Pairing in Cold Atoms and other Applications for Quantum Monte Carlo methods

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We discuss the importance of the fermion nodes for the quantum Monte Carlo (QMC) methods and find two cases of the exact nodes. We describe the structure of the generalized pairing wave functions in Pfaffian antisymmetric form and demonstrate their equivalency with certain class of configuration interaction wave functions. We present the QMC calculations of a model fermion system at unitary limit. We find the system to have the energy of \( E = 0.425 E_{\text{free}} \) and the condensate fraction of \( \alpha = 0.48 \). Further we also perform the QMC calculations of the potential energy surface and the electric dipole moment along that surface of the LiSr molecule. We estimate the vibrationally averaged dipole moment to be \( \langle D \rangle_{\nu=0} = -0.4(2) \).

1. Introduction

The electronic structure is in general a very important characteristic of systems described by electron-ion Hamiltonians. One of the popular many-body electronic structure approaches is the quantum Monte Carlo (QMC) method, which employs stochastic techniques for solving the fully interacting stationary Schrödinger equation and for evaluation of expectation values [1–4]. The QMC methodology has an important advantage of employing variety of many-body wave functions (WFs) with explicit electron-electron correlations. These highly accurate wave functions enable us to understand the complicated nature of many-body effects. They are also relevant to QMC fixed-node errors arising from the necessity to circumvent the fermion sign problem [5; 6].

The QMC methods have proven record of highly accurate results for many real systems such as molecules [7], clusters, solids [4] and model systems [8; 9]. However, the crucial challenge in the QMC community is to develop approaches capable of systematic elimination of the fixed-node errors. This goal might be accomplished first by careful analysis of the sources of the fixed-node errors, second by the employment of more accurate and possibly novel many-body wave functions and last by the development of methods with

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In the first part of this article, we address the two former points by discussing the properties of fermion nodes in Sec. 2 and the implementation of the novel Pfaffian pairing wave functions in Sec. 3. In the second part of the article, we apply the QMC methodology to model system of fermionic ultra-cold atoms (Sec. 5). The results of model QMC calculations of the electron dipole moment of the LiSr molecule are reported in the Sec. 6. The last section contains the conclusions and outlook for future work.

2. Fermion Nodes

For a long time, the nodes of fermionic wave functions and their related objects, density matrices, were considered uninteresting. For real many-body state \( \Psi(\mathbf{R}) \) the node is defined as a subspace of \( \mathbb{R} \) where \( \Psi(\mathbf{R}) = 0 \). The configuration space is therefore divided into nodal domains of a constant “+” or “−” sign. The importance of the nodes of eigenstates were first realized by Hilbert and Courant. The electronic nodes have been first analyzed by Breit in 1930. He actually also found the first exact node for the atomic \( ^3P(2p^2) \) state [10]. From QMC point of view, the knowledge of exact nodes of fermionic wave functions leads to elimination the nodal errors.

The general properties of fermion nodes were first analyzed in an extensive study by Ceperley [11], which included a proof of the tiling property and generalizations of the fermion nodes to density matrices. In addition, for some free particle systems, it was numerically shown [11] that there are only two nodal cells. The fermion nodes for degenerate and excited states were further studied by Foulkes and co-workers [12]. Recently, one of us (L.M.) used the property of connectivity from Ref. 11 to show that a number of spin-polarized non-interacting and mean-field systems (homogeneous electron gas, atomic states, fermions in the box, in the harmonic well and on the sphere) has ground state wave functions (given as Slater determinants) with minimal number of nodal cells [13; 14]. Further, he demonstrated that for spin-unpolarized systems an arbitrarily weak interaction introduced by Bardeen–Cooper–Schrieffer (BCS) wave function reduces the four non-interacting nodal cells to just two. Finally, he has also shown that the minimal number of nodal cells property extends to the temperature density matrices.

