Optimal orbitals from energy fluctuations in correlated wave functions

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(March 24, 2022)

A quantum Monte Carlo method of determining Jastrow-Slater wave functions for which the energy is stationary with respect to variations in the single-particle orbitals is presented. A potential is determined by a least-squares fitting of fluctuations in the energy with a linear combination of one-body operators. This potential is used in a self-consistent scheme for the orbitals whose solution ensures that the energy of the correlated wave function is stationary with respect to variations in the orbitals. The method is feasible for atoms, molecules, and solids and is demonstrated for the carbon and neon atoms.

PACS numbers: 71.15.-m, 31.25.-v, 02.70.Lq

Over the past decade, quantum Monte Carlo (QMC) methods have been used to calculate the structural and electronic properties of a variety of atoms, molecules, clusters and solids. For systems with large numbers of electrons, QMC methods at present provide the most accurate benchmark calculations of structural energies. In both variational (VMC) and diffusion (DMC) calculations, a key step is the construction of a trial correlated many-electron wave function. In many such calculations, the trial wave function $\Psi$ is chosen to be of the Jastrow-Slater form, i.e., $\Psi = JD$, where $D$ is a determinant of single-particle orbitals and $J$ is the (positive) Jastrow correlation factor. Although considerable progress has been made (principally using the variance minimization approach) in the numerical construction of optimal Jastrow factors, relatively little attention has been given to the physical understanding and numerical optimization of the antisymmetric part of the wave function. In few-electron systems, variance minimization has been applied to the optimization of the determinant but, in larger systems, local density functional (LDA) or Hartree-Fock (HF) orbitals have generally been used as the only practical and numerically accurate way of constructing the determinantal part of the wave function. It has not been clear why LDA (or HF) orbitals, which have little formal justification in this context, do so well or how one might in practice do better.

A physical understanding of this issue and a practical method of approach to the calculation of such orbitals is bound to be particularly important to a wide and successful application of QMC methods.

In this Letter, a new iterative method is demonstrated which successively updates the determinant $D$ in Jastrow-Slater wave functions so that, at convergence, the energy of the full correlated wave function is stationary with respect to variations in the single-particle orbitals in the Slater determinant. The method is cast in the framework of a self-consistent field problem for the determinant and can make use of the standard numerical codes (either LDA or HF), combined with VMC sampling methods of many-body wave functions.

We will first derive Euler-Lagrange equations satisfied when the energy is stationary with respect to the single-particle orbitals in the determinant. Then, we will present the numerical approach for an iterative scheme which solves those equations exactly, demonstrate it in some numerical examples, and show that it can be conveniently combined with existing variance minimization methods for the optimization of the Jastrow factor.

Euler-Lagrange Equations: We assume that $J$ is held fixed and that only the single-particle orbitals $\phi_i$ of the determinant $D$ are varied. A general infinitesimal variation of the orbital $\phi_i$ can be written as $\phi_i \rightarrow \phi_i + \sum_{ji} \eta_{ji} \phi_j$ where $\eta_{ji}$ are infinitesimal coefficients and the sum is over a set of orthonormal orbitals which excludes all $\phi_j$ already in $D$. The corresponding variation in $D$ is given by $D \rightarrow [1 + \sum_{ji} \eta_{ji} c_j^i c_i^j]D$ where $c_j^i$ and $c_i$ are the fermion creation and destruction operators for the orbitals $j$ and $i$, respectively. The energy is stationary with respect to all variations of the orbitals $\phi_i$ if and only if the Euler-Lagrange equations,

$$\Delta E_{ji} = \frac{\partial}{\partial \eta_{ji}} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = 0,$$

are satisfied for all $i$ and $j$. $H$ is the many-body Hamiltonian. Explicit evaluation of the derivatives shows that

$$\Delta E_{ji} = \langle \Psi | (H - \tilde{E}) \left[ \frac{c_j^i c_i^j D}{D} \right] | \Psi \rangle,$$

where $\tilde{E} = \langle \Psi | H | \Psi \rangle$ and $| \Psi \rangle$ is assumed normalized.

