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Quantum Monte Carlo with variable spins: fixed-phase and fixed-node approximations

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We study several aspects of the recently introduced fixed-phase spinor diffusion Monte Carlo (FPSODMC) method, in particular, its relation to the fixed-node method and its potential use as a general approach for electronic structure calculations. We illustrate constructions of spinor-based wave functions with the full space-spin symmetry without assigning up or down spin labels to particular electrons, effectively “complexifying” even ordinary real-valued wave functions for Hamiltonians without spin terms. Interestingly, with proper choice of the simulation parameters and spin variables, such fixed-phase calculations enable one to reach also the fixed-node limit. The fixed-phase approximation has several desirable properties when compared to the fixed-node approximation. The fixed-phase solution provides a straightforward interpretation as the lowest bosonic state in a given effective potential generated by the many-body approximate phase, whereas nodal boundary conditions are defined through less intuitive and complicated hypersurfaces with one dimension less than the original configuration space. In addition, the divergences of the local energy and drift at real wave function nodes are smoothed out to lower dimensionality when the wave function is complexified, thus decreasing the variation of sampled quantities and eliminating artificial nodal domain issues that can occur in the fixed-node formalism. We illustrate some of these properties on calculations of selected first-row systems that recover the fixed-node results with quantitatively similar levels of the corresponding biases. At the same time, the fixed-phase approach opens new possibilities for more general trial wave functions with further opportunities for increasing accuracy in practical calculations.

I. INTRODUCTION

Recently, we introduced a projector quantum Monte Carlo (QMC) method for calculating quantum systems with both spatial and spin degrees of freedom [1]. The approach is based on an overcomplete representation for spin variables such that the sampling is similar to the spatial variables. Given our choice of spin representation, the method involves the fixed-phase [2] approximation, hence its acronym fixed-phase spin-orbit/spinor diffusion Monte Carlo (FPSODMC). This approach enabled us to carry out QMC calculations of atoms and molecules with spin-orbit interactions in the spinor formalism including cases where high accuracy was needed for both spin-orbit and electron correlation effects. In a subsequent work we studied simple cases of fixed-phase vs. fixed-node [3] approximations in order to compare the corresponding biases in these two related possibilities [4, 5]. We constructed simple cases where both fixed-phase and fixed-node conditions were equivalent or very similar and we found comparable biases in the total energies using the two approximations.

In this work we explore this direction further by investigating a unification and smooth transition between the fixed-node and fixed-phase methods. While the FPSODMC method was originally used to study spin-orbit interactions in various systems, the spin-orbit interaction itself was introduced via a relativistic effective core potential. Here we study another aspect of the method, in particular, how the complex spin representation we introduced can be used in the absence of the spin-orbit interactions. As we show below, this provides a framework

for using complex wave functions under the fixed-phase approximation in cases that would normally be described by *real-valued wave functions used within the fixed-node approximation*. It has been known for some time that the fixed-node approximation is a special case of the fixed-phase approximation. Here we make this relationship explicit through a straightforward construction of trial wave functions that in a particular limit recover the fixed-node counterparts. In addition, we explicitly show how one can obtain the fixed-node result as a limit of the fixed-phase calculation. We use this property for QMC fixed-phase calculations of several systems and we directly compare the fixed-phase biases to the corresponding fixed-node biases. Another aspect of the proposed method is that it provides a general framework for complexifying trial wave functions. Given the success of complexification schemes, such as in quantum field theories, this avenue could prove to be a new tool for improving the accuracy of QMC calculations. Finally, we elaborate on the advantages and also point out some of the current limits of the fixed-phase approach.

II. FIXED-PHASE SPINOR DIFFUSION MONTE CARLO

Let us briefly outline the key notions of the FPSODMC approach: fixed-phase approximation, continuous spin representation and the corresponding importance sampling approach.

A. Fixed-Phase Approximation and the Upper Bound Property

For complex wave functions we present a brief sketch of the fixed-phase method (FPDMC) [2] and its relation to the fixed-node flavor of DMC.

Let us consider the Born-Oppenheimer Hamiltonian $H = -(1/2)\nabla^2 + V(\mathbf{R})$, where $\nabla = (\nabla_1, \nabla_2, \dots, \nabla_N)$ and V denotes the electron-ion and electron-electron Coulomb interactions. We denote spatial configurations as $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \in \mathbb{R}^{dN}$, where N is the number of particles and d is dimensionality (here we assume $d = 3$). We assume a complex wave function $\Psi(\mathbf{R}, \tau) = \rho(\mathbf{R}, \tau)e^{i\Phi(\mathbf{R}, \tau)}$ and substitute it into the imaginary-time Schrödinger equation. For the amplitude $\rho(\mathbf{R}, \tau)$ and phase $\Phi(\mathbf{R}, \tau)$ we obtain

$$-\frac{\partial \rho(\mathbf{R}, \tau)}{\partial \tau} = \left[T_{kin} + V(\mathbf{R}) + \frac{1}{2} |\nabla \Phi(\mathbf{R}, \tau)|^2 \right] \rho(\mathbf{R}, \tau) \quad (1)$$

$$-\frac{\partial \Phi(\mathbf{R}, \tau)}{\partial \tau} = \left[T_{kin} - \frac{\nabla \rho(\mathbf{R}, \tau) \cdot \nabla}{\rho(\mathbf{R}, \tau)} \right] \Phi(\mathbf{R}, \tau) \quad (2)$$

where $T_{kin} = -(1/2)\nabla^2$. The fixed-phase approximation is given by imposing the phase to be equal to the phase of trial or variational wave function $\Psi_T(\mathbf{R}) = \rho_T(\mathbf{R})e^{i\Phi_T(\mathbf{R})}$ that is independent of τ

$$\Phi(\mathbf{R}, \tau) = \Phi_T(\mathbf{R}). \quad (3)$$

The fixed-phase approximation is variational since the repulsive potential $V_{ph} = \frac{1}{2} |\nabla \Phi_T|^2$ can only raise the energy for an approximate phase [2]. This is easy to see from the energy expectation with $\rho \exp(i\Phi_T)$ that must be an upper bound to the exact energy for an arbitrary symmetric $\rho \geq 0$. The amplitude ρ that minimizes the energy expectation value for the given phase Φ_T is obtained by solving the first equation. The accuracy of this method clearly depends on the accuracy of the trial phase and the convergence towards the exact eigenvalue scales with the square of the difference between the exact and approximate trial function. In the present work the second equation is not considered any further.

