VARIATIONAL MONTE CARLO IN SOLIDS

S. FAHY
Department of Physics,
University College Cork, Ireland

Abstract. Physical and computational issues related to correlated Jastrow-Slater wavefunctions for the electrons in solids are discussed. The physics of short- and long-range correlation terms in the Jastrow factor is reviewed. The representation and evaluation of single-particle orbitals is also discussed. Pseudopotentials are used to give a separation of valence and core electron degrees of freedom so that QMC methods can then be used to treat the correlation of valence electrons only. Methods for the evaluation of non-local, angular-momentum-dependent pseudopotentials, along with general methods for the evaluation of local potentials in periodically extended systems are presented. The use of modified boundary conditions and electron-electron interactions for the reduction of finite-size effects is briefly discussed. Applications of these methods to the calculation of cohesive energies, correlation functions, and Compton profiles for solids are reviewed.

1. Introduction

In this chapter, I will discuss technical and computational issues with are of specific interest when one applies variational Monte Carlo methods to the electronic structure of periodic solids. Many of the issues will also be of practical or qualitiative relevance to the calculation of electronic energies in other systems too: e.g., pseudopotentials are frequently used in atomic and molecular calculations; the evaluation of the many-body hamiltonian in a periodic system must also be tackled in diffusion Monte Carlo calculations for solids; and qualitative issues related to the form of the correlated wavefunctions which are used in solids are also relevant for variational calculations of atoms and molecules. The Monte Carlo sampling methods for the evaluation of many-particle integrals throughout the variational approach are discussed at length elsewhere in this volume.

The quality of any variational calculation depends crucially on the form of wavefunction used. A physical understanding of the nature the mean-field behavior and of correlation in the system under study is of great help in constructing a suitable form for the trial variational wavefunction. For solids, LDA and Hartree-Fock wavefunctions have already provided considerable insight into the mean-field behaviour, and correlation factors from the uniform electron gas provide a useful starting point for correlation factors in many real, inhomogeneous solids. Indeed, it is rather remarkable how well one can do with such approximate wavefunctions [1] which I will discuss below. For more accurately determined wavefunctions, methods such as direct energy and variance minimization, as well as indirect energy minimization by Monte Carlo solution of the associated Euler-Lagrange equations have been applied to solids as well as other systems.

The computational tractability of the variational many-electron wavefunction approach depends not only on our ability to construct suitable, accurate wavefunctions, but also on our ability to evaluate these wavefunctions and their physical properties (e.g. their energy) accurately and efficiently. The use of pseudopotentials to describe the interaction between the ionic cores and the valence electrons is particularly important here. I will also discuss the efficient evaluation of single-particle wavefunctions for solids and Ewald summation methods for the calculation of interactions in periodic systems.

The variational Monte Carlo method, as applied to quantum mechanical many-body problems in extended systems (the forerunner of applications in solids), was pioneered by McMillan [2] to study liquid ^{4}He and first applied to fermion problems by Ceperley, Chester, and Kalos [3]. Prior to the introduction of pseudopotential methods to quantum Monte Carlo work, the Green's function quantum Monte Carlo approach to the many-electron problem had been applied very successfully to the electron gas [4], to light molecules [5], and solid hydrogen [6]. However, a straightforward application of the method to materials, with fully realistic treatment of the ionic potentials containing heavier atoms is severely hampered by the very rapid growth in the required computation time with increasing atomic number [7,8]. This growth is caused primarily by the fluctuations in the energies of electrons in the core region. The motivation to overcome this restriction on quantum many-body calculations is high, especially for strongly correlated electronic systems with d- and f-electrons that are of major current interest and importance. Even in condensed matter systems where the electronic structure can be said to be reasonably well understood, the standard approach of local keyworddensity functional theory [9] (LDA) had consistently failed to give accurate binding energies [10] although other structural properties were generally in good agreement with experiment.

A natural scheme for solving (or at least avoiding) the problems associated with Monte Carlo calculations for the heavier elements is to factor out in some manner the relatively inert core electrons, leaving only the chemically active valence electrons to be treated in the Monte Carlo simulation. This idea of treating the valence behavior only of solids has traditionally been implemented in single-particle theories (e.g., in local density functional theory) by the pseudopotential or effective core potential approach [11-14]. Using pseudopotentials, the effective atomic number is reduced by including the inert core electrons with the nucleus and treating the interaction of the valence electrons with the core and nucleus combined via an effective potential. The "atomic charge" associated with the pseudopotential is approximately that of the nucleus plus the core electrons, rather than that of the nucleus alone. Thus, in the case of silicon, for example, the effective "atomic charge" for the system is reduced from 14 to 4.

However, in the standard pseudopotential approach, the price paid for this removal of the core electrons from the problem is that the resulting effective potential is angular momentum dependent [11]. Angular momentum dependence has usually been achieved by allowing a pseudopotential which involves angular momentum projection operators and which is thus non-local in the angular coordinates. Such a non-local potential poses severe problems for the Green's Function Monte Carlo approach and substantial effort has been made to try to circumvent this non-locality in various ways in the Green's Function QMC method [8,15-18]. Within the conceptually and computationally simpler variational Monte Carlo approach, the non-locality of the pseudopotential poses less of a problem. As in all variational methods, the applicability of this approach hinges largely on one's ability to employ trial wavefunctions sufficiently accurate for the level required in estimating the energy (or other quantities) associated with the ground state of the many-body system. In this regard, the conceptual and technical machinery of standard band-structure methods for generating accurate single-particle wavefunctions and charge densities proves to be a very important ingredient. An accuracy can be achieved in calculating the binding energy of carbon- and silicon-based systems which is substantially better than that achieved by density functional theory within the local density approximation and close to that obtained in Green's Function Monte Carlo calculations.

With the combination of non-local pseudopotentials and appropriate variational wavefunctions for solids and atoms, the range of practical applicability of the QMC method for many-fermion systems can be extended to real solid-state systems involving heavier ($Z > 2$) elements. Overall, with our present class of variational Jastrow-Slater wavefunctions, the results indicate that the method can obtain 80-95% of the valence electron correlation energies in many atomic and solid state systems involving s and p electrons.

Because any Monte Carlo calculation must be carried out for a system with a finite number of particles, the infinite periodic solid must be approximated by a finite system. The usual approach is to use a finite simulation region but impose periodic boundary conditions to reproduce the properties of the infinite system as well as possible. This approach is approximate and the correction of finite-size errors is important to the use of Monte Carlo methods for solids. Considerable progress has been made recently in the reducing finite-size errors by the use of generalized periodic boundary conditions [19,20] and modified forms of the effective electron-electron interaction [21,22].

2. The Many-Body Wavefunction

In electronic structure problems one has a fermion system where the many-body wavefunction is anti-symmetric [3]. The nuclei in the solid will be treated simply as sources of an external potential and will be held fixed at their ideal lattice positions. In using pseudopotentials, only the many-body wavefunction of the valence electrons will be considered. Thus, only the degrees of freedom associated with the valence electrons are included in the many-body wavefunction.

In the Hartree-Fock approximation, the simplest anti-symmetric function is used, viz., a single Slater determinant. One of the advantages of this approximation is that the variational problem can be expressed in terms of a set of self-consistent single-particle equations, the Hartree-Fock equations, which can be solved directly. However, apart from the antisymmetric form of the wavefunction, there is no correlation between the electrons in this approximation. The introduction of correlation should keep the electrons from coming close together, particularly those of opposite spin, which are not correlated in any way in the Hartree-Fock approximation, thus reducing the Coulomb interaction energy.

2.1. TWO-BODY JASTROW TERMS

A convenient and physically appealing way of introducing correlation to the Fermion state is to multiply the Slater determinant by a Jastrow factor

[23], of the form:

$$\Psi_J(R) \quad = \quad \exp\left\{-\sum_{i<j} u(r_{ij})\right\} , \tag{1}$$

where R denotes the set of all electron coordinates and r_{ij} is the distance between the ith and jth electrons. This form of correlated wavefunction has been used as the starting point for many methods [3,23-25]. The first fermion variational Monte Carlo calculation for a model extended system was the work of Ceperley, Chester, and Kalos [3] on uniform fermion systems. When $u(r)$ is a positive and decreasing function of r, the probability of two electrons coming close together is reduced and the repulsive electron-electron interaction energy is reduced. The kinetic energy and other terms in the energy are increased by the introduction of the Jastrow factor and so $u(r)$ is chosen variationally to obtain the optimum energy. This many-body wavefunction can be conveniently sampled using the variational quantum Monte Carlo approach, although in practice its optimal form has not been determined exactly via a self-consistent single-particle theory, as the Hartree-Fock wavefunction has.