By considering arbitrary linear combinations of the variations $\eta_{ji}$, we can see that solving the set of Euler-Lagrange equations is equivalent to requiring that

$$\Delta E_{\mathcal{O}} = \langle \Psi | (H - \tilde{E}) \left[ \frac{\mathcal{O} D}{D} \right] | \Psi \rangle = 0$$

for all possible one-body operators $\mathcal{O}$. As discussed below, it is sometimes convenient or sufficient to consider a
restricted class of variations of the orbitals in $D$ so that Eq. (3) is satisfied only for a restricted class of one-body operators.

Iterative Solution of the Euler-Lagrange Equations: We wish to find $D$ such that $\Delta E_{\partial_k} = 0$ for a set of $n$ one-body operators $\partial_k$. We sample $N_c$ configurations $\{R(i)\}$ with local energies $\{E(i) = H\Psi(R(i))/\Psi(R(i))\}$ from the square of the wave function $\Psi = JD$. We perform a least-squares fit of the local energies with the sum $E_0 + \sum_{k=1}^n V_k \partial_k D$, where $E_0$ and $V_k$ are fitting parameters and $\partial_k$ is a least-squares fit of the local energies with the sum $\sum_{k=1}^n V_k \partial_k$. In the limit of $N_c \to \infty$, this is equivalent to minimizing the integral

$$\langle \Psi \rangle \left\{ H - E_0 - \sum_{k=1}^n V_k \frac{\partial_k D}{D} \right\}^2 \langle \Psi \rangle (4)$$

with respect to the fitting parameters. This is in turn equivalent to solving the set of linear equations:

$$\sum_{k=1}^n V_k \langle \Delta \partial_k \Delta \partial_k \rangle = \langle \Delta E \Delta \partial_k \rangle, \quad \text{for } l = 1, \ldots, n, (5)$$

where $\langle \rangle$ denotes the average over the $N_c$ configurations, $\Delta \partial_k(i) = \partial_k(i) - \langle \partial_k \rangle$ and $\Delta E(i) = E(i) - \langle E \rangle$. For $N_c \to \infty$, $\langle \Delta E \partial_k \rangle \to \Delta E_{\partial_k}$ and the fitting coefficients $V_k$ are all zero if and only if all $\Delta E_{\partial_k} = 0$.

Suppose we determined a set of $V_k^{(1)}$ for a wave function $\Psi^{(1)} = JD^{(1)}$ according to the above procedure. How do we use the coefficients $V_k^{(1)}$ to obtain the orbitals $\phi_i^{(2)}$ for the determinant $D^{(2)}$ of the next iteration?

Let’s first suppose we have a non-interacting system with Hamiltonian $H_{\text{eff}}$ and eigenfunctions $\phi_i$ but that we start from the eigenstates $\phi_i^{(1)}$ of an incorrect Hamiltonian $H^{(1)} = H_{\text{eff}} - \sum_{k=1}^n A_k \partial_k$. If we follow the above fitting procedure (Eq. 3) and determine the coefficients $V_k$, it is easy to see that $V_k = A_k$ for all $k$ and $H_{\text{eff}}$ may be found (if not known in advance) as $H_{\text{eff}} = H^{(1)} + \delta H$ where $\delta H = \sum_{k=1}^n V_k \partial_k$. The correct single-particle orbitals $\phi_j$ are then eigenstates of the Hamiltonian $H^{(1)} + \delta H$.

