PHYSICAL REVIEW B **77**, 115112 (2008)

Pfaffian pairing and backflow wavefunctions for electronic structure quantum Monte Carlo methods

M. Bajdich,* L. Mitas, and L. K. Wagner
Center for High Performance Simulation and Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, USA

K. E. Schmidt
Department of Physics, Arizona State University, Tempe, Arizona 85287, USA

(Received 1 November 2006; revised manuscript received 9 February 2008; published 10 March 2008)

We investigate pfaffian trial wavefunctions with singlet and triplet pair orbitals by quantum Monte Carlo methods. We present mathematical identities and the key algebraic properties necessary for efficient evaluation of pfaffians. Following upon our previous study [Bajdich *et al.*, Phys. Rev. Lett. **96**, 130201 (2006)], we explore the possibilities of expanding the wavefunction in linear combinations of pfaffians. We observe that molecular systems require much larger expansions than atomic systems and linear combinations of a few pfaffians lead to rather small gains in correlation energy. We also test the wavefunction based on fully antisymmetrized product of independent pair orbitals. Despite its seemingly large variational potential, we do not observe additional gains in correlation energy. We find that pfaffians lead to substantial improvements in fermion nodes when compared to Hartree-Fock wavefunctions and exhibit the minimal number of two nodal domains in agreement with recent results on fermion nodes topology. We analyze the nodal structure differences of Hartree-Fock, pfaffian, and essentially exact large-scale configuration interaction wavefunctions. Finally, we combine the recently proposed form of backflow correlations [Drummond *et al.*, J. Phys. Chem. **124**, 22401 (2006); Rios *et al.*, Phys. Rev. E. **74**, 066701 (2006)] with both determinantal and pfaffian based wavefunctions.

DOI: 10.1103/PhysRevB.77.115112 PACS number(s): 71.15.Nc, 02.70.Ss

I. INTRODUCTION

One of the most promising many-body electronic structure approaches is the quantum Monte Carlo (QMC) method, which employs stochastic techniques for solving the stationary Schrödinger equation and for evaluation of expectation values.[4–7] QMC methodology has an important virtue that it enables us to test and employ variety of many-body wavefunctions (WFs) with explicit electron-electron correlation. This opens a possibility to explore wavefunctions, which are very difficult to use with traditional methods based on one-particle basis expansions and on orthogonality of one-particle orbitals. These high accuracy wavefunctions enable us to understand the nature of many-body effects and also to decrease the QMC fixed-node errors which come from the necessity to circumvent the fermion sign problem.[8,9] Fixed-node QMC has been very effective in providing high accuracy results for many real systems, such as molecules, clusters, and solids with hundreds of valence electrons. Typically, for cohesive and binding energies, band gaps, and other energy differences, the agreement with experiments is within 1%–3%.[7,10] The key challenge for successful application of fixed-node QMC is to develop methods, which can eliminate the fixed-node bias or at least make it smaller than experimental error bars for the given quantity. This is a difficult task, once we realize that the fermion nodes (the subset of position space where the wavefunction vanishes) are complicated high-dimensional manifolds determined by the many-body effects. So far, improvement in the accuracy of trial wavefunctions has proved to be one realistic approach to finding better approximations for the nodes. This approach has an additional benefit in forcing us to think about the relevant correlation effects and their compact and computationally efficient description.

The commonly used QMC trial wave functions have the Slater-Jastrow form, which can be written as $\Psi_T = \Psi_A \exp[U_{corr}]$, where Ψ_A is the antisymmetric part while U_{corr} describes the electron-electron and higher-order correlations. The antisymmetric component is typically one or a linear combination of several Slater determinants of one-particle orbitals, such as configuration interaction (CI) expansion.[11] To overcome the limit of one-particle orbitals, the two-particle or pair orbital has been suggested. In condensed systems, one such example is the Bardeen-Cooper-Schrieffer (BCS) wavefunction,[12] which is an antisymmetrized product of identical singlet pairs.

The pair orbital is also referred to as geminal and the resulting wavefunction as the antisymmetrized product of geminals (APG).[13,14] In its full variational limit, say, for a system with M pairs of fermions, such a wavefunction is an antisymmetrized product of M distinct pair orbitals. However, this freedom leads to computationally very demanding form, since the number of terms grows exponentially with the number of pairs. In this work, we have actually tested the APG wavefunctions on a few-particle systems, as will be reported later. On the other hand, if all the geminals in the product are identical, then this special case of APG is called the antisymmetrized geminal power (AGP).[15] It can be shown that for a singlet type geminal with a fixed number of particles, the AGP and BCS wavefunctions are identical[16] and can be expressed in the form of single determinant.[17]

The BCS wavefunction has been recently used to calculate several atoms and molecules as well as superfluid Fermi gases.[18–20] The results show promising gains when compared to the single-determinant Hartree-Fock (HF) wavefunctions; nevertheless, in partially spin-polarized systems, the improvements are less pronounced due to the lack of pair correlations in the spin-polarized subspace.[18,19] The spin-polarized (triplet) pairing wavefunctions naturally lead to pfaffians (instead of determinants). In this respect, pfaffians have been mentioned a few times and applied to model systems[21–23] in the past.

In this paper, we follow upon our previous letter,[1] in which we have proposed the description of electron systems by pfaffian wavefunctions with variational freedom beyond the HF and BCS wavefunctions. The pfaffian form proved to be the right algebraic form, which can accommodate pair orbitals with singlet and triplet pair channels, together with unpaired one-particle orbitals, into a single compact wavefunction. Here, we present a set of key mathematical identities and formulas for pfaffians, some of them derived for the first time. We investigate generalizations to linear combinations of pfaffians and to antisymmetrized independent singlet pairs and compare the results from the point of view of recovered energies and compactness of the wavefunctions. We analyze the fermion nodes for some of the wavefunctions and point out the topological differences between HF, pfaffian, and essentially exact wavefunctions for a given test example. Finally, we explore the possibility of further improvements of nodal structure of pfaffians by using the recently proposed form of backflow correlations.[2,3]

II. ALGEBRA OF PFAFFIANS

A. Definitions

First introduced by Cayley in 1852,[24] the pfaffian is named after German mathematician Johann Friedrich Pfaff. Given a $2n\times 2n$ skew-symmetric matrix $A=[a_{i,j}]$, the pfaffian of A is defined as antisymmetrized product

$$\mathrm{pf}[A]=\mathcal{A}[a_{1,2}a_{3,4}\ldots a_{2n-1,2n}]=\sum_{\alpha}\mathrm{sgn}(\alpha)a_{i_1,j_1}a_{i_2,j_2}\ldots a_{i_n,j_n}, \tag{1}$$

where the sum runs over all possible $(2n-1)!!$ pair partitions $\alpha=\{(i_1,j_1),(i_2,j_2),\ldots,(i_n,j_n)\}$ of $\{1,2,\ldots,2n\}$ with $i_k<j_k$. The sign of permutation associated with the partition α is denoted as $\mathrm{sgn}(\alpha)$. The pfaffian for a matrix of odd order equals to zero. The following example gives pfaffian of a $A(4\times 4)$ skew-symmetric matrix:

$$\mathrm{pf}\begin{bmatrix}0 & a_{12} & a_{13} & a_{14}\\ -a_{12} & 0 & a_{23} & a_{24}\\ -a_{13} & -a_{23} & 0 & a_{34}\\ -a_{14} & -a_{24} & -a_{34} & 0\end{bmatrix}=a_{12}a_{34}-a_{13}a_{24}+a_{14}a_{23}. \tag{2}$$

It can be also evaluated recursively as

$$\begin{aligned}\mathrm{pf}[A]&=\sum_{j=2}^{2n}a_{1,j}\sum_{\alpha_{1,j}}\mathrm{sgn}(\alpha_{1,j})a_{i_1,j_1}a_{i_2,j_2}\ldots a_{i_{n-1},j_{n-1}}\\ &\equiv\sum_{j=2}^{2n}a_{1,j}P_c(a_{1,j}),\end{aligned} \tag{3}$$

where $\alpha_{1,j}$ is partition with $i_k,j_k\neq 1,j$ and $P_c(a_{1,j})$ is defined as pfaffian cofactor of $a_{1,j}$. The cofactor for an element $a_{j,k}$ is given by a formula

$$P_c(a_{j,k})=(-1)^{j+k+1}\mathrm{pf}[A(j,k;j,k)], \tag{4}$$

where the matrix $A(j,k;j,k)$ has the rank $2(n-1)\times 2(n-1)$ and is obtained from A by eliminating rows j and k and columns j and k.