Several considerations arise in connection with the Jastrow factor for inhomogeneous systems which are not present in homogeneous systems. In principle, the two-body term in the Jastrow factor for an inhomogenous system is not simply a function $u(r_{ij})$ of the distance r_{ij} between electrons i and j, but rather a function $u(\mathbf{r}_i, \mathbf{r}_j)$ of each coordinate separately. Formally, the solution of the Euler-Lagrange equation associated with energy minimization for arbitrary $u(\mathbf{r}_i, \mathbf{r}_j)$ may be stated as follows [3]: for the optimal u, the energy of the system when particle 1 is constrained at position $\mathbf{r}_1$ and particle 2 at $\mathbf{r}_2$ is independent of the values of $\mathbf{r}_1$ and $\mathbf{r}_2$. To see this, consider u to be written as a linear combination of a complete set of 2-particle (i.e., 6-dimensional) functions:

$$u(\mathbf{r}_1, \mathbf{r}_2) \quad = \quad \sum_{k=1}^{\infty} \alpha_k f_k(\mathbf{r}_1, \mathbf{r}_2) , \tag{2}$$

where the α_k are variational parameters. Then the average energy

$$E \quad = \quad \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{3}$$

is stationary with respect to variations in α_k when

$$-\frac{1}{2}\frac{\partial E}{\partial \alpha_k} \quad = \quad \frac{\langle\Psi|\{\sum_{i,j} f_k(\mathbf{r}_i, \mathbf{r}_j)\}(H-E)|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad = \quad 0 . \tag{4}$$

Since the wavefunction is anti-symmetric in the electron coordinates, this condition is equivalent to

$$\langle\Psi|f_k(\mathbf{r}_1,\mathbf{r}_2)[H-E]|\Psi\rangle = 0 . \tag{5}$$

If this is true for *all* functions f_k, then

$$\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)[H-E]\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)d\mathbf{r}_3\ldots d\mathbf{r}_N = 0 \tag{6}$$

for all values of $(\mathbf{r}_1,\mathbf{r}_2)$. Thus,

$$\bar{E}_2(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)H\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)d\mathbf{r}_3\ldots d\mathbf{r}_N}{\int|\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)|^2 d\mathbf{r}_3\ldots d\mathbf{r}_N}$$

is independent of $\mathbf{r}_1$ and $\mathbf{r}_2$. This is equivalent to our original statement of the Euler-Lagrange equation. In most variational Monte Carlo calculations for solids to date, $u(\mathbf{r}_1,\mathbf{r}_2)$ is assumed to depend only on $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$, as in the homogeneous system. There are some indications that the effects of this approximation on the energy is small but its effect on other quantities (e.g., pair-correlation functions) is not well understood.

An even more serious consideration [1] is that the introduction of the Jastrow factor, as in Eq. (1), alters the single-particle density obtained from the Slater determinant alone in an inhomogenous system. This can be understood roughly as follows: if an electron i is in a high density region, the sum $\sum_{j\neq i}u(r_{ij})$ tends to be larger than when electron i is in a low density region. This is because there tends to be a greater number of nearby electrons j in a high density region and since $u(r)$ is a decreasing function of r, the terms $u(r_{ij})$ in the sum are larger on average when $\mathbf{r}_i$ is in a high-density region than when it is in a low-density region. Thus, the Jastrow factor $\exp[-\sum_{j<i}u(r_{ij})]$ supresses the average amplitude-squared of the many-body wavefunction when $\mathbf{r}_i$ lies in a high density region. The two-body term then tends to make the charge density more uniform than that obtained from the Slater determinant alone, reducing charge density in higher density regions and increasing that in lower density regions.

Even neglecting three- and higher-body terms in the Jastrow factor, which can be envisaged but might be guessed on physical grounds to be relatively unimportant in homogeneous and inhomogenous systems alike, the interplay between the one- and two-body terms in the Jastrow factor and the single-particle wavefunctions of the Slater determinant in minimizing the energy is complex and has not been solved exactly. The Fermi Hypernetted Chain (FHNC) approach allows one to develop a self-consistent approach to this problem [25], but only within the approximations of that method for the energy as a functional of the Jastrow factor and Slater determinant. Moreover, the FHNC approach has not been applied to fully realistic, three dimensional solids.

In most applications of the variational Monte Carlo approach to date, restrictions are placed on the forms of the one- and two-body terms used in the Jastrow factor although the energy is evaluated exactly for any given form, so that the results remain variational. Perhaps a central result of the early variational Monte Carlo work on carbon and silicon solids [1] is that a surprisingly simple form of the Jastrow factor can give excellent results for the energies of the inhomogeneous systems considered. In particular, the many-body wavefunction used there was of the form

$$\Psi(R) \quad = \quad \Psi_J(R)\, d^{\uparrow}(R)\, d^{\downarrow}(R)\ . \tag{7}$$

The Jastrow factor Ψ_J is of the form [3],

$$\Psi_J(R) \quad = \quad \exp\left\{ \sum_{(s,i)=(\uparrow,1)}^{(\downarrow,N)} \chi_s(\mathbf{r}_i^s) - \sum_{(\uparrow,1)\le(s,i)<(s',j)}^{(\downarrow,N)} u_{ss'}(r_{ij}) \right\}\ . \tag{8}$$

The two-body term $u(r_{ij})$ is assumed to depend only on the distance r_{ij} between the particles and on their relative spin. The results clearly demonstrate the adequacy of this form in calculating energies, at least in the *sp* electron systems, where 80-95% of the correlation energies are obtained. The term d^s is the Slater determinant for electrons with spin s. The one-body term $\chi(\mathbf{r}_i)$ in the Jastrow factor could be formally incorporated into the Slater determinant by multiplying each single-particle orbital by $\exp[\chi(\mathbf{r})]$. However, it has been found convenient in many calculations to keep it (partly or wholly) in the Jastrow factor, using it to vary the single-particle density to minimize the energy or the variance of the energy.

The two-body function $u(r_{ij})$ in the Jastrow factor was chosen in Ref. [1] to be of the form [26]

$$u(r) \quad = \quad A(1\ -\ e^{-r/F})/r \quad , \tag{9}$$

where A and F are variational parameters. This function has the general behavior one intuitively expects: u is large and positive for $r = 0$ and decreases to zero as $r \to \infty$. Moreover, it satisfies some important exact limiting conditions. From the Euler-Lagrange equation for u discussed above, it follows [26] that, as two electrons approach one another, the divergence of the Coulomb interaction between them must be accompanied by an equal and opposite divergence of the kinetic energy. This yields the "cusp" condition (for 3-dimensional systems) on the derivative of u (in atomic units) at $r = 0$:

$$\left.\frac{du}{dr}\right|_{r=0} \quad = \quad \begin{cases} -1/2 & \text{for opposite spin} \\ -1/4 & \text{for parallel spin} \end{cases} \tag{10}$$

This cusp condition holds in both the atom and the solid and is independent of electron density. A relative-spin dependent value of F is used to satisfy this condition. The short-range part of $u(r)$ can be viewed as giving an exact solution to the two-body scattering problem at short distances. It appears that this short-range aspect of the Jastrow factor is the most important numerically for the reduction of energy of the interacting system since rather large changes in A (with the corresponding change in F so that the cusp condition remains satisfied) changes the system energy very little.

The long-range part of the two-body Jastrow factor is more appropriately thought of in terms of correlation in the collective modes of the charge in the system. Writing the Fourier coefficients of the charge

$$\rho_q = \sum_i \exp[-iq \cdot \mathbf{r}_i] , \tag{11}$$

we may rewrite the 2-body Jastrow factor as a sum of quadratic terms in the collective charge coordinates:

$$\sum_{i<j} u(r_{ij}) = \frac{1}{2\Omega} \sum_q \tilde{u}(q) \rho_q^* \rho_q , \tag{12}$$

where $\tilde{u}$ is the Fourier transform of u and Ω is the system volume. As discussed in the early work of Bohm and Pines on the uniform electron gas [27], the long-wavelength modes ($q \to 0$) behave in the random phase approximation (RPA) as independent simple harmonic oscillators with a classical frequency equal to the plasma frequency ω_p. For these modes to be in their quantum ground state, it can be shown that

$$\tilde{u}(q) = \frac{4\pi e^2}{\hbar \omega_p q^2} . \tag{13}$$

The behavior of u as $r \to \infty$ is dominated by the zero-point motion of the long-wavelength plasmons in the solid, leading to a $1/r$ dependence in $u(r)$ with a coefficient equal to $A = e^2/\hbar\omega_p$. Although the solids may be insulators, this condition should not be expected to change much there since the plasma frequency is substantially larger than the band gap [28]. Indeed, the experimentally measured plasma frequency in *sp* systems like diamond and silicon is virtually identical to that obtained from the uniform electron gas with a density equal to the average valence charge density for the crystal. We note that these long-range collective charge correlations are the physical origin of the van der Waals interaction. These energies are very small, compared to the contribution of the short-range part of Jastrow factor to the correlation energy.