Motivated by this argument for non-interacting systems, we construct the determinant $D^{(1)}$ of the correlated wave function $\Psi^{(1)}$ from orbitals $\phi_i^{(1)}$ which are eigenstates of a non-interacting Hamiltonian $H^{(1)}$. We compute $V_k^{(1)}$ from Eq. 3 and, as in the non-interacting case, use $\delta H^{(1)} = \sum_{k=1}^n V_k^{(1)} \partial_k$ as an increment to the physical external potential $V_{\text{ext}}$ in $H^{(1)}$ to determine a set of orbitals $\phi_i^{(2)}$. A new increment $\delta H^{(2)}$ is similarly derived from $JD^{(2)}$ and the external potential $V_{\text{ext}} + \delta H^{(1)} + \delta H^{(2)}$ is used for the next iteration to obtain the orbitals $\phi_i^{(3)}$. Convergence is reached when $\delta H^{(i)}$ is negligible. For accelerated convergence, the orbitals $\phi_i^{(m)}$ at the $m$th iteration are determined by performing a standard self-consistent LDA calculation with the external potential $V_{\text{ext}} + \sum_{i=1}^{m-1} \delta H^{(i)}$. The scheme converges within two or three iterations for the applications studied here. It should be noted that the LDA potential here is used purely for computational convenience and that the final orbitals $\phi_i^{(m)}$, the Hartree potential and the final energy-fluctuation potential (EFP) part of the non-interacting Hamiltonian, $H^{EFP} = \sum_{i=1}^n \delta H^{(i)} + V_{\text{ext}}^{\text{LDA}}$, are independent of the LDA.

One may wonder why this approach, based on an argument for non-interacting systems, would give rapid convergence in the interacting case. To see this, we consider the combined action of the many-body Hamiltonian $H$ and the Jastrow factor $J$ on the determinant $D$ by defining $H_{J}D(R) \equiv [H(J(R)D(R))]/J(R)$. The eigenvalues of $H$ and $H_{J}$ are identical and the eigenfunctions $\Psi$ of $H$ satisfy $\Psi = Jf$ where $f$ is the corresponding eigenfunction of $H_{J}$. With a suitable choice of $J$, the two-body terms in $H_{J}$ can be made weak. For the uniform electron gas, Bohm and Pines determined the long-wavelength part of the two-body Jastrow factor to remove the long-range fluctuations of the two-body interaction in $H_{J}$. Similarly, the short-range cusp condition removes the $e^2/r_{ij}$ divergence in $H_{J}$. If $H_{J}$ were truly a non-interacting Hamiltonian $H_{\text{eff}}$, its exact eigenfunctions would be Slater determinants $D$. Thus, the motivation for choosing a trial Jastrow-Slater wave function $JF$ is directly related to the approximation that two- and higher-order terms in $H_{J}$ can be neglected. This, in turn, motivates our iterative approach to the solution of the Euler-Lagrange equations.

In order to specify the full numerical implementation of the method, we need to choose an appropriate set of one-body operators $\partial_k$. We consider three possible choices:

1. $\partial_k$ is a local potential $f_k(r)$ so that $\partial_k(i) = \sum_{j=1}^{N} f_k(r_j)$ for the configuration $R(i) = (r_1, \ldots, r_N)$. The evaluation of such an operator and of the averages required in Eq. 3 and the increment of $V_{\text{ext}}$ by $\delta V(r) = \sum_{k=1}^n V_k \delta f_k$ in the self-consistent LDA calculation is then straightforward. This case corresponds to the variational freedom of multiplying all orbitals $\phi_i$ in $D$ by a common function $1 + \eta_k f_k(r)$ and is equivalent to minimizing the energy with respect to the one-body term in the Jastrow factor.

2. $\partial_k$ is an angular-momentum-dependent potential $f_{k}(r)P_l$ with $P_l$ the projection operator for angular momentum $l$. The evaluation of the coefficients in Eq. 3 can be made using the standard methods for the integration of non-local pseudopotentials in VMC and incrementing the external potential in the LDA code by an angular-momentum-dependent potential is also straightforward. This case corresponds to the variational freedom of multiplying different angular momentum orbitals $\phi_i$ in $D$ by different factors.