The fermion nodes of small systems, mostly atoms, were investigated in several previously published papers [5; 10; 15–19]. Interesting work by Bressanini, Reynolds and Ceperley revealed differences in the nodal surface topology between Hartree–Fock and correlated wave functions for the Be atom explaining the large impact of the \( 2s, 2p \) near-degeneracy on the fixed-node DMC energy [20]. More recently, improvement in fixed-node DMC energies of small systems using CI expansions [21; 22], and pairing wave functions [23–26] were also reported.

2.1. Exact Nodal Surfaces

The fermionic wave functions with the exact nodes do not contain any fixed node errors and therefore lead to exact energies and other properties. The exact nodes for states of fully interacting (attractive of repulsive) fermions are in general very difficult to find. There is however a handful of known cases when the node is completely enforced by the high symmetry of the state. This subsection is aimed on such cases. We assume the usual electron-ion Hamiltonian and we first investigate few-electron ions focusing on fermion
nodes for sub-shells of one-particle states with s, p, d, f... symmetries using coordinate transformations, symmetry operations and explicit expressions for the nodes.

2.2. Three-Electron Quartet $^4S(p^3)$ State

The three-electron quartet $^4S(p^3)$ state is the lowest quartet state of $S$ symmetry and odd parity. In order to analyze the wave function in an unambiguous manner, it is convenient to define new coordinates. Let us denote $r_{12}^+ = r_1 + r_2$, $r_{12}^- = |r_{12}|$, together with the customary $r_{12} = r_1 - r_2$, $r_{12} = |r_{12}|$. We can now introduce the following map of the Cartesian coordinates

$$(r_1, r_2, r_3) \rightarrow (r_{12}^+, r_{12}^-, r_3, \cos \alpha, \cos \beta, \gamma, \Omega)$$

(1)

with definitions: $\cos \alpha = r_3 \cdot (r_1 \times r_2)/(r_3|r_1 \times r_2|)$, $\cos \beta = r_{12}^+ \cdot r_{12}/(r_{12}^+ r_{12})$ and $\gamma$ being an azimuthal angle of $r_3$ in the relative coordinate system with unit vectors $e_x = r_{12}^+ / r_{12}^+$, $e_z = r_1 \times r_2/|r_1 \times r_2|$, $e_y = e_z \times e_x$. For completeness, $\Omega$ denotes three Euler angles, which fix the orientation of the three-particle system in the original coordinates (e.g., two spherical angles of $r_1 \times r_2$ and an azimuthal angle of $r_{12}^+$). Since the angles $\Omega$ are irrelevant in $S$ symmetry, the first six variables fully specify the relative positions of the three particles and the wave function dependence simplifies to $\Psi(r_{12}^+, r_{12}^-, r_3, \cos \alpha, \cos \beta, \gamma)$. Consider now two symmetry operations which change the sign of the wave function and keep the distances unchanged: parity $P_1$ and exchange $P_{12}$ between particles 1 and 2. The exchange flips the sign of all three $\cos \alpha, \cos \beta, \gamma$ while the parity changes only the sign of $\cos \alpha$. The action of $P_1 P_{12}$ on $\Psi$ leads to

$$\Psi(..., \cos \alpha, -\cos \beta, -\gamma) = \Psi(..., \cos \alpha, \cos \beta, \gamma)$$

(2)

showing that the wave function is even in the simultaneous sign flip $(\cos \beta, \gamma) \rightarrow (-\cos \beta, -\gamma)$. Applying the exchange operator $P_{12}$ to the wave function and taking advantage of the previous property gives us

$$\Psi(..., -\cos \alpha, \cos \beta, \gamma) = -\Psi(..., \cos \alpha, \cos \beta, \gamma)$$

(3)

suggesting that there is a node determined by the condition $\cos \alpha = 0$. It is also clear that the same arguments can be repeated with exchanged particle labels $2 \leftrightarrow 3$ and $3 \leftrightarrow 1$ and we end up with the same nodal condition, $r_3 \cdot (r_1 \times r_2) = 0$. This shows that the node is encountered when all three electrons lie on a plane passing through the origin. Note that it is identical to the node of Hartree–Fock wave function of $2p$ orbitals given by $\Psi_{HF} = \det[\rho(r)x, \rho(r)y, \rho(r)z]$ where $\rho(r)$ is a radial function.