Although the very short- and long-range aspects of the two-body Jastrow factor u are correctly satisfied by the simple form given above, there is no guarantee that intermediate range behaviour is optimal. Recent calculations [29] have used variance minimization to optimize the intermediate-range behavior of u. Polymonial terms $\Delta u_k(r)$ are added to $u(r)$ for $r < r_{max}$, where r_{max} is a suitably chosen cut-off radius. The functions $\Delta u_k(r) = 0$ at $r = r_{max}$ and have zero derivative at $r = 0$ and $r = r_{max}$. The effects of these terms on the energy are small, although the effects on the pair-correlation functions can be significant.

2.2. ONE-BODY JASTROW TERMS

The one-body term $\chi(\mathbf{r})$ in the Jastrow factor allows a variational adjustment of the electron charge density in the presence of the two-body term $u(r_{ij})$. Its importance has been observed in the context of FHNC calculations [23] for inhomogeneous systems. An alteration of the single-particle density is an unavoidable effect of the introduction of the two-body term in an inhomogeneous system, although the intuitive motivation for its introduction is to change the pair-correlation function, *not* the single-particle density, which may be already assumed to be quite well optimized by the solution of the mean-field single-particle (Hartree-Fock or LDA) problem. In the solid, $\chi(\mathbf{r})$ has the full space group symmetry of the solid, so that it can be written conveniently as a Fourier series with wavevectors $\mathbf{G}$ in the reciprocal lattice. The sum of the one-body terms can then be written as,

$$\sum_i \chi(\mathbf{r}_i) \quad = \quad \sum_{\mathbf{G}} \tilde{\chi}(\mathbf{G}) \rho_{\mathbf{G}} \; . \tag{14}$$

Using the full crystal symmetry, the function χ can be parameterized with a relatively small number of independent Fourier coefficients $\tilde{\chi}(\mathbf{G})$.

In the early VMC calculations [1], the one-body term used was calculated explicitly using the charge density of the mean-field solution (usually the LDA charge density) to guide the choice of χ. Thus, χ was taken to be of the form:

$$\chi(\mathbf{r}) \quad = \quad \alpha/2 \, \log[\rho_{\chi,u=0}(\mathbf{r})/\rho_{\chi=0}(\mathbf{r})] \; , \tag{15}$$

where $\rho(\mathbf{r})$ is the charge density and α is a variational parameter. In this approach, the charge density with $u \neq 0$ is calculated by Monte Carlo sampling. This approach must be used with considerable care, since noise in sampling the large-wavevector components of the charge density can give rise to nonphysical aspects of the wavefunction and spurious increases in the kinetic energy of the many-body wavefunction. More recent calculations [29,30] have used variance minimization to find the optimal Fourier components $\tilde{\chi}(\mathbf{G})$ of χ, which reduces the energy slightly from the form of χ determined directly from the LDA charge density.

A particularly simple form of χ has recently been observed [30] to give energies almost as good as variance minimization. This form is determined directly from the Fourier transform of the two-body term in the Jastrow factor and the LDA density and is set equal to

$$\chi_0(\mathbf{G}) \quad = \quad \tilde{u}(\mathbf{G})\langle\rho^*_{u=0}(\mathbf{G})\rangle \ , \tag{16}$$

where $\langle\rho_{u=0}(\mathbf{G})\rangle$ is the average charge Fourier component for the reciprocal lattice $\mathbf{G}$ when no Jastrow factor is used (i.e., the LDA charge density if the LDA wavefunctions are used in the Slater determinant). This form is far easier to calculate than the logarithmic expression in Eq. (15) since it involves no Monte Carlo evaluation of charge densities.

It can be argued [30] that this part χ_0 of the one-body term, defined in Eq. (16), can be viewed very naturally as an integral part of the RPA correlation term. We observe that in an inhomgeneous system the Bohm-Pines argument for the form $\tilde{u}(q)\rho^*_q\rho_q$ of the correlation terms should strictly be applied using the charge *fluctuations* $\Delta\rho_q = \rho_q - \langle\rho_q\rangle$ (i.e. the difference between a charge component and its average value) as the plasma oscillation mode coordinates, rather than the entire charge component. For the inhomogeneous, periodic solid, $\langle\rho_q\rangle$ is non-zero when $q = \mathbf{G}$ is a reciprocal lattice vector. The Jastrow factor then becomes

$$-\frac{1}{2}\sum_q \tilde{u}(q)\Delta\rho^*_q\Delta\rho_q \quad = \quad -\frac{1}{2}\sum_q \tilde{u}(q)\rho^*_q\rho_q + \sum_{\mathbf{G}} \tilde{u}(\mathbf{G})\langle\rho_{\mathbf{G}}\rangle^*\rho_{\mathbf{G}} + \text{constant} \ , \tag{17}$$

which contains a one-body term with $\tilde{\chi}(\mathbf{G}) = \tilde{u}(\mathbf{G})\langle\rho_{\mathbf{G}}\rangle$, as in Eq. (14). Further details concerning the construction of the one-body term χ_0 in both atoms and solids are given in Ref. [30].

Besides appearing as the natural correlation term in the Bohm-Pines RPA theory, it can be seen that the Jastrow correlation term given in Eq. (17) has a much smaller effect on the charge density than the corresponding two-body term alone. To see this, consider the term $\tilde{u}_q\Delta\rho^*_q\Delta\rho_q$ as a variational term in the many-body wavefunction. Then the derivative of any Fourier component of the charge density $\langle\rho_{q'}\rangle$ with respect to the parameter u_q is given by

$$\frac{\partial\langle\rho_{q'}\rangle}{\partial\tilde{u}_q} \quad = \quad \frac{\langle\Psi|\Delta\rho_{q'}\Delta\rho^*_q\Delta\rho_q|\Psi\rangle}{\langle\Psi|\Psi\rangle} \ . \tag{18}$$

This expression involves only fluctuations $\Delta\rho$ of the charge components from their average values and is therefore much smaller than the corresponding derivative,

$$\frac{\partial \langle \rho_{q'} \rangle}{\partial \tilde{u}_q} = \frac{\langle \Psi | \Delta\rho_{q'} \rho_q^* \rho_q | \Psi \rangle}{\langle \Psi | \Psi \rangle} , \tag{19}$$

which occurs when the pure two-body term $\tilde{u}_q \rho_q^* \rho_q$ is used in the Jastrow factor. Thus the introduction of a non-zero value of $\tilde{u}_q$ gives rise to relatively small changes in the charge density when the form $\tilde{u}_q \Delta\rho_q^* \Delta\rho_q$ (i.e., the two-body term with its associated one-body term) is included in the Jastrow factor.

The form χ_0 above is found to be very useful as a starting χ in the variance minimization approach and in recent calculations which directly solve the Euler-Lagrange equations associated with energy minimization for the one-body term, which we now discuss.

2.3. EULER-LAGRANGE EQUATIONS FOR ONE-BODY TERMS

It has already been observed that the one-body term of the Jastrow factor could be incorporated into the orbitals in the Slater determinant by multiplying each orbital by the factor $\exp[\chi(\mathbf{r})]$. Thus, it is perhaps not too surprising that a solution of the energy minimization problem for the one-body term in the Jastrow factor can be effectively solved by varying the orbitals in the Slater Determinant. Such an approach has very recently been developed [31] and we review the principal ideas of that method here, after first discussing the use of more standard LDA or Hartree-Fock methods to generate orbitals for the Slater determinant of the Jastrow-Slater wavefunction.

The Slater determinant d^s for electrons with spin s is the determinant of the Slater matrix, $\mathbf{D}$, where $D_{ji} = \phi_j(\mathbf{r}_i^s)$. Here the ϕ_j are a set of N single-particle wavefunctions. In practice, a reasonably good choice of such single particle wavefunctions has been found to be the set of wavefunctions obtained from the corresponding local density functional calculation [9]. It is not possible to rigorously justify the use of either LDA or Hartree-Fock wavefunctions in the Slater determinant when a Jastrow factor is present. However, important atomic (electron-ion) information is embodied in these wavefunctions which would otherwise be difficult to reproduce with a simple parameterisation of the single-particle wavefunctions.

