to come up with a good function for this nonlocal potential than it is for a pair potential.

III. THE TRIAL FUNCTION

The trial function used in our calculation has the form

$$\Psi = D_1 D_2 \exp \left[\sum_T \sum_{i < j} u(r_{iT}, r_{jT}, r_{ij}) \right], \quad (20)$$

where D_1 and D_2 are Slater determinants of single electron orbitals for spin up and down electrons, respectively. LDFT atomic orbitals obtained by a numerical self-consistent solution of the Kohn–Sham equations on a radial grid were used for the atoms and ions. The Ceperley–Alder¹⁷ exchange–correlation as parametrized by Perdew and Zunger¹⁸ was used. Molecular orbitals were built from a linear combination of atomic orbitals to which a Gaussian, centered at middle of the bond, was added. We used a correlation part, $u(r_{iT}, r_{jT}, r_{ij})$, similar to that proposed by Boys and Handy¹⁹ and recently successfully applied to the first row atoms by Schmidt and Moskowitz²⁰

$$u(r_{iT}, r_{jT}, r_{ij}) = p(\tilde{r}_{iT}) + p(\tilde{r}_{jT}) + s(\tilde{r}_{ij}) + c_8 \tilde{r}_{iT}^2 \tilde{r}_{jT}^2 + c_9 (\tilde{r}_{iT}^2 + \tilde{r}_{jT}^2) \tilde{r}_{ij}^2, \quad (21)$$

where

$$\tilde{r}_{iT} = \frac{r_{iT}}{(1 + br_{iT})}, \quad \tilde{r}_{jT} = \frac{r_{jT}}{(1 + br_{jT})}, \quad (22)$$

and

$$s(y) = c_1 y + c_2 y^2 + c_3 y^3 + c_4 y^4, \quad (23)$$

$$p(y) = c_5 y^2 + c_6 y^3 + c_7 y^4. \quad (24)$$

In some cases (Si^{++} , Si^+ , Cu^+ , Cu , Cu^-) we added the following terms to describe better the correlations in the region near the pseudo-ion where the wave function changes more rapidly,

$$u^*(r_{iT}, r_{jT}, r_{ij}) = u(r_{iT}, r_{jT}, r_{ij}) + d_1 [\exp(-\zeta_1 r_{iT}^2) + \exp(-\zeta_1 r_{jT}^2)] + d_2 [\exp(-\zeta_2 r_{iT}^2) + \exp(-\zeta_2 r_{jT}^2)] \tilde{r}_{ij}^2 + d_3 \exp[-\zeta_3 (r_{iT}^2 + r_{jT}^2)]. \quad (25)$$

This was particularly helpful for Cu because of the strong localization of the d electrons. The presence of the electron–electron–nucleus terms in Eqs. (21) and (25) (i.e., those multiplied by the coefficients c_8 , c_9 , d_2 , and d_3) were found to be just as important for the cases considered here as they were for the all-electron variational treatment of the first row atoms.^{20–22}

The parameter c_1 was determined by the exact cusp condition so that value 0.5 (0.25) was used for unlike (like) spin pairs, respectively.³ All other parameters (b , $c_2 - c_9$, $\zeta_1 - \zeta_3$, $d_1 - d_3$) were optimized with the reweighting method¹ which allows one to quickly judge the effect in the energy or variance of a change in a trial function parameter. A set of N_{conf} configurations, sampled from the square of the trial function, was generated. Then the variational energy and its variance were evaluated as [Eq. (4)]

$$E_V = \frac{1}{N_{\text{conf}}} \sum_{k=1}^{N_{\text{conf}}} \frac{H_{\text{val}} \Psi(R_k)}{\Psi(R_k)}, \quad (26)$$

$$\sigma_H = \left\{ \frac{1}{N_{\text{conf}} - 1} \sum_{k=1}^{N_{\text{conf}}} \left[\frac{H_{\text{val}} \Psi(R_k)}{\Psi(R_k)} - E_V \right]^2 \right\}^{1/2}. \quad (27)$$

The variance of the local energy was minimized with respect to the parameters with a strategy similar to that proposed by Umrigar *et al.*^{21,22} New variational runs were carried out with the new parameters and the whole procedure was repeated until the variance converged.

