

Nodal variational principle for excited statesFederico Zahariev,^{1,*} Mark S. Gordon,^{1,†} and Mel Levy^{2,3,4,‡}¹*Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA*²*Department of Chemistry, Duke University, Durham, North Carolina 27708, USA*³*Department of Physics, North Carolina A&T State University, Greensboro, North Carolina 27411, USA*⁴*Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118, USA*

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It is proven that the exact excited-state wave function and energy may be obtained by minimizing the energy expectation value of trial wave functions that are constrained only to have the correct nodes of the state of interest. This excited-state nodal minimum principle has the advantage that it requires neither minimization with the constraint of wave-function orthogonality to all lower eigenstates nor the antisymmetry of the trial wave functions. It is also found that the minimization over the entire space can be partitioned into several interconnected minimizations within the individual nodal regions, and the exact excited-state energy may be obtained by a minimization in just one or several of these nodal regions. For the proofs of the theorem, it is observed that the many-electron eigenfunction (excited state as well as ground state), restricted to a nodal region, is equivalent to a ground-state wave function of one electron in a higher-dimensional space; and, alternatively, an explicit excited-state energy variational expression is utilized by generalizing the Jacobi method of multiplicative variation. In corollaries, error functions are constructed for cases for which the nodes are not necessarily exact. The exact nodes minimize the energy error functions with respect to nodal variations. Simple numerical illustrations of the error functions are presented.

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Variational principles have provided the most popular and effective ways to compute the properties of electronic systems. In this connection, it is well known that the minimization of the expectation value of the Hamiltonian yields the wave function and energy of the k th eigenstate, if the trial wave function for the k th state is constrained to be orthogonal to the wave functions for the $0, 1, 2, \dots, k - 1$ states, where the energy of state $n + 1$ is understood to be at least as high as the energy of state n . A related notion is the Hylleraas-Undheim-MacDonald theorem [1]. This theorem states that the eigenvalues of the Hamiltonian matrix in any finite-dimensional subspace of the Hilbert space are bounded from below by the true eigenvalues of the Hamiltonian. High-quality results typically require relatively large finite-dimensional subspaces, where the eigenvalue problem becomes computationally expensive. In fact, the computational cost of the best eigenvalue solver algorithms scales quadratically with the dimension of the subspace.

With this in mind, it is the purpose of this paper to present a nodal variational principle for excited states. Specifically, we prove that in order to obtain the energy and wave function of the k th state, it is sufficient that the minimization takes place with the constraint that the trial wave function has the same nodes as the wave function of the k th eigenstate. It is not necessary to impose the difficult orthogonality constraint. It is also not

necessary to impose explicitly antisymmetry. The imposition of the nodal constraint is sufficient.

While interest in nodes of eigenfunctions goes back at least to the proof that the k th eigenfunction of the one-electron Schrödinger equation, in any multidimensional space, has no more than k nodal regions [2], and although research regarding nodes and their properties continued [3], it is the ground-state fixed-node variational principle [4] and tiling theorem [5] of the Quantum Monte Carlo (QMC) method that has aroused substantial interest in nodes and their properties [6–11]. The ground-state fixed-node variational principle states that an energy minimization in a nodal region of an arbitrary antisymmetric wave function gives an upper bound to the ground-state energy, and if a nodal region is bounded by the exact nodes, the energy minimization gives the ground-state energy. The proof of the ground-state fixed-node variational principle indirectly relies on the tiling theorem [5].

The QMC method is now being commonly used for excited states as well as ground states. In fact, the nodal variational principle for excited states presented in this paper is being implied *without a proof* for a number of QMC applications, such as the computations of optical gaps in nanostructures [12] and solids [13], diffusive properties of the vacancy defects in diamond [14], diamondoid excitation energies and Stokes shifts [15], excitation spectra of localized Wigner states [16], quasi-particle excitations of the electron gas [17], and electronic [18] and rovibrational excitations [19] of molecules. As the QMC experience demonstrates, even approximations to the correct nodal surfaces typically result in accurate excited-state values.

The ground-state fixed-node variational principle has been extended to nondegenerate [6] and degenerate [7] excited states that are ground states within certain symmetry classes of

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trial wave functions. More precisely, the trial wave functions are supposed to transform according to the one-dimensional irreducible representation of the symmetry point group of the Hamiltonian. The proofs that are used therein are symmetry-restricted generalizations of the ground-state fixed-node proof [4] and rely on symmetry-restricted generalizations of the ground-state tiling theorem [5]. Although symmetries are not uncommon in molecules consisting of a handful of atoms, larger molecules are less likely to possess any symmetry, and no tiling theorem currently exists that would be applicable to an arbitrary excited state. The proofs of the theorem, its corollaries, and the supporting lemma in the current paper do not require a tiling theorem and are applicable to any eigenstate. In contrast with the original fixed-node approach though, variance type error functions are minimized here for the case of approximate nodes.

We prove the theorem and its corollaries by means of two complementary routes, A and B. Proof A is based on our observation that a many-electron wave function, with a domain of definition that is restricted to a single nodal region, is equivalent to a single-electron wave function in a higher-dimensional space. Proof B extends the ground-state Jacobi method of multiplicative variation to excited states.

Moreover, when the exact nodes are not known, corollaries to the proofs given here construct two different error functions that assess the quality of approximate nodes. These error functions incorporate energy minimization with the given approximate nodes. The minimization of the error functions, with respect to variations of the nodes, achieves zero once the geometries of the nodes become exact. We show that *the explicit antisymmetry is not required*, even when the nodes are approximate. In fact, it is important to emphasize that we prove in a lemma that the minimization results in an antisymmetric wave function. Numerical examples illustrate the use of the error functions.

II. NODAL VARIATIONAL PRINCIPLE

Given below are two different proofs of our *theorem* that expresses the following nodal variational principle for excited states:

(i) *The minimum of the energy expectation value of trial wave functions that are analytically well behaved and have the nodes of the exact eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ of N electrons is the exact eigenvalue E_k . The minimum of the energy expectation value is achieved at the exact eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$.*

(ii) *In addition, even the minimization in just one or several nodal regions also yields E_k .*

Note that it has been shown [20,21] that spin-free wave functions are sufficient in the context of the present work.

