Pfaffian Pairing Wave Functions in Electronic-Structure Quantum Monte Carlo Simulations

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We investigate the accuracy of trial wave functions for quantum Monte Carlo based on Pfaffian functional form with singlet and triplet pairing. Using a set of first row atoms and molecules we find that these wave functions provide very consistent and systematic behavior in recovering the correlation energies on the level of 95%. In order to get beyond this limit we explore the possibilities of multi-Pfaffian pairing wave functions. We show that a small number of Pfaffians recovers another large fraction of the missing correlation energy comparable to the larger-scale configuration interaction wave functions. We also find that Pfaffians lead to substantial improvements in fermion nodes when compared to Hartree-Fock wave functions.

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Wave functions of interacting quantum systems such as electrons in matter are notoriously difficult to calculate despite decades of effort. One of the most productive many-body methods for electronic-structure problems is the quantum Monte Carlo (QMC) procedure, which employs stochastic approaches both for solving the stationary Schrödinger equation and for evaluation of expectation values [1–3]. The key advantage of QMC is its capability to use explicitly correlated wave functions which allow the study of many-body effects beyond the reach of mean-field approaches. The most important limit on QMC accuracy is the fixed-node approximation which is used to circumvent the fermion sign problem [4,5]. Even with this approximation, the fixed-node QMC has been very successful for a host of real systems such as molecules, clusters, and solids with up to hundreds of valence electrons and has provided an agreement with experiments (1%–3%) for cohesive energies, band gaps, and other energy differences [3]. However, reaching beyond the fixed-node limit has proven to be challenging since fermion nodes (subset of position space where the wave function vanishes) are complicated high-dimensional manifolds which are affected by correlation as well. Accuracy of QMC trial wave functions is therefore crucial for both fundamental and also computational reasons.

The state-of-the-art QMC calculations employ accurate Slater-Jastrow wave functions that can be written as $\Psi_T = \Psi_A \exp[U_{\rm corr}]$ where Ψ_A is the antisymmetric part while $U_{\rm corr}$ describes the electron-electron and higher-order correlations. The antisymmetric part is either a single Hartree-Fock (HF) determinant of one-particle orbitals or a multireference sum of excited determinants such as a limited configuration interaction (CI) expansion [6]. A natural generalization of a one-particle orbital is a two-particle or pair orbital, sometimes called a geminal. In particular, the Bardeen-Cooper-Schrieffer (BCS) wave function, which is an antisymmetrized product of singlet pairs, has been recently used to calculate several atoms and molecules as well as superfluid Fermi gases [7–9]. The results show significant improvements over the single-determinant HF wave functions. Nevertheless, for partially spin-polarized systems the energy gains are less pronounced due to the lack of pairing correlations in the spin-polarized subspace [8]. The spin-polarized triplet pairing wave functions based on Pfaffians have been tried a few times on model systems [10,11].

In this Letter, we propose to describe systems of electrons by Pfaffian wave functions with variational freedom beyond HF and also BCS wave functions. The Pfaffian allows us to incorporate pair orbitals for both singlet and triplet pairing channels together with unpaired one-particle orbitals into a single, compact wave function. These Pfaffian wave functions are tested on atomic and molecular systems in variational and fixed-node diffusion Monte Carlo methods. The results show significant gains in correlation energy both for spin-polarized and unpolarized cases. Furthermore, we explore the multi-Pfaffian wave functions and we find that they recover a large fraction of the missing correlation energy while being much more compact than expansions in determinants.