IV. THE EVALUATION OF $\mathcal{W}\Psi/\Psi$

The numerical integration of the trial function over a sphere to determine the nonlocal pseudopotential energy, $\mathcal{W}\Psi/\Psi$, is the main computational difference between this method and those with local Hamiltonians. One simply has to determine the relative change in the trial function as one electron is rotated about the nearest ion. For notational convenience we discuss the situation with only one ion at the origin. The quantity $\mathcal{W}\Psi/\Psi$ is the sum of one-electron terms [see Eq. (3)] and the contribution from i th electron is given by⁸

$$\left(\frac{\mathcal{W}\Psi}{\Psi} \right)_i = \sum_{\Gamma} \frac{(2l+1)}{4\pi} v_l(r_i) \times \int_{4\pi} P_l[\cos(\theta'_i)] \frac{\Psi(r_1, \dots, r'_i, \dots, r_N)}{\Psi(r_1, \dots, r_i, \dots, r_N)} d\Omega'_i, \quad (28)$$

where P_l denotes a Legendre polynomial and the axes orientation is such that the i th electron is on the z axis. Hammond *et al.*⁵ developed the formulas to integrate exactly a pure determinantal trial function. While exact integration may be somewhat faster, we believe it is better to allow the full many-body trial function to determine the local model potential and perform the above integral numerically.

We have investigated a number of quadrature rules for a sphere, either of the Gaussian type (both weights and position of the points are optimized), or Chebyshev type (weights are equal, only positions of the points are optimized).^{23–26} Their deviation is based on the properties of the tetrahedron, octahedron or icosahedron rotation groups and they are exact for the integration of spherical harmonics Y_{lm}

with $l < l_{\text{exact}}$ (l_{exact} is the order of the rule). With any quadrature rule, one can choose how to orient the axes and thereby place the quadrature points. If the orientation of the axes is chosen randomly then the result is an unbiased Monte Carlo estimation of the two-dimensional integral, Eq. (28). We have used this property for testing quadrature formulas on the Si atom (s^2p^2 , 3P) and Cu^+ ion (d^{10} , 1S) using the LDFT s and p pseudopotentials (see Sec. V for details) and our optimized VMC trial functions. We have investigated the accuracy of a given rule by repeatedly randomizing the axes' orientation homogeneously over the sphere⁸ and finding the rms error of the nonlocal pseudopotential contribution

$$\sigma_{\mathcal{W}}(N_p) = \left\{ \frac{1}{N_{\text{conf}} - 1} \sum_{k=1}^{N_{\text{conf}}} \left[\left\langle \frac{W_{N_p} \Psi(R_k)}{\Psi(R_k)} \right\rangle - \left\langle \frac{W_{N_p} \Psi(R_k)}{\Psi(R_k)} \right\rangle^2 \right]^2 \right\}^{1/2}, \quad (29)$$

where the index N_p means that the integrals (28) in $\mathcal{W}\Psi/\Psi$ were replaced by the N_p point quadratures, the angle brackets denote averaging over the quadrature points orientation, and k labels the configuration of electrons sampled from $\Psi^2(R)$. Table I shows the parameters and symmetries of the tested rules while Fig. 1 shows the rms error as a function of N_p . First, one sees that the error decreases asymptotically as const/N_p^2 , with the same power as the trapezoidal rule on a line segment. One might have thought that the error would decrease exponentially fast, but the trial functions have non-analytic points when two electron positions are coincident and it is likely that these control the asymptotic error. Second, the errors are one hundred times larger for Cu^+ because the pseudopotentials are about an order of magnitude stronger compared with Si.⁹ However, the contribution of $\mathcal{W}\Psi/\Psi$ to the total energy is, in fact, smaller for Cu^+ than for Si because the d -electron contribution with s and p pseudopotentials is relatively small. (If only the determinantal part of the trial function was used for the evaluation of $\mathcal{W}\Psi/\Psi$, this contribution would be zero.)

Because the high accuracy rules are computationally very demanding we have carried out some preliminary cal-

TABLE I. The parameters and symmetries of the selected quadrature rules for a sphere (Refs. 23–26) together with the nonlocal pseudopotential evaluation errors for Si atom and Cu^+ ion. N_p is the number of quadrature points, l_{exact} is the order of the rule, the next column shows the symmetry group and the errors $\sigma_{\mathcal{W}}$ were estimated by Eq. (29). The weights and points of the rules are listed in the Appendix.