B. Calculation of a pfaffian

There exist several identities involving pfaffians and determinants. For any $2n\times 2n$ skew-symmetric matrix A and arbitrary matrices $B(2n\times 2n)$ and $M(n\times n)$, we have the following relations:

$$\mathrm{pf}[A^T]=(-1)^n\mathrm{pf}[A] \tag{5a}$$

$$\mathrm{pf}[A]^2=\det[A] \tag{5b}$$

$$\mathrm{pf}\begin{bmatrix}A_1 & 0\\ 0 & A_2\end{bmatrix}=\mathrm{pf}[A_1]\mathrm{pf}[A_2] \tag{5c}$$

$$\mathrm{pf}[BAB^T]=\det[B]\mathrm{pf}[A] \tag{5d}$$

$$\mathrm{pf}\begin{bmatrix}0 & M\\ -M^T & 0\end{bmatrix}=(-1)^{n(n-1)/2}\det[M] \tag{5e}$$

Proofs. (5a) Each permutation contains product of n pairs resulting in an overall $(-1)^n$ factor. (5b) This is well-known Cayley's relationship between the pfaffian and the determinant of a skew-symmetric matrix. Since it has been proved many times before in variety of ways,[25–27] we do not give this proof here. Using this relation, we rather prove a more general version of Cayley's identity[27] in the Appendix, which we were not able to find anywhere else except in original Cayley's paper.[27] (5c) Use the expansion by pfaffian cofactors. (5d) By squaring (5d), using Eq. (5b), and taking the square root, one finds $\mathrm{pf}[BAB^T]=\pm\det[B]\mathrm{pf}[A]$. Substituting the identity matrix I for B, one finds $+$ to be the correct sign. (5e) Assume

$$B=\begin{pmatrix}M & 0\\ 0 & I\end{pmatrix}\quad\text{and }A=\begin{pmatrix}0 & I\\ -I & 0\end{pmatrix}$$

in Eq. (5d). The overall sign is given by value of $\mathrm{pf}[A]$.

The identities listed above imply several important properties. First, Eqs. (5d) and (5e) show that every determinant can be written as a pfaffian, but on the contrary, only the absolute value of pfaffian can be given by determinant [Eq. (5b)]. The pfaffian is therefore a generalized form of the determinant. Second, by substituting suitable matrices[28] for

M in Eq. (5d), one can verify the following three properties of pfaffians,[29] similar to the well-known properties of determinant:

(a) multiplication of a row and a column by a constant is equivalent to multiplication of pfaffian by the same constant,

(b) simultaneous interchange of two different rows and corresponding columns changes the sign of pfaffian, and

(c) a multiple of a row and corresponding column added to another row and corresponding column does not change the value of pfaffian.

Any real skew-symmetric matrix can be brought to block-diagonal form by an orthogonal transformation. Recursive evaluation [Eq. (3)] then implies that the pfaffian of block-diagonal matrix is directly given by

$$\mathrm{pf}\begin{bmatrix} 0 & \lambda_1 & & & & & \\ -\lambda_1 & 0 & & & & 0 & \\ & & 0 & \lambda_2 & & & \\ & & -\lambda_2 & 0 & & & \\ & & & & \ddots & & \\ & 0 & & & & 0 & \lambda_n \\ & & & & & -\lambda_n & 0 \end{bmatrix} = \lambda_1\lambda_2\cdots\lambda_n. \tag{6}$$

Therefore, by employing a simple Gaussian elimination technique with row pivoting, we can transform any skew-symmetric matrix into block-diagonal form and obtain its pfaffian value in $O(n^3)$ time.

However, in QMC applications, one often needs to evaluate the wavefunction after a single electron update. Since Cayley[27] showed [for proof see Appendix] that

$$\det\begin{bmatrix} 0 & b_{12} & b_{13} & \dots & b_{1,n} \\ -a_{12} & 0 & a_{23} & \dots & a_{2,n} \\ -a_{13} & -a_{23} & 0 & \dots & a_{3,n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -a_{1,n} & -a_{2,n} & -a_{3,n} & \dots & 0 \end{bmatrix}$$
$$= \mathrm{pf}\begin{bmatrix} 0 & a_{12} & a_{13} & \dots & a_{1,n} \\ -a_{12} & 0 & a_{23} & \dots & a_{2,n} \\ -a_{13} & -a_{23} & 0 & \dots & a_{3,n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -a_{1,n} & -a_{2,n} & -a_{3,n} & \dots & 0 \end{bmatrix}$$
$$\times \mathrm{pf}\begin{bmatrix} 0 & b_{12} & b_{13} & \dots & b_{1,n} \\ -b_{12} & 0 & a_{23} & \dots & a_{2,n} \\ -b_{13} & -a_{23} & 0 & \dots & a_{3,n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -b_{1,n} & -a_{2,n} & -a_{3,n} & \dots & 0 \end{bmatrix}, \tag{7}$$

we can relate the pfaffian of original matrix pf$[A]$ to the pfaffian of a matrix with updated first row and column pf$[B]$ using the inverse matrix A^{-1} in only $O(n)$ operations by

$$\mathrm{pf}[B] = \frac{\det[A]\Sigma_j b_{1j}A^{-1}_{j1}}{\mathrm{pf}[A]} = \mathrm{pf}[A]\sum_j b_{1j}A^{-1}_{j1}. \tag{8}$$

The second part of Eq. (8) was obtained by taking advantage of the identity in Eq. (5b). Slightly more complicated relation between pf$[A]$ and pf$[B]$ can be derived if one considers simultaneous change of two separate rows and/or columns, which represents a two electron update of the wavefunction.

C. Gradient and Hessian of pfaffian

If the elements of matrix A depend on some variational parameters $\{c_i\}$, one can derive the following useful expressions (see Sec. IV) for gradient and Hessian of pfaffian:

$$\frac{1}{\mathrm{pf}[A]}\frac{\partial \mathrm{pf}[A]}{\partial c_i} = \frac{1}{2}\mathrm{tr}\left[A^{-1}\frac{\partial A}{\partial c_i}\right] \tag{9}$$

and

$$\frac{1}{\mathrm{pf}[A]}\frac{\partial^2 \mathrm{pf}[A]}{\partial c_i \partial c_j} = \frac{1}{2}\mathrm{tr}\left[A^{-1}\frac{\partial^2 A}{\partial c_i \partial c_j}\right] - \frac{1}{2}\mathrm{tr}\left[A^{-1}\frac{\partial A}{\partial c_i}A^{-1}\frac{\partial A}{\partial c_j}\right] + \frac{1}{4}\mathrm{tr}\left[A^{-1}\frac{\partial A}{\partial c_i}\right]\mathrm{tr}\left[A^{-1}\frac{\partial A}{\partial c_j}\right], \tag{10}$$

where A^{-1} is again the inverse of A.

III. PAIRING WAVEFUNCTIONS

In order to contrast the properties of pair wavefunctions with the wavefunctions build from one-particle orbitals, we will first recall the well-known fact from the Hartree-Fock theory. The simplest antisymmetric wavefunction for N electrons constructed from one-particle orbitals is the Slater *determinant*

$$\Psi_{HF} = \det[\tilde{\varphi}_k(\mathbf{r}_i, s_i)] = \det[\tilde{\varphi}_k(i)], \quad i,k = 1, \dots, N, \tag{11}$$

where the tilde means that the one-particle states depend on both space and spin variables. Clearly, for N electrons, this requires N linearly independent spin-orbitals which form an orthogonal set in canonical HF formulation.

Let us now consider the generalization of the one-particle orbital to a two-particle (or pair) orbital $\tilde{\phi}(i,j)$, where the tilde again denotes dependence on both spatial and spin variables. The simplest antisymmetric wavefunction for $2N$ electrons constructed from the pair orbital is a *pfaffian*,

$$\Psi = \mathcal{A}[\tilde{\phi}(1,2), \tilde{\phi}(3,4) \cdots \tilde{\phi}(2N-1,2N)] = \mathrm{pf}[\tilde{\phi}(i,j)]. \tag{12}$$

The antisymmetry is guaranteed by the definition (1), since the signs of pair partitions alternate depending on the parity of the corresponding permutation. The important difference from Slater determinant is that in the simplest case only *one* pair orbital is necessary. (This can be generalized, of course, as will be shown later.) If we further restrict our description to systems with collinear spins, the pair orbital $\tilde{\phi}(\mathbf{r}_i, s_i; \mathbf{r}_j, s_j)$ for two electrons in positions $\mathbf{r}_i$ and $\mathbf{r}_j$ and with spin projections s_i and s_j can be expressed as

$$\begin{aligned}\tilde{\phi}(\mathbf{r}_i,s_i;\mathbf{r}_j,s_j) = {} & \phi(i,j)\langle s_is_j|[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]/\sqrt{2} + \chi^{\uparrow\uparrow}(i,j)\langle s_is_j|\uparrow\uparrow\rangle \\ & + \chi^{\uparrow\downarrow}(i,j)\langle s_is_j|[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle]/\sqrt{2} \\ & + \chi^{\downarrow\downarrow}(i,j)\langle s_is_j|\downarrow\downarrow\rangle. \end{aligned} \quad (13)$$

Here, $\phi(i,j) = \phi(\mathbf{r}_i,\mathbf{r}_j)$ is even, while $\chi^{\uparrow\uparrow}$, $\chi^{\uparrow\downarrow}$, and $\chi^{\downarrow\downarrow}$ are odd functions of spatial coordinates. In the rest of this section, we will discuss special cases of wavefunction (12).