Let us consider $1, 2, \ldots, N$ spin-up and $N+1, \ldots, 2N$ spin-down electrons in a singlet state with electron spatial coordinates denoted simply as $R = (1, 2, \ldots, 2N)$. An antisymmetrized product of singlet pair orbitals $\phi(i, j) = \phi(j, i)$ is the BCS wave function

$$\Psi_{\rm BCS} = \mathcal{A}[\phi(i, j)] = \det[\phi(i, j)] = \det[\mathbf{\Phi}], \quad (1)$$

which is simply a determinant of $N \times N$ matrix. The BCS wave function is efficient for describing systems with single-band correlations such as Cooper pairs in conven-

tional BCS superconductors where pairs form from one-particle states close to the Fermi level. For partially spin-polarized states one can augment the matrix by columns/rows of one-particle orbitals. However, the spin-polarized subspace is then uncorrelated and for a fully spin-polarized system one ends up with the usual Hartree-Fock wave function. In order to correlate spin-polarized electrons it is necessary to generalize the wave function form and introduce effects of triplet pairing.

For a system of $2N$ fully spin-polarized electrons the pairing wave function is formed as an antisymmetrized product of triplet pair orbitals $\chi(i,j) = -\chi(j,i)$ and is given by [10,11]

$$\mathcal{A}\,[\chi(1,2)\chi(3,4)\ldots] = \mathrm{Pf}[\chi(i,j)] = \mathrm{Pf}[\boldsymbol{\xi}], \qquad (2)$$

which defines a Pfaffian of degree $2N$, e.g., for $N = 2$

$$\mathrm{Pf}\,[\chi(i,j)] = \chi(1,2)\chi(3,4) - \chi(1,3)\chi(2,4) + \chi(1,4)\chi(2,3). \qquad (3)$$

Any Pfaffian of an odd degree vanishes, however, the Pfaffian wave function can be easily generalized to an odd number of electrons by extending the Pfaffian by a row/column of one-particle (unpaired) orbital. For example, for three spin-up electrons, replace the last row/column in the equations above as $\chi(i,4) \to \varphi(i)$ and $\chi(4,i) \to -\varphi(i)$. We note that the Hartree-Fock wave function is a special case of both BCS singlet and Pfaffian triplet pairing wave functions as discussed [12].

The square of the Pfaffian is related to the determinant of a skew-symmetric matrix as

$$\{\mathrm{Pf}[\chi(i,j)]\}^2 = \det[\chi(i,j)]. \qquad (4)$$

However, the QMC applications require also the knowledge of the wave function sign, e.g., for enforcing the fixed-node restriction. Therefore, we have implemented a direct evaluation of Pfaffian based on an $O(N^3)$ algorithm which is analogous to Gauss elimination for determinants. Note that Pfaffians can be expanded in Pfaffian minors and by exploring Cayley's results [13] one can calculate the Pfaffian and its updates for electron moves in computer time similar to the calculation of determinants [12].

Let us now consider a partially spin-polarized system with unpaired electrons. Remarkably, the Pfaffian form can accommodate both singlet and triplet pairs as well as one-particle unpaired orbitals into a single, compact wave function. The singlet/triplet/unpaired (STU) orbital Pfaffian wave function is given by

$$\Psi_{\mathrm{STU}} = \mathrm{Pf}\begin{bmatrix} \boldsymbol{\xi}^{\uparrow\uparrow} & \boldsymbol{\Phi}^{\uparrow\downarrow} & \boldsymbol{\varphi}^{\uparrow} \\ -\boldsymbol{\Phi}^{\uparrow\downarrow T} & \boldsymbol{\xi}^{\downarrow\downarrow} & \boldsymbol{\varphi}^{\downarrow} \\ -\boldsymbol{\varphi}^{\uparrow T} & -\boldsymbol{\varphi}^{\downarrow T} & 0 \end{bmatrix}, \qquad (5)$$

where the bold symbols are block matrices/vectors of corresponding orbitals and T denotes transposition. For a spin-restricted STU wave function the pair and one-particle orbitals of spin-up and spin-down channels would be identical.