N_p	l_{exact}	Group	$\sigma_{\mathcal{W}}$ (Si)	$\sigma_{\mathcal{W}}$ (Cu^+)
4	2	Tetrahedron	0.075	53.4
6	3	Octahedron	0.016	2.18
12	5	Icosahedron	0.001 9	0.19
18	5	Octahedron	0.001 2	0.12
26	7	Octahedron	0.000 43	0.035
32	9	Icosahedron	0.000 21	0.016
50	11	Octahedron	0.000 094	0.007 3
194	23	Octahedron	0.000 007 5	0.000 70

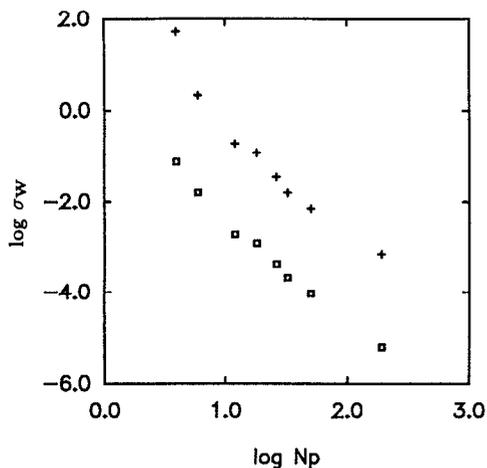


FIG. 1. The error of the nonlocal pseudopotential evaluation σ_W [Eq. (29)] as a function of the number of quadrature points N_p (+ is for Cu⁺ ion, □ is for Si atom).

culations to see the impact of the integration rule on energy averages. We have found that the systematic errors of the medium accuracy (18- or 26-point) octahedron rules were smaller than the statistical errors of VMC and DMC estimations even if the orientation of the quadrature points was not randomized (the octahedron vertices were fixed on the axes and the p and d orbitals were in their “natural” orientation: $p_x, p_y, p_z, d_{xy}, d_{yz}, \dots$). In order to minimize the computer time we have used the fixed 18-point rule. For a few cases we checked the VMC and DMC results with the fixed 26- and 50-point rules and by 18-point rule with randomized orientation. The weights and points for rules with $4 < N_p < 50$ are listed in the Appendix.

In VMC, whichever rule is used, the estimate of the energy will be unbiased, as long as the orientation of the points is occasionally randomized. However, the efficiency of the calculation and the calculation of the variance of the local energy will be affected by the accuracy of the rule. The efficiency of a Monte Carlo estimation η measures the rate of decrease of the statistical error with computer time and we can roughly model its dependence on the integration rule as

$$\eta^{-1} \propto [1 + \sigma_W^2(N_p)/\sigma_H^2] (1 + \tau_W N_p), \quad (30)$$

where the first factor is proportional to the relative increase in variance and the second factor is the relative increase in computer time due to the nonlocal pseudopotential evaluation [σ_H is the local energy variance given by Eq. (27) provided $\mathcal{W}\Psi/\Psi$ is evaluated with negligible error and τ_W represents the computer time increase per quadrature point.] Performing some preliminary calculations it is easy to find the optimal N_p which minimizes η^{-1} . In our case the parameter τ_W was ≈ 0.1 and the optimal values were $N_p = 6$ for Si and $N_p = 12$ for Cu⁺. From Eq. (30) and Fig. 1 it is also clear that one will always gain more increasing the order of the rule than by simply resampling the axes as was suggested in Ref. 8 because in this case the error decrease is much slower.

However, for stable minimization of σ_H with respect to

trial function parameters with the reweighting method we require that the evaluation of the nonlocal terms is sufficiently accurate so that ratio of $\sigma_W(N_p)$ to σ_H should be ≈ 0.1 or smaller. This requirement is satisfied by the 6-point rule in Si and the 18-point rule in Cu⁺.

In DMC, the error of the nonlocal pseudopotential evaluation can bias the results if it is too large, since branching is a nonlinear operation.³ Let us suppose that the error in the integration formula for a given configuration R is $\omega(R)$. Clearly $\langle \omega(R) \rangle = 0$ and $\langle \omega^2(R) \rangle = \sigma_W^2(R)$ where the averaging is over the orientation of the axes. Let us assume that $\omega(R)$ is a normally distributed random variable. Then the bias in the branching in one time-step Δt can be exactly evaluated

$$\langle \exp[-\Delta t \omega(R)] \rangle = \exp[(\Delta t)^2 \sigma_W^2(R)/2]. \quad (31)$$