III. PROOFS OF THE THEOREM

Proof A. Consider the nodal hypersurface corresponding to the k th eigenfunction, i.e., all of the points in the $3N$ -dimensional coordinate space of N electrons that satisfy the condition $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0$. This nodal hypersurface, i.e., a $(3N - 1)$ -dimensional surface in the $3N$ -dimensional space of electron positions, partitions the configuration space into m

nodal regions L_j ($j = 1, 2, \dots, m$). $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is either strictly positive or strictly negative in each of the m nodal regions. Some technical aspects of the nodal constraint are in Appendix A.

Now consider a trial wave function $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ that is not necessarily antisymmetric with respect to the exchange of like-spin electrons and has the same nodes as the k th eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. The trial wave function $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, which is normalized to unity, could be the exact k th eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ itself. The integration over the entire $3N$ -dimensional space can be partitioned into a sum of integrations over the m nodal regions,

$$\langle \Psi^{(k)} | \Psi^{(k)} \rangle = \sum_{j=1}^m \langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j} = \sum_{j=1}^m p_{L_j} = 1, \quad (1)$$

where $\langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j}$ signifies $\langle \Psi^{(k)} | \Psi^{(k)} \rangle$ in the nodal region L_j .

The energy expectation value of $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ can be similarly partitioned as

$$E^{(k)} = \langle \Psi^{(k)} | \hat{H} | \Psi^{(k)} \rangle = \sum_{j=1}^m \langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j} \frac{\langle \Psi^{(k)} | \hat{H} | \Psi^{(k)} \rangle_{L_j}}{\langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j}}. \quad (2)$$

The expression $\frac{\langle \Psi^{(k)} | \hat{H} | \Psi^{(k)} \rangle_{L_j}}{\langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j}}$, which we denote as $E_{L_j}^{(k)}$, on the right-hand side of Eq. (2) is the energy expectation value of $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ in the individual nodal region L_j and $p_{L_j} = \langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j}$ is the respective probability of finding the N -electron system in the individual nodal region L_j . Consequently, the right-hand side of Eq. (2) is an average over the nodal energies that are weighted by the respective probabilities. If the trial wave function $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the exact eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ itself, then $E_{L_j}^{(k)} = E^{(k)} = E_k$. (A similar partitioning of the energy expectation value of a one-dimensional Hamiltonian was used in Ref. [11] in the proof of a different variational principle involving nodes.)

It is important to observe here that the k th eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ in a nodal region is, in fact, the ground-state solution for the given nodal region. This is because an eigenfunction that is either strictly positive or strictly negative is a ground state according to an extension presented here of a theorem of Courant and Hilbert [2]. Although the original theorem is for a one-electron wave function in a space of arbitrary dimension, the many-electron eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, restricted to a nodal region, can be equivalently interpreted as a ground-state wave function of one electron in $3N$ -dimensional space, even when $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is an excited state.¹ In such

¹Note that the interchange symmetry of $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ does not play a role for an individual nodal region for the following reason: If $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N$ belongs to a nodal region, then $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N$, in which the spatial coordinates corresponding to two spin-equivalent electrons are interchanged, is outside the nodal region, as the interchange changes the sign of the wave function.

an interpretation, the many-electron Hamiltonian is regarded as an effective Hamiltonian of one electron in $3N$ -dimensional space and, similarly, $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ may also be regarded as an eigenfunction of one electron in $3N$ -dimensional space.

According to the foregoing ground-state minimum principle for each nodal region, the nodal region normalized energy expectation value of $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ cannot be lower than the nodal region normalized energy expectation value of the k th eigenvalue of $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$:

$$E_{L_j}^{(k)} = \frac{\langle \Psi^{(k)} | \hat{H} | \Psi^{(k)} \rangle_{L_j}}{\langle \Psi^{(k)} | \Psi^{(k)} \rangle_{L_j}} \geq \frac{\langle \Psi_k | \hat{H} | \Psi_k \rangle_{L_j}}{\langle \Psi_k | \Psi_k \rangle_{L_j}} = E_k. \quad (3)$$

Multiplication on both sides of the inequality in Eq. (3) by p_{L_j} followed by a summation over j gives

$$\begin{aligned} E^{(k)} &= \langle \Psi^{(k)} | \hat{H} | \Psi^{(k)} \rangle = \sum_{j=1}^m p_{L_j} E_{L_j}^{(k)} \geq \sum_{j=1}^m p_{L_j} E_k \\ &= \left(\sum_{j=1}^m p_{L_j} \right) E_k = E_k. \end{aligned} \quad (4)$$

The inequality in Eq. (4) arises because each p_{L_j} is non-negative, the use of the normalization expression given by Eq. (1), and the fact that the weighted average increases if any of the contributing energies increases. Equation (4) proves part (i) of the above theorem.

The analytic restriction on the trial wave functions guarantees *smooth patching* of the wave functions that achieve energy minima in the different nodal regions. This smooth patching is *necessary* because each nodal-region energy minimizing wave function has the freedom of a multiplicative constant.

Equation (3) demonstrates that an energy minimization in an isolated nodal region actually gives the exact energy E_k of the entire eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. More generally, consider an energy minimization over some of the nodal regions, such as over an isolated region of space bounded by nodes. An appropriately normalized nodal energy minimization over just some of the nodal regions also yields the exact energy E_k , as demonstrated by a generalization of Eq. (4),

$$\frac{\sum_j p_{L_j} E_{L_j}^{(k)}}{\sum_j p_{L_j}} \geq \frac{\sum_j p_{L_j} E_k}{\sum_j p_{L_j}} = E_k, \quad (5)$$

where the partial sum is over one or more nodes that participate in the minimization. Equation (5) proves part (ii) of the above theorem. ■

Proof B. Consider trial wave functions of the type $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, where the k th state $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is kept fixed and the function $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is varied. The function $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is assumed to be well behaved. That is, $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is smooth (in particular, everywhere finite) and such that $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is a well-behaved wave function. It is important to note that $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is not assumed here to be necessarily antisymmetric with respect to the exchange of like-spin electrons.