3. Arbitrary variations of the orbitals $\phi_i$ may be allowed by using the one-body operators $\partial_{ji} = c_i^\dagger c_j$, where
labels an occupied orbital of the determinant $D$ and $j$ an unoccupied orbital. $O_{ji}$ acting on $D$ simply replaces the orbital $\phi_i$ in $D$ with the orbital $\phi_j$. The averages in Eq. 2 can be efficiently calculated using the relations in Ref. [9] for replacing a row in a Slater determinant. The Hamiltonian in the self-consistent LDA calculation is then incremented by $\delta H = \sum_{ji} V_{ji} |\phi_j\rangle \langle \phi_i| + c.c.$.

Thus, while the approach can use, with trivial modifications, all the computational techniques to determine LDA orbitals, the final orbitals $\phi^{(m)}_i$ minimize the energy for the many-body wave function $J D^{(m)}$ with no restriction on the form of $J$.

FIG. 1. The incremental EFP potentials, $\delta H(r)$, for the ground state of the carbon and neon pseudo-atoms. The potentials corresponding to the Jastrow factors $J_1$ and $J_2$ are shown for the first and last iteration. $\delta H(r)$ at the first iteration is calculated using LDA orbitals in the determinant.

In this Letter, we present results for the carbon and neon pseudo-atoms (pseudopotentials are used to eliminate the 1s core electrons [3]). The application of the approach to extended systems will be discussed in detail elsewhere [12]. In optimizing the orbitals, we have investigated method (1) with a local EFP potential, and method (2) with both $s$ and $p$ EFP potentials. Because there is only one type of $s$ orbital (spin up and down) and only one radial function for the $p$ orbitals, methods (2) and (3) are equivalent and all variations of the orbitals consistent with the ground state symmetry are allowed in method (2). For simplicity, we will focus on results obtained using the local potentials (1). Interestingly, the orbitals, charge density, and energies differ only very slightly when the full variational freedom of the orbitals is allowed using separate $s$ and $p$ non-local potentials.

The initial atomic orbitals in the Jastrow-Slater wave function are determined from a LDA calculation. Because of self-interaction in the LDA, $\delta H(r)$ computed at the first iteration must behave like $-e^2/r$ at large distances. Since, at large radii, the sampling of $\delta H$ has large statistical noise due to the very low electron density, we constrain $\delta H^{(1)}(r)$ to behave like $-e^2/r$ at large $r$ while allowing full variational freedom at smaller $r$. This is achieved by writing $\delta H^{(1)}(r) = V_0(r) + \sum_{E=1}^{n_E} V_k f_k(r)$, where $f_k(r) = \cos((k-1)\pi r/r_c) \exp[-(r/r_c)^2]$ and $V_0(r)$ goes like $-e^2/r$ for $r > r_c$ and smoothly becomes constant for $r < r_c$. The parameters $V_k$ are determined by least-square fitting, as in Eq. 4. After the first iteration, $V_0(r)$ is not included in fitting $\delta H^{(1)}$.

We performed the calculations for two different types of Jastrow factor, $J_1$ and $J_2$. The Jastrow factor $J_1$ only contains electron-nucleus and electron-electron terms (see Appendix A of Ref. [5]) and the value of its single free parameter was determined by minimizing the energy. $J_2$ includes electron-electron, electron-electron-nucleus and electron-nucleus terms (modified from Ref. [6] to deal with a pseudo-atom) and variance minimization was used to optimize its 25 parameters.

In Fig. 1, we show the first and last incremental EFP potentials for carbon and neon, obtained using the two Jastrow factors $J_1$ and $J_2$. The cut-off radius $r_c$ is equal to 3 a.u. for neon and 5 a.u. for carbon and the number of basis functions, $n_f$, is always less than 50. In each case, the final iteration is almost indistinguishable from zero, except for statistical sampling noise near the origin. The potential depends on the choice of the correlated component of the wave function: the superiority of $J_2$ over $J_1$ is reflected in the much smaller initial potential $\delta H^{(1)}(r)$.