If the axes are randomized after each step, this will be the only bias introduced into the algorithm. Its effect is to enhance the density at places in configuration space where there is a large quadrature error. Clearly it is important to keep $\Delta t \sigma_W \ll 1$ where σ_W is configurational average of $\sigma_W(R)$. This condition is easily fulfilled in our calculations (see Sec. V for the values of the DMC time steps). In principle, one should require this inequality at all points R but the use of the average error and the assumption of Gaussian statistics is probably qualitatively justified with accurate integration formula. Equation (31) suggests that the approximate evaluation of the nonlocal potential introduces a time step error of order $(\Delta t)^2$. In Green's function Monte Carlo one can completely eliminate the time step bias as long as one can find an upper bound to the quadrature error, since in that algorithm the potential appears linearly.¹

In actual simulations we have found that because of the nonlocal term evaluations the computer time for atoms and ions was increased roughly by a factor of 3 (for molecules more). Furthermore, for large systems of itinerant electrons, containing in excess of 200 electrons, the computer time will be dominated by the updating of the inverse Slater determinant which is proportional to N^3 while the angular integration is proportional to N^2 (to find all of the changed pair correlation factors) so that asymptotically the angular integration will impose a relatively small computational burden.

V. RESULTS

For all the results to be described here we have used the standard norm-conserving pseudopotentials generated by LDFT.⁹ The local pseudopotential was chosen to be that of the d pseudopotential and the differences $v_s(r) - v_d(r)$, $v_p(r) - v_d(r)$ were used as the s, p nonlocal pseudopotentials, respectively. Our simulations were nonrelativistic but the pseudopotentials were generated within the relativistic version of LDFT.⁹ The time steps of the DMC simulations were 0.01, 0.0025, and 0.0005 (a.u.) for the Si, Sc, and Cu systems, respectively. Other practical details of the DMC simulations of Eq. (11) are described, e.g., by Reynolds *et al.*³

For some cases we computed HF and CI energies with the valence Hamiltonian [Eqs. (1)–(3)]. The HF results were obtained by solving the HF equations on a radial mesh

TABLE II. The total valence energies (a.u.) of selected ions, atoms, and Si₂ molecule as computed with the LDFT pseudopotentials (Ref. 9). HF, VMC, DMC, and CI denote the Hartree-Fock, VMC, fixed-node diffusion Monte Carlo, and restricted configurational interaction methods, respectively. σ_H is the VMC variance of the local energy [Eq. (27)]. The statistical errors are given in the parentheses.

	HF	VMC	DMC	CI	σ_H
Si ⁺⁺	-2.8454	-2.8919(1)	-2.8940(4)	-2.8951	0.10
Si ⁺	-3.4328	-3.4985(5)	-3.5035(7)	-3.5049	0.13
Si	-3.7188	-3.7976(7)	-3.8065(4)	-3.8071	0.14
Si ⁻	...	-3.8495(2)	-3.8587(9)	...	0.15
Si ₂	...	-7.693 (2)	-7.733 (2)	...	0.31
Sc ⁺ (¹ D)	-1.3553	-1.3755(3)	-1.3792(6)	-1.3793	0.09
Sc ⁺ (³ D)	-1.3799	-1.3832(1)	-1.3847(4)	-1.3847	0.05
Sc	-1.5785	-1.6093(4)	-1.6251(6)	-1.6244	0.12
Cu ⁺	-47.656	-48.346(3)	-48.457(3)	...	1.2
Cu	-47.923	-48.653(3)	-48.782(4)	...	1.2
Cu ⁻	...	-48.689(3)	-48.839(4)	...	1.2

by standard methods. The CI computations restricted to single and double substitutions were carried out using the following basis functions for each calculation: (1) the HF orbitals; (2) orbitals from other configurations; and (3) orbitals obtained by multiplying the HF orbitals by the powers of radius and simple exponentials (used to compress them radially). All orbitals were orthogonalized to each other and had the correct leading powers. The above basis set gave typically all but 2–3% of the correlation energy in the lightest elements in full-core CI tests.