A. Singlet pairing wavefunction

Let us consider the first $i=1,2,\ldots,N$ electrons to be spin-up and the rest $j=N+1,\ldots,2N$ electrons to be spin-down and allow only $\phi(\mathbf{r}_i,\mathbf{r}_j)$ in $\tilde{\phi}(\mathbf{r}_i,s_i;\mathbf{r}_j,s_j)$ to be nonzero. Using the pfaffian identity [Eq. (5e)], we can write the wavefunction for N singlet pairs, also known as the BCS wavefunction, in the following form:

$$\Psi_{BCS} = \mathrm{pf}\begin{bmatrix} 0 & \mathbf{\Phi}^{\uparrow\downarrow} \\ -\mathbf{\Phi}^{\uparrow\downarrow T} & 0 \end{bmatrix} = \det[\mathbf{\Phi}^{\uparrow\downarrow}], \quad (14)$$

which is simply a determinant of the $N\times N$ matrix $\mathbf{\Phi}^{\uparrow\downarrow} = [\phi(i,j)]$, as was shown previously.[17]

It is straightforward to show that the BCS wavefunction contains the restricted HF wavefunction as a special case. Let us define the Slater matrix $C=[\varphi_i(j)]$, where $\{\varphi_i\}$ is a set of HF occupied orbitals. Then, we can write

$$\Psi_{HF} = \det[C]\det[C] = \det[CC^T] = \det[\mathbf{\Phi}_{HF}^{\uparrow\downarrow}], \quad (15)$$

where

$$(\mathbf{\Phi}_{HF}^{\uparrow\downarrow})_{i,j} = \phi_{HF}(i,j) = \sum_{k=1}^{N} \varphi_k(i)\varphi_k(j). \quad (16)$$

On the other hand, we can think of the BCS wavefunction as a natural generalization of the HF one. To do so, we write the singlet pair orbital as

$$\phi(i,j) = \sum_{k,l}^{>N} S_{k,l}\varphi_k(i)\varphi_l(j) = \boldsymbol{\varphi}(i)\mathbf{S}\boldsymbol{\varphi}(j), \quad (17)$$

where the sum runs over all (occupied and virtual) single-particle orbitals and **S** is some symmetric matrix. Therefore, we can define one-particle orbitals which diagonalize this matrix and call them *natural orbitals of a singlet pair*.

The BCS wavefunction is efficient for describing systems with single-band correlations such as Cooper pairs in conventional BCS superconductors where pairs form from one-particle states close to the Fermi level.

B. Triplet pairing wavefunction

Let us assume, in our system of $2N$ electrons, that the first M_1 are spin-up and remaining $M_2 = 2N - M_1$ are spin-down. Further, we restrict M_1 and M_2 to be even numbers. Then by allowing only $\chi^{\uparrow\uparrow}(i,j)$ and $\chi^{\downarrow\downarrow}(i,j)$ in (13) to be nonzero, we obtain from (12) by the use of Eq. (5c)

$$\Psi_T = \mathrm{pf}\begin{bmatrix} \boldsymbol{\xi}^{\uparrow\uparrow} & 0 \\ 0 & \boldsymbol{\xi}^{\downarrow\downarrow} \end{bmatrix} = \mathrm{pf}[\boldsymbol{\xi}^{\uparrow\uparrow}]\mathrm{pf}[\boldsymbol{\xi}^{\downarrow\downarrow}], \quad (18)$$

where we have introduced $M_1\times M_1(M_2\times M_2)$ matrices $\boldsymbol{\xi}^{\uparrow\uparrow(\downarrow\downarrow)} = [\chi^{\uparrow\uparrow(\downarrow\downarrow)}(i,j)]$. To our knowledge, this result was never explicitly stated and only the weaker statement that the square of wavefunction simplifies to a product of determinants has been given.[17]

The connection to a restricted HF wavefunction for the above state can be again established as follows. In accord with what we defined above, $\det[C^{\uparrow(\downarrow)}]$ are spin-up (-down) Slater determinants of some HF orbitals $\{\varphi_i\}$. Then, by taking advantage of Eq. (5e), we can write

$$\Psi_{HF} = \det[C^{\uparrow}]\det[C^{\downarrow}] = \frac{\mathrm{pf}[C^{\uparrow}A_1C^{\uparrow T}]\mathrm{pf}[C^{\downarrow}A_2C^{\downarrow T}]}{\mathrm{pf}[A_1]\mathrm{pf}[A_2]}, \quad (19)$$

given A_1 and A_2 are some skew-symmetric nonsingular matrices. In the simplest case, when A_1 and A_2 have block-diagonal form with all values $\lambda_i = 1$, one gets

$$\Psi_{HF} = \mathrm{pf}[\boldsymbol{\xi}_{HF}^{\uparrow\uparrow}]\mathrm{pf}[\boldsymbol{\xi}_{HF}^{\downarrow\downarrow}]. \quad (20)$$

The pair orbitals can be then expressed as

$$\begin{aligned}(\boldsymbol{\xi}_{HF}^{\uparrow\uparrow(\downarrow\downarrow)})_{i,j} &= \chi_{HF}^{\uparrow\uparrow(\downarrow\downarrow)}(i,j) \\ &= \sum_{k=1}^{M_1(M_2)/2} [\varphi_{2k-1}(i)\varphi_{2k}(j) - \varphi_{2k-1}(j)\varphi_{2k}(i)]. \end{aligned} \quad (21)$$

Similar to the singlet pairing case, one can also think of triplet pairing as a natural generalization of the HF wavefunction. To do so, we write the triplet pair orbitals as

$$\chi(i,j)^{\uparrow\uparrow(\downarrow\downarrow)} = \sum_{k,l}^{>M_1(M_2)} A_{k,l}^{\uparrow\uparrow(\downarrow\downarrow)}\varphi_k(i)\varphi_l(j) = \boldsymbol{\varphi}(i)\mathbf{A}^{\uparrow\uparrow(\downarrow\downarrow)}\boldsymbol{\varphi}(j), \quad (22)$$

where again the sum runs over all (occupied and virtual) single-particle orbitals and $\mathbf{A}^{\uparrow\uparrow(\downarrow\downarrow)}$ are some skew-symmetric matrices. Therefore, we can define one-particle orbitals which block diagonalize these matrices and call them *natural orbitals of a triplet spin-up-up (down-down) pair*.

C. Generalized pairing wavefunction

Let us now consider a partially spin-polarized system with unpaired electrons. In order to introduce both types of pairing, we allow $\chi^{\uparrow\uparrow}(i,j)$, $\chi^{\downarrow\downarrow}(i,j)$ and $\phi(i,j)$ in (13) to be nonzero. However, we omit the $\chi^{\uparrow\downarrow}(i,j)$ term. Then our usual ordered choice of electron labels, with all spin-up electrons first and remaining electrons spin-down, enables us to directly write from (12) the singlet-triplet-unpaired (STU) orbital pfaffian wavefunction,[1]

$$\Psi_{STU} = \mathrm{pf}\begin{bmatrix} \boldsymbol{\xi}^{\uparrow\uparrow} & \mathbf{\Phi}^{\uparrow\downarrow} & \boldsymbol{\varphi}^{\uparrow} \\ -\mathbf{\Phi}^{\uparrow\downarrow T} & \boldsymbol{\xi}^{\downarrow\downarrow} & \boldsymbol{\varphi}^{\downarrow} \\ -\boldsymbol{\varphi}^{\uparrow T} & -\boldsymbol{\varphi}^{\downarrow T} & 0 \end{bmatrix}, \quad (23)$$

TABLE I. Total energies for C, N, and O atoms and their dimers with amounts of the correlation energy recovered in VMC and DMC methods with wavefunctions as discussed in the text. Unless noted otherwise, the numbers in parentheses are the statistical errors in the last digit from corresponding QMC calculation. Energies are in Hartree a.u. For C, N, and O atoms, we used the correlation energies by Dolg (Ref. 55) (0.1031, 0.1303, and 0.1937 a.u.). For the estimation of correlation energies of dimers, we needed accurate HF energies at experimental distances (Ref. 56) and the estimated exact total energies. Each exact total energy was estimated as a sum of total energies of constituent atoms minus experimental binding energy (Ref. 55–58) adjusted for experimental zero-point energy (Ref. 58).