TABLE I. Total energies in VMC ($E_{\text{VMC}}$) and DMC ($E_{\text{DMC}}$) and root mean square fluctuation ($\sigma$) of the local energy in VMC. $E_N$ and $E_D$ are the percentages of correlation energies recovered in VMC and DMC. Hartree units are used. (For carbon, the HF energy is $E_{\text{HF}} = -5.3530$ and the ground state energy $E_0$ is $E_0 = -5.4561$ Hartree. For neon, $E_{\text{HF}} = -34.6930$ and $E_0 = -35.0106$ Hartree).

| $\Psi$ | $J_1 D_{\text{LDA}}$ | $J_1 D_{\text{EFP}}$ | $J_2 D_{\text{LDA}}$ | $J_2 D_{\text{EFP}}$ | $E_N$ (%) | $E_D$ (%) | $\sigma$ |
|--------|----------------|----------------|----------------|----------------|----------|----------|--------|
| C      | -5.4345(1)     | -5.4376(1)    | -5.4371(1)     | -5.4373(1)     | 79.1(1)  | 82.0(1)  | 0.255  |
| Ne     | -34.9554(2)    | -34.9674(3)   | -34.9912(2)    | -34.9913(2)    | 82.6(1)  | 86.4(1)  | 1.150  |
| Ne     | -34.6930       | -35.0106      | 93.9(1)        | 97.9(1)        | 0.630    | 0.624    |        |

From Table 1, we see that for each atom and for each type of Jastrow factor, the energy is lowered in going from LDA to EFP orbitals. Since $J_2$ has greater flexibility than $J_1$, this lowering of energy is negligible for $J_2$. For carbon (an open shell system) a multideterminant wave function is required to accurately represent the correlations and the use of a more flexible Jastrow factor $J_2$ gains little over $J_1$. (The very small difference in energy between $J_2 D_{\text{EFP}}$ and $J_1 D_{\text{EFP}}$ may be due either to the
different parametric forms of \( J_1 \) and \( J_2 \) or to intrinsic differences between variance minimization and energy minimization.) In DMC, the energy gain in using EFP instead of LDA orbitals is negligible for both systems.

In conclusion, we have demonstrated, for the first time, a numerically stable, rapidly convergent method which combines Monte Carlo sampling with existing self-consistent field techniques to minimize the energy with respect to the orbitals in a correlated Jastrow-Slater wave function. The approach may be combined with variance minimization methods for the optimization of the Jastrow factor. The resulting variational many-body wave functions have electron densities very close to the most accurate densities available for atoms, using variance minimization and DMC methods. Preliminary tests show that the approach, in modified form, is also applicable to multi-determinant wave functions. We thank C. Umrigar for useful discussions and E. Shirley for the use of his Hartree-Fock code. This work was supported by Enterprise Ireland, Contract SC/98/748.

![Graph](image-url)

**FIG. 2.** Valence charge density \( 4\pi r^2 \rho(r) \) for carbon and neon. The upper panel for each atom shows the “exact” density \( \rho(r) \). The lower panel shows the differences from the HF density of the “exact”, LDA, GGA (PW91) and the densities for the wave functions \( J_1 D_{\text{EFP}} \) (VMC1) and \( J_2 D_{\text{EFP}} \) (VMC2).

In Fig. 2 the densities are shown for carbon and neon. In both systems and for both Jastrow factors, the VMC density obtained with the EFP approach is substantially closer to the best estimate of the true density than HF, and much closer than either LDA or the Perdew-Wang ’91 (PW91) generalized gradient approximation (GGA). In carbon, neither \( J_1 \) nor \( J_2 \) can capture the intrinsic multi-configuration correlation and the accuracy in the densities cannot rival that obtained in neon with \( J_2 D_{\text{EFP}} \).

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