The theorem will now be proven by showing that the explicit form of the g variations around the excited state $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, which can be considered to be a generalization to excited states of the Jacobi method of multiplicative variation,² is

$$\frac{\langle g \Psi_k | \hat{H} | g \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} = E_k + \frac{\frac{1}{2} \sum_{i=1}^N \sum_{\alpha=x,y,z} \langle (\frac{\partial g}{\partial r_{i,\alpha}}) \Psi_k | (\frac{\partial g}{\partial r_{i,\alpha}}) \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} \geq E_k. \quad (6)$$

Note that the inequality in Eq. (6) occurs because the sums are non-negative.

The equality on the left in Eq. (6) is derived by the following chain of equalities:

$$\begin{aligned} \frac{\langle g \Psi_k | \hat{H} | g \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} &= \frac{\langle g \Psi_k | \hat{T} | g \Psi_k \rangle + \langle g \Psi_k | \hat{V} | g \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} = \frac{\langle g \Psi_k | \hat{T} | g \Psi_k \rangle + \langle g^2 \Psi_k | \hat{V} | \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} \\ &= \frac{\langle g \Psi_k | \hat{T} | g \Psi_k \rangle + \langle g^2 \Psi_k | (\hat{H} - \hat{T}) | \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} = E_k + \frac{\langle g \Psi_k | \hat{T} | g \Psi_k \rangle - \langle g^2 \Psi_k | \hat{T} | \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle} \\ &= E_k + \frac{\frac{1}{2} \sum_{i=1}^N \sum_{\alpha=x,y,z} \langle (\frac{\partial g}{\partial r_{i,\alpha}}) \Psi_k | (\frac{\partial g}{\partial r_{i,\alpha}}) \Psi_k \rangle}{\langle g \Psi_k | g \Psi_k \rangle}. \end{aligned} \quad (7)$$

Additional details of the derivation of Eq. (7) can be found in Appendix B.

At this stage, the inequality in Eq. (6) has been proved. But in order for the inequality to constitute a proof of the theorem, each trial wave function $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ that has the same nodes as the k th eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ should be presentable as $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. In other words, the well-behaved scaling function must be presentable as $\frac{\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}$. Since $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ vanishes at the nodes, the finiteness of the ratio may not appear to be guaranteed. However, the ratio is, in fact, finite, as shown in Appendix C.

Thus, the inequality in Eq. (6), together with the fact that each trial wave function $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ that has the same nodes as the k th eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is presentable as $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, proves part (i) of the above theorem.

²On pp. 458 and 459 of Vol. I of Ref. [2], the Jacobi's method of multiplicative variation is introduced and applied to the ground-state problem only.

As with Proof A, Proof B can be adapted to a single nodal region or, more generally, to several nodal regions with an appropriate normalization of the energy expectation value. Equation (6) implies that the analog of Eq. (5) is

$$\frac{\sum_j \langle g \Psi_k | \hat{H} | g \Psi_k \rangle_{L_j}}{\sum_j \langle g \Psi_k | g \Psi_k \rangle_{L_j}} = E_k + \frac{\frac{1}{2} \sum_j \sum_{i=1}^N \sum_{\alpha=x,y,z} \left(\left(\frac{\partial g}{\partial r_{i,\alpha}} \right) \Psi_k \left| \left(\frac{\partial g}{\partial r_{i,\alpha}} \right) \Psi_k \right\rangle_{L_j}}{\sum_j \langle g \Psi_k | g \Psi_k \rangle_{L_j}} \geq E_k, \quad (8)$$

where each sum in j could be replaced by simply one term when only one nodal region is used, which proves part (ii) of the above theorem. ■

IV. ANTISYMMETRY LEMMA AND COROLLARIES TO THE THEOREM

Now assume that the m nodal regions \tilde{L}_j ($j = 1, 2, \dots, m$) are not necessarily the exact nodes of Ψ_k . It is assumed that the approximate nodes are variations around the exact ones, i.e., that the approximate nodes can be continuously deformed back to the exact ones.

In this case, the minimizing energies within the different nodal regions,

$$\tilde{E}_{\tilde{L}_j, \min}^{(k)} = \frac{\langle \tilde{\Psi}_{\min}^{(k)} | \hat{H} | \tilde{\Psi}_{\min}^{(k)} \rangle_{\tilde{L}_j}}{\langle \tilde{\Psi}_{\min}^{(k)} | \tilde{\Psi}_{\min}^{(k)} \rangle_{\tilde{L}_j}}, \quad (9)$$

may differ from each other. Although the trial wave functions $\tilde{\Psi}^{(k)}$ are not *constrained* to be antisymmetric, the energy-minimizing trial wave function $\tilde{\Psi}_{\min}^{(k)}$ will always be antisymmetric if the nodes come from *some* antisymmetric wave function, as the following lemma demonstrates.

Lemma. The minimizing wave function $\tilde{\Psi}_{\min}^{(k)}$ is antisymmetric. (The spin-free wave functions that are antisymmetric are such with respect to the interchange of electron coordinates that correspond to the same spin.)

Proof. Define Φ to be an antisymmetric wave function such that the nodes of Φ divide the N -electron configuration space into m nodal regions \tilde{L}_j ($j = 1, 2, \dots, m$). The nodes of the trial wave functions $\tilde{\Psi}^{(k)}$ are assumed to be the nodes of Φ .

Choose a point $\vec{R} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ in the configuration space of N electrons. Label the nodal region, where the point \vec{R} lies, as A . An interchange of two electrons having the same spin, say the first and the second electrons, maps the point \vec{R} to a new point $\vec{R}' = (\vec{r}_2, \vec{r}_1, \dots, \vec{r}_N)$. Label the nodal region, where the point \vec{R}' lies, as A' .

The nodal regions A and A' are different because $\Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ and $\Phi(\vec{r}_2, \vec{r}_1, \dots, \vec{r}_N)$ have different signs (as a reminder, Φ is antisymmetric). If \vec{R} and \vec{R}' are connected with a straight line, there has to be an odd number of nodal crossings along the line as there is a sign change at each nodal crossing.

The interchange of the first and second electrons, in fact, maps every point of A to a point of A' , making the two nodal regions “isomorphic,” i.e., of the same form and size. Since the nodal regions A and A' are isomorphic, the ground state in A is mapped to the ground state in A' by the interchange of the first and second electrons (up to a normalization factor). In the same manner, another nodal region, say B , is mapped to an isomorphic nodal region B' , C to C' , D to D' , and so

on. In other words, one-half of the space (A, B, C, D, \dots) is mapped to its isomorphic other half (A', B', C', D', \dots). The uncertainty in the normalization factor of the ground state is reduced to just an uncertainty in the sign due to the perfect mirror symmetry between the two isomorphic halves.