Method	WF	C	E_{corr} (%)	N	E_{corr} (%)	O	E_{corr} (%)
HF	S	−5.31471	0	−9.62892	0	−15.65851	0
VMC	SJ	−5.3939(4)	76.8(4)	−9.7375(1)	83.3(1)	−15.8210(6)	83.9(3)
	BCS	−5.4061(2)	88.6(2)	−9.7427(3)	87.3(2)	−15.8250(3)	86.0(2)
	STU	−5.4068(2)	89.3(2)	−9.7433(1)	87.8(1)	−15.8255(3)	86.2(2)
DMC	SJ	−5.4061(3)	88.6(2)	−9.7496(2)	92.6(2)	−15.8421(2)	94.8(1)
	BCS	−5.4140(2)	96.3(2)	−9.7536(2)	95.7(2)	−15.8439(4)	95.7(2)
	STU	−5.4139(2)	96.2(2)	−9.7551(2)	96.8(1)	−15.8433(3)	95.4(2)
Est.	Exact	−5.417806	100	−9.759215	100	−15.85216	100
Method	WF	C_2	E_{corr} (%)	N_2	E_{corr} (%)	O_2	E_{corr} (%)
HF	S	−10.6604	0	−19.4504	0	−31.3580	0
VMC	SJ	−10.9579(4)	72.9(1)	−19.7958(5)	80.0(1)	−31.7858(6)	79.6(1)
	BCS	−11.0059(4)	84.7(1)	−19.8179(6)	85.0(1)	−31.8237(4)	86.7(1)
	STU	−11.0062(3)	84.8(1)	−19.821(1)	85.8(2)	−31.8234(4)	86.6(1)
DMC	HF	−11.0153(4)	87.0(1)	−19.8521(3)	93.0(1)	−31.8649(5)	94.3(1)
	BCS	−11.0416(3)	93.5(1)	−19.8605(6)	94.9(1)	−31.8664(5)	94.6(1)
	STU	−11.0421(5)	93.6(1)	−19.8607(4)	95.0(1)	−31.8654(5)	94.4(1)
Est.	Exact[a]	−11.068(5)[b]	100.0(10)	−19.8825(6)[c]	100.0(1)	−31.8954(1)[c]	100.0(1)

[a] The error bars on estimated exact total energies are due to experiment.

[b] There is rather large discrepancy in the experimental values of C_2 binding energy [141.8(9) (Ref. 56), 143(3) (Ref. 58), and 145.2(5) kcal/mol] (Ref. 57). For the estimation of exact energy, we have taken the average value of 143(3) kcal/mol.

[c] Experimental binding energies taken from Ref. 56

where the bold symbols are block matrices and vectors of corresponding orbitals as defined in Secs. III A and III B and T denotes transposition. Let us note that for a spin-restricted STU wavefunction the pair and one-particle orbitals of spin-up and -down channels would be identical.

The above pfaffian form can accommodate both singlet and triplet pairs as well as one-particle unpaired orbitals into a single, compact wavefunction. The correspondence of STU pfaffian wavefunction to HF wavefunction can be established in a similar way to the pure singlet and triplet pairing cases.

IV. PAIRING WAVEFUNCTION RESULTS

We perform the variational and fixed-node diffusion Monte Carlo (VMC and DMC) calculations[6,7] with the pfaffian pairing wavefunctions. As we mentioned earlier, the trial variational wavefunction is a product of an antisymmetric part Ψ_A times the Jastrow correlation factor

$$\Psi_T(\mathbf{R}) = \Psi_A(\mathbf{R})\exp[U_{corr}(\{r_{ij}\},\{r_{iI}\},\{r_{iJ}\})], \tag{24}$$

where U_{corr} depends on electron-electron, electron-ion and, possibly, on electron-electron-ion combinations of distances.[7,30,31] Previously, we have reported[1] the results with antisymmetric part being equal to $\Psi_A = \Psi_{HF}$, $\Psi_A = \Psi_{BCS}$, and $\Psi_A = \Psi_{STU}$. We extend this work to different linear combinations of pfaffians. The pair orbitals were expanded in products of a one-particle orbital basis according to Eqs. (17) and (22). The expansions include both occupied and virtual one-particle orbitals from either Hartree-Fock or CI correlated calculations.[11] The pair orbital expansion coefficients were then optimized in VMC by minimizations of energy, variance, or a combination of energy and variance.[30] The optimization procedure requires the calculation of gradient and the Hessian of the wavefunction according to Eqs. (9) and (10). We used pseudopotentials[32] to eliminate the atomic cores.

A. Single- and multipfaffian calculations

The results of a single-pfaffian wavefunction calculations when applied to the first row atoms and dimers were reported in our previous paper.[1] However, for completeness, we summarize all total and correlation energies in Table I. A systematic high percentage of recovered correlation energy on the level of 94%–97% in DMC method with generally low triplet contributions was observed.

Further, the tests of multipfaffian (MPF) wavefunction of the form

$$\Psi_{MPF} = \mathrm{pf}[\chi_1^{\uparrow\uparrow}, \chi_1^{\downarrow\downarrow}, \phi_1, \varphi_1] + \mathrm{pf}[\chi_2^{\uparrow\uparrow}, \chi_2^{\downarrow\downarrow}, \phi_2, \varphi_2] + \dots \tag{25}$$

for atomic systems were also discussed in our previous study.[1] A small number of pfaffians were shown to recover another significant fraction of the missing correlation energy comparable to much more extensive configuration interaction expansions in determinants.

In this work, we extend the application of MPF wavefunctions to the diatomic cases (Table II). However, only very limited gain over single STU pfaffian WF was achieved for MPF wavefunctions with few pfaffians. We therefore conclude that for obtaining significantly larger gains in correlation energy, the molecular wavefunctions require much larger expansions.

B. Antisymmetrized product of geminals

We have also tested the fully antisymmetrized product of geminals (or singlet independent pairs) wavefunction, which introduces one pair orbital per each electron pair. For system of $2N$ fermions in singlet state, the APG wavefunction can be written as

$$\begin{aligned}\Psi_{APG} &= \mathcal{A}[\tilde{\phi}_1(1,2), \tilde{\phi}_2(3,4), \dots, \tilde{\phi}_N(2N-1,2N)] \\ &= \sum_P \mathrm{pf}[\tilde{\phi}_{i_1}(1,2), \tilde{\phi}_{i_2}(3,4), \dots, \tilde{\phi}_{i_N}(2N-1,2N)],\end{aligned} \tag{26}$$

where the last equation corresponds to the sum over all $N!$ possible permutations of N different pair orbitals $\tilde{\phi}_i$ for each pfaffian. Recently, the APG wavefunction was used also by Rassolov[33] in the form of an strongly orthogonal geminals. Our results for C and N dimers using APG wavefunctions in the VMC and DMC methods are given in Table II.

Consideration of independent pairs results in an exponential increase of number of pfaffians. However, captured correlation energy is on the level of small MPF expansion and significantly less than CI with reoptimized weights using the same one-particle orbitals. This suggests that to achieve more correlation energy in larger systems, we have to go beyond double pairing.

C. Nodal properties

The fermion node is defined by an implicit equation $\Psi(R)=0$ and for N electrons it is a $(3N-1)$-dimensional hypersurface. With exception of few exact cases, the nodes of trial and/or variational wavefunctions introduce bias into fixed-node DMC energies. Recently, a number of authors have reported improvement in nodal structure of trial wavefunctions.[1,2,18,19,34,35]

The effect of pairing correlations on nodes can be highlighted by direct comparison. Figure 1 shows the example of nodal structure of oxygen atom. Here, we compare the nodal surfaces of HF (no pairing), MPF pfaffian (STU pairing), and a high accuracy CI wave function with more than 3000 determinants, which gives essentially exact fermion nodes [i.e., 99.8(3)% of correlation energy in fixed-node DMC].

It is clear that the changes in the nodal surfaces are significant, the most important one being the elimination of artificial four nodal cells resulting from the independence of spin-up and -down channels in HF. The pfaffian smooths out the crossings and fuses the compartments of the same sign into the single ones. These topology changes therefore lead to the minimal number of two nodal cells, an effect observed in correlated context previously.[36–39] However, the nodes of the pfaffian wavefunctions could be further improved if the scheme for direct optimization of nodes of trial wavefunctions were used.[20,40] Additional result from our work is that despite such a substantial change in the nodal structure the amount of missing correlation energy is still non-negligible.

V. BACKFLOW CORRELATED WAVEFUNCTIONS

Another route to improvement of the trial wavefunction and its nodal structure is through the introduction of back-

TABLE II. Total energies for C and N dimers with amounts of correlation energy recovered in VMC and DMC methods with wavefunctions as discussed in the text. The corresponding number of pfaffians and/or determinants n for each wavefunction is also shown. See caption of Table III for a more detailed description.