B. Fixed-node as a special case of the fixed-phase in general

The fixed-phase approximation is a generalization of the more familiar fixed-node approximation, which can be demonstrated in several ways. Let us present perhaps the simplest such construction [4], where we add a complex amplitude to a real-valued $\Psi_T(\mathbf{R})$ as follows. We denote the nodes of Ψ_T as the set of configurations

$$\Gamma = \{ \mathbf{R} \in \mathbb{R}^{dN} | \Psi_T(\mathbf{R}) = 0 \}. \quad (4)$$

Now we add to Ψ_T another function (for simplicity, a non-negative bosonic ground state of H)

$$\tilde{\Psi}_T = \Psi_T + i\varepsilon \Psi_B \quad (5)$$

Taking the limit $\varepsilon \rightarrow 0$ leads to [4]

$$V_{ph}(\mathbf{R}) = V_\infty \delta(\mathbf{R} - \mathbf{R}_\Gamma) \quad (6)$$

where $\mathbf{R}_\Gamma \in \Gamma$ and V_∞ diverges as $\propto 1/\varepsilon$, therefore V_{ph} enforces any wave function to vanish at the node Γ , i.e., it is equivalent to the fixed-node boundary condition.

C. Spin Representation

Let us denote one-particle spinors as

$$\chi(\mathbf{r}, s) = \alpha \varphi^\uparrow(\mathbf{r}) \chi^\uparrow(s) + \beta \varphi^\downarrow(\mathbf{r}) \chi^\downarrow(s) \quad (7)$$

where s is the coordinate of the spin projection along the z -axis. Note that the spinor lives in the full $SU(2)$ Hilbert space since α, β are complex and $|\alpha|^2 + |\beta|^2 = 1$ as usual. In its minimal representation the spin variables (“coordinates”) are discrete $s = \pm 1/2$ so that for S_z eigenstates $\chi^\uparrow(1/2) = \chi^\downarrow(-1/2) = 1$, $\chi^\downarrow(1/2) = \chi^\uparrow(-1/2) = 0$. Due to its discrete nature, this representation has the potential to introduce large variations of sampled quantities during stochastic updates as well as loss of efficiency in propagation due to the decreased acceptance rate. Besides the fluctuations of various quantities of interest (local energy, drifts, values of the wave function, etc.), the discrete sampling would eventually lead to exponential efficiency barrier in the many-particle limit.

One possibility to address this obstacle is to make the spin configuration space continuous, which allows for continuous evolution as well as importance sampling [3, 4]. We choose an *overcomplete* spin representation through the utilization of a 1D ring (i.e. a $U(1)$ representation) with the lowest pair of degenerate, orthogonal eigenstates as follows:

$$\langle s_j | \chi^\uparrow \rangle = e^{is_j}, \quad \langle s_j | \chi^\downarrow \rangle = e^{-is_j} \quad (8)$$

where the spin variable $s_j \in [0, 2\pi)$. Clearly, the paths in this space are continuous and resemble paths for spatial coordinates. As will be shown below, this particular choice of representation coupled with our modified Hamiltonian allows the spin variables to evolve and be updated in the exact same fashion as the spatial variables.

D. Importance sampling

Rewriting the Schrödinger equation in an integral form with importance sampling by ρ_T leads to the following equation for the mixed distribution $g = \rho \rho_T$

$$g(\mathbf{R}', t + \tau) = \int d\mathbf{R} \frac{\rho_T(\mathbf{R}')}{\rho_T(\mathbf{R})} G(\mathbf{R}' \leftarrow \mathbf{R}, \tau) g(\mathbf{R}, t) \quad (9)$$

which is well-known from the fixed-node QMC [3, 4].

Spin variables are sampled by introducing a spin “kinetic” energy with a corresponding energy offset such that for all $s_i, i \in \{1, 2, \dots, N\}$ we write

$$T_i^s = -\frac{1}{2\mu_s} \left[\frac{\partial^2}{\partial s_i^2} + 1 \right]. \quad (10)$$

where μ_s is an effective mass. The full Hamiltonian then becomes $H' = H + \sum_{i=1}^N T_i^s$. Clearly, $T_i^s \psi(\mathbf{r}_i, s_i) = 0$ due to the introduced offset so that there is no energy contribution from the spin Laplacian. The inclusion of the spin kinetic energy leads to the following importance sampled Green’s function

$$\tilde{G}(\mathbf{X}' \leftarrow \mathbf{X}; \tau) \simeq T_{\mathbf{X}', \mathbf{X}} e^{-\tau[E_L(\mathbf{X}) + E_L(\mathbf{X}') - 2E_T]/2} \quad (11)$$

with

$$T_{\mathbf{X}', \mathbf{X}} \propto \exp \left[\frac{-|\mathbf{R}' - \mathbf{R} - \tau \mathbf{v}_D^{\mathbf{R}}(\mathbf{R})|^2}{2\tau} \right] \times \exp \left[\frac{-|\mathbf{S}' - \mathbf{S} - \tau_s \mathbf{v}_D^{\mathbf{S}}(\mathbf{S})|^2}{2\tau_s} \right] \quad (12)$$

where $\mathbf{X} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N) = (\mathbf{R}, \mathbf{S})$. Here we have introduced a spin time step $\tau_s = \tau/\mu_s$ as well as $\mathbf{v}_D^{\mathbf{R}} = \nabla_{\mathbf{R}} \ln \rho_T(\mathbf{X})$ and $\mathbf{v}_D^{\mathbf{S}} = \nabla_{\mathbf{S}} \ln \rho_T(\mathbf{X})$ which correspond to the spatial and spin drifts. The local energy is given by $E_L = \text{Re}[(H'\Psi_T)/\Psi_T^*]$ [1, 3]. With this choice of spin representation, implementation into existing codes is rather straightforward. The spin variable can be treated essentially like another spatial degree of freedom, except that the effective spin mass implies two evolutions: one for the spins and another for the spatial degrees of freedom. That in turn introduces two types of time steps when implementing the dynamics of the whole system.