2.3. Two-Electron Triplet $^3P(p^2)$ and $^3\Sigma_g(p^2)$ States

Apparently, the exact node of this case was derived in a different context by Breit in 1930 [10; 21; 27]. Here we offer an independent proof which enables us to apply the analysis to some molecular states with the same symmetries. The exact node for the $^3P(p^2)$ state can be found in a similar way as in the case of quartet above. The state has even parity, cylindric symmetry, say, around z-axis, and is odd under rotation by $\pi$ around $x, y$ axes, $R(\pi x), R(\pi y)$. The mapping of Cartesian coordinates which enables to analyze the wave function symmetries is given by

$$(r_1, r_2) \rightarrow (r_{12}^+, r_{12}^- \cos \omega, \cos \beta, \varphi, \varphi')$$

(4)
where \( \cos \omega = z_0 \cdot (r_1 \times r_2)/|r_1 \times r_2| \) with \( z_0 \) being the unit vector in the \( z \)-direction and \( \varphi' \) being the azimuthal angle of \( r_1 \times r_2 \); \( \varphi' \) can be omitted due to the cylindric symmetry. Further, \( \varphi \) is the azimuthal angle of \( r_1^+ \) in the relative coordinate system with the \( x \)-axis unit vector given by a projection of \( z_0 \) into the plane defined by \( r_1, r_2 \), i.e., \( e_x = z_0 \cdot |z_0| \), \( e_y = e_z \times e_x \) and \( e_z = (r_1 \times r_2)/(r_1 \times r_2) \). Action of \( P_{12}R(\pi x) \) reveals that the wave function is invariant in the simultaneous change \((\cos \beta, \varphi) \rightarrow (-\cos \beta, -\varphi)\). This property and action of \( P_{12} \) to the wave function together lead to

\[
\Psi(\ldots, -\cos \omega, \ldots) = -\Psi(\ldots, \cos \omega, \ldots)
\]  

with the rest of the variables unchanged. The node is therefore given by \( \cos \omega = 0 \) and is encountered when an electron hits the plane which contains the \( z \)-axis and the other electron. As in the previous case, the nodal plane fulfills the tiling property and manifestly divides the space into two nodal cells so that we can conclude that this node is exact. The exact node again agrees with the node of Hartree–Fock wave function \( \Psi = \det[\rho(r)x, \rho(r)y] \). In addition, our fixed-node QMC calculations for \( ^3P(p^2) \) and \( ^4S(p^3) \) states with Hartree–Fock wave functions had numerically confirmed the proofs [28].

3. Pairing wave functions

So far, the work on improvement in the accuracy of trial wave functions has proved to be one working method to decrease the fixed-node errors [22; 29; 30]. This approach has also an additional benefit in forcing us to think about the relevant correlation effects and their compact and computationally efficient description.

The trial wave functions in QMC have usually the Slater–Jastrow form, which can be written as \( \Psi_T = \Psi_A \exp[U_{\text{corr}}] \), where \( \Psi_A \) is the antisymmetric part while \( U_{\text{corr}} \) 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 a configuration interaction expansion [for details see e.g. Ref. 31].

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) wave function, which is an antisymmetrized product of singlet pairs. It has been recently used to calculate several atoms and molecules as well as superfluid Fermi gases [9; 23; 24]. The results show promising gains when compared to the single-determinant Hartree–Fock (HF) wave functions, nevertheless, in partially spin-polarized systems the improvements are less pronounced due to the lack of pair correlations in the spin-polarized subspace [23; 24]. The spin-polarized (triplet) pairing wave functions lead to Pfaffians (instead of determinants) and have been mentioned a few times before and applied to model systems [32–34].