From the point of view of the variational Monte Carlo approach in real materials, the all-important contribution of the standard mean-field (principally LDA) calculations for solids is to provide numerically accurate single-particle wavefunctions for a potential which includes the major single-particle terms in the solid as well as a reasonable mean-field approximation to the two-body interactions. In the absence of a practical scheme for handling the single-particle terms accurately, a variational wavefunction approach to the interacting system is hopelessly complicated. Thus, although the variational wavefunction approach is conceptually quite distinct from the density functional approach, in practice its success is heavily dependent on the technical machinery developed for calculating LDA single-particle wavefunctions.

We now outline a new iterative method which successively updates the determinant d in Jastrow-Slater wavefunctions so that, at convergence, the full correlated many-particle wavefunction satisfies the Euler-Lagrange equation for energy minimization with respect to the one-body term in the Jastrow factor; viz., that the conditional average $\bar{E}_1(\mathbf{r})$ of $E(R) = H\Psi(R)/\Psi(R)$, given that $\mathbf{r}_1 = \mathbf{r}$, does not depend on the position $\mathbf{r}$. (This Euler-Lagrange condition is derived in an analogous way to the corresponding Eq. (5) for the two-body Jastrow factor, above.) In this approach, the orbitals in the final determinant are eigenfunctions of a single-particle Schrödinger equation whose mean-field potential is constructed to ensure that $\bar{E}_1(\mathbf{r})$ does not depend on $\mathbf{r}$ for the Jastrow-Slater wavefunction $d\Psi_J$. (A similar condition enters into the Fermi hypernetted chain approach [25], but the implementation here is very different.)

The details of the method are as follows: we assume that initial single-particle orbitals $\phi_j^{(1)}$ for the determinant $d^{(1)}$ have been determined using a reasonable mean-field potential $V^{(1)}(\mathbf{r})$ (e.g., from a self-consistent LDA calculation). Although the form of the Jastrow factor Ψ_J is not constrained by the present approach, for rapid convergence, Ψ_J is chosen with appropriate two-body terms and with a one-body term (χ_0 of Eq. (16)) which ensures that the single-particle density for the wavefunction $\Psi^{(1)} = d^{(1)}\Psi_J$ does not differ greatly from that for $d^{(1)}$ [30]. A set of random configurations $R(i)$, $i = 1, N_c$, of the particles with local energies $E(i) = H\Psi^{(1)}(R(i))/\Psi^{(1)}(R(i))$ are generated by Monte Carlo importance sampling of the initial many-body wavefunction $\Psi^{(1)}$. A least-squares fit of the energies $E(i)$ is made with a sum of terms $E_0 + \sum_{k=1}^{n_f} V_k f_k(i)$, where $f_k(i) = \sum_{j=1}^{N} f_k(\mathbf{r}_j)$ is the kth collective charge coordinate for the configuration $R(i)$. The $f_k(\mathbf{r})$, $k = 1, n_f$, are a set of linearly independent non-constant functions. The choice of these functions is determined by physical considerations and computational convenience. Thus, the coefficients V_k of the least-squares fit satisfy the linear equations

$$\sum_{k=1}^{n_f} V_k \langle \Delta f_k \Delta f_l \rangle \quad = \quad \langle \Delta E \Delta f_l \rangle \,, \qquad \text{for } l = 1, \ldots, n_f, \tag{20}$$

where $\langle \cdot \rangle$ denotes the average of any quantity over the N_c configurations, $\Delta f_k(i) = f_k(i) - \langle f_k \rangle$, and $\Delta E(i) = E(i) - \langle E \rangle$.

Note that, as $N_c \to \infty$, $\langle \Delta E \Delta f_l \rangle \to \int \bar{E}_1(\mathbf{r}) \Delta f_l(\mathbf{r}) \rho(\mathbf{r})\, d\mathbf{r}$, where $\rho(\mathbf{r})$ is the single-particle density for the wavefunction $\Psi^{(1)}$. Hence, for a complete set of non-constant functions f_k, the coefficients V_k are all zero if and only if $\bar{E}_1(\mathbf{r})$ is a constant function.

To understand how to obtain the orbitals $\phi_j^{(2)}$ of the next iteration, consider a hypothetical *non-interacting* system in an external potential $V(\mathbf{r})$, with eigenfunctions $\phi_j(\mathbf{r})$. Suppose we construct a determinant d with single-particle orbitals $\phi'_j(\mathbf{r})$ which are solutions (with eigenvalues ϵ'_j) of the single-particle Schrödinger equation with an *incorrect* potential $V'(\mathbf{r})$. Then, for the non-interacting many-particle Hamiltonian H_0, the local energy $H_0 d(R)/d(R) = \sum_{j=1}^{N} [V(\mathbf{r}_j) - V'(\mathbf{r}_j) + \epsilon'_j]$. If we follow the above least-squares fitting procedure for determining V_k, then $\delta V(\mathbf{r}) = \sum_{k=1}^{n_f} V_k\, f_k(\mathbf{r})$ will fit the function, $V(\mathbf{r}) - V'(\mathbf{r})$+constant, and the exact single-particle orbitals ϕ_j are solutions of the Schrödinger equation with the potential, $V'(\mathbf{r}) + \delta V(\mathbf{r})$.

Motivated by this argument for non-interacting systems, in the interacting case we use $\delta V^{(1)}$, derived from the energy fluctuations $\Delta E(i)$ in $\Psi^{(1)}$, as an increment to the physical external potential V_{ext} in a standard self-consistent field determination of the single-particle orbitals, determining the Hartree potential (and, for accelerated convergence, the LDA exchange-correlation potential) self-consistently with the new single-particle orbitals $\phi_j^{(2)}$. A new potential increment $\delta V^{(2)}$ is similarly derived from the the new wavefunction $d^{(2)} \Psi_J$ and is added to the external potential $V_{ext} + \delta V^{(1)}$ for the next iteration to obtain the orbitals $\phi_j^{(3)}$. At the ith iteration, the orbitals $\phi_j^{(i)}$ are determined by performing a standard self-consistent LDA calculation with the external potential $V_{ext} + \sum_{l=1}^{i-1} \delta V^{(l)}$. Convergence is reached when $\delta V^{(i)}$ is negligible.

It should be noted that the LDA potential here is used purely for acceleration of convergence and that the final total "energy-fluctuation" potential $V^{EFP} \equiv \sum_{l=1}^{i} \delta V^{(l)} + V_{xc}^{LDA}$ and the final wavefunctions $\phi_j^{(i)}$ are independent of the LDA. The total energy-fluctuation potential $V^{EFP}(\mathbf{r})$ depends only on the external potential V_{ext}, the form of the Jastrow factor Ψ_J, and the functions f_k used in the expansion of δV. Thus, while the approach can use, with trivial modification, all of the computational techniques developed for determining numerically accurate LDA single-particle orbitals, the final orbitals $\phi_j^{(i)}$ are directly related to the many-particle wavefunction $d^{(i)} \Psi_J$ through the solution of the Euler-Lagrange equation for the Jastrow one-body term, $\bar{E}_1(\mathbf{r}) = $ constant. Moreover, the method uses the conceptually familiar framework of a self-consistent mean-field theory to optimize the orbitals.

In very recent applications of the method to diamond [31], the potentials V^{EFP} can be determined with sufficient accuracy in the solid using approximately 10^4 configurations in the Monte Carlo averages for Eq. (20). The method converges to sufficient accuracy in less than three iterations. The reduction of the variational energy, compared with a Jastrow-Slater wavefunction using the LDA orbitals and χ_0 (defined above) as the one-body term, is of the order of 0.1 eV/atom. A small difference in the charge density from the LDA charge density can be well resolved in this approach. It is found that the variational energy and the variance of the local energy is reduced (or does not increase, within statistical error) in successive iterations of the potential V^{EFP}. Thus, we see that the iterative solution of the Euler-Lagrange equation is numerically consistent with the minimization of both the average and variance of the local energy.

