Many-body nodal hypersurface and domain averages for correlated wave functions

Shuming Hu, Kevin Rasch, Lubos Mitas
Department of Physics, North Carolina State University, Raleigh, NC 27695.
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We outline the basic notions of nodal hypersurface and domain averages for antisymmetric wave functions. We illustrate their properties and analyze the results for a few electron explicitly solvable cases and discuss possible further developments.

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Quantum Monte Carlo is one of the most effective many-body methodologies for the study of quantum systems. It is based on a combination of analytical insights, robustness of stochastic approaches, and performance of parallel architectures [1-10]. The approach has been applied to a variety of challenging problems in electronic structure of atoms, small molecules, clusters, solids, ultracold condensates, and beyond [1-15]. The two most commonly used QMC methods are variational Monte Carlo and diffusion Monte Carlo (DMC). Let us briefly recapitulate the basics of the DMC method.

It is straightforward to show that for $\tau \to \infty$, the operator $\exp(-\tau H)$ projects out the ground state of a given symmetry from any trial function with nonzero overlap. We assume that the Hamiltonian $H$ is time-reversal symmetric so that the eigenstates can be chosen to be real. This projection is most conveniently carried out by solving the Schrödinger equation in an imaginary time integral form so that the product $f(\mathbf{R}, t) = \Phi(\mathbf{R}, t)\Psi_T(\mathbf{R})$ obeys

$$f(\mathbf{R}, t + \tau) = \int G(\mathbf{R}, \mathbf{R}', \tau)f(\mathbf{R}', t)d\mathbf{R'},$$

where

$$f(\mathbf{R}, t) = \Phi(\mathbf{R}, t)\Psi_T(\mathbf{R}).$$

The Green’s function is given by

$$G(\mathbf{R}, \mathbf{R}', \tau) = \frac{\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R}')}(\mathbf{R})|\exp[-\tau(H - E_T)]|\mathbf{R'},$$

where $\mathbf{R} = (r_1, ..., r_N)$ denotes positions of $N$ particles and $E_T$ is an energy offset. In the DMC method, the function $f(\mathbf{R}, t)$ is represented by a set of $10^2$-$10^4$ random walkers (sampling points) in the $3N$-dimensional space of electron configurations. The walkers are propagated for a time slice $\tau$ by interpreting the Green’s function as a transition probability from $\mathbf{R}' \to \mathbf{R}$. The kernel is known for small $\tau$, and the large time $t$ limit is obtained by iterating the propagation. The method is formally exact provided that the boundary conditions, i.e., the fermion nodes of the antisymmetric solution defined as $\Phi(\mathbf{R}, \infty) = 0$, are known [1,5,14]. Unfortunately the antisymmetry does not specify the nodes completely, and currently we have to use approximations. The commonly used fixed-node approximation [14] enforces the nodes of $f(\mathbf{R}, t)$ to be identical to the nodes of $\Psi_T(\mathbf{R})$ which then implies that

$$f(\mathbf{R}, t) \geq 0$$

everywhere. It is therefore clear that the accuracy of the fixed-node DMC is determined by the quality of the trial wave function nodes. The commonly used form for $\Psi_T$ is the Slater-Jastrow wave function given as

$$\Psi_T(\mathbf{R}) = \sum_n d_n \det^+_{\phi_n} \det^\dagger_{\phi_n} \exp[U_{corr}]$$

where $U_{corr}$ is the correlation factor explicitly depending on interparticle distances thus describing pair or higher order correlations explicitly. The typical number of Slater determinants is between 1 and $10^4$, and the corresponding weights $\{d_n\}$ are usually estimated in multi-reference Hartree-Fock (HF) or Configuration Interaction (CI) calculations and then re-optimized in the variational framework.

It is quite remarkable that the nodes of such Slater-Jastrow wave functions (often with a single-determinant product only) lead to unexpectedly small errors and that the typical amount of obtained correlation energy in fixed-node DMC is $\approx 95\%$. This is true for essentially all systems we have studied: atoms, molecules, clusters and solids [1-15].