3.1. General pairing wave function

The simplest antisymmetric wave function for \( N \) electrons constructed from one-particle orbitals is the Slater determinant

\[
\Psi_{HF} = \det[\tilde{\varphi}_k(r_i, s_i)] = \det[\tilde{\varphi}_k(i)]; \quad i, k = 1, \ldots, N,
\]
where 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.

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

\[
\Psi = \mathcal{A}[\tilde{\phi}(1,2), \tilde{\phi}(3,4) \ldots \tilde{\phi}(2N-1,2N)] = \text{pf}[\tilde{\phi}(i,j)]. \tag{7}
\]

The antisymmetry is guaranteed by the definition, since the signs of pair partitions in Pfaffian form 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 \( \tilde{\phi}(r_i, s_i; r_j, s_j) \) for two electrons in positions \( r_i \) and \( r_j \) and with spins projections \( s_i \) and \( s_j \) and can be expressed as

\[
\tilde{\phi}(r_i, s_i; r_j, s_j) = \phi(i, j)\langle s_i s_j|[[\uparrow\downarrow] - |\downarrow\uparrow]\rangle/\sqrt{2} \tag{8}
\]

\[
+ \chi_{\uparrow\downarrow}(i, j)\langle s_i s_j|[[\uparrow\uparrow] + |\downarrow\downarrow]\rangle/\sqrt{2} \\
+ \chi_{\downarrow\uparrow}(i, j)\langle s_i s_j|[[\uparrow\downarrow]\rangle.
\]

Here \( \phi(i, j) = \phi(r_i, r_j) \) is even, while \( \chi_{\uparrow\uparrow} \), \( \chi_{\downarrow\downarrow} \) and \( \chi_{\downarrow\uparrow} \) are odd functions of spatial coordinates.

For fixed number of electrons and ordered choice of electron labels, with all spin-up electrons first and remaining electrons spin-down, we can readily write down the spatial part of singlet–triplet–unpaired (STU) Pfaffian wave function [25] as

\[
\Psi_{STU} = \text{pf}\begin{bmatrix}
\xi_{\uparrow\uparrow} & \Phi_{\uparrow\downarrow} + \xi_{\downarrow\downarrow} \\
-\Phi_{\uparrow\downarrow}^T & \xi_{\downarrow\downarrow} \\
-\Phi_{\downarrow\uparrow}^T & \varphi_{\downarrow\downarrow}
\end{bmatrix} \tag{9}
\]

using expressions (7 and 8). The bold symbols \( \Phi, \xi \) and \( \varphi \) are block matrices of \( \phi(i,j) \), \( \chi(i,j) \) and \( \varphi(i) \), respectively and \( T \) denotes transposition.

4. Pairing wave function results

We perform the variational and fixed-node diffusion Monte Carlo (VMC and FN-DMC) calculations [3; 4] with the Pfaffian pairing wave functions. We also extend this work to different linear combinations of Pfaffians. The pair orbitals were expanded in products of a one-particle orbital basis. The expansions include both occupied and virtual one-particle orbitals from either Hartree–Fock or CI correlated calculations [31]. The pair orbital expansion coefficients were then optimized in VMC by minimizations of energy, variance or a combination of energy and variance [35]. We used pseudopotentials [36] to eliminate the atomic cores.
4.1. Multi-Pfaffian calculations

The results of single-Pfaffian wave function calculations when applied to the first row atoms and dimers were reported in our previous two papers [25; 26]. The employed STU Pfaffian pairing wave function of the form Eq. (9) with $\chi^{\uparrow\downarrow} = 0$ yielded systematic percentage of recovered correlation energy on the level of 94-97% in FN-DMC method. In general, the triplet contribution to correlation was very small, on the order of 1%. In order to capture the correlation energy missing from the single STU Pfaffian wave function and to test the limits of the Pfaffian functional form, we have also proposed to expand the $\Psi_A$ in the linear combination of STU Pfaffian wave functions.