Method	WF	n	C_2	E_{corr} (%)	n	N_2	E_{corr} (%)
VMC	MPF	5	−11.0187(2)	87.8(1)	5	−19.8357(3)	89.2(1)
	APG	4!	−11.0205(4)	88.3(1)	5!	−19.8350(3)	89.0(1)
	CI[a]	148	−11.0427(1)	93.7(1)	143	−19.8463(9)	91.6(2)
DMC	MPF	5	−11.0437(4)	94.0(1)	5	−19.8623(5)	95.3(1)
	APG	4!	−11.0435(7)	94.0(2)	5!	−19.8611(3)	95.0(1)
	CI[a]	148	−11.0573(2)	97.3(1)	143	−19.875(2)	98.3(5)

[a] The determinantal weights were reoptimized in the VMC method.

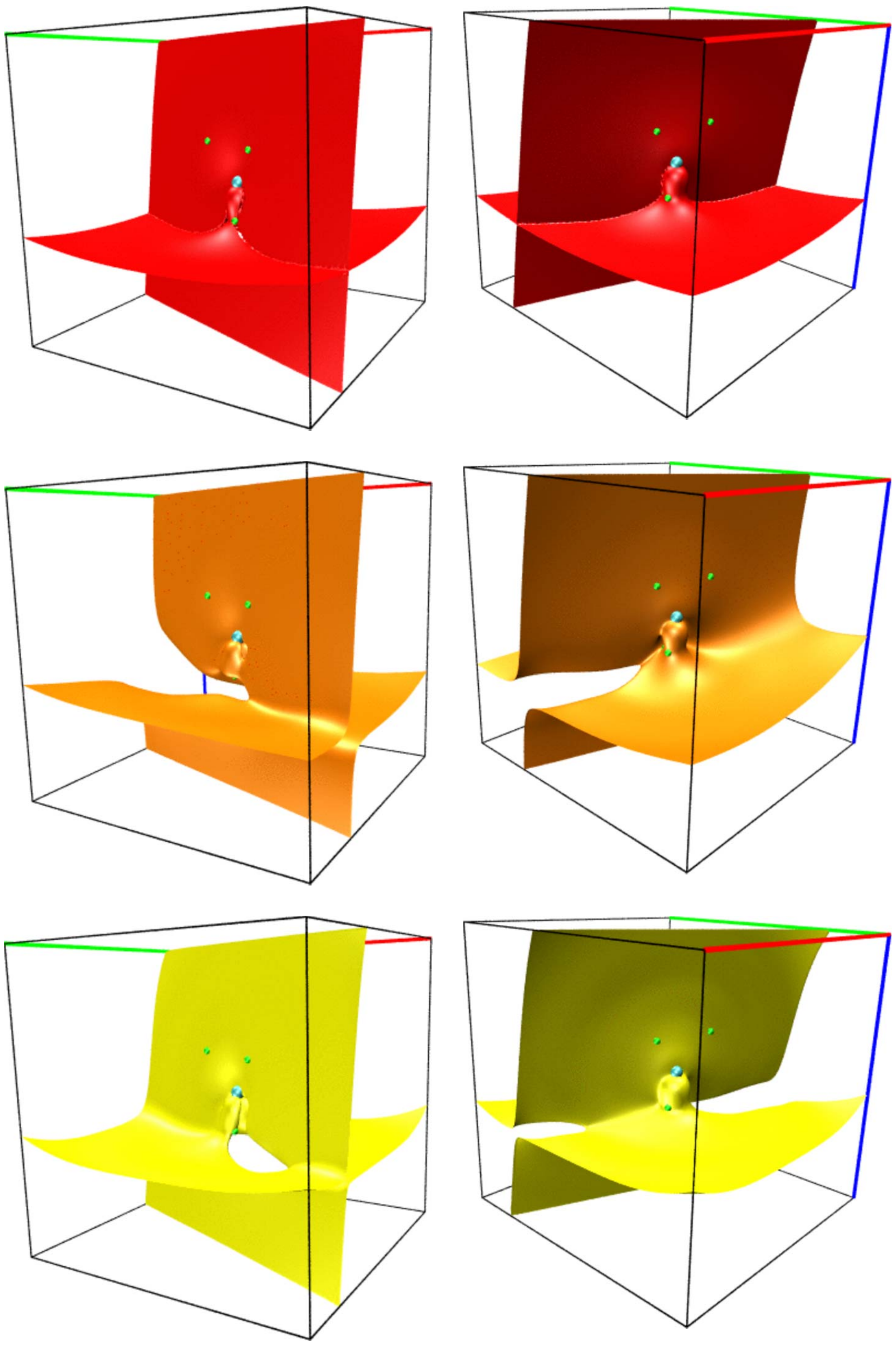

FIG. 1. (Color online) A three-dimensional cut through the fermion node hypersurface of oxygen atom obtained by scanning the wavefunction with a spin-up and -down (singlet) pair of electrons at equal positions, while keeping the rest of electrons at a given VMC snapshot positions (small green spheres). Nucleus is depicted in the center of the cube by the blue sphere. The three colors (from left to right) show nodes of: Hartree-Fock (red and/or dark gray), multipfaffian nodes (orange and/or medium gray), and the nodes of the CI wave function (yellow and/or light gray) in two different views (upper and lower rows). The CI nodal surface is very close to the exact one (see text). The HF node clearly divides the space into four nodal cells while pfaffian and CI wavefunctions partitioning leads to the minimal number of two nodal cells. The changes in the nodal topology occur on the appreciable spatial scale of the order of 1 a.u.

flow correlations.[2,3,41–49] Given the form of our trial wavefunction, Eq. (24), its nodal structure is completely defined by the nodes of the antisymmetric part $\Psi_A(\mathbf{R})$. The backflow correlations are then introduced by replacing $\Psi_A(\mathbf{R})$ by $\Psi_A(\mathbf{X})$, where $\mathbf{X}=(\mathbf{x}_1,\mathbf{x}_2,\ldots)$ are some quasicoordinates dependent on all-electron positions $\mathbf{R}$, such that overall antisymmetry is preserved. Consequently, if $\mathbf{X}$ is made dependent on some variational parameters, we can decrease the fixed-node errors by further optimizing $\Psi_A(\mathbf{X})$.

The implementation of the backflow correlations into Slater determinant and pfaffian wavefunctions closely follows the approach of Kwon *et al.*[46] and Rios *et al.*[3] The quasicoordinate of ith electron at position $\mathbf{r}_i$ is given as

$$\mathbf{x}_i = \mathbf{r}_i + \boldsymbol{\xi}_i(\mathbf{R}) = \mathbf{r}_i + \boldsymbol{\xi}_i^{en}(\mathbf{R}) + \boldsymbol{\xi}_i^{ee}(\mathbf{R}) + \boldsymbol{\xi}_i^{een}(\mathbf{R}), \quad (27)$$

where $\boldsymbol{\xi}_i$ is the ith electron's backflow displacement divided to the contributions from one-body (electron-nucleus), two-body (electron-electron), and three-body (electron-electron-nucleus) terms. They can be further expressed as

$$\boldsymbol{\xi}_i^{en}(\mathbf{R}) = \sum_I \mu(r_{iI})\mathbf{r}_{iI},$$

$$\xi_i^{ee}(\mathbf{R}) = \sum_{j\neq i} \eta(r_{ij})\mathbf{r}_{ij},$$

$$\xi_i^{een}(\mathbf{R}) = \sum_{I} \sum_{j\neq i} [\theta_1(r_{ij},r_{iI},r_{jI})\mathbf{r}_{ij} + \theta_2(r_{ij},r_{iI},r_{jI})\mathbf{r}_{iI}], \tag{28}$$

where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, $\mathbf{r}_{iI}=\mathbf{r}_i-\mathbf{r}_I$ and we sum over all nuclei I and electrons j. The μ, η, and θ_1 with θ_2 terms are similar to one-, two-, and three-body Jastrow terms present in U_{corr} of trial wavefunction, Eq. (24), and are further expanded as

$$\mu(r) = \sum_k c_k a_k(r),$$

$$\eta(r) = \sum_k d_k b_k(r),$$

$$\theta_{1(2)}(r_{ij},r_{iI},r_{jI}) = \sum_{klm} g_{klm}^{1(2)} a_k(r_{iI}) a_l(r_{jI}) b_m(r_{ij}). \tag{29}$$

VI. BACKFLOW WAVEFUNCTION RESULTS

In this section, we present VMC and DMC results obtained with above implementation of backflow correlations for determinant and pfaffian wavefunctions. The Jastrow factors and pseudopotentials are identical to the ones used in Sec. IV. The distance-dependent basis functions $\{a\}$ and $\{b\}$ used in the Eq. (29) are chosen either as Gaussians centered on the nucleus or polynomial Padé functions[31] to preserve the electron-electron and electron-nucleus (when used with pseudopotentials) cusp conditions.[50,51] The sets of variational parameters $\{c\}$, $\{d\}$, and $\{g\}$ are minimized in the similar fashion as in Sec. IV with respect to energy or mixture of energy and variance.[30] In addition, all electron-electron coefficients $[\{d_k\}$ and $\{g_{klm}^{1(2)}\}$ with fixed k and $l]$ are allowed to be different for spinlike and for spin-unlike electron pairs.