The fixed-node approximation is perhaps the single most important unsolved problem which hampers the progress in further improvement of accuracy and efficiency of the QMC calculations. One of the key difficulties is that the fixed-node bias is actually very small on the scale of the total energy. A comparison of the total energy components for a typical electronic structure problem is given in Table I.
Characterization of the nodes can be of significant interest in another context. Very recently, very interesting developments (cent developments) have difficulties picking up the nodal shapes. It is straightforward to show that the total energy is given as a sum of kinetic and potential components, which we call nodal (hypersurface) and domain averages (nda, in short). They are defined as follows:

\[ E_{\text{nda}} = \int_{\partial \Omega} \nabla R \Psi(R) \cdot dS + \int V(R)\Psi(R) dR = E \int |\Psi(R)| dR. \]

The obtained equation shows that the total energy is expressed more directly than the expectation values. In fact, the expectation values measure properties of the quantum amplitudes, whereas the nodal (domain) and not on the wave function. Note that although the sum of kinetic and potential components produces the total energy, the corresponding node \( \partial \Omega \). We integrate the equation over the \( \Omega^+ \) domain only, and using the Gauss-Stokes-Green theorem we get

\[ \int_{\partial \Omega^+} (V(R) - E)\Psi(R) dR - \frac{1}{2} \int_{\partial \Omega} \nabla R \Psi(R) \cdot dS_n = 0. \]

Similarly, we can integrate over the \( \Omega^- \) domain and if we put it together (assuming either free or periodic boundary conditions) then we get

\[ \int_{\partial \Omega} |\nabla R \Psi(R)| dS + \int V(R)\Psi(R) dR = E \int |\Psi(R)| dR. \]

So that

\[ E = E_{\text{kin}} + E_{\text{pot}}. \]

This derivation and definitions deserve some comments. First, we tacitly assumed that there is only one positive and one negative nodal domain, however, this generally applies only to fermionic ground states. Generalization to more domains is straightforward: one integrates domain by domain and sums the results. It therefore applies to any eigenstate including excitations, both fermionic and bosonic (the bosonic ground state is an exception since it is nodeless). It is important that \( E_{\text{nda}} \) depends solely on the gradient of the wave function on the node (domain boundary) and not on the wave function values inside the domain. The key idea is that these expressions measure properties of the quantum amplitudes more directly than the expectation values. In fact, the expectations suppress the nodal signal since both the square of the exact eigenstate and also its Laplacian vanish at the node. Note that although the sum of kinetic and potential nda components produces the total energy,
the expression has no variational property, i.e., it is not quadratic in the wave functions as is the usual expectation value. It is rather a “one-sided expectation” which enables one to probe the nodal structure as we will show in what follows.

The nda values are not trivial to calculate, and for illustration we will present just a few simple cases. Let us first consider a toy model, an electron in $2p$ orbital so that the state is $^3P(2p)$. For the Coulomb potential $V(r) = -Z/r$ we have

$$
\Psi = z \rho_{2p}(r) = z \exp(-Zr/2)
$$

and we can write

$$
E_{\text{pot}}^{\text{nda}}(2p) = \frac{\int V(r) \rho_{2p}(r)r |\cos(\vartheta)| r^2 \sin(\vartheta) d\theta dr}{\int \rho_{2p}(r)r |\cos(\vartheta)| r^2 \sin(\vartheta) d\theta dr} = -\frac{Z^2}{6}.
$$

The node is the plane given by $z = 0$, and we can easily evaluate also the kinetic energy part since

$$
|\nabla \Psi|_{z=0} = \rho_{2p}(r)
$$

so that we can write

$$
E_{\text{kin}}^{\text{nda}}(2p) = \frac{2\pi \int \rho_{2p}(r) r x dy}{\int \rho_{2p}(r)r |\cos(\vartheta)| r^2 \sin(\vartheta) d\theta dr} = \frac{Z^2}{24}.
$$

Note that the integral in the numerator is over the plane while the integration domain of the denominator is the full 3D volume. One can also verify that the sum of the two components gives $E = -Z^2/8$ as expected.

Much more interesting are cases with more than one particle. We mentioned the two excitations of the He atom, namely $^3S(1s2s)$ and $^3P(1s2p)$, and also the corresponding four-particle singlets $^1S(1s2s2s)$ and $^1S(1s2p2p)$. Actually, these are quite nontrivial to calculate even in noninteracting cases. The state $^3S(1s2s)$ is straightforward but rather involved, and one ends up with numerous integrals. The states with $2p$ orbitals are even more complicated since the node is given by a combination of exponentials and linear functions so that the integration domains become complicated. Therefore for this case we have used Monte Carlo integration. The resulting values are listed in Table II.