2.4. EVALUATION OF SINGLE-PARTICLE ORBITALS

Although trivial in principle, the evaluation of the single particle wavefunctions in the Slater determinant is a matter of considerable computational importance and difficulty. In order to avoid excessive computation time in their evaluation, they must be expressed in a reasonably compact representation suitable for rapid numerical calculation. On the other hand, the representation must give accurate numerical values if useful information is to be obtained from the Monte Carlo simulation. In crystals, the single-particle orbitals may be written in Bloch form, $\phi_{n\mathbf{k}}(\mathbf{r}) = \exp[i\mathbf{k}\cdot\mathbf{r}]u_{n\mathbf{k}}(\mathbf{r})$, where u is periodic. A very general approach, which allows one to make use of a number of current single-particle band-structure codes in the initial determination of the orbitals (as in Section 2.3, above) is to adopt a composite of LCAO and plane-wave representations for ϕ. In limiting cases, the representation may be entirely plane-wave-like or entirely local-orbital-like. The method is in some ways reminiscent of the Ewald summation technique and is similar to the mixed-basis approach to single-particle electronic structure calculations. Either density functional calculations, Hartree-Fock calculations, or solution of the Euler-Lagrange equations (as in Section 2.3, above) provide the wavefunctions in the appropriate representation (gaussian orbitals or plane-waves, as the case may be) as output.

Even when the band-structure codes use an entirely localized-orbital representation, it is not necessary to use them in precisely that form in the VMC calculations. In the evaluation of the wavefunctions in the Monte Carlo program, Ref. 1 leaves the short-range Gaussian orbitals in their original representation and takes the plane wave representation of the long-range orbitals prior to the Monte Carlo calculation.

In the most general case, each single-particle wavefunction is expressed as a sum of both localized gaussian orbitals and plane waves. Thus, to evaluate the single-particle wavefunctions at a particular point, we need to determine the Gaussian orbital sites within a cut-off radius large enough to ensure that the short-range orbitals from sites outside that radius are negligibly small at the point. The Gaussian part can be evaluated directly from the LCAO representation of the single-particle orbitals:

$$u_{\rm loc}(\mathbf{r}) \quad \equiv \quad \sum_{\substack{\mathbf{R}\alpha lm \\ |\mathbf{r}-\mathbf{R}|<R_{cut}}} C_{\alpha lm}\, f_{\alpha lm}(\mathbf{r}-\mathbf{R}) \exp\{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r})\}\ , \tag{21}$$

where u denotes the periodic part of the wavefunction, $f_{\alpha lm}$ are the LCAO basis functions, $C_{\alpha lm}$ are the LCAO expansion coefficients of the wavefunction, $\mathbf{k}$ is the $\mathbf{k}$-point to which the wavefunction belongs, and R_{cut} is the appropriately chosen cut-off radius. The plane-wave part is evaluated directly as a sum of exponentials:

$$u_{\rm pw}(\mathbf{r}) \quad \equiv \quad \sum_{\substack{\mathbf{G} \\ |\mathbf{G}|<G_{cut}}} C_{\mathbf{G}}\ \exp[i\mathbf{G}\cdot\mathbf{r}]\ \ , \tag{22}$$

where $\mathbf{G}$ are vectors of the reciprocal lattice with length less than an appropriate cut-off, G_{cut}. Several hundred plane-waves can be used in practice in this summation since the exponentials and dot-products can be evaluated very efficiently.

Considerable care must be exercised to ensure that the calculation of the kinetic energy from the representation of the single-particle wavefunctions is consistent with the calculated values of the wavefunctions. Surprisingly small discontinuities in the wavefunction due to too small a cut-off radius for the inclusion of neighboring sites can cause substantial errors in the total energy obtained. Internal consistency in the evaluation of the kinetic energies and values of the wavefunctions is even more important than the accuracy of the representation of the LDA single-particle wavefunctions.

In the atoms, the wavefunctions are tabulated on a very fine radial grid of several thousand points and calculated by interpolation.

3. The Hamiltonian

In this section we describe the many-body Hamiltonian used for infinite crystals within the pseudopotential formalism [12]. The essential ingredients in the Hamiltonian are an external potential (due to the ions in the crystal), the kinetic energy of the valence electrons, and the Coulomb interaction between the valence electrons.

The external potential has two parts to it: a local part, and a non-local part. The kinetic energy has the usual form,

$$E_{\text{kinetic}} = -\frac{\hbar^2}{2m}\sum_{(s,i)} \nabla^2_{(s,i)} , \tag{23}$$

and the Coulomb interaction between the electrons is given by

$$E_{\text{el-el}} = \frac{1}{2}\sum_{(s,i)}\sum_{(s',j)\neq(s,i)} \frac{e^2}{|\mathbf{r}_j^{s'} - \mathbf{r}_i^{s}|} . \tag{24}$$

where, in keeping with the periodic boundary conditions of the simulation region, the sum over (s', j) is taken over all images of the particle (s', j) in the simulation region.

3.1. PSEUDOPOTENTIALS

The pseudopotentials used in the variational Monte Carlo calculations are generated within a mean-field approach, for example by the scheme of Hamann, Schlüter, and Chiang [12] for use in local density functional calculations [9]. These smooth ionic potentials tend rapidly to the all-electron electrostatic potential of the nucleus plus core electrons, $-Z_{\text{ion}}/r$, beyond a cutoff radius r_c of the order of one atomic unit and give valence eigenvalues (and eigenfunctions outside of r_c) virtually identical to the all-electron density functional calculations.

A fundamental objection might perhaps be raised to the use of these potentials on the grounds that they are objects derived from density functional theory calculations of the atom and should only be used within the context of density functional theory in the solid. From a purely logical standpoint, this objection is well founded and the use of such pseudopotentials cannot be rigorously justified. Presumably, for systems in which core-valence exchange and correlation play a very important role, this approach could give poor results. However, calculations such as those of Hybertsen and Louie [31] for quasiparticle energies indicate that this is not the case in many insulators, semiconductors, and metals. We expect that the pseudopotentials generated from density functional theory will give a reasonable description of the core-valence interaction for the variational calculations. Also, since the ground-state properties are determined by differences in total energies, the dominant many-body contributions to these differences would be from changes in the valence-valence electron correlations, and the core-valence effects are expected to cancel out or to play a relatively minor role.

At worst, we can consider these to be model calculations designed to approximate the behavior of the corresponding real system. The validity of the model can then be judged *a posteriori* by the accuracy of the predictions it makes for the properties of the real system. Shirley *et al.* [33] have formulated the problem for many-body pseudopotentials and have generated pseudopotentials for some atoms in their approach.

3.2. EVALUATION OF THE LOCAL PSEUDOPOTENTIAL

The local pseudopotential at any point in the crystal is a sum of the potentials of the ions evaluated at that point:

$$V(\mathbf{r}) \quad = \quad \sum_{\mathbf{R}_{\rm ion}} V_{\rm ion}(|\mathbf{r}-\mathbf{R}_{\rm ion}|) \ , \tag{25}$$

where $\mathbf{R}_{\rm ion}$ are the positions of the ions and $V_{\rm ion}(r)$ is the (spherically symmetric) potential due to the ion at a distance r. In fact, as it stands the sum in Eq. (25) does not even converge for the infinite crystal because of the long range $1/r$ tail of the ionic pseudopotential. However, we implicitly assume that we include the electrostatic potential of a counterbalancing uniform negative background charge equal in density to the average charge density of the ions. (The interaction of the electron at the point $\mathbf{r}$ with this uniform background charge is in turn balanced by an equal and opposite interaction with the positive backgound introduced in the evaluation of the electron-electron interaction. When these are added we are left only with the true interaction of the electron with the combined electron-ion system.)

Even with the addition of the uniform negative background, the sum in Eq. (25) converges very slowly as a function of the number of nearest neighbours included. A much more satisfactory approach is to divide each ion potential into a $-Z_{\rm ion}/r$ part and a deviation from $-Z_{\rm ion}/r$ behaviour. As we mentioned above, this deviation from $-Z_{\rm ion}/r$ has a range of only a few atomic units and can be expressed at any point in the crystal as a sum of contributions from a small number of neighbouring ions. The $1/r$ part can be evaluated by the usual Ewald summation technique [34], in which the sum is divided into a "real space" part and a "Fourier space" part, each of which converges rapidly. The terms in the real space sum converge like $\mathrm{erfc}\{-\sqrt{\alpha}r\}/r$, where erfc is the complimentary error function, and those in Fourier space like $(e^{-G^2/4\alpha})/G^2$. Here α is a parameter which can be varied to optimize the efficiency of the method. (The converged value of the real plus Fourier space sums is independent of α.)