The Pfaffian wave functions were used in QMC calculations by variational and fixed-node diffusion Monte Carlo (VMC and DMC) methods [2,3]. The VMC trial/variational wave function is a product of an antisymmetric part Ψ_A times a Jastrow correlation factor

$$\Psi_{\mathrm{VMC}}(R) = \Psi_A(R)\exp[U_{\mathrm{corr}}(\{r_{ij}\},\{r_{iI}\},\{r_{iJ}\})], \qquad (6)$$

where U_{corr} depends on electron-electron, electron-ion, and electron-electron-ion combinations of distances [3,14] with a maximum of 22 variational parameters. For the antisymmetric part we have used $\Psi_A = \Psi_{\mathrm{HF}}$ and $\Psi_A = \Psi_{\mathrm{STU}}$ as well as some tests with $\Psi_A = \Psi_{\mathrm{BCS}}$ to compare with recent results [8,9]. The pair orbitals were expanded in products of one-particle orbital basis [8] as

$$\phi(i,j),\ \chi(i,j) = \sum_{k,l} c_{kl}\varphi_k(i)\varphi_l(j). \qquad (7)$$

The coefficients are symmetric ($c_{kl} = c_{lk}$) for the singlet $\phi(i,j)$, and antisymmetric ($c_{kl} = -c_{lk}$) for the triplet $\chi(i,j)$ functions. The expansions include both occupied and unoccupied (virtual) one-particle orbitals. The one-particle atomic and molecular orbitals used in expansions, which we tested, were either Hartree-Fock orbitals or natural orbitals [6] from CI correlated calculations. Typically, we used about 10 virtual orbitals and the natural orbitals produced better and more systematic results than the HF ones. The pair orbital expansion coefficients were then optimized in VMC by minimizations of energy using recently published methods [14].

We have applied these developments to several first row atoms and dimers (Fig. 1). Except for the Be atom, we used

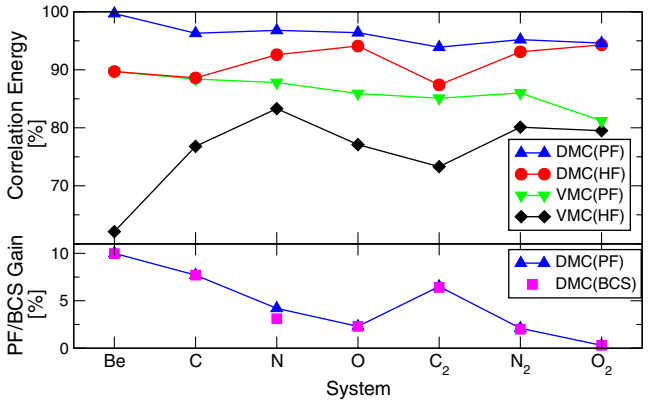

FIG. 1 (color online). Correlation energies obtained by QMC methods with the different trial wave functions: VMC and fixed-node DMC with HF nodes and STU Pfaffian nodes (PF). The lower plot shows the fixed-node DMC correlation energy gains over HF nodes for BCS and STU Pfaffian wave functions. The statistical error bars are of the symbol sizes or smaller. Except for the Be atom all the calculations used the same pseudopotentials [15].

pseudopotentials to eliminate the atomic cores [15] while the previous calculations with BCS wave functions were done with all electrons [8]. Nevertheless, our BCS wave functions produced percentages of correlation energies rather close to the ones obtained with all electrons [8]. Perhaps the most striking result is a systematic percentage of recovered correlation energy (94%–97%) for systems heavier than Be (see Fig. 1). The triplet contribution for these single Pfaffian STU wave functions are small, with the only exception being the nitrogen atom, where we see a gain of additional 1% in correlation energy (Table I) when compared to the trial wave function without triplet pairs. We believe that this is due to the fact that the nitrogen atom is quartet and therefore has the highest spin polarization from all studied cases.

Our results show that the single Pfaffian form is capable of capturing single-band near degeneracies and mixing of excited states for both spin-polarized and unpolarized systems. Considering multideterminantal expansions, such as the CI method, the overall trade-off between accuracy and computational cost seems to be in favor of more compact and physically based Pfaffian wave functions. A similar opinion was also expressed by Sorella and co-workers [8].