Note that there are two possible limiting cases with regard to μ_s vs the ordinary m_e .

The first limit corresponds to $\mu_s \ll m_e$, i.e., spin mass being much smaller than the electron mass. The spin degrees of freedom then evolve much faster so that effectively the spins are integrated out much faster than is the pace of the spatial propagation. That guarantees to provide the fixed-phase limit and it is expected that it will lead to the higher energy since the fixed-phase potential is non-zero in the whole space. Therefore it should lead to the larger bias when compared with the fixed-nodes that are codimension 1. Indeed, this is what we have presented already in our previous work, see Ref. [4], Fig. 3.

The opposite limit, that is relevant for our present study, corresponds to the very slow spin evolution, i.e., $\mu_s \gg m_e$. The spin configurations then appear as almost static external constraints in a (relatively) much faster spatial evolution. In the results section we come to this point again and we show that in this mode the simulations will enable us to recover the fixed-node solution. Before fully appreciating this point we need to explain the trial function forms and corresponding choices of spin coordinates as outlined below.

We close this section with the note that the practical implementation of different masses is done through the different time steps for spins and spatial variables. Note that the extrapolation to the zero time step limit should be done in such a way that the ratio of the two time steps is constant as given by the choice of μ_s/m_e . Alternatively, one of the time steps can be chosen sufficiently small so that its bias is negligible overall, while the other can vary within an acceptably low-bias range, as we have chosen to do in this study.

III. TRIAL WAVE FUNCTIONS

The FPSODMC trial functions are built from spinors $\chi(\mathbf{r}, s) = \alpha\varphi^\uparrow(\mathbf{r})\chi^\uparrow(s) + \beta\varphi^\downarrow(\mathbf{r})\chi^\downarrow(s)$ where orbitals $\varphi^\uparrow, \varphi^\downarrow$ are calculated in spinor-based DFT, HF/DHF or correlated methods. The full configuration space for particles is $\mathbf{X} = \{(\mathbf{r}_1, s_1), \dots, (\mathbf{r}_N, s_N)\} \in \mathbb{R}^{3N} \times [0, 2\pi)^N$ and we write the trial wave function as

$$\Psi_T(\mathbf{X}) = e^{U(\mathbf{R})} \sum_{\alpha} c_{\alpha} \det_{\alpha} [\dots, \chi_i(\mathbf{r}_k, s_k), \dots]. \quad (13)$$

with $i, k = 1, \dots, N$. The particle correlations are explicitly approximated by the Jastrow factor $U(\mathbf{R})$ that captures two-particle and, possibly, higher order correlations, as is customary in QMC calculations [3, 4, 6, 7].

A. From fixed-phase to fixed-nodes

In this work we are particularly focused on the limit of vanishing complex component of the wave function and how the single-reference spinor determinant simplifies to the product of spin-up and spin-down determinants, i.e., to the usual fixed-node form. We emphasize that in the present exploration of the FPSODMC method the spin-orbit interactions are disregarded in both all-electron and pseudopotential settings. Let us show that this is indeed what happens for our spin representation as briefly sketched earlier [4]. Note that our previous exposition of this aspect was not formulated precisely [4], so that we clarify it in detail here. For the sake of consistency with the previous paper we consider N occupied spinors that can be grouped as $N/2$ Kramer’s pairs (for simplicity assuming N to be even). We can write the Kramer’s pair as

$$\chi^+ = (\varphi + \Delta\varphi)\chi^\uparrow + (\varphi - \Delta\varphi)\chi^\downarrow \quad (14)$$

$$\chi^- = (\varphi - \Delta\varphi)\chi^\uparrow - (\varphi + \Delta\varphi)\chi^\downarrow \quad (15)$$

where the $\Delta\varphi$ is the spin-orbit induced splitting of the spatial orbital φ . The block of the first four rows/columns from the corresponding Slater determinant

reads as follows

$$\det \begin{bmatrix} \chi_1^+(1) & \chi_1^+(2) & \chi_1^+(3) & \chi_1^+(4) & \dots \\ \chi_1^-(1) & \chi_1^-(2) & \chi_1^-(3) & \chi_1^-(4) & \dots \\ \chi_2^+(1) & \chi_2^+(2) & \chi_2^+(3) & \chi_2^+(4) & \dots \\ \chi_2^-(1) & \chi_2^-(2) & \chi_2^-(3) & \chi_2^-(4) & \dots \\ \dots & & & & \dots \end{bmatrix}. \quad (16)$$