Combining the deviation from $-Z_{\rm ion}/r$ behaviour with the real space part of the Ewald sum gives the potential at a point in the crystal as a sum over the positions of the ions plus a sum over reciprocal lattice vectors:

$$V(\mathbf{r}) = \sum_{\substack{\mathbf{R}_{\text{ion}} \\ |\mathbf{r}-\mathbf{R}_{\text{ion}}|<R_{max}}} V^R_{\text{ion}}(|\mathbf{r}-\mathbf{R}_{\text{ion}}|) + \sum_{\substack{\mathbf{G} \\ G<G_{max}}} V^F(G)\, S(\mathbf{G}) \exp\{i\mathbf{G}\cdot\mathbf{r}\} . \tag{26}$$

Here R_{max} and G_{max} are cut-off radii in real and Fourier space, respectively, chosen to give the required accuracy in the value of $V(\mathbf{r})$. The potentials in real and Fourier space are given by,

$$V^R_{\text{ion}}(r) = V_{\text{ion}}(r) + \frac{Z_{\text{ion}}}{r}\left(1 - \text{erfc}(\sqrt{\alpha} r)\right) , \tag{27}$$

$$V^F(G) = \begin{cases} \dfrac{4\pi \exp(-G^2/4\alpha)}{G^2 V_{cell}} , & \text{for } G \neq 0, \\ -\dfrac{\pi}{V_{cell}\,\alpha} , & \text{for } G = 0, \end{cases} \tag{28}$$

where V_{cell} is the volume of the crystal unit cell. Comparable convergence is obtained for the real and Fourier space sums when $\alpha R^2_{max} = G^2_{max}/4\alpha$. The structure factors $S(\mathbf{G})$ of the ionic charge are

$$S(\mathbf{G}) \equiv \sum_{\mathbf{R}_{\text{ion}} \in \text{unit cell}} -Z_{\text{ion}} \exp\{-i\mathbf{G}\cdot\mathbf{R}_{\text{ion}}\} . \tag{29}$$

The real-space potential $V^R_{\text{ion}}(r)$ is tabulated on a fine radial mesh and evaluated by interpolation at each step of the random walk. The Fourier-space potential is also calculated in advance.

In the atomic calculations, the local potential is evaluated at the position of the electron by interpolation from values tabulated in advance on a fine uniform radial grid.

3.3. THE NON-LOCAL PSEUDOPOTENTIAL

The part of the many-body Hamiltonian which arises from the non-local pseudopotential of the ions must be a simple (linear) sum over all the ions of terms due to the pseudopotential of each individual ion. Also, it must be symmetric in the electronic variables and linear in the number of electrons. These are nothing more than the usual conditions for any external potential acting on a system of indistinguishable particles. We state them explicitly here in order to make clear that the non-locality of the pseudopotential in the coordinate representation of electrons does not invalidate them. Thus, the non-local part of the Hamiltonian must have the form,

$$\mathbf{H}_{non-local} = \sum_{\mathbf{R}} \sum_{s,i} \mathbf{H}^{s,i}_{\mathbf{R}}, \tag{30}$$

where $\mathbf{R}$ varies over the sites of the ions, s varies over the electron spin, and $i = 1, N$ varies over the electrons of spin s. $\mathbf{H}^{s,i}_{\mathbf{R}}$ is the non-local pseudopotential due to the ion at $\mathbf{R}$ acting on the (s, i) electron coordinates.

Since the total crystal non-local potential is a sum over the potentials of the ions, for notational simplicity we will concentrate on evaluating the energy due to a single potential centered at the origin. The potential at the origin has the form [11],

$$\mathbf{H}^{s,i} \quad = \quad \sum_l \int_0^\infty dr\ V_l(r) \mathbf{P}^{s,i}_{l,r} \ . \tag{31}$$

Here $\mathbf{P}^{s,i}_{l,r}$ is the angular momentum l projection operator acting at a distance r from the origin on the (s, i) electron variable. (The action of $\mathbf{H}^{s,i}$ can be understood as follows: fix at particular values all the electron variables in the argument of the many-body wavefunction except the (s, i) variable and consider the resulting function $f(\mathbf{r}^s_i)$; the action of $\mathbf{H}^{s,i}$ on f is precisely the same as the action of the usual (one-body) pseudopotential on single-particle wavefunctions in, for example, the Kohn-Sham equations [12]. This is always the way the action of a single-particle operator is generalized from the "independent particle" situation to the "interacting particle" case.)

The contribution of this term in the Hamiltonian to the energy of a many-body state $|\Psi\rangle$ is given by,

$$E(|\Psi\rangle) \quad = \quad \langle\Psi|\{\sum_{s,i} \mathbf{H}^{s,i}\}|\Psi\rangle \quad = \quad \sum_{s,i} \langle\Psi|\mathbf{H}^{s,i}|\Psi\rangle \ .$$

The Monte Carlo random walk technique with importance sampling automatically integrates all quantities with respect to the weight $|\Psi|^2$. Thus, in order to calculate the one particle energy $E^{s,i}$, we want to perform importance sampling on the quantity, $[\mathbf{H}^{s,i}\Psi]/\Psi$. Making use of Eq. (31) we can see that the value of this function at any point $\{\mathbf{r}^\uparrow_1, \ldots, \mathbf{r}^s_i, \ldots, \mathbf{r}^\downarrow_N\}$ in configuration space is given by,

$$\begin{aligned} E^{s,i}_l(\mathbf{r}^s_i = \mathbf{r}) \quad &= \\ V_l(r) Y_{l0}(0,0) \int_{r'=r} Y^*_{l0}(\Omega_{\mathbf{r}'}) &\frac{\Psi(\mathbf{r}^\uparrow_1, \ldots, \mathbf{r}^s_i = \mathbf{r}', \ldots, \mathbf{r}^\downarrow_N)}{\Psi(\mathbf{r}^\uparrow_1, \ldots, \mathbf{r}^s_i = \mathbf{r}, \ldots, \mathbf{r}^\downarrow_N)}\, d\Omega_{\mathbf{r}'} \ , \end{aligned} \tag{32}$$

where $\Omega_{\mathbf{r}'}$ is the angular part of the spherical coordinates of the vector $\mathbf{r}'$ when $\mathbf{r}$ points along the z-axis.

In principle, the expression for the energy due to one atom should be summed over *all* the atoms in the crystal to give the total non-local energy for electron (s, i) from Eq. (30). However, the non-local potentials are very short ranged ($\simeq 2$ atomic units) [12] and so we need only sum Eq. (32) over one or two neighbouring atoms in most cases.

It is immediately clear that the integral in Eq. (32) cannot be evaluated analytically and must be performed numerically. One approach would be to use a fixed grid of values for $\Omega_{\mathbf{r}'}$ and use a summation over values of the many-body wavefunction at those points to estimate the integral. However, this method is clearly subject to systematic bias which may converge very slowly with respect to the grid size. A more satisfactory approach in the present context is to evaluate the integral in a statistical fashion; i.e., we choose values for $\Omega_{\mathbf{r}'}$ at random according to an appropriate probability distribution and use the summation over the values of the many-body wavefunction at those points (with appropriate weighting factors) to obtain a statistically unbiased estimator of the integral.

The variance of such an estimator can be greatly reduced by a judicious choice of sampling scheme. We expect the many-body wavefunction (as a function of $\mathbf{r}'$, keeping the other electrons fixed) to have predominantly the angular momentum character of the single particle wavefunctions in the Slater determinant; viz., in most cases of interest, largely s, p, or d character. The variance of the estimator of the integral in Eq. (32) will thus be greatly reduced if the estimator is exact (i.e., has zero variance) for functions of pure s, p, or d character. Any fluctuations in the estimate of the integral will then come only from higher angular momentum components in the many-body wavefunction.

Such sampling schemes can easily be developed [1] to give exact evaluation of the s and p pseudopotentials for all s, p, and d wavefunctions, as follows: we randomly select a grid of n points, $\{\Omega_i\}_{i=1}^n$, on the unit sphere and associated weights, $\{W_i\}_{i=1}^n$, for use in the projection of the lth angular momentum component of an arbitrary function. The grid is to have the following properties:

1. The sum over the grid points of any function defined on the unit sphere will give an *unbiased estimator* of the integral of the function over the sphere; i.e.,

$$\langle \sum_{i=1}^{n} W_i \, f(\Omega_i) \rangle \quad = \quad \int f(\Omega) \, d\Omega \ , \tag{33}$$

where the notation $\langle \ \rangle$ denotes the average value taken over grids chosen at random according to the selection scheme.

2. The grid scheme for integration of the l angular momentum potential is to be *exact* for projection of functions of angular momentum up to $l_{\max}$ in the following sense: the relation,

$$\sum_{i=1}^{n} W_i \, Y_{l0}^*(\Omega_i) \, Y_{l'm}(\Omega_i) \quad = \quad \delta_{ll'} \, \delta_{0m} \ , \tag{34}$$

is to be satisfied exactly for *any* particular grid chosen, for values of l' up to $l_{\max}$ and m between $-l'$ and l'.

