Implications of the two nodal domains conjecture for ground state fermionic wave functions

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The nodes of many-body wave functions are mathematical objects important in many different fields of physics. They are at the heart of the quantum Monte Carlo methods but outside this field their properties are neither widely known nor studied. In recent years a conjecture, already proven to be true in several important cases, has been put forward related to the nodes of the fermionic ground state of a many-body system, namely that there is a single nodal hypersurface that divides configuration space into only two connected domains. While this is obviously relevant to the fixed node diffusion Monte Carlo method, its repercussions have ramifications in various fields of physics as diverse as density functional theory or Feynman and Cohen's backflow wave function formulation. To illustrate this we explicitly show that, even if we knew the exact Kohn-Sham exchange correlation functional, there are systems for which we would obtain the exact ground state energy and density but a wave function quite different from the exact one. This paradox is only apparent since the Hohenberg-Kohn theorem relates the energy directly to the density and the wave function is not guaranteed to be close to the exact one. The aim of this paper is to stimulate the investigation of the properties of the nodes of many-body wave functions in different fields of physics. Furthermore, we explicitly show that this conjecture is related to the phenomenon of avoided nodal crossing but it is not necessarily caused by electron correlation, as sometimes has been suggested in the literature. We explicitly build a many-body uncorrelated example whose nodal structure shows the same phenomenon.

I. INTRODUCTION

The properties of the nodes of wave functions are important in many different fields: e.g., the study of quantum dots, the fixed node diffusion Monte Carlo method, the quantum Hall effect, and quantum chaos, to name a few. However, despite the fundamental importance of wave function nodes (as opposed to orbital nodes) only recently have a few papers[1–9] begun to investigate their properties for both exact and approximate many-body wave functions.

The *nodal surface*, (sometimes called *nodal set* in the mathematical literature or simply the node), is the set of points **R** for which a wave function vanishes, i.e., $\Psi(\mathbf{R}) = 0$. With **R** we indicate the collective coordinates of the N particles in D dimensions. The nodal set implicitly defines two or more *nodal domains* (sometimes called nodal cells or nodal pockets), i.e., a connected set of points bounded by the nodal set where the wave function has the same sign.

In one dimension it is well known[10] that the so called "nodal theorem" holds, i.e., the ground state has no nodes and a nondegenerate Mth excited state has exactly M nodes, dividing the real axis into $M + 1$ nodal domains. A common textbook example of the nodal theorem is the simple harmonic oscillator. In two-dimensional (2D) and higher-dimensional systems, the nodal theorem is no longer valid: it is not necessarily true that the Mth excited state has $M + 1$ nodal domains.[11] Courant and Hilbert[10] were able to prove a weaker version of the nodal theorem: The nodes of the Mth excited state divide the space into at most $M + 1$ nodal domains.

The many-body fermionic ground state of an N-electron system can, in principle, have a large number of nodal domains, depending how many bosonic and mixed symmetry states are below the fermionic one. In recent years, however, a body of evidence has accumulated showing that in several cases the ground fermionic state has only two nodal domains, the minimum possible, and it has been conjectured[1,2,9] that

this property might be a general property of fermionic systems.

The properties of the many-body nodal surfaces, and in particular the two nodal domains conjecture, are well known in the field of quantum Monte Carlo, since they are at the heart of the fixed node diffusion Monte Carlo (FN-DMC) method, but are usually little known in other fields. Far from being only a mathematical curiosity, if a wave function must have only two nodal domains this fact puts a severe constraint on its shape, which in turn can have various implications worth exploring in different fields of physics. In the following we will show two such implications: one related to density functional theory (DFT) and the other to the construction of backflow wave functions in the hope to further stimulate the study of nodal surfaces in different fields of physics where they usually are only marginally considered or not considered at all. Furthermore we will show that this conjecture is not necessarily related to electron correlation, as it is often assumed.

Bressanini *et al.*[4] showed, both numerically and analytically, the differences in the topology of the nodal surfaces between Hartree-Fock (HF) and configuration interaction (CI) wave functions for the beryllium atom. They showed that the HF wave function has four nodal domains while both the CI and the exact wave functions have only two nodal domains. In the following we briefly recall, for the benefit of the general reader, the properties of the nodal surfaces of the beryllium atom that we will use to define and illustrate the concepts needed in later sections.

