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Comments on the quantum Monte Carlo method and the density matrix theory

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Density matrix theory is implemented in a variational quantum Monte Carlo computation of electronic properties of atoms and molecules. Differences between electronic densities from conventional and density matrix methods are detected. However, calculated properties present similar behavior and partial antisymmetry can be ignored in the cases studied. © 2003 American Institute of Physics. [DOI: 10.1063/1.1558393]

In the last few years, quantum Monte Carlo methods (QMC) have been widely applied in atomic and molecular studies of many different systems such as electron gas,¹ liquid He,² molecular and metallic hydrogen,³ carbon clusters,^{4,5} and several molecules including LiH, H₂O, H₃, and others.⁶⁻⁹

The simplest form of quantum Monte Carlo is the variational method (VMC), which determines atomic and molecular properties from approximate solutions of the electronic Schrödinger equation through the expectation value of the corresponding operator. If a Hamiltonian (\hat{H}) operates on a trial wave function (ψ), the variational principle states that the expected value to the energy ($E_{(\psi)}$) is an upper bound to the exact ground state energy (E_o),

$$E_o \leq \frac{\int \Psi^* \hat{H} \Psi d\mathbf{R}}{\int \Psi^* \Psi d\mathbf{R}} = E_{(\psi)}. \quad (1)$$

To perform Monte Carlo integration, Eq. (1) is written in an appropriate form,

$$E_{(\psi)} = \frac{\int \psi^* \psi (\hat{H} \psi / \psi) d\mathbf{R}}{\int \psi^* \psi d\mathbf{R}} = \frac{\int \psi^* \psi E_L d\mathbf{R}}{\int \psi^* \psi d\mathbf{R}}, \quad (2)$$

where the local energy is defined as

$$E_L = \frac{\hat{H} \psi}{\psi}. \quad (3)$$

The total energy (E) can be obtained by Metropolis algorithm sampling points of the configuration space $\{\mathbf{R}_i\}$ from the probability distribution $|\psi|^2$ providing the well-know averaged energy

$$E_{(R)} = \langle E_L \rangle_{\psi^2} = \lim_{N \rightarrow \infty} \left(\frac{1}{N} \sum_{i=1}^N E_L(\mathbf{R}_i) \right). \quad (4)$$

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In order to perform the integration of the electronic properties, trial wave functions are considered as the product of two determinants built from spin-orbital functions φ_i and a correlation factor, Ψ_{corr} , as

$$\Psi_{\alpha,\beta} = N \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_1(\mathbf{r}_2) & \cdots & \varphi_1(\mathbf{r}_j) \\ \varphi_2(\mathbf{r}_1) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_2(\mathbf{r}_j) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_j(\mathbf{r}_1) & \varphi_j(\mathbf{r}_2) & \cdots & \varphi_j(\mathbf{r}_j) \end{vmatrix} \times \begin{vmatrix} \varphi_{j+1}(\mathbf{r}_{j+1}) & \varphi_{j+1}(\mathbf{r}_{j+2}) & \cdots & \varphi_{j+1}(\mathbf{r}_n) \\ \varphi_{j+2}(\mathbf{r}_{j+1}) & \varphi_{j+2}(\mathbf{r}_{j+2}) & \cdots & \varphi_{j+2}(\mathbf{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_n(\mathbf{r}_{j+1}) & \varphi_n(\mathbf{r}_{j+2}) & \cdots & \varphi_n(\mathbf{r}_n) \end{vmatrix} \Psi_{\text{corr}}. \quad (5)$$