In order to test the limits of Pfaffian functional form, we propose a simple extension: a multiple Pfaffian (MPF) wave function having a form

$$\Psi_{\mathrm{MPF}} = \mathrm{Pf}[\chi_1, \phi_1, \varphi_1] + \mathrm{Pf}[\chi_2, \phi_2, \varphi_2] + \cdots, \quad (8)$$

so that in Eq. (6) we have $\Psi_A = \Psi_{\mathrm{MPF}}$. In actual calculations we start with all pairing functions such that each Pfaffian is equal to the HF wave function, $\mathrm{Pf}[\chi_i, \phi_i, \varphi_i] = \Psi_{\mathrm{HF}}$. The pairing orbitals [see Eq. (7)] are expanded in the basis of HF or natural occupied orbitals, e.g., for the carbon atom we have $2s$, $2p_x$, and $2p_y$. The choice of singlet $\phi_1(1,2) = 2s(1)2s(2) \equiv \phi_1[2s, 2s]$ and triplet $\chi_1(1,2) = 2p_x(1)2p_y(2) - 2p_y(1)2p_x(2) \equiv \chi_1[2p_x, 2p_y]$ pairing orbitals then gives $\mathrm{Pf}[\chi_1, \phi_1] = \Psi_{\mathrm{HF}}[2s^{\uparrow\downarrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}]$. However, one can construct the equivalent combinations of pairs as: $\phi_2[2s, 2p_x]$, $\chi_2[2s, 2p_y]$ and $\phi_3[2s, 2p_y]$, $\chi_3[2s, 2p_x]$. We can therefore include all three Pfaffians into our Ψ_{MPF} and further optimize independently all the pairing functions in VMC on the space of occupied and virtual orbitals. This construction allows us to incorporate the excitations which are not present in the single Pfaffian STU wave function based only on a single ϕ and a single χ pairing function. In the leading order the resulting MPF wave function then corresponds to the CI wave function with singles and doubles with the same active orbital space. The disadvantage of this approach is that we perform the VMC optimizations of M^2 pairing coefficients for each Pfaffian given that M is the total size of our orbital basis. However, this can be improved by a factor of M if we rotate the one-particle orbitals to make the pairing functions diagonal. The total number of Pfaffians in the expansion is then subject to the required symmetry of state and desired accuracy. In the most general case it would be proportional to the number of distinct pairs. For large systems one can restrict the number of pairs by including only the ones which have significant contributions, e.g., pairs formed from states close to the Fermi level, or considering pairs only within a given band or a subband.

The results (Table II) show that our MPF wave functions are able to recover close to 99% of the correlation energy. Furthermore, comparison with the CI results shows that it is possible to obtain similar quality of wave functions with corresponding improvements of the fermion nodes at much smaller calculational cost. This is another indication that the inclusion of singlet and triplet pairing enables us to treat the correlation in both spin-polarized and spin-unpolarized channels in a consistent manner.

The quality of fermion nodes is crucial for accurate energies in the fixed-node DMC. The fermion node manifold is defined by an implicit equation $\Psi(R) = 0$. For N electrons the manifold has $(3N - 1)$ dimensions and divides the configuration space into compact nodal cells. The HF spin-polarized ground states typically show two nodal cells, while HF unpolarized or partially polarized states have $2 \times 2 = 4$ nodal cells since the wave function is a product of spin-up and spin-down determinants [17–19]. Changes in the HF nodal structures from the inclusion of correlation were recently investigated by D. Bressanini *et al.* [18,19]. Here we observe that the pairing correlations

TABLE I. Total energies (a.u.) for N atoms and dimers, with amounts of correlation energy recovered, in VMC and DMC methods with wave functions as discussed in the text.