II. THE NODAL SURFACE OF THE GROUND STATE OF BERYLLIUM ATOM

The beryllium atom has four electrons ($N = 4$) and its wave function is an object defined by all spin-space coordinates of the electrons. The ground state has ^1S symmetry and in the

absence of magnetic field, since the Hamiltonian does not explicitly depend on spin, with no loss of generality we can arbitrarily assign spin α to electrons 1 and 2 and spin β to electrons 3 and 4 and study the properties of the associated space component of the full wave function specified by the twelve coordinates of the electrons:

$$\begin{aligned}\Psi(\mathbf{R}) &= \Psi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) \\ &= \Psi(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3, x_4, y_4, z_4),\end{aligned} \quad (1)$$

where $\mathbf{R}_i$ indicates the coordinates of electron i. The spatial wave function in Eq. (1) can be viewed as the projection of the full spin-space wave function against the spin function $\alpha\alpha\beta\beta$. Projecting using a different spin function results in a spatial function that differs only by a different labeling of the coordinates.

In order to satisfy the Pauli principle the function must be antisymmetric with respect to the interchange of electrons with the same spin. For example,

$$\begin{aligned}P_{12}\Psi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) &= -\Psi(\mathbf{R}_2, \mathbf{R}_1, \mathbf{R}_3, \mathbf{R}_4), \\ P_{34}\Psi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) &= -\Psi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_4, \mathbf{R}_3),\end{aligned} \quad (2)$$

where P_{12} and P_{34} are permutation operators.

The general properties of fermion nodes were investigated by Ceperley.[1] In this seminal paper he proved the tiling theorem: All nodal domains in a ground fermionic state are equivalent, i.e., they all have the same shape, and the various permutation operators P_{ij} that exchange electron i with electron j transform one nodal domain into another. Note that this theorem does not specify the total number of nodal domains.

In the restricted Hartree-Fock approximation, the beryllium ground state wave function is described by the electronic configuration $1s^2 2s^2$ whose Slater determinant, after spin projection, factors into the product of two determinants

$$\begin{aligned}\Psi_{\mathrm{HF}} &= |1s(r_1)2s(r_2)|_\alpha \, |1s(r_3)2s(r_4)|_\beta \\ &= [1s(r_1)2s(r_2) - 1s(r_2)2s(r_1)] \\ &\quad \times [1s(r_3)2s(r_4) - 1s(r_4)2s(r_3)],\end{aligned} \quad (3)$$

where r_i is the distance from electron i to the nucleus.

The wave function is the product of two independent determinants, so the nodal set is the union of the nodal sets of the individual determinants. Each determinant has the structure of the $1s2s\,^3S$ state of Be^{2+} and it is easy to see that the equations defining the two nodes are $r_1 - r_2 = 0$ and $r_3 - r_4 = 0$. The nodal set of Ψ_{HF} thus is defined by the equation $(r_1 - r_2)(r_3 - r_4) = 0$: The HF wave function is zero whenever two like electrons are at the same distance from the nucleus. It is not difficult to see that the nodal set of Ψ_{HF} divides the space into four equivalent nodal domains: two where the wave function is positive and two where the wave function is negative. These domains are related to each other by permutations and satisfy the tiling theorem.

Note that the node is completely independent from the actual shape of the $1s$ and $2s$ orbitals (although orbitals with a completely arbitrary shape could introduce further spurious nodes into the wave function).

Note also that Ψ_{HF} belongs to a higher symmetry group than the exact wave function, since it neither depends on
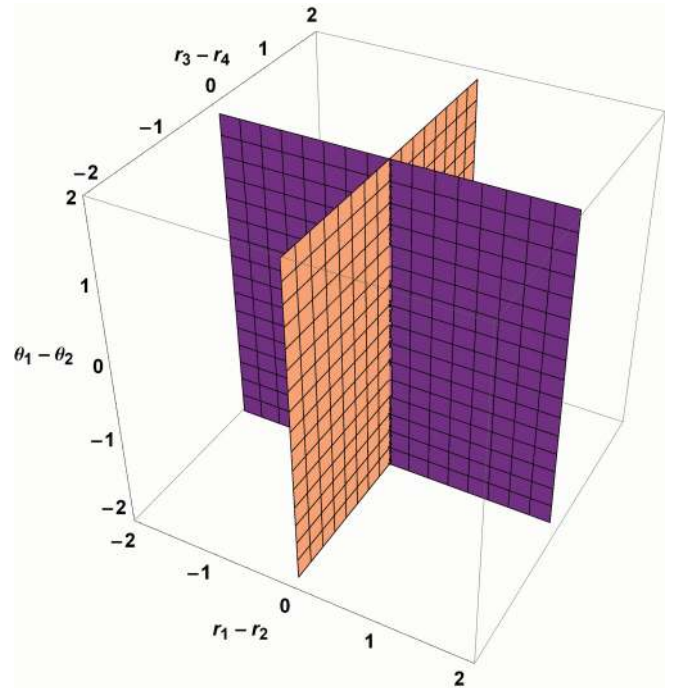

FIG. 1. (Color online) Three-dimensional cut of the full 11D node of the HF wave function for the Be atom with four nodal domains.

the interparticle distances nor the angular coordinates of the individual electrons. For this reason its node has a particular simple form.