A. Homogeneous electron gas

We benchmark our implementation of the backflow correlations on the homogeneous electron gas (HEG). The HEG system of 54 unpolarized electrons in the simple cubic simulation cell with periodic boundary conditions was studied before.[3,48,49] We use the backflow displacement, Eq. (27), with only ξ_i^{ee} being nonzero and let $\eta(r)$ in Eq. (28) to be different for spinlike and for spin-unlike electron pairs. These functions are further expanded in the basis of polynomial Padé functions[31] with cutoff equal to half of the simulation cell.

We compare our results for the following three densities of $r_s=1$, 5, and 20 (see Table III). First, it is clear that the HF and Slater-Jastrow (SJ) fixed-node DMC energies are in good agreement with previous results.[3,48,49] Second, due to the omission of the three-body correlations from Jastrow factor and also from backflow displacement, it is expected that we obtain higher VMC energies and variances for SJ and backflow displaced SJ (SJBF) trial wavefunctions. Nevertheless, our fixed-node DMC energies for SJBF trial wavefunctions closely match the results of Kwon *et al.*,[48] and only slightly deviate at higher densities from results of Rios *et al.*[3]

TABLE III. VMC and fixed-node DMC energies per electron and variances of local energies for various trial wavefunctions (S, Slater; SJ, Slater-Jastrow; SJBF, backflow correlated SJ) for three-dimensional unpolarized HEG of 54 electrons.

r_s	Method	WF	E/N (a.u./electron)	σ^2 (a.u.)
1.0	HF	S	0.56925(2)	19.3(1)
	VMC	SJ	0.53360(4)	1.26(4)
		SJBF	0.53139(4)	0.81(4)
	DMC	SJ	0.53087(4)	
		SJBF	0.52990(4)	
5.0	HF	S	−0.056297(7)	0.776(4)
	VMC	SJ	−0.075941(6)	0.0636(1)
		SJBF	−0.078087(4)	0.0236(1)
	DMC	SJ	−0.07862(1)	
		SJBF	−0.07886(1)	
20.0	HF	S	−0.022051(2)	0.0482(1)
	VMC	SJ	−0.031692(2)	0.000711(4)
		SJBF	−0.031862(1)	0.000437(1)
	DMC	SJ	−0.031948(2)	
		SJBF	−0.032007(2)	

B. Carbon atom and dimer

The backflow correlations in single-determinant Slater-Jastrow trial wavefunctions were recently applied also to inhomogeneous systems.[2,3,52] They were demonstrated to capture additional few percent of the correlation energy but being somewhat shy of the goal of more than 99%, with the only exception of Li atom. It was also suggested that the backflow by itself is unlikely to change the number of nodal cells. These observations let to further studies of backflow combined with the wavefunctions that have the minimal number of nodal cells—an important topological property associated with ground state wavefunctions.[36–39] One of the successes of this scheme are the very recent results of Brown *et al.*[53] obtained from backflow correlated CI-Jastrow wavefunctions applied to first row all-electron atoms. In this study, we further test the limits of the backflow correlations to decrease the fixed-node errors of the CI-Jastrow wavefunctions and, for the first time, also include backflow into the pfaffian-Jastrow pairing wavefunctions. Below is a brief discussion of our implementation and results for carbon atom and dimer systems.

In the inhomogeneous backflow, each electron's coordinate is correlated by the displacement as given by Eq. (27), while the functions η and $\theta_{1,2}$ are allowed to be spin dependent. We use up to 11 Gaussian basis functions to fit the μ and η functions, while the three-body functions $\theta_{1,2}$ are limited to a product of $4\times4\times4$ Gaussians. The main results are plotted in Figs. 2 and 3 and detailed numerical results are

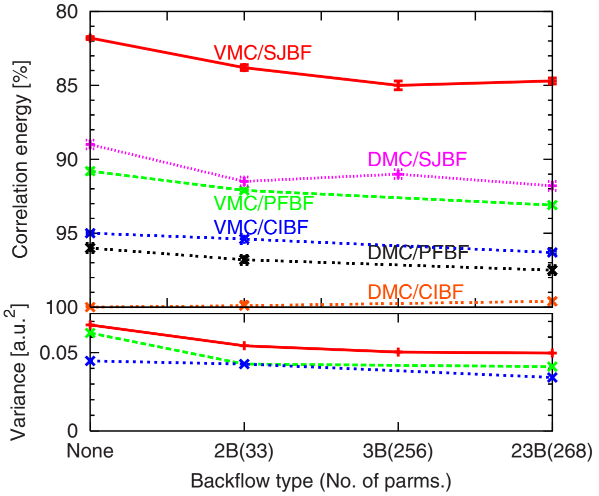

FIG. 2. (Color online) Upper figure: Percentages of correlation energy from VMC and DMC methods versus a number of backflow parameters with backflow correlated Slater-Jastrow (SJBF), pfaffian-Jastrow (PFBF), and CI-Jastrow (CIBF) trial wavefunctions for C atom (2B, electron-nucleus and electron-electron terms; 3B, all electron-electron-nucleus terms; 23B for all terms together). Lines connecting the points serve only as a guide to the eye. Lower figure: Variance of the local energy versus a number of backflow parameters.

summarized in Tables IV and V. The backflow correlations are able to capture additional few percent of the correlation energy for both Slater-Jastrow and pfaffian-Jastrow wavefunctions. Another important feature of backflow is 20%–30% decrease in variances of local energy with respect to the wavefunctions without backflow correlations. We find that for the fully optimized backflow, the spin-unlike electron-electron functions are almost order of magnitude larger than spinlike ones as well as electron-nucleus functions. The gains are systematic with increasing number of parameters; however, we do not find the three-body terms as important as reported in previous study.[3] This difference can be attributed to two main reasons—we use a different basis to expand the three-body functions $\theta_{1,2}$ and we also eliminate atomic cores by pseudopotentials. It is plausible that for systems with core electrons the three-body correlations are more important due to the strong variations of orbitals close to the nucleus.

Finally, let us discuss the difference between the two systems with respect to missing correlation energy. For the C atom, we have shown previously[1] that less than 100 determinants give more than 99% of correlation energy (E_{corr}). The C dimer's fixed-node errors are more pronounced, since the 148 determinants with reoptimized weights give only 97.5(1)% in a close agreement with recent calculations by Umrigar *et al.*[35] Employing backflow correlations for our 148 determinant CI-Jastrow wavefunction gives no apparent gain in E_{corr} except for decrease in the variance of local energy. The improvement for the pfaffian-Jastrow wavefunction is also very modest (less than 1%). Our results suggest that to reach beyond 99% of correlation, one still needs complicated multireference wavefunctions, even after including quite general forms of the backflow correlations.

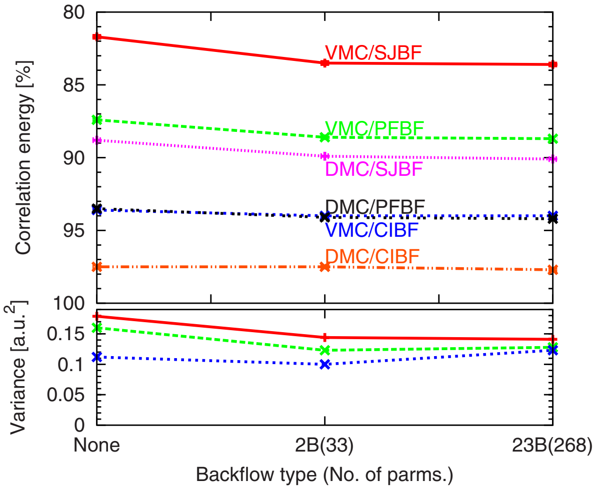

FIG. 3. (Color online) Same as Fig. 2 but for C dimer.

VII. CONCLUSIONS

To summarize, we have proposed pfaffians with singlet pair, triplet pair, and unpaired orbitals as variationally rich and compact wavefunctions. They offer significant and systematic improvements over commonly used Slater determinant-based wavefunctions. We have included a set of key mathematical identities with proofs, which are needed for the evaluation and update of the pfaffians. We have also shown connections of HF and BCS wavefunctions to more general pfaffian wavefunction. Further, we have explored multipfaffian wavefunctions, which enabled us to capture additional correlation. While for atomic systems the results are comparable to large-scale CI wave functions,[1] equivalent accuracy in molecular systems most probably require much larger multipfaffian expansions than we have explored. As another test of the variational potential of pairing, we have employed the fully antisymmetrized independent pair wavefunction in pfaffian form and we have found that it does not lead to additional gains in correlation energy. We therefore conclude that more general functional forms together with more robust large-scale optimization methods might be necessary in order to obtain further improvements. The gains in correlation energy for pfaffians come from improved fermion nodes which are significantly closer to the exact ones than the HF nodes and exhibit the correct topology with the minimal number of two nodal cells.