Following the approach adopted from the CI correlated calculations, accurate $\Psi_A$ can be expressed as a linear combination of reference state $\Psi_0$ and single $\Psi_i^k$ and double $\Psi_{ij}^{kl}$ excitations:

$$
\Psi_{CISD} = c_0 \Psi_0 + \sum_i \sum_k c_i^k \Psi_i^k + \sum_{ij} \sum_{kl} c_{ij}^{kl} \Psi_{ij}^{kl},
$$

(10)

where $i$-th and $j$-th electrons are being excited into $k$ and $l$ virtual orbitals. Note that the number of determinants in the expansion will be of the order of $N^2 \times M^2$. Analogously, we postulate the multi-Pfaffian (MPF) wave function as a linear combination of STU Pfaffians:

$$
\Psi_{MPF} = c_0 \Psi_0 + \sum_i \text{pf}[\tilde{\phi}_i] + \sum_{ij} \text{pf}[\tilde{\phi}_{ij}],
$$

(11)

where each $\tilde{\phi}_{ij}$ is the generalized paring orbital [Eq. (8)] containing all possible $M^2$ excitations of $i$ and $j$ electrons. The resulting wave function will in general consist of only $N^2$ Pfaffians. Further, if the reference state $\Psi_0$ is the most dominant state (i.e., $c_0 \gg c_{ij}^{kl}$), it is possible to show by expanding $\tilde{\phi}_{ij}$ into orders of $c_{ij}^{kl}/c_0$ that

$$
\Psi_{MPF} = \Psi_{CISD} + \mathcal{O} \left( \left( \frac{c_{ij}^{kl}}{c_0} \right)^2 \right).
$$

(12)

In fact, the only difference between the $\Psi_{MPF}$ and $\Psi_{CISD}$ wave functions is in presence of the higher order excitations, which are approximately present in the $\Psi_{MPF}$.

The mapping of the MPF wave functions onto equivalent CISD wave functions was also verified numerically in the variational and FN-DMC methods using the above first row atoms and molecules [25; 26]. The results in Table 1 show that for the atomic systems the MPF wave functions are able to recover close to 99% of correlation energy—very similarly to CISD wave functions, while requiring an order of magnitude less terms.

Our latest results for diatomic cases (see Table 2) exhibit comparable behavior. The correlation energy recovered is on the order of 98% with MPF wave functions closely matching the CISD wave functions—despite much richer electronic structure than in atomic cases. The comparison with the CI results therefore demonstrates that it is possible to obtain similar quality wave functions with corresponding improvements of the fermion nodes at much smaller calculational cost.
Table 1
Percentages of correlation energies recovered for C, N and O atoms by VMC and DMC methods with wave functions as discussed in the text. The corresponding number of Pfaffians or determinants $n$ for each wave function is also shown. For C, N, O atoms we used the correlation energies by Dolg [37] (0.1031, 0.1303, 0.1937 H). Unless noted otherwise, the numbers in parentheses are the statistical errors in the last digit from corresponding QMC calculation.

| Method/WF | C $n$ | N $n$ | O $n$ |
|-----------|-------|-------|-------|
| VMC/MPF   | 3     | 5     | 11    |
|           | 92.3(1) | 90.6(1) | 92.6(3) |
| VMC/CI    | 98    | 85    | 136   |
|           | 89.7(4) | 91.9(2) | 89.7(4) |
| DMC/MPF   | 3     | 5     | 11    |
|           | 98.9(2) | 98.4(1) | 97.2(1) |
| DMC/CI    | 98    | 85    | 136   |
|           | 99.3(3) | 98.9(2) | 98.4(2) |

$^a$The determinantal weights were taken directly from CI calculation without re-optimization in VMC.

5. Pairing in Ultra-Cold Fermi Gases

Strongly paired fermions have been recently experimentally observed in cold atom systems in the gas phase (see for example Ref. 42). At very low temperatures, the particle-particle correlations play crucial role in bringing the gas into a superfluid state. In dilute systems with spherically symmetric inter-particle potentials, the interactions are fully characterized by a single parameter, the two-body $s$-wave scattering length $a$. Utilizing Feshbach resonance, the scattering length $a$ can be tuned via external magnetic field. The system can be continuously interpolated from the so-called BCS superfluid constituted of weakly bound Cooper pairs ($1/a \to -\infty$) to the Bose–Einstein condensate (BEC) of tightly bound bosonic dimers ($1/a \to \infty$).