Since the nodal set is a high-dimensional object we can only plot portions of it by taking cuts, by fixing some of the coordinates, and plot where this subset of the wave function is zero.

To better show the features of the nodal set we express the electronic positions in spherical coordinates and rewrite the wave function using sum and differences of those. Figure 1 shows a cut through the node of the HF wave function fixing nine out of twelve coordinates, showing where $\Psi_{\mathrm{HF}} = 0$ for the remaining three coordinates. The x, y, and z axes show, respectively, $r_1 - r_2$, $r_3 - r_4$, and $\theta_1 - \theta_2$.

The plot is only a three-dimensional cut of the full 11-dimensional (11D) ($3N-1$) node but it nicely shows the four distinct nodal domains separated by the two intersecting nodes. The two independent nodes, one from each determinant, cross forming angles of $\pi/2$. It can be shown[12] that this is a general feature of intersecting nodes of eigenfunctions: If n independent nodes cross, they form equal angles of π/n. The intersection is a ten-dimensional (10D) set ($3N-2$) where both the wave function and its gradient vanish: $\Psi = 0, \nabla\Psi = 0$. The double permutation operator $P_{12}P_{34}$ transforms a point in a positive (negative) domain into a point in the other disconnected positive (negative) domain.

In the HF picture the ground state spatial wave function is always the product of α and β determinants which means that the nodal structure of Ψ_{HF} is always composed by two or more intersecting nodal surfaces,[2] even if not necessarily as simple as those of beryllium. An important consequence is that the number of nodal domains in the HF description is at least 4 for systems with more than three electrons (the ground state
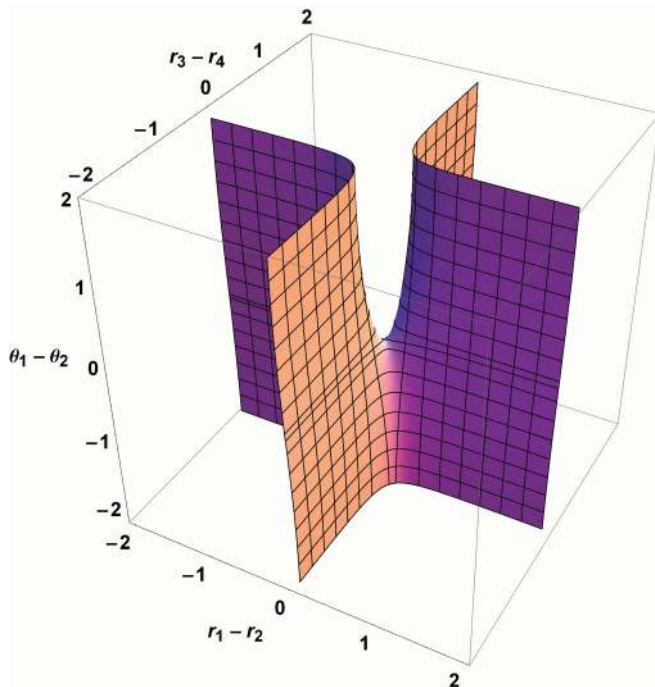
FIG. 2. (Color online) Three-dimensional cut of the full 11D node of the CI wave function for the Be atom with two nodal domains.

of helium has only one domain since it is positive everywhere while the ground state of Li has a single nodal surface and two nodal domains[4]). The same of course applies to any single Slater determinant generated from any single-particle theory.

It is well known that the quality of the HF wave function for four electron atoms can be greatly improved by adding the $1s^2 2p^2$ configuration to the ground state one, generating a small CI expansion:

$$\Psi_{CI} = \varphi(1s^2 2s^2) + c\varphi(1s^2 2p^2). \tag{4}$$

The nodal set of Ψ_{CI} is completely different from that of Ψ_{HF}: As soon as the parameter c is different from zero, the two independent nodal surfaces of the HF configuration merge, an "opening" appears where the two surfaces previously crossed, and only one hypersurface is left, with only two nodal domains: one positive and one negative. Figure 2 shows a three-dimensional (3D) cut of the full 11D node of Ψ_{CI}.