The minimizing wave function $\tilde{\Psi}_{\min}^{(k)}$ is a ground state within each nodal region. As a result, $\tilde{\Psi}_{\min}^{(k)}$ restricted to A is mapped to $\tilde{\Psi}_{\min}^{(k)}$ restricted to A' by the interchange of the first and second electrons, i.e., $\tilde{\Psi}_k(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \pm \tilde{\Psi}_k(\vec{r}_2, \vec{r}_1, \dots, \vec{r}_N)$.

On the one hand, every minimizing wave function, antisymmetric or not, changes sign across a node because it is with a nonzero slope at the node (Appendix C). On the other hand, as stated above, there is an odd number of nodal crossings along the straight line connecting \vec{R} and \vec{R}' . Hence, $\tilde{\Psi}_k(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = -\tilde{\Psi}_k(\vec{r}_2, \vec{r}_1, \dots, \vec{r}_N)$. ■

A relevant “error expression,” corresponding to $\tilde{\Psi}_{\min}^{(k)}$ is

$$\sum_{j=1}^m [\tilde{E}_{\tilde{L}_j, \min}^{(k)} - \tilde{E}_{\min}^{(k)}]^2 \langle \tilde{\Psi}_{\min}^{(k)} | \tilde{\Psi}_{\min}^{(k)} \rangle_{\tilde{L}_j}, \quad (10)$$

where

$$\tilde{E}_{\min}^{(k)} = \langle \tilde{\Psi}_{\min}^{(k)} | \hat{H} | \tilde{\Psi}_{\min}^{(k)} \rangle = \sum_{j=1}^m \tilde{E}_{\tilde{L}_j, \min}^{(k)} \langle \tilde{\Psi}_{\min}^{(k)} | \tilde{\Psi}_{\min}^{(k)} \rangle_{\tilde{L}_j}. \quad (11)$$

Note that the larger nodal regions are weighted higher in expression (10). This error expression achieves its minimum of zero if and only if the trial wave function $\tilde{\Psi}_{\min}^{(k)}$ is the true eigenfunction Ψ_k because then all the nodal-region minimizing energies in Eq. (9) are equal.

Corollary I to the theorem. The minimization of error expression (10), with respect to nodal variations, yields the correct nodes of Ψ_k .

Another nodal error expression is dictated by the use of $g \Psi_k$ in Proof B. The expression is

$$\left[\frac{\langle g \tilde{\Psi}_{\min}^{(k)} | \hat{H} | \tilde{\Psi}_{\min}^{(k)} \rangle}{\langle g \tilde{\Psi}_{\min}^{(k)} | \tilde{\Psi}_{\min}^{(k)} \rangle} - \langle \tilde{\Psi}_{\min}^{(k)} | \hat{H} | \tilde{\Psi}_{\min}^{(k)} \rangle \right]^2. \quad (12)$$

Corollary II to the theorem. Minimization of error expression (12) with respect to nodal variations, for all allowable scaling functions g , yields the correct nodes of Ψ_k . Note that the allowable g 's from Proof B are such that $g \tilde{\Psi}_{\min}^{(k)}$ preserves the nodes of $\tilde{\Psi}_{\min}^{(k)}$.

When only a subset of the nodal regions is employed, for which zero values of error expressions (10)–(12) serve as necessary eigenstate conditions, it is understood that expressions (10)–(12) are adjusted to incorporate the particular scalar products in the nodal regions.

TABLE I. The energies and corresponding errors of the wave function for the 4S state of the hydrogen atom with approximate nodes. The energies are in Hartrees. The squared norms of the wave function in the four nodal regions are, respectively, 0.007 188, 0.030 936, 0.128 878, and 0.832 998.

Nodal regions	$\tilde{E}_{\min}^{(k)}$	$[E_k - \tilde{E}_{\min}^{(k)}]^2$ with $\tilde{E}_{\min}^{(k)}$ over the nodal regions	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over 1,2,3,4	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over the nodal regions
1	-0.14010	1.1849×10^{-2}	1.1819×10^{-2}	0
2	-0.01000	4.5153×10^{-4}	4.5743×10^{-4}	0
3	-0.03261	1.8427×10^{-6}	1.4862×10^{-6}	0
4	-0.03106	3.7671×10^{-8}	1.1052×10^{-7}	0
1,2	-0.03453	1.0764×10^{-5}	2.5995×10^{-3}	2.5897×10^{-3}
1,3	-0.03829	4.9508×10^{-5}	6.2577×10^{-4}	5.7819×10^{-4}
1,4	-0.03199	5.4590×10^{-7}	1.0122×10^{-4}	1.0086×10^{-4}
2,3	-0.02823	9.1122×10^{-6}	8.9746×10^{-5}	7.9779×10^{-5}
2,4	-0.03030	8.9878×10^{-7}	1.6486×10^{-5}	1.5306×10^{-5}
3,4	-0.03126	1.9032×10^{-10}	2.9484×10^{-7}	2.7933×10^{-7}
1,2,3	-0.03305	3.2276×10^{-6}	5.9458×10^{-4}	5.9184×10^{-4}
1,2,4	-0.03121	1.7651×10^{-9}	1.1387×10^{-4}	1.1384×10^{-4}
1,3,4	-0.03207	6.7424×10^{-7}	8.7959×10^{-5}	8.7493×10^{-5}
2,3,4	-0.03060	4.2089×10^{-7}	1.4539×10^{-5}	1.3920×10^{-5}
1,2,3,4	-0.03139	1.9140×10^{-8}	1.0167×10^{-4}	1.0167×10^{-4}

V. SIMPLE NUMERICAL EXAMPLES

It was observed earlier that a many-electron wave function, with a domain of consideration that is restricted to a single nodal region, is equivalent to a single-electron wave function in a higher-dimensional space. As a result, a single-electron example is worthwhile for demonstrating the qualitative features of approximate nodal regions. As an illustration, consider the exact and approximate 4S state of the hydrogen atom. The approximate wave functions minimize the total energy, while being constrained to approximate nodes. Tables I–IV present the energies and corresponding errors of the minimizing wave functions in single, double, triple, and quadruple combinations of nodal regions for four 4S state wave functions of the hydrogen atom with approximate nodes. The utility of error expression (10) for helping to select the best wave function is reflected in the fact that the wave function with the best average energy, which is associated with the bottom row of Table III, is the one that gives the lowest value for error expression (10); compare the bottom rows of Tables I–IV. Comparison of the bottom rows in Table I and Table IV also reveals, however, that it is possible for a wave function with a higher value for error expression (10) to actually give a better average energy.