The first condition tells us that the average of the estimator is correct for *all* functions and the second condition that the variance of the estimator is zero for functions of angular momentum less than or equal to $l_{\max}$.

We can achieve the first objective by taking *any* fixed grid of points on the sphere with fixed weights summing to unity and rotating the coordinate axes in which the set is fixed so that the rotated z-axis has a uniform solid angle distribution and the final x and y axes are rotated with a uniform planar angle about the final z axis. The grid in this rotated set of axes is used to evaluate the average in Eq. (33). It is easy to show that each point of the original grid covers the entire sphere with a uniform solid angle distribution by this rotation scheme. Thus the integration scheme samples all functions without bias.

In order to achieve exact l-angular momentum of all functions up to angular momentum l', it is sufficient to to find a fixed grid which sums all $Y_{l''m}$ to zero, for $1 \leq l'' \leq l + l'$. McLaren [35] has discussed such grids in detail. The vertices of the regular tetrahedron, octohedron, and icosahedron with constant weighting factors provide grids of 4, 6, and 12 points which give exact integration of all functions with $l'' \leq 2$, 3, and 5, respectively. In cartesian coordinates, the four tetrahedral grid points are: $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$, $(1/\sqrt{3}, -1/\sqrt{3}, -1/\sqrt{3})$, $(-1/\sqrt{3}, 1/\sqrt{3}, -1/\sqrt{3})$, and $(-1/\sqrt{3}, -1/\sqrt{3}, 1/\sqrt{3})$. The six octohedral grid points are: $(\pm 1, 0, 0)$, $(0, \pm 1, 0)$, and $(0, 0, \pm 1)$. The twelve icosahedral points are: $(0, \pm\lambda, \pm\rho)$, $(\pm\lambda, 0, \pm\rho)$, and $(\pm\lambda, \pm\rho, 0)$, where $\lambda = [(5 - \sqrt{5})/10]^{1/2}$ and $\rho = [(5 + \sqrt{5})/10]^{1/2}$. For many applications, the tetrahedral grid is found to be sufficient. More complicated angular sampling schemes [36] have been used to sample even higher angular momenta exactly.

3.4. FINITE SIZE EFFECTS

The goal of any VMC calculation for solids is to obtain the quantities calculated (energy, charge density, pair-correlation functions, etc.) for the *infinite* solid. Clearly, in any VMC simulation only a finite number of particles can be used. As mentioned above, periodic boundary conditions are usually used to mimic the effects of the infinite system as well as possible. If the many-body wavefunction is required to satisfy periodic boundary conditions, then this is most simply implemented by using those Bloch single-particle states in the Slater determinant which themselves have periodic boundary conditions on the simulation region. In this way, only single-particle states at a discrete set of momentum k-points within the Brillouin Zone will be used in the many-body wavefunctions. (If a simulation region contains M primitive unit cells of the crystal, then only M k-points in the Brillouin Zone will be allowed under periodic boundary conditions.)

The dominant finite size effect in this case is what may be called the single-particle band structure correction: the single-particle (potential, mean-field, and kinetic energy) contributions to the energy of the system are only sampled at discrete k-points in the Brillouin Zone, rather than integrated over all points in the Zone, as would be the case for an infinite system. Because LDA calculations include exchange and correlation in an approximate way, one may expect that (at least for large simulation cells) the size-dependence of the VMC calculations should approximately track that of the LDA calculations performed with the k-point sampling corresponding to periodic boundary conditions on the VMC simulation region. Thus, the simplest practical correction [1] to the VMC energy for a finite size simulation is to add the difference between the k-point converged LDA calculation and the LDA calculation using the k-points compatible with periodic boundary conditions on the simulation region.

However, strictly periodic boundary conditions are not the only physically reasonable choice for the many-body wavfunction. It is also allowable to have a more general type of aperiodic boundary condition applied to the wavefunction [19,20], where translation of one electron to one of the periodic images of the simulation region introduces a phase factor into the wavefunction, as follows:

$$\Psi(\mathbf{r}_1 + \mathbf{L}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \quad = \quad \exp[i\mathbf{Q} \cdot \mathbf{L}]\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \; , \tag{35}$$

where $\mathbf{L}$ is a vector of the Bravais Lattice which has the simulation region as its primitive unit cell and $\mathbf{Q}$ is an arbitrary vector which specifies the type of boundary condition on the many-body wavefunction. In some cases, taking $\mathbf{Q} \neq 0$ leads to more rapid convergence to the infinite-size limit.

Finally, it has recently been suggested [21,22] that the use of periodically repeated images of the particles in the simulation region (with associated interactions with the other particles) is not always the most rapidly convergent representation of interactions in the infinite system. A modification of the interaction has been suggested by Fraser *et al.* [21], where particle i interacts with the nearest image only of particle j. Convergence of the total energy per particle to the infinite-size limit is found to be more rapid than when the periodically-repeated images method is used. For inhomogeneous systems [22], the mean-field (Hartree) contribution of the charges outside the simulation region must be included in this case as part of the single-particle potential.

TABLE 1. Ionization energy and electron affinity of carbon and silicon (in eV). The expected statistical error in the last digits is in parentheses. [From Reference 1.]

		VMC	Experiment[a]
Carbon			
	Ionization Energy	11.43(5)	11.26
	Electron Affinity	1.20(10)	1.27
Silicon			
	Ionization Energy	8.20(5)	8.15
	Electron Affinity	1.40(10)	1.39

[a]see Ref. [16].

4. Results for Carbon and Silicon Systems

In order to give a general impression of the level of accuracy obtained and the complexity in the VMC computations, in this section we review some of the early VMC results for energies of carbon and silicon systems using pseudopotentials. The results presented are by no means exhaustive.

4.1. ATOMS

Early VMC calculations were carried out for the total energy of the neutral, positively, and negatively charged carbon and silicon atoms. The results for the ionization energies and electron affinities are presented in Table 1.

It is found that both the one-body and two-body terms are equally important in lowering the energy of the system when compared to that of the single Slater determinant wavefunction. Without the one-body term $\chi(\mathbf{r})$ in the Jastrow factor, the presence of a non-zero $u(r_{ij})$ significantly alters the charge density from that of the Slater determinant alone. Since the correlation term $u(r_{ij})$ reduces the probability of two electrons getting close to each other, its effect is to reduce the charge density in the high-density regions and increase it in the low-density regions. The optimal one-body term $\chi(\mathbf{r})$ brings the charge density back to a distribution which is very close to the LDA result. The lowering of energy due to the one-body term keeping the two-body term constant at the final optimal parameters is 4.5 eV in the neutral carbon atom.

Since the number of three-body interactions is very different for these atoms in the three different charge states shown, the results show that three-body terms in the Jastrow factor appear to be not significant at the level of accuracy of the pseudo-potential approximation itself, and can lower the energy by no more than approximately 0.2 eV/atom. A similar conclusion is suggested by comparison of the VMC results for the Si atom with those from the Green's Function Monte Carlo pseudo-Hamiltonian calculation of Bachelet, Ceperley, and Chiocchetti [15]. Allowing for the fact that the two many-body Hamiltonians are not identical, nevertheless, it is reasonable to conclude that the amount of correlation energy absent in the variational wavefunction of the form we have used is no more than approximately 0.2 eV/atom.

4.2. SOLIDS

The method has been applied [1] to study the binding energy and structural properties of diamond and graphite using simulation cells with periodic boundary conditions, as described in Section 3.4, above. Cell sizes containing up to 216 electrons (or 54 carbon atoms) were used. It is found that the size dependence for larger simulations is mainly determined by the convergence of the single-particle terms in the total energy, as given in LDA band theory by the k-point sampling of the Brillouin zone.

The introduction of the one-body term into the Jastrow factor lowers the energy of diamond, but only by 0.6 eV/atom, compared to 4.5 eV in the carbon atom (as discussed above). In graphite, where the charge density is substantially more susceptible to change by the two-body term in the Jastrow factor (due to the presence of large, very low density regions in the interlayer region) the lowering of the energy by the one-body term χ is 4.2 eV/atom, much larger than in diamond. Thus we see that the influence of the one-body term on the energy varies greatly from system to system.

The total energies calculated with and without the full Jastrow factor (i.e., both the u and χ terms are included) in the wavefunction are presented in Table 2 for diamond at the minimum-energy lattice constant, together with the atomic results. The QMC results for the solid include a finite-size correction beyond the 216 electron simulation obtained from the difference between the LDA energy calculated using k-points compatible with periodic boundary conditions on this simulation region and that calculated with a fully-converged k-point set. This energy difference is 0.2 eV/atom. It is found that the finite-size correction to the QMC energy calculations for regions containing between 64 and 216 electrons follows within 20% that of the corresponding LDA calculation. This fact merely demonstrates the relatively localized nature of the exchange-correlation hole in this system.