In the second part of the paper, we have presented the application of pfaffian and multideterminantal wavefunctions with backflow correlations to chemical systems. The results for two testing cases of C atom and its dimer show promising gains in correlation energies, decreases in variances, and improvements in the nodal structure. Our results also indicate that accurate description of molecular systems with fixed-node errors below 1% of correlation energy requires optimized multireference wavefunctions and inclusion of backflow then appears less favorable considering significant computational cost, especially for evaluation of the nonlocal pseudopotential operators.

TABLE IV. VMC and DMC energies and variances of local energy for Slater-Jastrow (SJ), pfaffian-Jastrow (PF), and CI-Jastrow (CI) trial wavefunctions with backflow (BF) correlations for C atom. Notation is the same as in Fig. 2.

Method	WF	N_μ	N_η	N_{θ_1}	N_{θ_2}	N_p	E (a.u.)	σ^2 (a.u.)	E (%)
HF	S						−5.31471		0.0
VMC	SJ						−5.3990(1)	0.0677	81.8(1)
	SJBF2B	11	22			33	−5.4011(2)	0.0544	83.8(2)
	SJBF3B			128	128	256	−5.4023(3)	0.0504	85.0(3)
	SJBF23B	4	8	128	128	268	−5.4020(2)	0.0498	84.7(2)
	PF						−5.4083(2)	0.0626	90.8(2)
	PFBF2B	11	22			33	−5.4097(1)	0.0427	92.1(1)
	PFBF23B	4	8	128	128	268	−5.4107(1)	0.0411	93.1(1)
	CI[a]						−5.4127(1)	0.0447	95.0(1)
	CIBF2B	11	22			33	−5.4131(3)	0.0427	95.4(3)
	CIBF23B	4	8	128	128	268	−5.4140(1)	0.0342	96.3(1)
DMC	SJ						−5.40653(3)		89.0(3)
	SJBF2B	11	22			33	−5.4090(3)		91.5(3)
	SJBF3B			128	128	256	−5.4085(3)		91.0(3)
	SJBF23B	4	8	128	128	268	−5.4094(3)		91.8(3)
	PF						−5.4137(3)		96.0(3)
	PFBF2B	11	22			33	−5.4145(3)		96.8(3)
	PFBF23B	4	8	128	128	268	−5.4152(3)		97.5(3)
	CI						−5.4178(1)		100.0(1)
	CIBF2B	11	22			33	−5.4177(3)		99.9(3)
	CIBF23B	4	8	128	128	268	−5.4174(2)		99.6(2)
Est.	Exact						−5.417806		100.0

[a] Wavefunction consists of 100 determinants reoptimized in VMC.

ACKNOWLEDGMENTS

We gratefully acknowledge the support by NSF Grant Nos. DMR-0121361, PHY-0456609, and EAR-0530110 and the computer time at PAMS NCSU and NCSA facilities as well the INCITE allocation at ORNL.

APPENDIX: PROOF OF CAYLEY'S IDENTITY

In order to prove the statement in Eq. (7), we will proceed by induction. For $n=2$, it is true that

$$\det\begin{bmatrix} 0 & b_{12} \\ -a_{12} & 0 \end{bmatrix} = \mathrm{pf}\begin{bmatrix} 0 & b_{12} \\ -b_{12} & 0 \end{bmatrix}\mathrm{pf}\begin{bmatrix} 0 & a_{12} \\ -a_{12} & 0 \end{bmatrix}.$$

For even n greater than 2, determinant of the matrix of interest can be expanded through its cofactors as

$$\det\begin{bmatrix} 0 & b_{12} & b_{13} & \dots & b_{1,n} \\ -a_{12} & 0 & a_{23} & \dots & a_{2,n} \\ -a_{13} & -a_{23} & 0 & \dots & a_{3,n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -a_{1,n} & -a_{2,n} & -a_{3,n} & \dots & 0 \end{bmatrix} = \sum_k -a_{1,k}C(k,1) = \sum_k \sum_l -a_{1,k}b_{1,l}C(k,1;1,l). \tag{A1}$$

The cofactor can be written as

$$C(k,1;1,l) = (-1)^{k+l+1}\det[A(k,1;1,l)], \tag{A2}$$

where the cofactor matrix is given by

TABLE V. Slater-Jastrow (SJ), pfaffian-Jastrow (PF), and CI-Jastrow (CI) wavefunctions with backflow (BF) correlations for C dimer. Notation is the same as in Fig. 2.

Method	WF	N_μ	N_η	N_{θ_1}	N_{θ_2}	N_p	E (a.u.)	σ^2 (a.u.)	E_{corr} (%)
HF	S						−10.6604		0.0
VMC	SJ[a]						−10.9936(4)	0.179	81.7(1)
	SJBF2B	11	22			33	−11.0012(3)	0.144	83.5(1)
	SJBF23B	4	8	128	128	268	−11.0014(2)	0.141	83.6(1)
	PF[b]						−11.0171(2)	0.160	87.4(1)
	PFBF2B	11	22			33	−11.0223(3)	0.123	88.7(1)
	PFBF23B	4	8	128	128	268	−11.0223(2)	0.128	88.7(1)
	CI[c]						−11.0420(4)	0.112	93.6(1)
	CIBF2B	11	22			33	−11.0440(3)	0.100	94.0(1)
	CIBF23B	4	8	128	128	268	−11.0438(3)	0.123	94.0(1)
DMC	SJ						−11.0227(2)		88.8(1)
	SJBF2B	11	22			33	−11.0269(4)		89.9(1)
	SJBF23B	4	8	128	128	268	−11.0280(3)		90.1(1)
	PF						−11.0419(9)		93.5(2)
	PFBF2B	11	22			33	−11.0443(6)		94.1(2)
	PFBF23B	4	8	128	128	268	−11.0447(3)		94.2(1)
	CI						−11.0579(5)		97.5(1)
	CIBF2B	11	22			33	−11.0580(4)		97.5(1)
	CIBF23B	4	8	128	128	268	−11.0585(5)		97.7(1)
Est.	Exact						−11.068(5)		100.0

[a] Slater determinant contains PBE DFT orbitals.

[b] Same PBE DFT orbitals are used also in PF wave function.

[c] Uses natural orbitals with weights of the 148 determinants reoptimized in VMC.

$$A(k,1;1,l) = \begin{bmatrix} 0 & a_{23} & \dots & a_{2,k} & \dots & a_{2,n} \\ -a_{23} & 0 & \dots & a_{3,k} & \dots & a_{3,n} \\ \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ -a_{2,l} & -a_{3,l} & \dots & -a_{k,l} & \dots & a_{l,n} \\ \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ -a_{2,n} & -a_{3,n} & \dots & -a_{k,n} & \dots & 0 \end{bmatrix}. \tag{A3}$$

At this point, we would like to use an induction step and rewrite the determinant cofactor as a product of two pfaffians [Cayley's identity, Eq. (7)]. This would allow us to demonstrate that the expansion is identical to the expansion of pfaffians in minors. In order to do so, however, we have to shift the kth column by pair column exchanges, so it becomes the *last* column and, similarly, we have to shift the lth row by pair exchanges, so it becomes the last row. This involves k pair exchanges of columns and l pair exchanges or rows and can be represented by unitary matrices U_k and U_l. It is necessary to invoke these operations so that the matrix gets into a form directly amenable for Cayley's identity, i.e., the matrix has to be in a manifestly skew-symmetric form. (The sign change from the row and/or columns exchanges will prove irrelevant as we will show below.) The transformed matrix is given by

$$A'(k,1;1,l) = U_k A(k,1;1,l) U_l \tag{A4}$$

and has all zeros on the diagonal with the exception of the last element which is equal to $-a_{k,l}$. The last row is given by

$$\mathbf{v}_r = (-a_{2,l}, \dots, -a_{k-1,l}, -a_{k+1,l}, \dots, \\ -a_{l-1,l}, a_{l,l+1}, \dots, a_{l,n}, -a_{k,l}), \tag{A5}$$

while the last column is given as follows:

$$\mathbf{v}_c^T = (a_{2,k}, \dots, a_{k-1,k}, -a_{k,k+1}, \dots, -a_{k,l-1}, \\ -a_{k,l+1}, \dots, -a_{k,n}, -a_{k,l})^T. \tag{A6}$$

The only nonzero diagonal element $-a_{k,l}$ can be eliminated, once we realize that its cofactor contains a determinant of a skew-symmetric matrix of odd degree which always vanishes (proof by Jacobi[54]).