5.1. Results for system at the unitary limit

At the Feshbach resonance, the scattering length $a$ diverges ($1/a = 0$) and the only relevant length scales remaining in the problem are the inverse of the Fermi wave vector $1/k_F$ and the thermal wavelength. All thermodynamic quantities should therefore be universal functions of the Fermi energy $E_F$ and the ratio $T/T_F$. At $T = 0$, there is only a single length scale left and the system is in the so-called unitary limit. The total energy can be written as

$$E = \xi E_{\text{free}} = \xi \frac{3}{5} E_F,$$

(13)

where $E_{\text{free}}$ denotes the energy of a non-interacting system and $\xi$ is a universal parameter.

One of the most accurate estimations of the parameter $\xi$ has been calculated by QMC methods [9; 43]. The original value of $\xi = 0.44(1)$ was subsequently improved to the current limit of about $\xi = 0.40(1)$ [44], which is in fair agreement with experiments.

In this work, we revisit these results and calculate the total energy of 38 spin unpolarized fermions interacting via attractive potential $V_{\text{eff}}(r) = -A_{2B} \exp\left[-(r/s)^2/2\right]/(s\sqrt{2\pi})$ with fixed $s = 0.4$ and variable $A_{2B}$. We employ trial wave-functions of the Slater–Jastrow and BCS-Jastrow forms. The latter can be expressed as $\Psi_T(R) = \Psi_{BCS}(R)\Psi_{\text{Jastrow}}(R)$,
Table 2
Total energies for C$_2$ and N$_2$ dimers with amounts of correlation energy recovered in VMC and DMC methods with wave functions as discussed in the text. Energies are in Hartree atomic units. The corresponding number of Pfaffians or determinants $n$ for each wave function is also shown. Unless noted otherwise, the numbers in parentheses are the statistical errors in the last digit from corresponding QMC calculation. For the estimation of correlation energies of dimers we needed accurate HF energies at experimental distances [38] 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 [38–40] adjusted for experimental zero-point energy [40].

| Method/WF  | $n$     | C$_2$  | $E_{corr}$ [%] | $n$     | N$_2$  | $E_{corr}$ [%] |
|------------|---------|--------|---------------|---------|--------|---------------|
| VMC/MPF$^c$| 11      | -11.0402(1) | 93.1(1)      | 16      | -19.8413(6) | 90.5(1)       |
| VMC/CI$^a$ | 404     | -11.0409(3) | 93.3(1)      | 535     | -19.8487(6) | 92.2(1)       |
| DMC/MPF$^c$| 11      | -11.0574(5) | 97.3(1)      | 16      | -19.8670(8) | 96.4(2)       |
| DMC/CI$^a$ | 404     | -11.0593(6)$^b$ | 97.8(2) | 535     | -19.8713(5) | 97.4(1)       |

$^a$The determinantal weights were re-optimized in the VMC method.
$^b$Recently, Umrigar et al. [22] published very accurate DMC result for fully optimized CI wave function with up to 500 determinants for C$_2$ molecule. The resulting well-depth of their calculation is 6.33(1) eV, which is only 0.03 eV from estimated exact value of Ref. 41. The well-depth resulting from our DMC/CI energy of $-11.0593(6)$ H equals to 6.08(3) eV.
$^c$One type of triplet-like excitations not included.

where $\Psi_{BCS}(R) = A[\phi(r_{ij})] = \det[\phi(r_{ij})]$. Our ansatz for the singlet pairing orbital $\phi(r_{ij})$ has the form

$$\phi(r_{ij}) = \sum_{\ell \in \text{closed shells}} c_\ell \sum_{k_m \in \ell-\text{th shell}} e^{ik_m \cdot r_{ij}} + \phi_s(r_{ij}),$$  \hspace{1cm} (14)$$

where $\{c_\ell\}$ as well as the short-range spherical term $\phi_s(r)$ are optimized on the VMC level by minimization of energy, variance or a combination of energy and variance [35].