| State          | $E_{\text{tot}}$ | $E_{\text{kin}}$ | $E_{\text{pot}}$ | $E_{\text{nda}}$ | $E_{\text{pot}}^{\text{nda}}$ |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $^3S(1s2s)$    | $-\frac{5}{4}$  | $\frac{5}{4}$   | $-\frac{5}{2}$  | $\frac{10}{27}$ | $-\frac{1185}{1884}$ |
| $^3P(1s2p)$    | $\frac{1}{4}$   | $\frac{1}{4}$   | $-\frac{1}{2}$  | $\frac{1768}{20}$ | $-\frac{1185}{1884}$ |
| $^1S(1s2s2s)$  | $-\frac{5}{4}$  | $\frac{5}{4}$   | $\frac{5}{2}$   | $\frac{20}{27}$  | $-\frac{1185}{1884}$ |
| $^1S(1s2p2p)$  | $\frac{1}{4}$   | $\frac{1}{4}$   | $-\frac{1}{2}$  | $\frac{1768}{20}$ | $-\frac{1185}{1884}$ |

into the three states $^3P_1^1S_1^1D$. For example, for the state $^3P(2p^2)$ the wave functions is given by

$$
\Psi(1,2) = \rho_{2p}(r_1) \rho_{2p}(r_2)(x_1 y_2 - x_2 y_1),
$$

and the nda potential energy can be written as

$$
E_{\text{pot}}^{\text{nda}}(2p^2) = 2 \left[ \int V(r_1) \rho_{2p}(r_1) \rho_{2p}(r_2) |x_1 y_2 - x_2 y_1| d\mathbf{r}_1 d\mathbf{r}_2 \right].
$$

The integrals can be factorized into radial and angular components. Since the angular parts cancel out, we get

$$
E_{\text{pot}}^{\text{nda}}(2p^2) = 2E_{\text{pot}}^{\text{nda}}(2p).
$$

It is perhaps somewhat unexpected that we get the same result also for the other two states $^1S(2p^2)$ and $^1D(2p^2)$.

| State          | $E_{\text{tot}}$ | $E_{\text{kin}}$ | $E_{\text{pot}}$ | $E_{\text{nda}}$ | $E_{\text{pot}}^{\text{nda}}$ |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $^3P_1^1S_1^1D$| $-\frac{1}{4}$  | $\frac{1}{4}$   | $-\frac{1}{2}$  | $\frac{1}{4}$   | $-\frac{1}{2}$   |

We therefore conclude that all the components are the same for all three states, although two of them are singlets and one is triplet and also have different spatial symmetries. Note that this is strictly true only for the non-interacting system. This implies that the states might have equivalent nodes, and a little bit of analysis actually shows that. One can find that the node for the $^3P$ state can be described from the perspective of one of the two electrons as the plane defined by the angular momentum axis and the second electron. Similarly, the node of the $^1D$ state looks to one of the electrons as the plane which contains the angular momentum axis and is orthogonal to a plane defined by the second electron and the angular momentum axis. Finally, for $^1S$ states one of the
electrons sees a plane which is orthogonal to the position vector of the second electron. In all three cases the node subset is therefore a plane which passes through the origin. Although these are only subsets of the complete 5D node, which is a hyperbolic hypersurface in 6D, the construction enables us to get an insight into their properties. In fact, this shows that there are only two nodal domains in all three cases: the scanning electron is either on one or the other side of the considered plane. Let us further define the equivalency for a set of nodes. By the equivalency we mean that the nodes in the given set can be transformed to each other by coordinate transforms which are unitary (the determinant of the transformation matrix is equal to +1 or -1). This includes not only rotations but also reflections around the origin since otherwise the triplet nodes cannot be transformed to the singlet nodes. This can be inspected, for example, by transforming the node of one of the 1D states

$$\Psi(1, 2) = \rho_{2p}(r_1)\rho_{2p}(r_2)(x_1y_2 + x_2y_1),$$

to the node of 3P state using the reflection of one coordinate component, say, $x_2 \rightarrow -x_2$ (see the wave function above). With some effort one could find that the nodes of the singlets are also equivalent. For this the reader might find useful to consult our previous papers on related topics of nodal structure and analysis [9].

Note that for interacting two electrons in these states the nda components will not be identical since the e-e Coulomb repulsion will distort the wave function gradients in different ways for different states, and energetically, it will favor the triplet over the singlets.

The previous case of two non-interacting electrons can be further generalized to a given subshell $l = n - 1$ for any $n$ and for any possible spin symmetry and occupations up to the maximum $2(l+1)$. The energies can be evaluated the same way as above, and it is revealing to explore the quasiclassical limit of the nda estimates. Consider the class of atomic (excited) states such that $k$ electrons occupy subshell $l = n - 1$ with any allowed spatial and spin symmetry. The state is $2^{S+l}L[\varphi_k^l]$ where $k$ is the occupation. One can find:

$$E_{\text{kin}}^{\text{nda}}(k, l) = kZ^2 \frac{l}{2(l+1)(l+2)}$$

and

$$E_{\text{pot}}^{\text{nda}}(k, l) = -kZ^2 \frac{1}{(l+1)(l+2)}$$

so that all the non-interacting nodes for various symmetries are equivalent. By checking out the quasiclassical limit $l \rightarrow \infty$, we find

$$\lim_{l \rightarrow \infty} E_{\text{kin}}^{\text{nda}}(k, l) = \lim_{l \rightarrow \infty} E_{\text{kin}}(k, l)$$

and

$$\lim_{l \rightarrow \infty} E_{\text{pot}}^{\text{nda}}(k, l) = \lim_{l \rightarrow \infty} E_{\text{pot}}(k, l).$$

Clearly, averages over $\Psi^2$ and $|\Psi|$ become identical since the quantum effects become irrelevant for $\lim_{l \rightarrow \infty}$.