Now we assume that the spin-orbit splitting $\Delta\varphi \rightarrow 0$ and then

$$\chi^+ = \varphi(e^{is} + e^{-is}) \rightarrow \varphi e^{is} \quad (17)$$

$$\chi^- = \varphi(e^{is} - e^{-is}) \rightarrow \varphi e^{-is} \quad (18)$$

by elementary rearrangements (adding, subtracting rows with the same φ). Explicitly, this gives

$$\det \begin{bmatrix} \varphi_1(1)e^{is_1} & \varphi_1(2)e^{is_2} & \varphi_1(3)e^{is_3} & \varphi_1(4)e^{is_4} & \dots \\ \varphi_1(1)e^{-is_1} & \varphi_1(2)e^{-is_2} & \varphi_1(3)e^{-is_3} & \varphi_1(4)e^{-is_4} & \dots \\ \varphi_2(1)e^{is_1} & \varphi_2(2)e^{is_2} & \varphi_2(3)e^{is_3} & \varphi_2(4)e^{is_4} & \dots \\ \varphi_2(1)e^{-is_1} & \varphi_2(2)e^{-is_2} & \varphi_2(3)e^{-is_3} & \varphi_2(4)e^{-is_4} & \dots \\ \dots & & & & \dots \end{bmatrix} \quad (19)$$

which is the usual Slater determinant of spin-orbital matrix with the size $N \times N$. This form effectively complexifies the usual real wave function due to particular choice of spin functions. Clearly, for arbitrary values of spin variables this wave function is *different* from the usual spin-up and spin-down product used on fixed-node calculations although in what follows we will demonstrate how to recover the fixed-node form using an appropriate choice for the spin coordinates. Let us now assume that $s_i = s_1, s_3, \dots$ will become the spin-up channel while $s_i = s_2, s_4, \dots$ will end up being the spin-down channel. In order to reach this spin-up/down partitioning explicitly we restrict $s_1, s_3, s_5, \dots = s$, and $s_2, s_4, \dots = s'$ where s, s' are distinct. Then we can write the determinant

$$\det \begin{bmatrix} \varphi_1(1)e^{is} & \varphi_1(2)e^{is'} & \varphi_1(3)e^{is} & \varphi_1(4)e^{is'} & \dots \\ \varphi_1(1)e^{-is} & \varphi_1(2)e^{-is'} & \varphi_1(3)e^{-is} & \varphi_1(4)e^{-is'} & \dots \\ \varphi_2(1)e^{is} & \varphi_2(2)e^{is'} & \varphi_2(3)e^{is} & \varphi_2(4)e^{is'} & \dots \\ \varphi_2(1)e^{-is} & \varphi_2(2)e^{-is'} & \varphi_2(3)e^{-is} & \varphi_2(4)e^{-is'} & \dots \\ \dots & & & & \dots \end{bmatrix} \quad (20)$$

and eliminating elements in each odd row we get

$$\det \begin{bmatrix} 0 & c_0\varphi_1(2) & 0 & c_0\varphi_1(4) & \dots \\ \varphi_1(1)e^{-is} & \varphi_1(2)e^{-is'} & \varphi_1(3)e^{-is} & \varphi_1(4)e^{-is'} & \dots \\ 0 & c_0\varphi_2(2) & 0 & c_0\varphi_2(4) & \dots \\ \varphi_2(1)e^{-is} & \varphi_2(2)e^{-is'} & \varphi_2(3)e^{-is} & \varphi_2(4)e^{-is'} & \dots \\ \dots & & & & \dots \end{bmatrix} \quad (21)$$

where

$$\begin{aligned} c_0 &= [e^{is'} - e^{i(2s-s')}] = e^{is} [e^{i(s'-s)} - e^{-i(s'-s)}] = \\ &= 2ie^{is} \sin(s' - s). \end{aligned}$$

Furthermore, by reshuffling the first two rows and columns and factorizing out the spins from the determinant we get

$$\propto [\sin(s' - s)]^{N/2} \det \begin{bmatrix} \varphi_1(1) & \varphi_1(3) & 0 & 0 & \dots \\ \varphi_2(1) & \varphi_2(3) & 0 & 0 & \dots \\ 0 & 0 & \varphi_1(2) & \varphi_1(4) & \dots \\ 0 & 0 & \varphi_2(2) & \varphi_2(4) & \dots \\ \dots & & & & \dots \end{bmatrix}. \quad (22)$$

After reshuffling the rest of rows and columns, the single determinant of spinors factorizes into the product of two determinants of spin-up and spin-down block matrices. Generalization to odd N with unpaired spinor(s) is straightforward. Therefore this decomposition strictly depends on the fact that all the spins have to acquire one of the two distinct values as expected when going from continuous to the fixed-label form that is traditionally used in FNDMC calculations.

B. Wave functions with full space-spin symmetries

In our recent paper we have probed into the behavior of such wave functions for simple cases [5]. It is useful to use an example such as the Li atom wave function to illustrate various wave function forms we consider here (assuming usual nucleus-electrons Hamiltonian without spin terms). The full symmetry exact wave function for the Li atom doublet is given by [8, 9]

$$\begin{aligned} \Psi(1, 2, 3) &= |\uparrow\rangle_1 |\uparrow\rangle_2 |\downarrow\rangle_3 F(1, 2, 3) \\ &+ |\uparrow\rangle_1 |\downarrow\rangle_2 |\uparrow\rangle_3 F(3, 1, 2) \\ &+ |\downarrow\rangle_1 |\uparrow\rangle_2 |\uparrow\rangle_3 F(2, 3, 1) \end{aligned} \quad (23)$$

where the function F depends only on the spatial coordinates. The function F is the exact, irreducible, spatial variables-only eigenstate for the three electrons in the doublet state. Indeed, it corresponds to the exact fixed-node solution sought after in the FNDMC method.

The single-configuration trial wave function in the fixed-node framework would look like

$$\Psi_T(1, 2, 3) = \det_{1,2}^{\uparrow}[1s, 2s] \det_3^{\downarrow}[1s] \quad (24)$$

where the electrons 1 and 2 are assigned as spin-up while the electron 3 is spin-down. Clearly, this is just a projection onto the spin state $|\uparrow\rangle_1 |\uparrow\rangle_2 |\downarrow\rangle_3$ with the single-reference term approximating the spatial part $F(1, 2, 3)$.