The electronic space and spin coordinates ($\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j$) and the one-electron functions ($\varphi_1, \varphi_2, \dots, \varphi_j$) refer to j electrons of α spin. The space and spin coordinates ($\mathbf{r}_{j+1}, \mathbf{r}_{j+2}, \dots, \mathbf{r}_n$) and the one-electron functions ($\varphi_{j+1}, \varphi_{j+2}, \dots, \varphi_n$) refer to $n-j$ electrons of opposite spin. N is normalization constant. This procedure is often used for the QMC methods because it allows for the calculation of the local properties by eliminating the spin functions. However, α - β trial wave functions represented by Eq. (5) ignore pure spin states and cannot fulfill the general antisymmetric requirement for multielectronic systems. Despite its fundamental deficiencies, the use of Eq. (5) provides correct electronic properties for most of the systems in the literature⁴⁻⁹ not only for VMQ but also for the diffusion quantum Monte Carlo (DQMC) method. The success of this formalism relies in the case of DQMC largely on the argument that the correct nodal properties of the wave function are preserved.⁶⁻⁹ On the other hand, space and spin variables can be properly treated restricting fundamental antisymmetry constraints and electronic indistinguishability by means of the density matrix theory.¹⁰⁻¹² In this model a well-behaved density matrix must satisfy the antisymmetry constraint for fermions and its integration over all the spatial and spin coordinates must be associated with the number of particles of the system. A convenient way to establish a link

between the density matrix concept and a well-behaved and arbitrary n electron wave function is through the n -order density matrix

$$\begin{aligned} \Gamma^{(n)}(\mathbf{r}'_1 \mathbf{r}'_2 \mathbf{r}'_3 \dots \mathbf{r}'_n | \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_n) \\ = \Psi^*(\mathbf{r}'_1 \mathbf{r}'_2 \mathbf{r}'_3 \dots \mathbf{r}'_n) \Psi(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_n). \end{aligned} \quad (6)$$

Any quantum mechanical operator applied on $\Gamma^{(n)}$ acts only on the unprimed coordinates $\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_n$, but not on $\mathbf{r}'_1 \mathbf{r}'_2 \mathbf{r}'_3 \dots \mathbf{r}'_n$. Subsequently, the dashed coordinates are replaced setting $\mathbf{r}'_1 = \mathbf{r}_1$, $\mathbf{r}'_2 = \mathbf{r}_2$, and so on. In this way, any local atomic or molecular property averaged over the spin coordinates can be defined as

$$O_L = \frac{\int \int \dots \int \hat{O} \Gamma^{(n)} d\xi_1 d\xi_2 \dots d\xi_n}{\int \int \dots \int \Gamma^{(n)} d\xi_1 d\xi_2 \dots d\xi_n}, \quad (7)$$

where ξ are the spin coordinates. Equation (7) defines a local property depending only on the spatial coordinates and it is formally exact, generally, preserves the correct spin state of the system, and does not violate indistinguishability of fermions or antisymmetry of a trial wave function. These features suggest that Eq. (7) is a formally superior representation to the local properties than Eq. (3) using wave functions defined by Eq. (5). The purpose of this Communication is to show that Eq. (7) can be suitably implemented in a VMC computation of electronic properties of atoms and molecules. The results reported here are restricted to the behavior of the electronic energy of simple systems in order to evaluate possible differences between the present alternative and the conventional mathematical treatment. It can be anticipated that our results show that both methods present similar behavior and possibly partial antisymmetry can be ignored in most of the properties studied. However, it must be said that differences between both electronic densities were detected but have not provided significant discrepancies between the traditional method and the more rigorous alternative introduced in this work. More complex systems and the use of the density matrix theory along with diffusion Monte Carlo methods will be treated in forthcoming works.

Most of the conventional properties investigated with variational Monte Carlo using density matrix from Hartree-Fock wave functions (d-VMC) are restricted to operators not depending of the spin coordinates. In this case, Eq. (7) can be simplified and the integration over the spin coordinates is carried out on the n -order density matrix providing

$$\begin{aligned} \Omega^{(n)}(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_n | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_n) \\ = \int \int \dots \int \Gamma^{(n)}(\mathbf{r}'_1 \mathbf{r}'_2 \dots \mathbf{r}'_n | \mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_n) d\xi_1 d\xi_2 \dots d\xi_n \end{aligned} \quad (8)$$

and the local property as

$$O_L = \frac{\hat{O} \Omega^{(n)}(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_n | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_n)}{\Omega^{(n)}(\mathbf{x}'_1 \mathbf{x}'_2 \dots \mathbf{x}'_n | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_n)}. \quad (9)$$

Other methods used along with quantum Monte Carlo simulations can also be associated with the spin averaged density matrix. For instance, substitution of $\Psi^* \Psi$ by Ω in a