Let us now turn to the case of a system with interactions. Consider the two-particle 3D harmonic problem with the Coulomb interaction. The Hamiltonian is given by

$$H = (P_1^2 + P_2^2)/2 + \omega^2(r_1^2 + r_2^2)/2 + g_0/r_{12},$$

where $g_0$ is the interaction strength. For certain values of $g_0$ and $\omega$, combined with particular symmetry, one can find simple analytical eigenstates. For $g_0 = 1$ and $\omega = 1/4$, the lowest triplet of $P$ symmetry $3P(sp)$ is given exactly as [19]

$$\Psi_{\text{exact}} = \Psi_0(1 + r_{12}/4),$$

where the noninteracting solution $\Psi_0$ (i.e., $g_0 = 0$) is as usual

$$\Psi_0 = e^{-(r_1^2 + r_2^2)/2}(z_1 - z_2).$$

The noninteracting energy for this particular state ($n_1 = n_2 = l_1 = l_2 = 1$) can be expressed as

$$E_0 = (2n_1 + 2n_2 + l_1 + l_2 + 3)\omega = 4\omega = 1,$$

while the interacting exact eigenvalue is

$$E_{\text{exact}} = E_0 + 1/4.$$

These analytical solutions are sufficiently simple so that we can evaluate the nda components for various combinations of Hamiltonians and wave functions.

a) Noninteracting Hamiltonian and noninteracting wave function. It is straightforward to find out that for $g_0 = 0$, we get

$$E_{\text{pot}}^{\text{nda}} = \frac{7\omega}{2} = \frac{7}{8},$$

and correspondingly

$$E_{\text{kin}}^{\text{nda}} = \frac{\omega}{2}.$$

b) Interacting Hamiltonian with $g_0 = 1$ and the exact eigenstate. After making transformation to center of mass and relative coordinates, one can find

$$E_{\text{pot}}^{\text{nda}} = \frac{7\omega}{2} + \frac{3}{8} \frac{\sqrt{3\pi}}{4 + 3\sqrt{\pi}} + \frac{1 + \sqrt{\pi}/2}{4 + 3\sqrt{\pi}}$$

and using the exact result above, we find

$$E_{\text{kin}}^{\text{nda}} = E - E_{\text{pot}}^{\text{nda}}.$$
the noninteracting wave function. This will give quite a poor estimate since the potential and kinetic energy will be “unbalanced,” but it will still be instructive. Taking \( \Psi_0 \) above, we get
\[
E_{\text{pot}}^{\text{nda}} = \frac{7\omega}{2} + \sqrt{\frac{7\omega}{4}}
\]
and
\[
E_{\text{kin}}^{\text{nda}} = \frac{\omega}{2}.
\]
This provides a clear demonstration that the energy obtained as nda sum is not necessarily an upper bound since
\[
E_{\text{kin}}^{\text{nda}} + E_{\text{pot}}^{\text{nda}} \approx \frac{9.77\omega}{2} < E_{\text{exact}} = \frac{10\omega}{2},
\]
which gives 1.226 ... vs. the exact value 5/4. Actually, the error is not very large considering how crude the trial state is. The dominant error is in the potential part, which comes out lower. This is caused by two effects: the noninteracting value of the exponent in the gaussian is not optimal and a secondary impact comes also from the absence of the correlation. The kinetic energy component is the same as in the noninteracting Hamiltonian, i.e., slightly larger than the exact. This results from the missing exchange hole which affects the gradient of the wave function on the nodal surface. Obviously, these ideas should be explored further and such investigations are currently in progress.

**Conclusions.** We have introduced the nodal hypersurface and domain averages, dubbed “nda”, as a tool for characterization of the nodes of trial wave functions. We have demonstrated their properties on a number of few-particle cases and analyzed implications of these results. For example, we were able to distinguish the nodal differences between degenerate states of the same and different symmetries. These characteristics enabled us to identify the equivalence of nodes in unexpected situations such as between noninteracting singlets and triplets. Clearly, the results show interesting potential and deserve further investigation. The theory can be further explored with much more powerful developments which will be presented elsewhere.

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