It is even possible to rigorously prove[4] that the exact beryllium ground state wave function has only two nodal domains. The proof is repeated in the Appendix for the convenience of the reader, to make the paper self-contained.

This property is not limited to the Be atom but seems to be a general feature of fermionic systems. It was hypothesized by Ceperley[1] numerically checking the ground state of the 2D and 3D noninteracting spin-polarized homogeneous electron gas with periodic boundary conditions, up to 200 electrons. Glauser *et al.*[2] showed that HF wave functions for a few first-row atoms have four nodal domains and conjectured that the CI wave functions might have only two. Mitas[9] proved that in two dimensions and higher, spin-polarized noninteracting fermions in a harmonic well have two nodal domains for arbitrary system size, and was able to extend the proof to a number of other models, such as fermions on a sphere or in a periodic box.

In the same paper Mitas showed, using a Bardeen-Cooper-Schrieffer (BCS) pairing wave function, that the two nodal domain property holds even for the ground state of 2D spin-unpolarized fermions in a closed-shell singlet state of arbitrary size.

The validity of the conjecture has been shown also for spin-polarized closed-shell ground states of noninteracting fermions and for spin-polarized atomic states with several electrons, both for noninteracting and HF wave function.[5]

In summary, even if a general mathematical proof is still lacking, there are reasons to believe that, at least for many important cases, the two nodal domains conjecture is true.

III. IMPLICATIONS OF THE CONJECTURE

Although it has not yet been established in general exactly in which cases the ground fermionic state has only two nodal domains, the above discussion suggests that the conjecture might be true for all ground states of electronic systems. If this is true it is well worth trying to understand its implications in different fields of physics through the constraints it puts on the exact wave function. The principal aim of this paper is to stimulate researchers in different fields to explore the nodal structure of their wave functions and in particular to investigate which consequences would have the two nodal domains conjecture in fields where the fermionic nature of the ground state wave function is important.

In the following we will assume that the conjecture is true and will explore a few implications and ramifications, hoping to stimulate further analysis. Some of the examples have already been discussed (albeit very briefly) in the literature, but in this paper they are brought together within a unifying framework.

A. Avoided nodal crossings

In recent years a few papers have been devoted to studying the phenomenon where two nodal lines (nodal sets in 2D) exhibit "avoided crossings." This phenomenon has been investigated in excited states of two-dimensional model potentials,[13] chaotic wave functions,[14,15] quantum stadium,[16] Gaussian random waves,[17] and other two-dimensional cases. The phenomenon, however, is not limited to one-particle excited states in two dimensions. The CI and exact beryllium wave function show the same phenomenon which seems to be a general feature, but so far little investigated, even of quantum many-body systems.

Taking two-dimensional plots of the nodes of the HF wave function (see Fig. 1) we observe two independent intersecting nodal lines, defining four nodal domains (See Fig. 3 dashed line). As soon as some mixing with the $|1s^2 2p^2|$ configuration is introduced the crossing of the two nodes disappears, except in a lower-dimensional subset of configurations, and the two nodes now show the avoided crossing phenomenon (solid line in Fig. 3). This is clearly intimately related to the fact that the CI and the exact wave function have only two nodal domains.

It is tempting to interpret the avoided crossing phenomenon as a correlation effect since in the beryllium wave function it appears as soon as we deviate from the simple HF wave function. However, this is not so and the appearances of
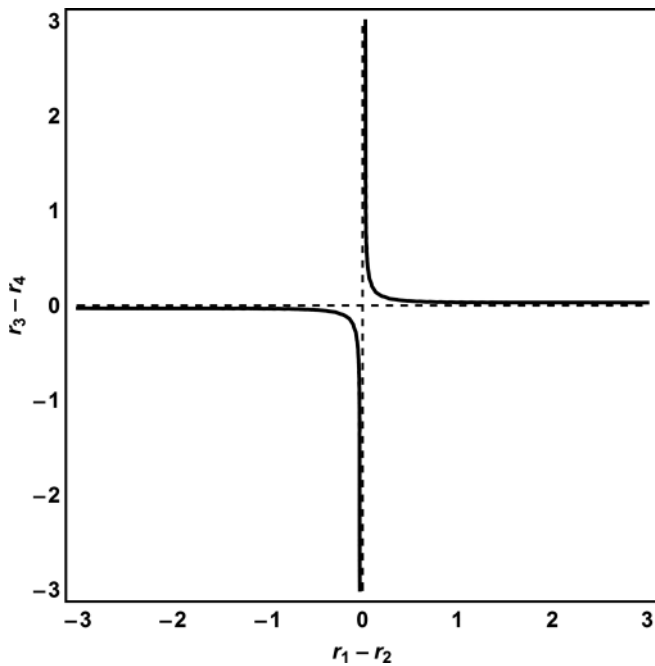
FIG. 3. Avoided nodal crossing in a beryllium CI wave function (solid line). The nodes of HF wave functions are shown in dashed lines.