Our wave function with variable spins is given by

$$\begin{aligned} \Psi &= \det[1s \times e^{is}, 1s \times e^{-is}, 2s \times e^{is}] \\ &= e^{i\Phi_1} \det_{1,2}^{\uparrow}[1s, 2s] \det_3^{\downarrow}[1s] - e^{i\Phi_2} \det_{3,1}^{\uparrow}[1s, 2s] \det_2^{\downarrow}[1s] \\ &+ e^{i\Phi_3} \det_{2,3}^{\uparrow}[1s, 2s] \det_1^{\downarrow}[1s]. \end{aligned} \quad (25)$$

It therefore results in a product of determinants approximating the function F with the phase factors from varying spins as coefficients. If one chooses, $s_1 = s_2 = s$

and $s_3 = s'$, the wave function collapses to a single determinant with a spin variable dependent coefficient as described above.

Sampling both spin and position spaces enables one to evolve between the spatial wave functions with permuted coordinates, i.e., eventually sampling all such equivalent possibilities. Note that the overall structure of the exact wave function and our variable spin formulation are analogous. While in this example the variable spins and corresponding phase factors appear superfluous, they enable us to use the fixed-phase formalism to reach the fixed-node limit as explained above. In addition, the form becomes fully operational whenever spin-dependent terms in the Hamiltonian are switched on.

For completeness, let us mention that in the limit of *fast spins* (small effective spin masses) the energy will be *higher* than in the fixed-node limit. This is straightforward to understand: we have complexified the wave function which is actually real. The added continuous spin space and corresponding phase potential “contaminate” the wave function and the expectation values. Note that this aspect was not our focus here. Further advances of the method in this limit are in progress, however, they are out of scope of the present study.

IV. FIXED-PHASE VARIABLE SPINS QMC AS A GENERAL METHOD

In fixed-node QMC calculations with real wave functions the node improvement is often very challenging since any general method proposed so far appears to have very unfavorable scaling. In several papers we have made some progress in understanding the relations between electron density, multiplicity of bonds and node curvatures that appear to be related with increased fixed-node bias [10]. In addition, we found relationships between nodes and eigenvalues that show the nodes carry information about the spectrum as presented elsewhere [11].

In this respect, the fixed-phase approximation opens new perspectives both in a better understanding of related issues with regard to antisymmetry and the corresponding fermion sign problem as well as possibilities for new constructions of more efficient approximations.

One important property of the fixed-phase approximation is that the sampled distribution ρ is non-negative everywhere and, as we mentioned, generically its zero locus is a subset of configurations with codimension 2, i.e., two dimensions lower than the full configuration space. In that case the sampling of the configuration space is ergodic. One then solves for the bosonic ground state in a given, state-dependent potential. A simple toy example is an atomic two-particle 3P state with the wave function

$$\Psi(1, 2) = r_1 r_2 g(r_1) g(r_2) [Y_{11}(1) - Y_{11}(2)]$$

where g are positive radial functions. Its phase-generated

potential is given by

$$V_{ph} = \frac{1}{2[(x_1 - x_2)^2 + (y_1 - y_2)^2]}$$

while the corresponding non-negative amplitude $\rho(r_1, r_2)$ vanishes only at $x_1 = x_2, y_1 = y_2$ [5]. This also has other consequences that make it favorable in comparison with the fixed-node approach, namely, the divergences of the local energy and drift are significantly diminished making them much smoother. For example, the drift for the importance sampled distribution given by $\nabla \ln \rho$ is smooth except at the point of vanishing ρ . This removes complications around nodes of real functions such as large local energy fluctuations, poor approximation of the Green's function, non-zero probability of crossing/re-crossing the node within a given time step, possible occurrences of stuck walkers and other difficulties, due to the fact that $\ln \Psi_T$ is non-analytic at the node. Of course, all these complications can be brought under the control by decreasing the time step in the fixed-node formalism. However, here these complications are simply absent in the fixed-phase formulation by being smoothed out into the lower dimension.

We note that in low-dimensional systems or for particular symmetry constraints one can end up with special or non-generic cases having zeros of ρ with codimension 1, i.e., one dimension higher than the generic codimension 2 mentioned above. A simple example is the lowest two-particle triplet in a periodic box with the wave function $\det[1, e^{ikx}]$. This leads to $\rho(x_1, x_2) = 2|\sin[(x_1 - x_2)/2]|$ that has a $(2d-1)$ -dimensional zero locus regardless of d , i.e., the dimensionality of the box. The reason is that this particular state effectively behaves as having 1D nodal structure that is non-generic. Interestingly enough, for $d > 1$ this node volume is smaller than in the corresponding fixed-node wave function given by the real (or imaginary) part, $\text{Re}\{\det[1, e^{ikx}]\}$. This aspect is more thoroughly investigated in our subsequent work [11] that explore the corresponding properties of nodes in such cases and further generalizations.

Perhaps the most appealing and yet unexplored property is that the approximation has a form of an additive effective many-body potential

$$V_{ph} = (1/2)[\nabla \Phi_T]^2 \quad (26)$$

so that the original Schrödinger equation changes to

$$(T + V)\Psi = E\Psi \quad \rightarrow \quad (T + V + V_{ph})\rho = E\rho \quad (27)$$

This effective potential formulation offers a clear conceptual understanding of the transformed problem that reminds us of effective potential/field methods used in other areas of quantum and high energy physics. It has a number of desired properties when thinking about the solution of the many-body problem, such as that the solution is non-negative everywhere, the state-dependent potential V_{ph} is purely repulsive (it only raises the energy) and it is explicitly and directly given by the approximate

phase. Consequently, it provides a constructive path for improvements with the perspective that the solution really exists, i.e., in the case of the exact phase one obtains the exact solution/eigenstate similarly to the fixed-node approximation (that is its special case). Interestingly, not much is known about the phases of stationary states. It is possible that more thorough analysis of the corresponding effective potentials will lead to a better understanding as well as to better approximations for practical calculations of realistic systems. What follows provides the first attempts to probe some aspects of this formulation.