Our results are shown in Fig. 1. We compare Slater–Jastrow and BCS–Jastrow trial wave function FN-DMC energies as functions of the two-body scattering length $a$. The mutual crossing of the curves, corresponding to different particle-number densities, demonstrates that there indeed exists a universal regime, where $\xi$ does not depend on the inter-particle distances. Moreover, for the best available wave function (BCS–Jastrow), this intersection is placed at the expected point of diverging two-body scattering length. On the energy scale, the crossing occurs at $\xi = 0.425$ for the BCS based trial wave function and at $\xi = 0.482$ for the Slater–Jastrow trial wave function. This clearly indicates that the FN-DMC energy of BCS based trial wave function is closer to the true ground state. Our number falls in between the first QMC estimate and the most current one, with the difference accounted for by a slightly different form of the singlet pairing orbital, Eq. (14).

Using the optimized BCS–Jastrow wave function, it is also possible to evaluate the condensate fraction $\alpha$ within the FN-DMC method. In unpolarized systems, $N_\uparrow = N_\downarrow = \alpha N_0$. The condensate fraction $\alpha$ is the fraction of all particles that are in the ground state (or, equivalently, the fraction of the macroscopic wave function that is localized on a single particle). In the context of the FN-DMC method, $\alpha$ is defined as the ratio of the number of particles in the ground state to the total number of particles. The expression for $\alpha$ in terms of the wave function is given by

$$\alpha = \frac{\int \phi_0^* \phi_0 \, d^3r}{\int |\psi|^2 \, d^3r},$$

where $\phi_0$ is the ground state wave function and $\psi$ is the full wave function. The condensate fraction $\alpha$ is a crucial quantity in many-body systems, as it characterizes the degree of Bose-Einstein condensation.
Figure 1. FN-DMC energies of 38 fermions at the Γ-point in units of $E_{\text{free}} = 3E_F/5$, where $E_F = k_F^2/2$, plotted as functions of the two-body scattering length $a$. Shown are three particle densities $\rho$ characterized by $r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$; $r_s = 3.5$, 4.0 and 4.5. Two types of trial wave functions are used: Slater–Jastrow (dashed lines) and BCS-Jastrow (solid lines).

Figure 2. Spherically averaged two-body density matrix (full symbols) and two-body density matrix without the uncorrelated contribution (open symbols) for 38 fermions at the Γ-point and $r_s = 4$ as described by the BCS wave function. Interaction is tuned to unitarity. Asymptotic value at $r \to \infty$ provides an estimate of the superfluid condensate fraction $\alpha = 0.48$.

\[
\alpha = \lim_{r \to \infty} \frac{N}{2} \rho_{2,11}^{P}(r) \quad \text{or} \quad \alpha = \lim_{r \to \infty} \frac{N}{2} \left[ \rho_{2,11}^{P}(r) - \rho_{11}^{sph}(r) \rho_{11}^{sph}(r) \right],
\]

where $\rho_{11}^{sph}$ and $\rho_{2,11}^{P}$ are spherically averaged one- and two-body density matrices as explained elsewhere [see Ref. 45 and references therein]. Both expressions in Eq. (15) are identical in the thermodynamic limit, but the latter is computationally more convenient, since it converges much faster to its asymptotic value (see Fig. 2). The calculated condensate fraction $\alpha = 0.48$ indicates that a large part of the fermions is indeed in the state of a (strongly) paired superfluid.