In the silicon case we have studied following ground states: Si⁺⁺ - $s^2(^1S)$, Si⁺ - $s^2p(^2P)$, Si - $s^2p^2(^3P)$, Si⁻ - $s^2p^3(^4S)$, and Si₂ - (³Σ_g⁻) at the equilibrium distance. The fixed-node energies together with the results from other methods are shown in Table II while comparison with experiment is given in Table III. Our optimized trial function parameters and LDFT orbitals on a coarse radial grid for the neutral atom are given in Tables IV and V. From the comparison with VMC and CI results it is clear that our trial functions recover ~90% of the correlation energy for atomic and ionic cases variationally and DMC usually recovers additional ~6–9%. In no instance is the DMC energy signif-

icantly lower than the CI energy (which is an upper bound to the exact energy). For the dimer the variational estimation has ~80% of the binding energy. The comparison with experiment is favorable in all cases although a small over-binding tendency of the pseudopotentials is visible. The values for the Si systems are quite similar to those obtained by the pseudo-Hamiltonian technique. The pseudo-Hamiltonian is slightly different from the pseudopotentials used here but one expects the differences to be small. For example, the pseudo-Hamiltonian release-node values for the energy of Si atom and Si₂ dimer are -3.8060(6) and -7.730(3), respectively.

In the case of Sc (the first transition metal atom) we computed Sc⁺ - $sd(^3D)$, Sc⁺ - $sd(^1D)$, and Sc - $s^2d(^2D)$ states. The trial function for the neutral atom was slightly less accurate than in the case of silicon. Perhaps this is due to an inadequate treatment of the correlation of electrons far away from the core. Nevertheless, the DMC results are in excellent agreement with those of CI. The comparison with experiment reveals the difficulties with using pseudopotentials to correctly calculate singlet-triplet splittings. (This is discussed in more detail elsewhere.²⁷)

To demonstrate that this method is capable of obtaining accurate results on large and more complicated systems we

TABLE III. Comparison of the energy differences from Table II with experiment (Refs. 29 and 30). IP and EA denote ionization potential and electron affinity of the atom, respectively, and E_B denotes the binding energy of the molecule.

	VMC	DMC	CI	Experiment
Si II. IP	0.6066(5)	0.6095(8)	0.6098	0.6007
Si I. IP	0.2991(9)	0.3030(8)	0.3022	0.2995
Si EA	0.0519(7)	0.0522(9)	...	0.0509
Si ₂ E _B	0.098 (2)	0.120 (2)	...	0.119
Sc ⁺ ³ D - ¹ D	0.0077(3)	0.0056(7)	0.0055	0.0118
Sc I. IP	0.2261(4)	0.2404(7)	0.2397	0.2403
Cu I. IP	0.307 (4)	0.325 (5)	...	0.283
Cu EA	0.036 (4)	0.057 (6)	...	0.045

TABLE IV. The optimized parameters of the correlation part of the trial function for Si and Cu. [Part of the variational parameters was not used for the Si atom (see Sec. III).]

Parameter	Si	Cu	Parameter	Si	Cu
c ₂	0.217 645	0.032 393	b	0.6	1.0
c ₃	0.034 826	-0.114 322	d ₁	0	0.157 575
c ₄	0.053 110	0.009 519	d ₂	0	-0.123 344
c ₅	-0.169 575	-0.031 701	d ₃	0	-0.286 816
c ₆	0.121 175	-0.091 222	ξ ₁	0	0.929 193
c ₇	-0.160 007	-0.212 868	ξ ₂	0	1.581 60
c ₈	0.106 469	-0.158 906	ξ ₃	0	0.842 634
c ₉	-0.045 930	0.175 737			

TABLE V. Radial parts of the one-particle LDFT orbitals for Si and Cu used in the determinantal part of the trial function. r denotes radius (a.u.) and s, p, d , denote orbitals of corresponding atoms.

r	s (Si)	p (Si)	s (Cu)	d (Cu)
0.000	0.190 30	0.000 00	0.109 44	0.000 00
0.100	0.193 08	0.036 73	0.110 74	0.738 58
0.137	0.195 49	0.050 17	0.111 80	1.213 58
0.187	0.200 02	0.068 48	0.113 74	1.775 44
0.256	0.208 52	0.093 28	0.117 35	2.175 49
0.350	0.224 49	0.126 61	0.124 38	2.212 92
0.478	0.254 34	0.170 54	0.138 44	1.949 02
0.654	0.308 46	0.225 94	0.165 59	1.476 00
0.894	0.394 20	0.288 49	0.213 18	0.960 03
1.223	0.473 50	0.339 63	0.281 84	0.545 41
1.673	0.438 17	0.340 91	0.324 67	0.276 44
2.287	0.288 76	0.269 63	0.274 39	0.125 96
3.128	0.136 15	0.165 54	0.172 63	0.050 49
4.278	0.044 45	0.078 36	0.081 83	0.016 94
5.850	0.009 27	0.027 33	0.027 80	0.004 39
8.000	0.001 09	0.006 49	0.006 21	0.000 79