V. RESULTS

We calculate the total energies for the first-row atoms using both the FN and FP approximations. For the FN calculations, we build our trial wave function from HF orbitals generated from GAMESS-US [12]. For the FP calculations, we build our trial wave function from the one-particle spinors generated from DIRAC14 [13]. For the FN calculations, we perform a linear time step extrapolation to zero time step. In all cases, a spatial time step of 0.001 Ha^{-1} is in agreement with the zero time step limit. Motivated by that, for all FP calculations we hold the spatial time step fixed at $\tau = 0.001 \text{ Ha}^{-1}$, rather than performing a spatial time step extrapolation.

We have previously studied some of the aspects of effective spin masses and the corresponding difference between the spin vs. spatial evolutions [1, 4]. The analysis of total energies as function of spin mass leads to the following conclusions:

a) With $\mu_s \ll m_e$, the spins are basically fully integrated out for each spatial step that is assumed to be much smaller. Then one sees higher fixed-phase bias since the repulsive potential acts in the full configuration space unlike the fixed-node condition that applies only on the configuration subspace.

b) With $\mu_s \gg m_e$ and for a small number of electrons, the propagation eventually finds the region(s) close to the pure fixed-node wave function. Apart from small spin fluctuations the energy therefore reaches very closely to the fixed-node solution.

In both limits and also for intermediate spin mass regimes the energy is an upper bound, since the energy is basically limited from below by the fixed-node limit. The complexified wave function and the fixed-phase only increases the energy since it acts in full space instead of fixed-node codimension 1 hypersurface and expands the configuration space in an ad hoc manner through the continuous spin as we argued in previous parts. This has also further implications that single reference wave functions will be, in general, less accurate, as we have actually observed in calculations of several systems [4, 5]. Here we are actually focused on the large spin mass limit that enables us to recover the fixed-node results although the calculations are carried out in FPSODMC setting.

As described in §III, we initialize the spin-

configurations to facilitate the decomposition into two independent determinants, as must be the case in a spin independent Hamiltonian. As an illustration of why this is necessary, consider the N atom using HF spatial orbitals and no Jastrow factor. The VMC energy should agree with the HF energy, within the statistical errors. This is because for any trial wave function using our spinor representation and $H_s = \sum_i T_i^s$, $\langle \Psi_T | H + H_s | \Psi_T \rangle = \langle \Psi_T | H | \Psi_T \rangle$ by construction since $H_s | \Psi_T \rangle = 0$. Therefore, the spin kinetic energy does not contribute to the energy expectation value. However, the trial wave function with included complex spin-orbitals is *different* from the usual fixed-node Ψ_T with spin-up and -down product of determinants. For arbitrary values of spin variables our Ψ_T cannot be factorized into such a fixed-node form. Consequently, if one randomly samples the spin variables and performs such VMC calculation, the obtained energy is $-54.3341(8) \text{ Ha}$ which clearly disagrees with the HF value of -54.40093 Ha . It is higher since we made the wave function complex in a way that for arbitrary values of spin variables does not allow direct separation of spin and space degrees of freedom (although the Hamiltonian does, since H and H_s do commute). Note however, that this is perfectly appropriate and, in fact necessary, for systems where spins truly vary such as with spin-orbit interactions.

On the other hand, if we initialize the spin variables such that $s_1 = s_3 = s_5 = s_6 = s_7 = s$ and $s_2 = s_4 = s'$, which yields a product of determinants with a trivial phase prefactor, and keep spins effectively static, we obtain variationally $-54.4003(7) \text{ Ha}$, which agrees with the energy obtained via HF as expected.

When performing FPSODMC for our systems here, we vary the spin mass until the energy is saturated for a fixed spatial time step. An example of the extrapolation is shown in Figure 1. For μ_s between 10^5 and 10^9 (ie, τ_s between 10^{-12} and 10^{-9}), the DMC energies all agree to within error bars and are converged. Performing the same procedure for all atoms, we list the total energies in Table I. By comparing the FN and FP total energies to the exact energies in the non-relativistic limit (NRL)[14], we calculate the fixed-node/phase correlation energy percentage error and is plotted in Figure 2.

Regardless of the approximation, the associated error decreases with atomic number subject to the choice of HF nodes/phases. Additionally, the FN and FP approximations yield essentially identical errors. A few comments to explain these results is warranted. While we are interested in the energy from the physical Hamiltonian $E_{\text{FPDMC}}(H)$, we are actually calculating $E_{\text{FPSODMC}}(H + H_s)$. Since $H_s \propto \mu_s^{-1}$, in the limit that $\mu_s \rightarrow \infty$ we obtain the desired physical limit, namely $E_{\text{FPSODMC}}(H + H_s) \rightarrow E_{\text{FPDMC}}(H)$. Additionally, by setting the initial spin variables to a desired configuration, we set the trial wave function/trial phase. As explained above, with a proper choice for the spin assignment coupled with heavy spins (i.e. $\mu_s \rightarrow \infty$) we are able to reproduce the FNMC results since the wave function then effectively reaches the

limit of the product of spin-up and -down determinants.

It is well known that using HF nodes, the Be atom exhibits a significant FN error [10]. The ground state symmetry of Be is 1S_0 , which is obtained with the electron configuration $1s^2 2s^2$. Using a HF trial wave function, the nodal surface $\partial\Omega = \{\mathbf{R} \in \mathbb{R}^{3N} | \Psi_T(\mathbf{R}) = 0\}$ separates the configuration space into 4 nodal domains, two of which give positive wave function while by symmetry the other two exhibit negative values. It is also well-known that by adding just one more configuration that corresponds to the near-degenerate state of the same symmetry one finds only two nodal domains as expected for generic fermionic ground state [15–17]. Previous calculations have found that it almost completely eliminates the fixed-node bias [16, 18]. The corresponding two-configuration trial function is given by

$$|\Psi_T\rangle = c_0 |1s^2 2s^2\rangle + c_1 \sum_{i \in \{x, y, z\}} |1s^2 2p_i^2\rangle \quad (28)$$

as with this choice of trial wave function and full optimization of all variational parameters one can reach almost zero bias in the FN calculation [18]. Instead we perform an optimization of this wave function with only the Jastrow parameters and expansion coefficient, keeping the HF orbitals fixed with resulting small increase in the energy compared to the nearly exact value. Total energies are shown in Figure 3. Again, by choosing the FP calculations to preserve the spin assignments of $s_1 = s_3 = s$ and $s_2 = s_4 = s'$ by using a large spin mass, the FN and FP calculations agree to within statistical uncertainty.