Wave function (WF)	N	E_{corr} [%]	N_2	E_{corr} [%]
HF	−9.628 915	0	−19.44 946	0
VMC/HF	−9.7375(1)	83.3(1)	−19.7958(5)	80.1(1)
VMC/BCS	−9.7427(3)	87.3(2)	−19.8179(6)	85.2(1)
VMC/STU	−9.7433(1)	87.8(1)	−19.821(1)	86.0(2)
DMC/HF	−9.7496(2)	92.6(2)	−19.8521(3)	93.1(1)
DMC/BCS	−9.7536(2)	95.7(2)	−19.8605(6)	95.1(1)
DMC/STU	−9.7551(2)	96.8(1)	−19.8607(4)	95.2(1)
Exact/est.	−9.759 215	100	−19.88 196	100

TABLE II. Percentages of correlation energies recovered for C, N, and O atoms by VMC and DMC methods with wave functions as discussed in the text. Corresponding number of Pfaffians or determinants n for each wave function is also shown. The estimated exact correlation energies for C, N, and O are 0.1031, 0.1303, and 0.1937 a.u. [16].

WF	n	C	n	N	n	O
VMC(MPF)	3	92.3(1)	5	90.6(1)	11	93.6(2)
VMC(CI)	98	89.7(4)	85	91.9(2)	136	89.7(4)
DMC(MPF)	3	98.9(2)	5	98.4(1)	11	97.5(1)
DMC(CI)	98	99.3(3)	85	98.9(2)	136	98.4(2)

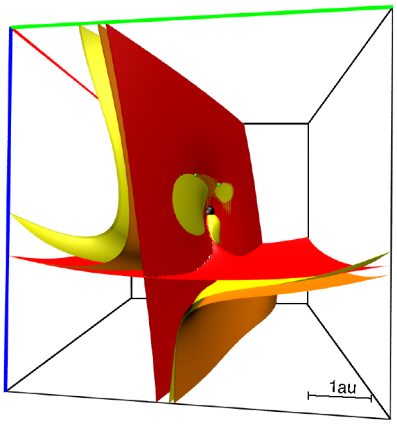

FIG. 2 (color online). A 3D cut through the fermion node hypersurface of an oxygen atom obtained by scanning the wave function with a pair of spin-up and spin-down of electrons, both sitting at the scanning point. The remaining electrons are fixed at a given VMC snaphsot position (small green spheres). The nucleus is depicted in the center of the cube by the black sphere. The three colors show nodes of: Hartree-Fock (red/dark gray), STU Pfaffian nodes (orange/medium gray), and the nodes of the CI wave function (yellow/light gray). The CI node is very close to the exact one (see text). The HF node clearly divides the space into four nodal cells while Pfaffian and CI wave functions partitioning leads to the minimal number of two nodal cells.

have an important effect on the nodal structure as well. A changes in the nodal manifold topology is illustrated in Fig. 2 on the example of an oxygen atom. As expected, the HF nodes show four nodal cells while the Pfaffian "opens" these artificial compartments and changes the topology to the minimal number of two nodal cells, similar to the effect of correlation observed for the Be atom [18]. A comparison of Pfaffian nodes with very accurate CI nodes shows that both are qualitatively similar. Further results on the properties of nodes and their improvement are given elsewhere [12,20].

In conclusion, we have proposed Pfaffians with singlet pair, triplet pair, and unpaired orbitals as variationally rich and compact wave functions which offer significant and systematic improvements over commonly used Slater determinant-based wave functions. We have demonstrated that these Pfaffian pairing wave functions are able to capture a large fraction of missing correlation energy with consistent treatment of correlation for both spin-polarized and unpolarized pairs. We have explored also multi-Pfaffian wave functions which enable us to obtain more correlation while keeping the wave functions compact. Our Pfaffian wave function results represent only the lower bound on the recovered correlation energies since we were focused on systematic trends using new functional forms. For example, a simultaneous reoptimization of one-particle orbitals used in representation of pairs could improve the results further. Finally, the Pfaffian wave functions exhibit qualitative improvements in fermion nodes and eliminate a significant portion of the Hartree-Fock node errors.

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