have studied the copper atom and its ions: $\text{Cu}^+ - d^{10}(^1S)$, $\text{Cu} - sd^{10}(^2S)$, $\text{Cu}^- - s^2d^{10}(^1S)$. In this atom the d electrons are strongly localized in a relatively small region of space so that very small time step (0.0005 a.u.) has to be used for the DMC simulations. Taking into consideration all the complications (many electrons, strong pseudopotentials, relatively large total energies, etc.) the results are encouraging, with error bars small enough, 0.004 a.u., to be chemically interesting. Our trial functions were remarkably good, obtaining in VMC $\sim 80\%$ of the correlation energy (if we consider that our DMC results have more than 95% of the correlation energy). The variational parameters and orbitals for the Cu atom are given in the Tables IV and V. The comparison with the experiment is not as good as it was, for example, in the Si case. There are two possible sources for the difference. We believe the major error comes from the inadequacy of the LDFT pseudopotentials for transition elements on the right half of the Periodic Table^{9,28} which can in principle be systematically improved.^{27,31,32} It is possible that a small part of the discrepancy is due to the two approximations used in this method, the fixed-node approximation and the locality approximation. Obviously, further improvement of the trial function is highly desirable to minimize these systematic errors and the statistical error.

VI. DISCUSSION AND CONCLUSIONS

Our results demonstrate that the DMC simulations with the local model potential gives a realistic description of valence electronic structure, but there is still room for further significant improvement. At a fundamental level, it has by no means been shown that the valence Hamiltonian of the form that we have assumed in Eqs. (1)–(3) is adequate for all atoms in the Periodic Table. We expect that the ability to compute accurate energies for this valence Hamiltonian will aid in understanding the limits of the pseudopotential method and in constructing pseudopotentials that can be used in many-electron theory. From this point of view the

DMC method with locality approximation is a valuable tool for the development and testing of the new generation of pseudopotentials. It is clear that one needs to seriously reconsider the methods for constructing the pseudopotentials which are accurate for both ground and excited states, and this work is already in progress.²⁷

It would be of great help to shorten the range of the nonlocal pseudopotentials. For example, for Si, small but non-negligible differences between the s, p , and d pseudopotentials of Bachelet, Hamann, and Schlüter⁹ persist up to the distance almost 3.0 a.u. from the pseudo-ion while the effective core radius is only ≈ 2.0 a.u. Obviously, this is more an artifact of the procedure used for the generation of the pseudopotentials than a real physical effect. The generation of pseudopotentials is notoriously nonunique but the flexibility in their construction can be used to minimize the nonlocality. It is of course possible to use an effective mass tensor in a certain region of the core, as is done in pseudo-Hamiltonian, to further minimize the nonlocality. The shorter range of pseudopotentials immediately means faster simulations and probably easier construction of the trial functions, and hopefully, better transferability of the pseudopotentials.

Finally, the improvement of the trial functions is an important issue for further progress with this technique, but this is true also for other QMC methods as well. Fortunately, there has been progress in recent years in this direction.^{19–21} We believe that a more systematic description of the correlation effects missing from the present trial function will improve the accuracy of the locality approximation, the fixed-node approximation, and the statistical error. For the cases where near-degeneracy effects are significant, it has been shown both within all-electron²¹ and pseudopotential⁶ approaches that the use of multiconfigurational trial functions is necessary for obtaining accurate results. In the nonlocal pseudopotential treatment of the Be atom, Christiansen⁶ found that the multiconfigurational trial function gave significantly lower energy and smaller variance when compared with the simple one-determinant trial function.

In conclusion, we have shown that rather accurate trial functions can be constructed for the cases of valence Hamiltonians with nonlocal pseudopotentials. Using these trial functions and nonlocal pseudopotentials, fixed-node DMC gave excellent values of the ground state energies, obtaining $> 95\%$ of the correlation energy. The DMC simulations were stable and feasible even for relatively complicated cases like atomic Cu. The statistical errors of this approach were small enough so that the systematic errors coming from the assumed pseudopotentials were dominant. This technique opens new possibilities for the use of QMC on transition metal systems.