6. Ultra Cold Polar Molecules

Recently, there has been a great deal of interest in the production of ultra-cold heteronuclear molecules having large electric dipole moments [46; 47]. This is of interest both for fundamental reasons having to do with the quantum phases and phase transitions such systems might undergo, as well as for applications such as qubits for quantum computing [48]. Dipolar quantum phases may include dipolar superfluids, striped and checkerboard phases, and various forms of quantum liquid crystals.
6.1. Results
In this work, we have calculated the dipole moment of a potentially implementable two-atom alkaline-alkaline-earth molecule, LiSr. We used CI and QMC methods to calculate the potential energy surface and dipole moment along that surface.

The dipole moment was studied with increasing accuracy of correlated wave-functions. The variationally re-optimized wave functions then served as the representation of the fermion nodes in the FN-DMC and reptation Monte Carlo (RMC) methods [49]. To treat the Sr atom we employed two types of effective core potentials (ECPs), one with a large core [50] and one with a small core [51]—to assess the impact of the effective core approximation. The large core ECP has only s-states in the valence space, while the small core valence space includes also the highest s and p semi-core sub-shells.

Our results from Fig. 3 indicate significant sensitivity of the dipole moment on the size of the valence space. For the larger core ECP, the predictions from the HF and the CI calculations differ very little, while for the smaller core ECP, the CI methods give much smaller dipole moment, due to the contribution of the highest semi-core sub-shells.

We have then performed the QMC calculations using only the smaller core ECP. The Fig. 4 shows the resulting RMC dipole moments for single-determinant and multi-determinant Slater–Jastrow trial wave functions compared to CI method. While the values for the single-determinant RMC method lie on the smooth curve, the multi-determinant RMC values exhibit unphysical fluctuations. This behavior is most likely caused by the uneven optimization of many determinant wave functions at each nucleon-nucleon distance. Even as the VMC energy data were reasonably smooth, and DMC method produced the most accurate binding curve up to date (inset of Fig. 4), the higher order sensitivity of dipole moment gave rise to systematic errors on the level of 0.2 D.

Finally, in Table 3 we list all the calculated spectroscopic data for the LiSr molecule. The used symbols are: \( D_e \) denotes binding energy, \( r_e \) equilibrium distance, \( E_{zpe} \) is the zero-point energy and finally the vibrationally averaged (zero mode only) electric dipole moment \( \langle D \rangle_{\nu=0} \). Due to the large systematic errors, we can only estimate the final value of the electric dipole moment (for the most accurate calculation) as \( \langle D \rangle_{\nu=0} = -0.4(2) \) D.

| \( D_e \) (eV) | 0.30(1) |
| \( r_e \) (a.u.) | 6.76(6) |
| \( E_{zpe} \) (cm\(^{-1}\)) | 81 |
| \( \langle D \rangle_{\nu=0} \) (D) | -0.4(2) |

7. Conclusions
In the first part of the article we have discussed the fermion nodes and Pfaffian pairing wave functions. First, using the coordinate transformations, we have found the exact
nodes for two particular states. Even if in general the nodes of integrating fermions are complicated, we have seen that for these cases, the interactions did not change the nodes enforced by the high symmetry.

Second, we have shown that for chemical systems the Pfaffian wave functions with pairing orbitals are viable alternative to multi-determinantal wave functions. However, the main virtue of the pairing wave functions still remains the capability of describing the pairing effects in quantum condensates and exhibit correct nodal topologies.

The second part of the article was dedicated to QMC applications. In the first application, we have revisited the calculations of total energy and condensate fraction of a model system at unitary limit. We have found that pairing wave functions of BCS type have better nodes and are suitable to describe the pairing effects. In the future, we hope to include the triplet pairing and describe novel phenomena such as $p$-wave superfluidity using the Pfaffian pairing wave functions.

Finally, the electron dipole moment calculation of LiSr highlighted the strengths as well as the weaknesses of the QMC methods. Using the VMC optimized many determinant trial wave functions we have been able to obtain the most accurate energy surface up to date. However, the variational bias was clearly visible in the RMC dipole moment.
calculation. We are currently working on the methods with direct nodal optimization, which in principle could project out the variational bias and minimize the fixed node errors.

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