The red (middle) lines on the right-hand side of Fig. 1 [23], which is associated with the wave function in Table I, depict the nodal-region energy minima (solid lines) and actual eigenvalue (dotted line) of the example. The ground-state energies in the different approximate nodal regions are not necessarily equal, making the energy discontinuous across the nodes.

The right-hand side of Fig. 1 depicts the split of the nodal-region energies into their local kinetic- and potential-energy components, obtained by rearranging the eigenvalue equation as $\frac{-\frac{1}{2}\nabla^2\Psi(\vec{r})}{\Psi(\vec{r})} + V(\vec{r}) = E$, which is the way it is utilized, for instance, in the familiar local energy and variance expressions

TABLE II. The energies and corresponding errors of the first alternative wave function for the 4S state of the hydrogen atom with approximate nodes. The energies are in Hartrees. The squared norms of the wave function in the four nodal regions are, respectively, 0.003 377, 0.029 859, 0.096 241, and 0.870 523.

Nodal regions	$\tilde{E}_{\min}^{(k)}$	$[E_k - \tilde{E}_{\min}^{(k)}]^2$ with $\tilde{E}_{\min}^{(k)}$ over the nodal regions	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over 1,2,3,4	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over the nodal regions
1	-0.01000	4.5153×10^{-4}	4.5442×10^{-4}	0
2	-0.04337	1.4700×10^{-4}	1.4536×10^{-4}	0
3	-0.02636	2.3944×10^{-5}	2.4611×10^{-5}	0
4	-0.03153	8.1424×10^{-8}	4.7355×10^{-8}	0
1,2	-0.03998	7.6272×10^{-5}	1.7676×10^{-4}	1.0167×10^{-4}
1,3	-0.02580	2.9677×10^{-5}	3.9181×10^{-5}	8.7611×10^{-6}
1,4	-0.03145	4.0860×10^{-8}	1.8031×10^{-6}	1.7850×10^{-6}
2,3	-0.03039	7.4593×10^{-7}	5.3203×10^{-5}	5.2335×10^{-5}
2,4	-0.03193	4.5963×10^{-7}	4.8663×10^{-6}	4.4939×10^{-6}
3,4	-0.03102	5.2981×10^{-8}	2.4927×10^{-6}	2.4039×10^{-6}
1,2,3	-0.02985	1.9470×10^{-6}	6.3667×10^{-5}	6.1526×10^{-5}
1,2,4	-0.03185	3.5525×10^{-7}	6.5460×10^{-6}	6.2670×10^{-6}
1,3,4	-0.03095	9.2014×10^{-8}	4.0657×10^{-6}	3.9280×10^{-6}
2,3,4	-0.03139	1.9591×10^{-8}	6.7730×10^{-6}	6.7678×10^{-6}
1,2,3,4	-0.03138	4.5884×10^{-9}	9.4020×10^{-6}	9.4020×10^{-6}

[25,26,27]. As can be seen in Fig. 1, about the same nodal deviation from an exact nodal position can have a dramatically different impact on the nodal energy, depending on the strength of the external potential at the position of a node. For this reason, energy-based error expressions (10) and (12) give measures for gauging nodal quality that should provide worthwhile alternatives to the use of the geometric notion of nodal distance error [28,29]. These energy-based error expressions

TABLE III. The energies and corresponding errors of the second alternative wave function for the 4S state of the hydrogen atom with approximate nodes. The energies are in Hartrees. The squared norms of the wave function in the four nodal regions are, respectively, 0.005 799, 0.037 427, 0.109 387, and 0.847 386.

Nodal regions	$\tilde{E}_{\min}^{(k)}$	$[E_k - \tilde{E}_{\min}^{(k)}]^2$ with $\tilde{E}_{\min}^{(k)}$ over the nodal regions	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over 1,2,3,4	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over the nodal regions
1	-0.02075	1.1023×10^{-4}	1.1123×10^{-4}	0
2	-0.03789	4.4137×10^{-5}	4.3511×10^{-5}	0
3	-0.02588	2.8840×10^{-5}	2.9350×10^{-5}	0
4	-0.03178	2.7825×10^{-7}	2.3057×10^{-7}	0
1,2	-0.03559	1.8868×10^{-5}	5.2595×10^{-5}	3.4136×10^{-5}
1,3	-0.02562	3.1680×10^{-5}	3.3473×10^{-5}	1.2577×10^{-6}
1,4	-0.03170	2.0479×10^{-7}	9.8504×10^{-7}	8.2084×10^{-7}
2,3	-0.02894	5.3250×10^{-6}	3.2960×10^{-5}	2.7415×10^{-5}
2,4	-0.03204	6.1811×10^{-7}	2.0613×10^{-6}	1.5154×10^{-6}
3,4	-0.03110	2.1550×10^{-8}	3.5598×10^{-6}	3.5221×10^{-6}
1,2,3	-0.02863	6.8585×10^{-6}	3.5934×10^{-5}	2.8826×10^{-5}
1,2,4	-0.03196	5.0796×10^{-7}	2.7722×10^{-6}	2.3294×10^{-6}
1,3,4	-0.03104	4.3752×10^{-8}	4.2085×10^{-6}	4.1427×10^{-6}
2,3,4	-0.03136	1.1844×10^{-8}	5.0638×10^{-6}	5.0600×10^{-6}
1,2,3,4	-0.03130	2.2384×10^{-9}	7.2620×10^{-6}	7.2620×10^{-6}

TABLE IV. The energies and corresponding errors of the third alternative wave function for the 4S state of the hydrogen atom with approximate nodes. The energies are in Hartrees. The squared norms of the wave function in the four nodal regions are, respectively, 0.007 466, 0.102 640, 0.240 274, and 0.649 620.