Since the electronic and geometric structure of graphite, which is a highly anisotropic semimetal with very large inhomogeniety of charge density, differ substantially from those of diamond, the calculation of its cohesive energy represents a significantly different challenge to the present

TABLE 2. Total energies (in eV/atom) of the carbon pseudo-atom and of diamond (with finite-size correction) for (a) LDA calculation, and for Monte Carlo calculations with (b) single Slater determinant of LDA wavefunctions and (c) Jastrow-Slater function with one- and two-body terms in the Jastrow factor. The experimental cohesive energy results (d) are adjusted to allow for the zero-point phonon energy (0.18 eV/atom) of the solid. The expected statistical error in the last digits is in parentheses. [From Reference 1.]

	Carbon Atom	Diamond	Cohesive Energy
(a) LDA	-146.79	-155.42	8.63
(b) Slater Det.	-145.55(7)	-151.3(2)	5.85(25)
(c) Jastrow-Slater	-147.93(3)	-155.38(6)	7.45(7)
(d) Experiment[a]	—	—	7.37

[a] see Ref. [37].

method. In particular, one might wonder in advance whether the spherically symmetric and translationally invariant form of the two-body term of the Jastrow factor in our wavefunction would be an adequate approximation for graphite. As we have already mentioned, the effect of the one-body term on the total energy is an order of magnitude greater in graphite than it is in diamond. However, the VMC result [1] for the cohesive energy is in excellent agreement with experiment, indicating that the simple variational wavefunction of the form discussed here works well in anisotropic systems.

Similar results are obtained for the cohesive energy of silicon, with a slightly larger discrepancy (0.18 ± 0.1 eV/atom) between the VMC results and experiment. In that case it has been shown that there is greater difficulty in the transferability of the pseudopotential to the many-body calculations than is the case for carbon. Li *et al.* [38] have compared VMC and diffusion Monte Carlo results for silicon, performed using pseudohamiltonians, and find that the energy difference in the solid between VMC and DMC is approximately 0.4 eV/atom.

More recent calculations for carbon and silicon systems have focused on many-body properties, other than the cohesive energy and have made extensive use of variance minimization to optimize many-parameter one-body and homogeneous two-body Jastrow terms. An early calculation [39] of the pair-correlation function and occupation numbers of single-particle states in diamond and silicon has been followed by extensive calculations [40] of the exchange and correlation functions in silicon and by calculations of the many-body corrections to the single-particle density matrix [41] and the Compton profile [42] of silicon, demonstrating the power of the method in extracting many-body properties of these solids which are inaccessible to standard band-structure methods.

5. Conclusion

It is now possible to calculate total energies of the valence electrons in atoms and solids using non-local pseudopotentials in conjunction with variational quantum Monte Carlo techniques. Using some the standard machinery of band-structure theory, we can construct a correlated many-body wavefunction of surprisingly simple form which can yield 80-95% of the correlation energy in the carbon- and silicon-based systems. The results give excellent agreement with experimental energy differences for carbon-based systems. The structural properties are also in good agreement with experiment. For silicon, the results are similarly in good agreement with experiment. With the full many-body wavefunction available, it is clear that many quantities other than the energy may be calculated. In particular, quantities inaccessible in the LDA approach, such as pair-correlation functions and single-particle occupation numbers, can be readily calculated in the present method.

The computational effort involved in VMC solid-state calculations of energies (at the 0.1 eV/atom level of statistical accuracy) is approximately 5 to 10 times that of the corresponding LDA calculation. This ratio is of course strongly dependent on the size of the crystal unit cell and also on the level of accuracy required in the QMC calculation. The LDA computation grows roughly as the cube of the cell size, while the dominant terms in the QMC computation grow roughly linearly with cell size (at least, in the current regime of QMC applications).

References

1. S. Fahy. X. W. Wang, and S. G. Louie, Phys. Rev. B **42**, 3503 (1990).
2. W. L. McMillan, Phys. Rev. **138**, A442 (1965).
3. D. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B **16**, 3081 (1977).
4. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
5. P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, J. Chem. Phys. **77**, 5593 (1982); R. M. Grimes, B. L. Hammond, P. J. Reynolds, and W. A. Lester, *ibid* **85**, 4749 (1986).
6. D. M. Ceperley and B. J. Alder, Phys. Rev. B **36**, 2092 (1987).
7. The amount of computation time increases at least as $Z^{5.5}$; see D. M. Ceperley, J. Stat. Phys. **43**, 815 (1986).
8. B. L. Hammond, P. J. Reynolds, and W. A. Lester, J. Chem. Phys. **87**, 1130 (1987).
9. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid* **140**, A1133 (1965).
10. O. Gunnarsson and R. O. Jones, Phys. Rev. B **31**, 7588 (1985), and references therein.
11. V. Heine, in *Solid State Physics*, Vol. 24 (Academic Press, New York, 1970), ed. by

H. Ehrenreich, F. Seitz, and D. Turnbull, p. 24, and references therein.
12. D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
13. P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. **71**, 4445 (1979).
14. C. M. Rohlfing and P. J. Hay, J. Chem. Phys. **83**, 4641 (1985).
15. G. B. Bachelet, D. M. Ceperley, and M. G. B. Chiocchetti, Phys. Rev. Lett. **62**, 2088 (1989).
16. M. M. Hurley and P. A. Christiansen, J. Chem. Phys. **86**, 1069 (1987); P. A. Christiansen, *ibid* **88**, 4867 (1988).
17. T. Yoshida and K. Iguchi, *ibid* **88**, 1032 (1988).
18. B. L. Hammond, P. J. Reynolds, and W. A. Lester, Phys. Rev. Lett. **61**, 2312 (1988).
19. G. Rajagopal *et al.*, Phys. Rev. Lett. **73**, 1959 (1994).
20. G. Rajagopal *et al.*, Phys. Rev. B **51**, 10591 (1995).
21. L. M. Fraser *et al.*, Phys. Rev. B **53**, 1814 (1996).
22. A. J. Williamson *et al.*, Phys. Rev. B **55**, 4851 (1997).
23. E. Feenberg, *Theory of Quantum Fluids*, (Academic Press, New York, 1969).
24. B. Kiel, G. Stollhoff, C. Weigel, P. Fulde, and H. Stoll, Z. Phys. B **46**, 1 (1982); G. Stollhoff and K. P. Bohnen, Phys. Rev. B **37**, 4678 (1988).
25. E. Krotscheck and W. Kohn, Phys. Rev. Lett. **57**, 862 (1986); E. Krotscheck, Phys. Rev. B **31**, 4267 (1985); E. Krotscheck, W. Kohn, and G.-X. Qian, Phys. Rev. B **32**, 5693 (1985).
26. D. Ceperley, Phys. Rev. B **18**, 3126 (1978).
27. D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).
28. H. Raether, *Excitation of Plasmons and interband transitions by Electrons*, (Springer, Berlin, 1980).
29. A. J. Williamson *et al.*, Phys. Rev. B **53**, 9640 (1996).
30. A. Malatesta, S. Fahy, and G. B. Bachelet, Phys. Rev. B **56**, 12201 (1997).
31. S. Fahy (unpublished).
32. M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985) and Phys. Rev. B **34**, 5390 (1986).
33. E. L. Shirley, L. Mitas, and R. M. Martin, Phys. Rev. B **44**, 3395 (1991).
34. P. P. Ewald, Ann. Physik **64**, 253 (1921); B. R. A. Nijboer and F. W. deWette, Physica **23**, 309 (1957).
35. A. D. McLaren, J. Math. Comp. **17**, 361 (1963).
36. L. Mitas, in *Computer Simulation in Condensed Matter Physics IV*, edited by D. P. Landau, K. K. Mon, and H. B. Schuttler, (Springer, Berlin, 1992).
37. L. Brewer, Lawerence Berkeley Report No. LB-3720 (unpublished).
38. X.-P. Li, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **44**, 10929 (1991).
39. S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. Lett. **65**, 1478 (1990).
40. R. Q. Hood, M. Y. Chou, A. J. Williamson, G. Rajagopal, and R. J. Needs, Phys. Rev. B **57**, 8972 (1998).
41. P. R. C. Kent *et al.*, Phys. Rev. B **57**, 15293 (1998).
42. B. Kralik, P. Delaney, and S. G. Louie, Phys. Rev. Lett. **80**, 4253 (1998).