Now we are ready to perform the induction step, namely, to use the property that the determinant of a $2(n-1)\times 2(n-1)$ matrix can be written as given by Cayley's identity, Eq. (7). We obtain

$$\det[U_k A(k,1;1,l) U_l] = \det[A'(k,1;1,l)] = \mathrm{pf}[A'(1,k;1,k)]\mathrm{pf}[A'(1,l;1,l)]. \tag{A7}$$

We can now apply the inverse unitary transformations and shift back the columns (and by the skew-symmetry of the corresponding rows) in the first pfaffian and, similarly, the rows (and corresponding columns) in the second. This enables us to write

$$\begin{aligned}&\mathrm{pf}[A'(1,k;1,k)]\mathrm{pf}[A'(1,l;1,l)]\\ &\quad = \mathrm{pf}[U_l^{-1}A(1,k;1,k)U_l]\mathrm{pf}[U_k A(1,l;1,l)U_k^{-1}]\\ &\quad = \mathrm{pf}[A(1,k;1,k)]\mathrm{pf}[A(1,l;1,l)],\end{aligned} \tag{A8}$$

where we have used the identity given by Eq. (5d). We can therefore finally write

$$\begin{aligned}C(k,1;1,l) &= (-1)^{k+l+1}\mathrm{pf}[A(1,k;1,k)]\mathrm{pf}[A(1,l;1,l)]\\ &= -P_c(a_{1,k})P_c(a_{1,l}),\end{aligned} \tag{A9}$$

where P_c denotes a pfaffian cofactor as defined in (4). Therefore, the determinant expansion in Eq. (A1) equals to

$$\begin{aligned}\sum_{k,l} - a_{1,k}b_{1,l}C(k,1;1,l) &= \sum_{k,l} a_{1,k}b_{1,l}P_c(a_{1,k})P_c(a_{1,l})\\ &= \mathrm{pf}[A]\mathrm{pf}[B],\end{aligned} \tag{A10}$$

with matrices A and B defined as in Eq. (8). This concludes the proof of the more general form of Cayley's identity. Note, if $B=A$, we trivially obtain well-known formula for the square of pfaffian [Eq. (5b)].

---

*mbajdic@ncsu.edu

[1] M. Bajdich, L. Mitas, G. Drobný, L. K. Wagner, and K. E. Schmidt, Phys. Rev. Lett. **96**, 130201 (2006).

[2] N. D. Drummond, P. L. Rios, A. Ma, J. R. Trail, G. G. Spink, M. D. Towler, and R. J. Needs, J. Phys. Chem. **124**, 224104 (2006).

[3] P. Lopez Rios, A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs, Phys. Rev. E **74**, 066701 (2006).

[4] D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binger (Springer, Berlin, 1979), pp. 145–194.

[5] K. E. Schmidt and D. M. Ceperley, in *Monte Carlo Methods in Statistical Physics 2*, edited by K. Binger (Springer, Berlin, 1984), pp. 279–355.

[6] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).

[7] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001).

[8] J. B. Anderson, J. Phys. Chem. **63**, 1499 (1975).

[9] P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., J. Phys. Chem. **77**, 5593 (1982).

[10] J. Grossman, J. Chem. Phys. **117**, 1434 (2002).

[11] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover, New York, 1996).

[12] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[13] V. A. Fock, Dokl. Akad. Nauk SSSR **73**, 735 (1950).

[14] A. C. Hurley, J. Lennard-Jones, and J. A. Pople, Proc. R. Soc. London, Ser. A **220**, 446 (1953).

[15] A. J. Coleman, J. Math. Phys. **6**, 1425 (1965).

[16] J. R. Schrieffer, *The Theory of Superconductivity* (Addison-Wesley, Reading, MA, 1994).

[17] J. P. Bouchaud, A. S. George, and C. L'huillier, J. Phys. (France) **49**, 553 (1988).

[18] M. Casula and S. Sorella, J. Phys. Chem. **119**, 6500 (2003).

[19] M. Casula, C. Attaccalite, and S. Sorella, J. Phys. Chem. **121**, 7110 (2004).

[20] J. Carlson, S.-Y. Chang, V. R. Pandharipande, and K. E. Schmidt, Phys. Rev. Lett. **91**, 050401 (2003).

[21] J. P. Bouchaud and C. L'huillier, Europhys. Lett. **3**, 1273 (1987).

[22] M. Bhattacharjee, Z. Phys. B: Condens. Matter **82**, 323 (1991); B. Weiner and J. V. Ortiz, J. Chem. Phys. **117**, 5135 (2002).

[23] A. Fabrocini, S. Fantoni, A. Y. Illarionov, and K. E. Schmidt, Phys. Rev. Lett. **95**, 192501 (2005); arXiv:nucl-th/0607034v1 (unpublished).

[24] A. Cayley, Cambridge and Dublin Math. Journal **7**, 40 (1852); reprinted in *The Collected Mathematical Papers of Arthur Cayley* (Cambridge University Press, Cambridge, 1889)., Vol. 2, p. 19.

[25] M. Nakahara, *Geometry, Topology and Physics* (Institute of Physics, Bristol, 2003).

[26] J. R. Stembridge, Adv. Math. **83**, 96 (1990).

[27] A. Cayley, J. Reine Angew. Math. **38**, 93 (1849); reprinted in *The Collected Mathematical Papers of Arthur Cayley* (Cambridge University Press, Cambridge, 1889), Vol. 1, pp. 410–413.

[28] F. R. Gantmacher, *The Theory of Matrices* (Chelsea, New York, 1959), Vol. 1.

[29] G. Galbiati and F. Maffioli, Discrete Appl. Math. **51**, 269 (1994).

[30] C. J. Umrigar and C. Filippi, Phys. Rev. Lett. **94**, 150201 (2005).

[31] L. K. Wagner, M. Bajdich, and L. Mitas, arXiv:0710.4361 (unpublished); http://www.qwalk.org/.

[32] I. Ovcharenko, A. Aspuru-Guzik, and W. A. Lester, Jr., J. Phys. Chem. **114**, 7790 (2001).

[33] V. A. Rassolov, J. Phys. Chem. **117**, 5978 (2002).

[34] D. Bressanini, G. Morosi, and S. Tarasco, J. Phys. Chem. **123**, 204109 (2005).

[35] C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, Phys. Rev. Lett. **98**, 110201 (2007).

[36] D. M. Ceperley, J. Stat. Phys. **63**, 1237 (1991).

[37] D. Bressanini, D. M. Ceperley, and P. J. Reynolds, in *Recent Advances in Quantum Monte Carlo Methods*, edited by W. A. Lester, S. M. Rothstein, and S. Tanaka (World Scientific, Singapore, 2002).

[38] L. Mitas, Phys. Rev. Lett. **96**, 240402 (2006).

[39] L. Mitas, arXiv:cond-mat/0605550v1 (unpublished).

[40] S. Y. Chang and V. R. Pandharipande, Phys. Rev. Lett. **95**, 080402 (2005).

[41] R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).

[42] K. E. Schmidt, M. A. Lee, M. H. Kalos, and G. V. Chester, Phys. Rev. Lett. **47**, 807 (1981).

[43] R. M. Panoff and J. Carlson, Phys. Rev. Lett. **62**, 1130 (1989).

[44] J. W. Moskowitz and K. E. Schmidt, J. Phys. Chem. **97**, 3382 (1992).

[45] Y. Kwon, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **48**, 12037 (1993).

[46] Y. Kwon, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **50**, 1684 (1994).

[47] Y. Kwon, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **53**, 7376 (1996).

[48] Y. Kwon, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **58**, 6800 (1998).

[49] M. Holzmann, D. M. Ceperley, C. Pierleoni, and K. Esler, Phys. Rev. E **68**, 046707 (2003).

[50] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[51] R. T. Pack and W. B. Brown, J. Phys. Chem. **45**, 556 (1966).

[52] I. G. Gurtubay and R. J. Needs, J. Chem. Phys. **127**, 124306 (2007).

[53] M. D. Brown, J. R. Trail, P. L. Ríos, and R. J. Needs, J. Chem. Phys. **126**, 224110 (2007).

[54] C. G. J. Jacobi, J. Reine Angew. Math. **2**, 347 (1827).

[55] M. Dolg, Chem. Phys. Lett. **250**, 75 (1996).

[56] M. W. Chase, Jr., NIST-JANAF Thermochemical Tables 4th ed. (American Institute of Physics, New York, 1998).

[57] Y. B. Randall, S. Urdahl, and W. M. Jackson, Chem. Phys. Lett. **178**, 425 (1991).

[58] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), Vol. 4.