Nodal regions	$\tilde{E}_{\min}^{(k)}$	$[E_k - \tilde{E}_{\min}^{(k)}]^2$ with $\tilde{E}_{\min}^{(k)}$ over the nodal regions	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over 1,2,3,4	Eq. (10) with $\tilde{E}_{\min}^{(k)}$ over the nodal regions
1	-0.01000	4.5153×10^{-4}	5.7794×10^{-4}	0
2	-0.05227	4.4195×10^{-4}	3.3239×10^{-4}	0
3	-0.03312	3.4957×10^{-6}	8.4886×10^{-7}	0
4	-0.03178	2.7835×10^{-7}	5.1235×10^{-6}	0
1,2	-0.04941	3.2965×10^{-4}	3.4904×10^{-4}	1.1295×10^{-4}
1,3	-0.03242	1.3758×10^{-6}	1.8240×10^{-5}	1.5622×10^{-5}
1,4	-0.03153	7.8434×10^{-8}	1.1632×10^{-5}	5.3270×10^{-6}
2,3	-0.03885	5.7797×10^{-5}	1.0008×10^{-4}	7.6934×10^{-5}
2,4	-0.03457	1.1048×10^{-5}	4.9776×10^{-5}	4.9492×10^{-5}
3,4	-0.03214	7.9189×10^{-7}	3.9694×10^{-6}	3.5507×10^{-7}
1,2,3	-0.03824	4.8828×10^{-5}	1.1027×10^{-4}	9.2654×10^{-5}
1,2,4	-0.03433	9.5012×10^{-6}	5.4966×10^{-5}	5.4882×10^{-5}
1,3,4	-0.03196	4.9800×10^{-7}	8.7447×10^{-6}	4.3961×10^{-6}
2,3,4	-0.03422	8.8319×10^{-6}	3.7932×10^{-5}	3.7899×10^{-5}
1,2,3,4	-0.03404	7.7898×10^{-6}	2.8065×10^{-5}	2.8065×10^{-5}

measure the cumulative deviation of the nodal-region energy minima from the average energy. When the nodes are exact,

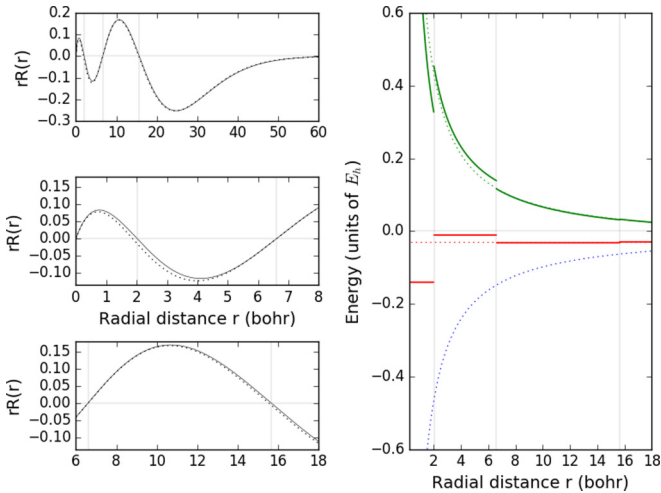


FIG. 1. The exact (dotted lines) and approximate (solid lines) wave functions corresponding to the 4S state of the hydrogen atom are depicted on the left-hand side of the figure on different radial distance scales. The exact wave function has nodes at $r = 1.8716$, 6.6108 , and 15.5180 bohr, while the approximate wave function has nodes at 2.0240 , 6.6068 , and 15.6442 bohr. The four nodal regions are enumerated from the nucleus outwards. The exact energy of the hydrogen atom in the 4S state is $-0.03125 E_h$, while the nodal-region energies of the approximate hydrogen-atom wave function are $-14.010 \times 10^{-2} E_h$ (first), $-1.000 \times 10^{-2} E_h$ (second), $-3.261 \times 10^{-2} E_h$ (third), and $-3.106 \times 10^{-2} E_h$ (fourth). The corresponding local energies are depicted on the right-hand side of the figure [kinetic: green (upper) curves; potential: blue (bottom) curve; total: red (middle) lines].

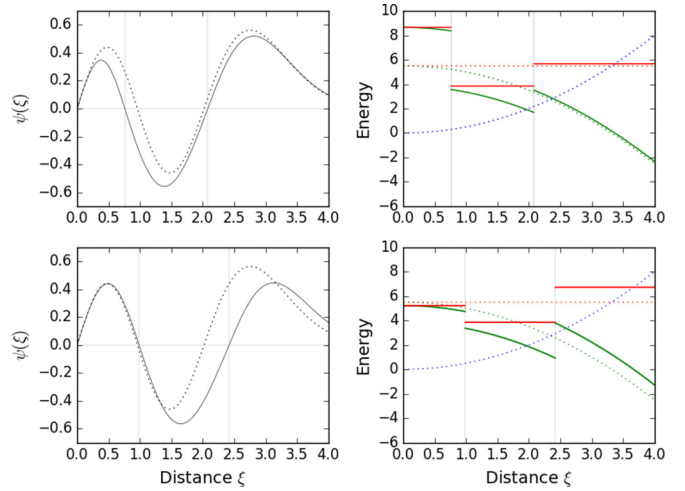


FIG. 2. The exact (dotted lines) and approximate (solid lines) wave functions corresponding to the fifth excited state of the harmonic oscillator (HO) are depicted on the left-hand side of the figure. The exact wave function (upper and lower left) has nodes at 0.959 and 2.020 , while the first approximate wave function (HO-1, upper left) has nodes at 0.759 and 2.080 and the second approximate wave function (HO-2, lower left) has nodes at 0.985 and 2.420 . The exact energy of HO is 5.5000 , while the nodal-region energies of the HO-1 are 8.6564 , 3.8478 , and 5.6742 and the nodal-region energies of HO-2 are 5.2218 , 3.8525 , and 6.7234 . The corresponding local energies are depicted on the right-hand side of the figure. The kinetic components are in green, the potential components are in blue, and the sum of the two is in red. Only the right halves of the wave functions are shown due to the antisymmetry with respect to the origin. A representation of the harmonic-oscillator problem with unitless distance and energy is chosen [24].

all of these nodal-region energy minima equal the excited-state eigenvalue, which is a constant throughout the entire space.