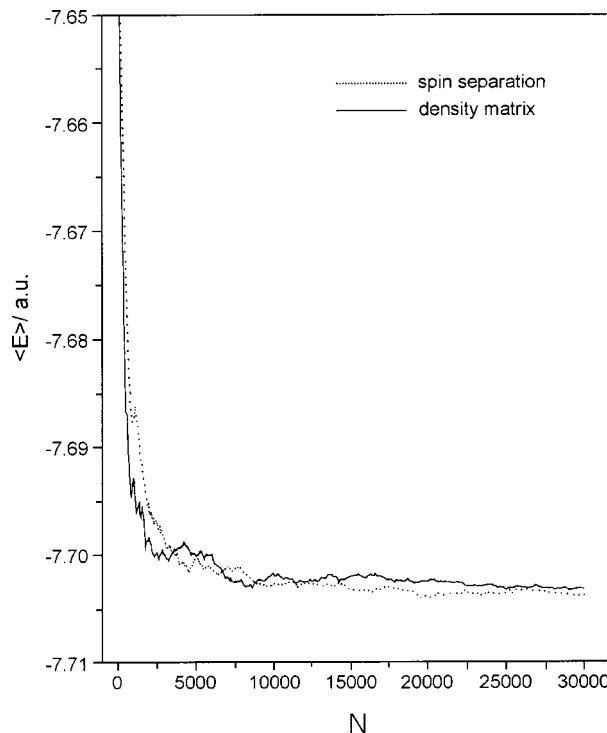


FIG. 1. Typical convergence of the accumulative average energy for LiH^+ using Hartree-Fock molecular orbitals.

Metropolis algorithm is straightforward. The same is correct regarding the use of the Fokker-Planck method to improve the importance sampling during the Monte Carlo simulation.

When Hartree-Fock wave functions are used, a convenient and efficient algorithm to compute the n -order density matrix [Eq. (8)] and the energy components [Eq. (9)] can be obtained from the Fock-Dirac first-order density matrix,¹³⁻¹⁵

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j=1}^n \varphi_j^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_2), \quad (10)$$

using the expression

$$\Omega_{\alpha, \beta} = N \begin{vmatrix} \rho(\mathbf{r}'_1, \mathbf{r}_1) & \rho(\mathbf{r}'_1, \mathbf{r}_2) & \dots & \rho(\mathbf{r}'_1, \mathbf{r}_n) \\ \rho(\mathbf{r}'_2, \mathbf{r}_1) & \rho(\mathbf{r}'_2, \mathbf{r}_2) & \dots & \rho(\mathbf{r}'_2, \mathbf{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \rho(\mathbf{r}'_n, \mathbf{r}_1) & \rho(\mathbf{r}'_n, \mathbf{r}_2) & \dots & \rho(\mathbf{r}'_n, \mathbf{r}_n) \end{vmatrix} \Psi_{\text{corr}}. \quad (11)$$

Tests for a set of atoms and simple diatomic molecules using either separation of spins or density matrix formalism showed, as expected, equivalent accuracy for both methods as well as numerical convergence. Figure 1 shows an example of the behavior of the accumulative average energy for a simulation of LiH^+ using Hartree-Fock molecular orbitals obtained from conventional *ab initio* calculation with single-zeta Slater type functions¹⁶ and bond length of 3.0495 a.u. The molecular orbitals obtained from STO-10G basis set are given by

$$1 \sigma_g = 0.99743.1 s_{\text{Li}}^{(S)} + 0.01385.2 s_{\text{Li}}^{(S)} + 0.00221.1 s_{\text{H}}^{(S)}$$

and

$$2\sigma_g = -0.09685.1s_{\text{Li}}^{(S)} - 0.02837.2s_{\text{Li}}^{(S)} + 1.01689.1s_{\text{H}}^{(S)}.$$

The exponents of the Slater functions are $\zeta_{1s,\text{Li}} = 2.69063$, $\zeta_{2s,\text{Li}} = 0.63961$ and $\zeta_{1s,\text{H}} = 1.0000$.