Thus far, we have only presented results for all-electron systems. We also consider the FN and FP approximation when nonlocal pseudopotentials are included [1, 4]. We calculate the binding curve for the nitrogen dimer in

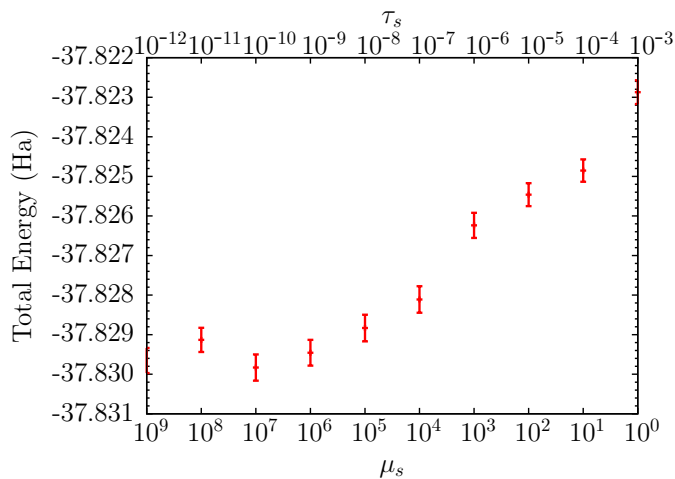


FIG. 1: FPDMC energy of the C atom with varying spin masses μ_s (or equivalently the spin time step $\tau_s = \tau/\mu_s$). The initial spin configurations were chosen so that the wave function decomposes into a product of determinants.

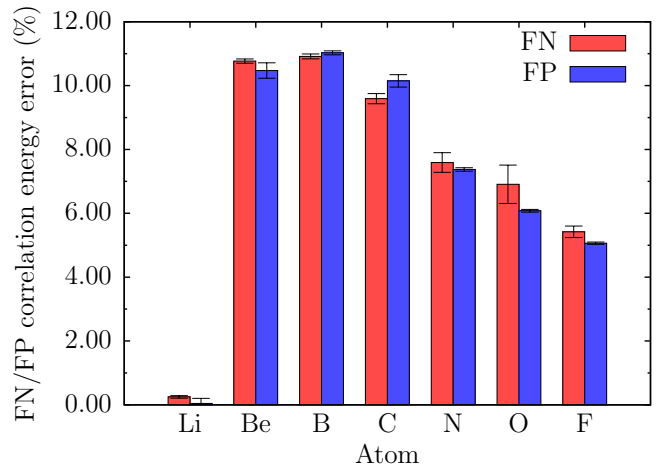


FIG. 2: Percentage error of the correlation energies in the fixed-node (FN) and fixed-phase (FP) extrapolated calculations.

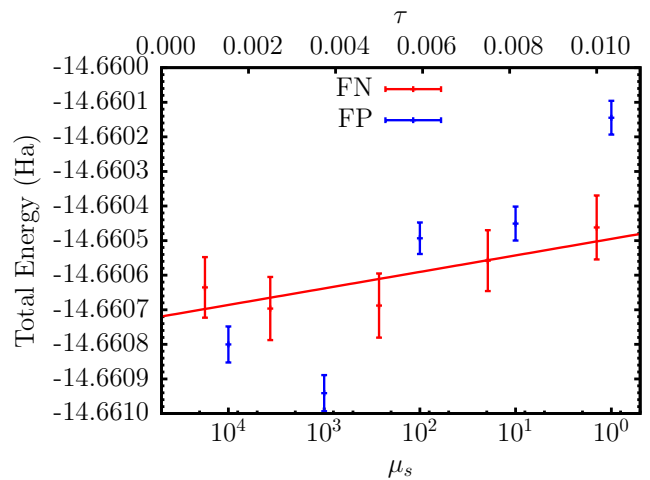


FIG. 3: Total energies for the Be atom with a two-configuration wave function. The top x -axis shows the actual spin time step for the FN calculation, which is linearly extrapolated to zero time step with an energy of $-14.66071(5)$ Ha. The bottom x -axis indicates the spin mass for the FP calculation, where with each value configurations are initialized such that $s_1 = s_3 = s$ and $s_2 = s_4 = s'$. We hold the spatial time step fixed at $\tau = 0.001 \text{ Ha}^{-1}$ throughout.

the $^1\Sigma_g$ state, using a single-reference trial wave function for each approximation built from PBE0 spatial orbitals. We utilize a BFD pseudopotential for N [19]. In order to calculate the binding curve, we first calculate the isolated N atom both in FN and FP. Under the locality approximation [20], we perform a time step extrapolation within FNDMC and obtain a total energy of $-9.79135(8)$ Ha. Using a fixed spatial time step, we perform a spin mass extrapolation as described above to facilitate decomposition into a product of two independent determinants using FPSODMC and obtained a total energy of $-9.7917(1)$ Ha.