It is interesting to note that the value of error expression (10) can be determined solely by the discontinuities of the local kinetic energy at the nodes. The value of error expression (10) is invariant with respect to a shift of all the nodal-region energy minima by the same constant and, as a result, this value depends only on the differences of the nodal-region energy minima. The differences of the neighboring nodal-region energy minima are, in turn, equivalent to the extent of the discontinuities of the local kinetic energy at the respective nodes.

TABLE V. The energies and error-expression evaluations of the approximate wave functions (HO-1 and HO-2 as defined previously) are shown in the table. The nodal regions, where the wave functions are considered, are indicated in the leftmost column (in parentheses). The harmonic oscillator energies are unitless.

Approx. wave func.	Energy	Error expr. 1, Eq. (10)	Error expr. 2, Eq. (12) [30]
HO-1 (1,2,3)	5.1974	1.9478	4.6713
HO-1 (3)	5.6742	0.2273	0.2273
HO-2 (1,2,3)	5.1319	1.6451	1.3926
HO-2 (1)	5.2218	0.0081	0.0081

If, through the use of error expressions (10) or (12), there is an indication that a particular subset of nodal regions might be preferred, then it would be reasonable to consider choosing this subset alone. For example, for the wave function associated with Table I, if only the third and fourth nodal regions (as counted from the nucleus outwards) are used, instead of all four nodal regions, the values of the error expressions of Eqs. (10) and (12) [30] go down from $1.0167 \times 10^{-4} E_h^2$ to $2.9484 \times 10^{-7} E_h^2$ and from $3.0694 \times 10^{-3} E_h^2$ to $7.9837 \times 10^{-7} E_h^2$, respectively, where E_h signifies the Hartree unit of energy. Simultaneously, the approximate energy estimate improves from $-0.03139 E_h$ to $-0.03126 E_h$ compared with the exact value of $-0.03125 E_h$. It becomes clear that a restriction to the third and fourth nodal regions of the approximate hydrogen atom 4S wave function improves the energy estimate. In fact, compared with all the nodal combinations in Table I, the use of the third and fourth regions gives both the lowest value for error expression (10) and the best average energy.

In addition to the exact and approximate wave functions for the 4S state of the hydrogen atom, consider also the exact and two approximate fifth excited states of the one-dimensional harmonic oscillator³ (Fig. 2) [23].

Table V summarizes the energy and error expression values of the minimizing wave functions with nodal approximations both in the entire space and in selected nodal regions only. It becomes clear that a restriction of HO-1 to the third nodal region and of HO-2 to the first nodal region improves the energy estimates.

While the mathematical results in this paper are general, the difficulty is that their applications to many-electron systems require flexible and robust numerical representations of the multidimensional nodes. For these purposes, one might use generalizations of the approach in Ref. [31]. In any case, our theorem justifies the interpretation that approximate excited-state energies and wave functions are obtained even when the exact nodes are only known approximately, as exemplified by the cases given in Sec. I.

VI. CONCLUDING REMARKS

In this paper, a minimum principle featuring nodes was proven for excited states. Aspects of this minimum principle are currently being actively utilized in practice, but here we provide a proof.

The excited-state theorem within provides the realization that the minimization over the entire space can be partitioned into interconnected minimizations in individual exact nodal regions, and an energy minimization over all space or over one or several nodal regions gives the exact excited-state energy. Moreover, the exact excited-state wave function is obtained when the minimization is performed over all space. The smoothness of the trial wave functions across the nodes is the *essential link* between the minimizations within each of the nodal regions for the construction of the correct mini-

minizing wave function, which is needed for the computation of properties. Explicit expressions for the wave-function variation around an excited state with the nodes constrained to the correct ones are given in Eqs. (6) and (8).

Expressions (10) and (12) of the corollaries extend the minimum principle to nodal variations when the exact nodes are unknown. The lemma supports the corollaries and establishes a key connection between the nodes and the antisymmetry of the minimizing wave functions.

The main results in this paper are formulated in the theorem, antisymmetry lemma, and corollaries. In addition, we have provided suggestions for calculations of excited states when approximate nodes are used in the nodal energy minimization process. With this in mind, simple numerical examples illustrate the use of expressions (10) and (12) as error estimates of approximate nodes.

It is expected that the excited-state minimum principle presented here and the extension of the minimum principle to nodal variation will have a wide range of new applications due to the general validity of these principles for excited states.

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APPENDIX A

The nodal constraint is imposed by restricting the variational space to the linear space of wave functions that are well behaved and have the nodes of the k th eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. See Ref. [22] for a definition of an analytically well behaved wave function. In the case of approximate nodes, slightly weaker conditions are assumed, namely, that the wave function is well behaved in the above sense in each nodal region and only first-order smooth, i.e., the wave function has continuous first derivatives, at the nodes. The restricted variational space is linear, as a linear combination of such trial wave functions is still a wave function with the properties that are assumed above. Alternatively to restricting the variational space, the Hamiltonian of interest, $\hat{H} = \hat{T} + \hat{V}$ [the kinetic part is $\hat{T} = -\frac{1}{2} \sum_{1 \leq i \leq N} \nabla_i^2$, where $\nabla_i = \frac{\partial}{\partial r_{i,x}} + \frac{\partial}{\partial r_{i,y}} + \frac{\partial}{\partial r_{i,z}}$ is acting on the i th electronic coordinates, and the potential part is $\hat{V} = \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{1 \leq j \leq N} v(\mathbf{r}_j)$, where $v(\mathbf{r})$ is the external potential], might be modified with the addition of δ -function-type infinite potential walls along the nodes. A replacement of \hat{H} with such a modified Hamiltonian \hat{H}' is an alternative way to ensure a nodal constraint on the trial wave functions upon energy minimization, as the eigenfunctions of \hat{H}' naturally have nodes at the places where the potential of \hat{H}' becomes infinite.

APPENDIX B

Here are the details for the derivation of Eq. (7).