ACKNOWLEDGMENTS

Many useful discussions with Professor R. M. Martin, Professor G. B. Bachelet, and Dr. M. Caffarel are gratefully acknowledged. This work was supported by NSF Grant No. DMR 88-08126 and Department of Energy Grant No. DEFG02-91ER-45439 and by the Department of Physics at the University of Illinois at Urbana-Champaign. One of us

(E.L.S.) is supported through a graduate fellowship from the Fannie and John Hertz Foundation.

APPENDIX

In this Appendix we list the weights and points of Gaussian quadratures for the integration on a unit sphere which were used for the evaluation of nonlocal pseudopotential term (see Sec. IV and Table I).

(a) Tetrahedron symmetry quadrature.²⁴ The integral J of the function f defined on the unit sphere is approximated as

$$J = \frac{1}{4\pi} \int_{4\pi} f(\Omega) d\Omega \cong A \sum_{i=1}^4 f(a_i)$$

and the Cartesian coordinates of the points are given by $a_i = [q, q, q]$, $[q, -q, -q]$, $[-q, q, -q]$, $[-q, -q, q]$, $q = 1/\sqrt{3}$, while the weight $A = 1/4$.

(b) Octahedron symmetry quadratures.²³⁻²⁶ We express the quadratures in a following form:

$$J = \frac{1}{4\pi} \int_{4\pi} f(\Omega) d\Omega \cong A \sum_{i=1}^6 f(a_i) + B \sum_{i=1}^{12} f(b_i) + C \sum_{i=1}^8 f(c_i) + D \sum_{i=1}^{24} f(d_i)$$

and the Cartesian coordinates of the points are given by $a_i = [\pm 1, 0, 0]$, $[0, \pm 1, 0]$, $[0, 0, \pm 1]$, $b_i = [\pm p, \pm p, 0]$, $[\pm p, 0, \pm p]$, $[0, \pm p, \pm p]$, $p = 1/\sqrt{2}$, $c_i = [\pm q, \pm q, \pm q]$, $q = 1/\sqrt{3}$, $d_i = [\pm r, \pm r, \pm s]$, $[\pm r, \pm s, \pm r]$, $[\pm s, \pm r, \pm r]$, $r = 1/\sqrt{11}$, $s = 3/\sqrt{11}$. The weights for the rules labeled by the (total) number of points N_p are as follows: $N_p = 6$: $A = 1/6$, $B = C = D = 0$, $N_p = 18$: $A = 1/30$, $B = 1/15$, $C = D = 0$, $N_p = 26$: $A = 1/21$, $B = 4/105$, $C = 27/840$, $D = 0$, $N_p = 50$: $A = 4/315$, $B = 64/2835$, $C = 27/1280$, $D = 14\,641/725\,760$. Very accurate rules of higher orders are tabulated in Refs. 25 and 26.

(c) Icosahedron symmetry quadratures.²⁴ The quadratures are expressed in the form

$$J = \frac{1}{4\pi} \int_{4\pi} f(\Omega) d\Omega \cong A \sum_{i=1}^2 f(a_i) + B \sum_{i=1}^{10} f(b_i) + C \sum_{i=1}^{20} f(c_i)$$

For the notational convenience we will write the points in spherical coordinates $[\theta, \varphi]$, $a_i = [0, 0]$, $[\pi, 0]$, $b_i = [\arctan 2, 2k\pi/5]$, $[\pi - \arctan 2, (2k + 1)\pi/5]$, $k = 0, 1, 2, 3, 4$, $c_i = [\theta_1, (2k + 1)\pi/5]$, $[\theta_2, (2k + 1)\pi/5]$, $[\pi - \theta_1, 2k\pi/5]$, $[\pi - \theta_2, 2k\pi/5]$ $k = 0, 1, 2, 3, 4$, where

$$\theta_1 = \arccos \frac{2 + \sqrt{5}}{(15 + 6\sqrt{5})^{1/2}},$$

$$\theta_2 = \arccos \frac{1}{(15 + 6\sqrt{5})^{1/2}}.$$

The weights are as follows: $N_p = 12$: $A = B = 1/12$, $C = 0$,

$N_p = 32$: $A = B = 5/168$, $C = 27/840$. Higher order rules of this symmetry can be found in Ref. 24.

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