Atom	HF	NRL[14]	FN	FP
Li	-7.43272	-7.47806	-7.47794(2)	-7.47804(7)
Be	-14.57302	-14.66736	-14.65720(6)	-14.6574(2)
B	-24.52906	-24.65393	-24.64030(9)	-24.64016(8)
C	-37.68861	-37.84500	-37.8300(3)	-37.8291(3)
N	-54.40093	-54.58930	-54.5750(6)	-54.5754(1)
O	-74.80939	-75.06700	-75.049(1)	-75.0513(1)
F	-99.40934	-99.73400	-99.7164(6)	-99.7175(1)

TABLE I: Total energies in Ha for the first-row elements using FN(FP) DMC with HF nodes (phases). FN calculations are extrapolated to zero time step. FP calculations take a spatial time step of 0.001 and decrease the effective spin mass (decrease the actual spin time step) until the energy is unchanged. NRL is the estimated nonrelativistic exact energy.

The dimer curve is shown in Figure 4 and shows the binding obtained from the FN and FP methods. The QMC data is fit to the Morse potential

$$V(r) = D_e \left[e^{-2a(r-r_e)} - 2e^{-a(r-r_e)} \right] \quad (29)$$

and the vibrational frequency can be obtained via

$$\omega_0 = \sqrt{\frac{2a^2 D_e}{\mu}} \quad (30)$$

where μ is the reduced mass of the dimer. The FN and FP solutions are quite similar, only differing by roughly 0.1–0.5 mHa throughout the entire curve. Coupled with the *slightly* different energies for the individual atom, the overall binding energy differs from the FN result by roughly ~ 0.02 eV, as shown in Table II. Clearly, the differences between the methods are very small, basically similar to variations in the fixed-node biases for different atoms and molecular systems and choices of orbitals used in single-reference trial functions.

It remains an interesting question whether the FP-SODMC energy could go below the corresponding FNDMC energy. On general grounds this cannot be *a priori* ruled out since we have expanded the configuration into a larger space through the introduction of an overcomplete spin representation. Overcompleteness can possibly compromise the upper bound property, i.e., the energy could go below the fixed-node limit at some values of $\mu_s < \infty$. In general, this is determined by the type of overcomplete construction. In our case, for Hamiltonians without spin terms we also make the trial wave function “worse” by making it non-separable in the spin and space variables, although for expectations (variational level) the Hamiltonian is separable. These two tendencies therefore go against each other. So far the indications are that the non-separability distortion appears stronger than the freedom gained from the overcompleteness, hence the energies obtained by FPSODMC are either higher or, in appropriate limit, equal to FNDMC. However, for heavy but not fully static spins it is difficult to dismiss the possibility that the DMC algorithm might find spin-space regions with favorable energies that could push the overall expectation below the FNDMC limit. Clearly, this aspect calls for further studies.

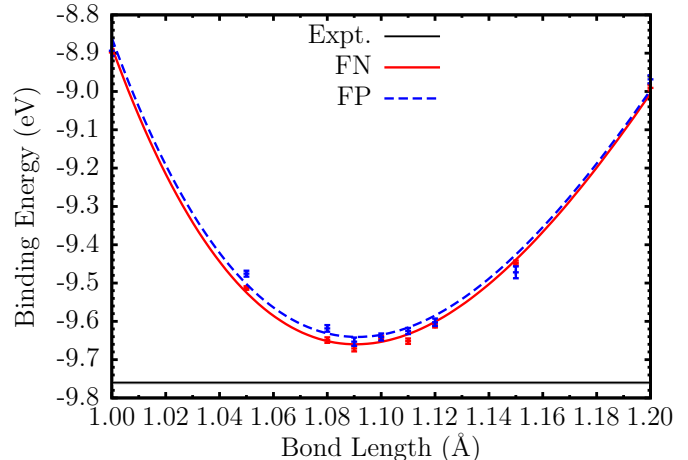


FIG. 4: N_2 binding curve for the $1\Sigma_g$ molecular state using a HF nodal surface/phase. The horizontal line indicates the experimental dissociation energy. The experimental error bar is too small to be visible on this scale. The small increase in FP underbinding comes from a slightly smaller fixed-phase bias in the N atom and a slightly larger bias in the dimer with the HF phase. We note that the results need not to be necessarily identical for Hamiltonians with ECPs due to marginal differences in localization errors from two close, but non-identical trial wave functions.

TABLE II: Equilibrium bond lengths (r_e), dissociation energies (D_e) and vibrational frequencies (ν_0) for the various approximations compared to experiment using a PBE0 nodal surface/phase. Parameters and uncertainties are obtained from a fit to the Morse potential.

Method	r_e (Å)	D_e (eV)	ω_0 (cm $^{-1}$)
FN	1.0905(7)	9.659(6)	2387(24)
FP	1.091(1)	9.64(1)	2377(45)
Expt.[21]	1.098	9.758(6)	2358.57(9)

VI. CONCLUSIONS

In this paper we elaborate in detail on a particularly important aspect of the fixed-phase spin-orbit/spinor DMC (FPSODMC) method that we have introduced recently [1]. We highlight some of the key aspects how the method can be useful even in cases with no spin-

orbit terms and with nominally real eigenstates. In particular, we illustrate how to obtain the fixed-node limit results from the fixed-phase setting both in theory and in practical calculations. This is enabled by complexifying the wave function through spinors that correspond to up/down spin states which are usually static and assigned in the beginning of common fixed-node calculations. We allow them to vary around the fixed values providing thus a complex “noise” that allows us to use fixed-phase rather than the fixed-node methodology.

We point out the promising features of such fixed-phase method and also analyze its behavior in our continuous spin formalism and we present the results for the first-row atoms and molecule calculations. The method enables us to write full space-spin symmetry wave functions for Hamiltonians with or without explicit spin terms and opens thus possibilities for possible further improvements of trial wave functions. We consider the results very encouraging since in a straightforward manner we were able

to obtain the fixed-node results in both all-electron and effective core potential settings as well as confirm essentially the same quality of both single and multi-reference trial wave functions. The method opens interesting new perspectives for many-body electronic structure calculations in complex wave function and spinor formalism that takes into account variable nature of the spin degrees of freedom and provides new possibilities for construction of more general trial wave functions.

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