³The two wave functions that minimize the energy-expectation value of the harmonic oscillator, while being constrained to nodes displaced from the exact positions, are abbreviated HO-1 and HO-2 (see the caption of Fig. 2 for more details).

$$\begin{aligned}
 \langle g\Psi_k|\hat{T}|g\Psi_k\rangle - \langle g^2\Psi_k|\hat{T}|\Psi_k\rangle &= -\frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\langle g\Psi_k|\frac{\partial^2}{\partial r_{i,\alpha}^2}|g\Psi_k\rangle + \frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\langle g^2\Psi_k|\frac{\partial^2}{\partial r_{i,\alpha}^2}|\Psi_k\rangle \\
 &= \frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\left\langle\frac{\partial(g\Psi_k)}{\partial r_{i,\alpha}}\left|\frac{\partial(g\Psi_k)}{\partial r_{i,\alpha}}\right.\right\rangle - \frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\left\langle\frac{\partial(g^2\Psi_k)}{\partial r_{i,\alpha}}\left|\frac{\partial\Psi_k}{\partial r_{i,\alpha}}\right.\right\rangle \\
 &= \frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\left\langle\left(\frac{\partial g}{\partial r_{i,\alpha}}\right)\Psi_k + g\left(\frac{\partial\Psi_k}{\partial r_{i,\alpha}}\right)\left|\left(\frac{\partial g}{\partial r_{i,\alpha}}\right)\Psi_k + g\left(\frac{\partial\Psi_k}{\partial r_{i,\alpha}}\right)\right.\right\rangle \\
 &\quad - \frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\left\langle\left(2g\frac{\partial g}{\partial r_{i,\alpha}}\right)\Psi_k + g^2\left(\frac{\partial\Psi_k}{\partial r_{i,\alpha}}\right)\left|\frac{\partial\Psi_k}{\partial r_{i,\alpha}}\right.\right\rangle \\
 &= \frac{1}{2}\sum_{i=1}^N\sum_{\alpha=x,y,z}\left\langle\left(\frac{\partial g}{\partial r_{i,\alpha}}\right)\Psi_k\left|\left(\frac{\partial g}{\partial r_{i,\alpha}}\right)\Psi_k\right.\right\rangle \\
 &= \frac{N_\uparrow}{2}\sum_{\alpha=x,y,z}\left\langle\left(\frac{\partial g}{\partial r_{N_\uparrow,\alpha}}\right)\Psi_k\left|\left(\frac{\partial g}{\partial r_{N_\uparrow,\alpha}}\right)\Psi_k\right.\right\rangle \\
 &\quad + \frac{N_\downarrow}{2}\sum_{\alpha=x,y,z}\left\langle\left(\frac{\partial g}{\partial r_{N_\uparrow+N_\downarrow,\alpha}}\right)\Psi_k\left|\left(\frac{\partial g}{\partial r_{N_\uparrow+N_\downarrow,\alpha}}\right)\Psi_k\right.\right\rangle. \tag{B1}
 \end{aligned}$$

The following arguments are used in Eq. (B1): (1) integration by parts in the second equality, (2) derivative of a product in the third equality, (3) algebraic simplification in the fourth equality, and (4) coordinate interchange symmetry of $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, if there is such symmetry, in the last equality.

APPENDIX C

This Appendix demonstrates that $g(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}$ is finite, assuming both the eigenfunction $\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and the trial wave function $\Psi^{(k)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ are analytic around the node.

An eigenfunction has $3N$ variables and its node, i.e., the positions in the $3N$ -dimensional space where the wave function

is zero, is a hypersurface of dimension $(3N - 1)$. For each point on the nodal hypersurface, there is a one-dimensional direction, perpendicular to the nodal hypersurface, that leads toward nonzero values, so the behavior of the eigenfunction in the vicinity of its node is effectively described by a one-dimensional Schrodinger equation,

$$\frac{d^2\Psi_k(r)}{dr^2} = f(r)\Psi_k(r), \tag{C1}$$

where $f(r) = -2[E_k - V(r)]$. Subsequent differentiation of Eq. (C1) gives

$$\begin{aligned}
 \frac{d^3\Psi_k(r)}{dr^3} &= \frac{df(r)}{dr}\Psi_k(r) + f(r)\frac{d\Psi_k(r)}{dr}, \\
 \frac{d^4\Psi_k(r)}{dr^4} &= \frac{d^2f(r)}{dr^2}\Psi_k(r) + 2\frac{df(r)}{dr}\frac{d\Psi_k(r)}{dr} + f(r)\frac{d^2\Psi_k(r)}{dr^2}, \dots \tag{C2}
 \end{aligned}$$

Now, we employ a proof by contradiction. If $\frac{d\Psi_k(r)}{dr}|_{r=0} = 0$ as well as $\Psi_k(0) = 0$, then Eqs. (C1) and (C2) dictate that all higher derivatives of the eigenfunction also vanish, i.e., $\frac{d^n\Psi_k(r)}{dr^n}|_{r=0} = 0$ for any n . Based on the assumption that $\Psi_k(r)$ is analytic around the node at $r = 0$, it follows that the eigenfunction identically vanishes everywhere around the origin, i.e., $\Psi_k(r) \equiv 0$, which is absurd. Consequently, $\Psi_k(0) = 0$ but $\frac{d\Psi_k(0)}{dr} \neq 0$. Hence, assuming the eigenfunction can be expanded in a Taylor series around the point at the node ($r = 0$), $\Psi_k(r) = a_1r + a_2r^2 + a_3r^3 + \dots = r(a_1 + a_2r + a_3r^2 + \dots)$, where $a_1 \neq 0$.

The Taylor expansion of a trial wave function around a point at the node has to be $\Psi^{(k)}(r) = b_nr^n + b_{n+1}r^{n+1} + b_{n+2}r^{n+2} + \dots = r^n(b_n + b_{n+1}r + b_{n+2}r^2 + \dots)$, where $b_n \neq 0$ and $n \geq 1$. The prefactor r^n guarantees the trial wave function $\Psi^{(k)}(r)$ vanishes at the node ($r = 0$).

As a result, $\frac{\Psi^{(k)}(r)}{\Psi_k(r)} = \frac{r^n(b_n + b_{n+1}r + b_{n+2}r^2 + \dots)}{r(a_1 + a_2r + a_3r^2 + \dots)}$ does not diverge at the node of the eigenfunction.

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