The acceptance ratio was 0.56 and two distinct set of steps were used to determine the average energy: a) 3×10^4 and b) 1×10^6 . The Hartree-Fock energy from *ab initio* calculation for this wave function is -7.7053 a.u. and the results obtained by the simulations using Eq. (3) and Eq. (9) and 3×10^4 steps are -7.7036 ± 0.0008 a.u. and -7.7029 ± 0.0008 a.u., respectively. The same total energy (-7.7046 ± 0.0001 a.u.) is obtained using either separation of spins or density matrix method and 1×10^6 steps. The results are essentially the same although better performance with respect to the *ab initio* result can be obtained incorporating importance sampling methods in the simulation. Variational Monte Carlo simulations, including d-VMC, present the best convergence rate with an acceptance ratio between 40% and 60%.

However, some intriguing differences in the electronic densities can be observed when simple Hartree-Fock atomic or molecular orbitals are used by both methods. The electronic density of the lithium atom is taken as example. The nucleus is fixed at the center of the coordinate system and all electrons are confined in the plane xy . Two electrons are held fixed with arbitrary coordinates ($x = 1.269867$ a.u., $y = 0.834961$ a.u.) for electron 1 and ($x = -1.669867$ a.u., $y = 0.834961$ a.u.) for electron 2. The third electron is allowed to move along the xy plane. Two density matrices are determined from the Hartree-Fock single-zeta wave function of Clementi and Roetti,¹⁶ each of them with different multielectronic wave functions: one using determinants with separation of spins and the other the complete Slater determinant. Both density matrices are integrated over the spin coordinates. Electrons 1 and 3 are assigned as alpha spin in separation of spins description and electron 2 is a beta spin. Systematic analysis shows that the cusps are well defined by both surfaces and tend to zero when the electron is moved away from the nucleus. The differences between the surface profiles arise when electron 3 is near electron 1 (see Fig. 2). Figure 2 shows that the density matrix with spin separation provides a surface with a minimum, while the use of the complete Slater determinant provides a maximum at the same coordinates. The electronic correlation in most Hartree-Fock calculation is comparatively small regarding the total energy of the system and, although differences exist between both treatments, they are apparently not significant for the cases studied.

In summary, the combination of density matrix and variational Monte Carlo is capable of recovering the antisymmetry and preserve indistinguishable characteristic of the electrons. The consistence of the combination can be easily demonstrated by reproducing Hartree-Fock calculations using the conventional Slater determinant to generate the den-

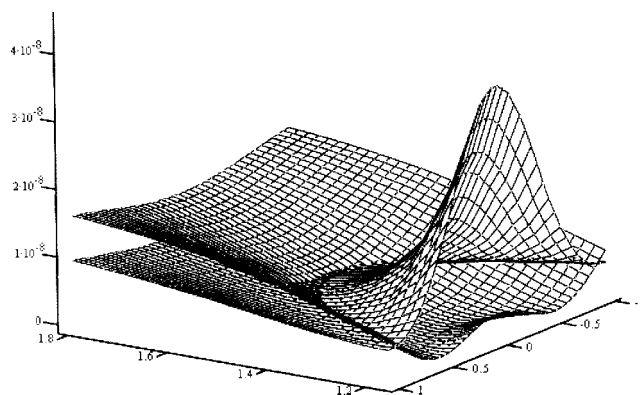


FIG. 2. Density matrices for Li in the ground state calculated from Hartree-Fock atomic orbitals with single-zeta basis functions and wave functions with separation of spins and conventional Slater determinant.

sity matrix. Tests show that the convergence of d-VMC is always reached independent of the acceptance ratio and initial configuration. The best accepted ratio is near to 50%, as it is common to most Monte Carlo simulations.

The reproducibility of the Hartree-Fock energies and some frequently calculated properties as dipole moment and higher moments suggest that the nodal properties are preserved by both methods and consequently the computationally most efficient method [Eq. (3)] should be used.

Differences between electronic densities calculated with the conventional method and the more rigorous alternative suggest that specific properties in highly correlated systems can present disagreement when calculated by both methods. Studies in this sense and exploring diffusion quantum Monte Carlo are in progress.

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