avoided nodal crossings are rather a manifestation of the fact that the wave function is no longer expressed as a simple product. To illustrate this we show in Fig. 4 the nodes of the $2s4s\,^1S$ doubly excited state of the helium atom where the interaction between the two electrons has been turned off. Other excited states have similar features.
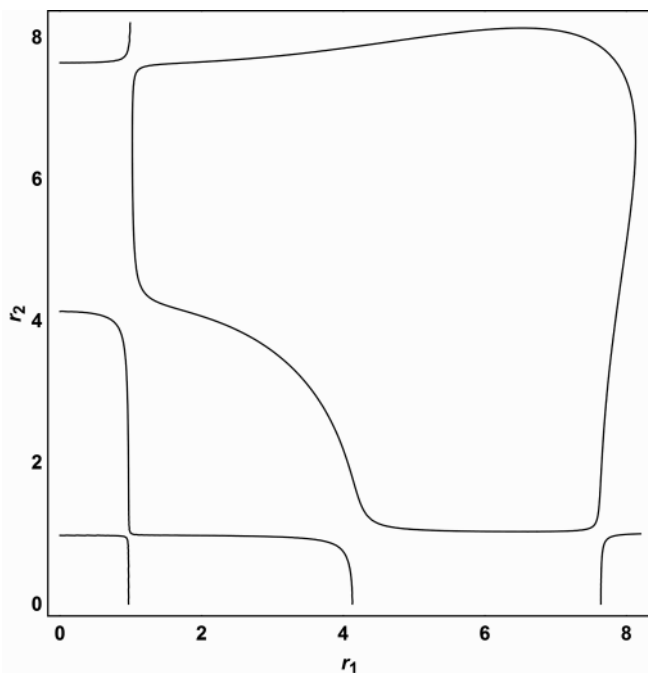

FIG. 4. Nodes of the $2s4s\,^1S$ doubly excited state of the helium atom where the interaction between the two electrons has been turned off.

Even if the interaction between the two electrons has been turned off, and so there is no correlation, a pattern of avoided crossings still shows up due to the fact that the wave function is symmetric with respect to the interchange of r_1 and r_2, and it cannot be written as a simple orbital product. It is important to notice this property, and it is likely that this feature survives even when the electronic interaction is turned on.

Uhlenbeck[18] showed that a generic property of eigenfunctions is that they are Morse functions and as a consequence different nodes do not generally intersect. The avoided intersection phenomenon and the two nodal domains conjecture are both clearly related to Uhlenbeck's theorem, which, however, is too general and cannot exclude that some state of some specific system has intersecting nodal surfaces. A counterexample is the $1s3s\,^3S$ excited state of helium, both with interacting or noninteracting electrons, that has two intersecting nodal surfaces and four nodal domains. The avoided crossing phenomenon is almost always present and crossing of nodal surfaces occurs only in special cases, e.g., when there are specific symmetry constraints as in many ^3S states of the He atom that have $r_1 = r_2$ as one nodal surface. The general properties of nodal surfaces for excited states will be the subject of a future paper.[19]

B. The DFT wave function

Density functional theory (DFT) has become quite popular in the last few decades. Its roots rest on the Hohenberg-Kohn theorem[20] which establishes the functional dependence of the system's ground state energy from the electron density. Strictly speaking there is no wave function in DFT; its practical implementation, however, almost always relies on the Kohn-Sham formulation,[21] where a system of N noninteracting particles in a fictitious potential is introduced and whose exact ground state wave function is a single Slater determinant whose density is, by construction, equal to the density of the real system of interacting particles. The orbitals which form the Slater determinant are the solutions of N single-particle equations. In its practical implementation the Kohn-Sham (KS) scheme introduces an approximation of the so called exchange-correlation potential.

Strictly speaking the Kohn-Sham orbitals and wave function have no real physical meaning. Their only connection with the real system is that they provide the exact density and energy, provided one has the exact exchange-correlation functional. While this is certainly true and well known, in recent years many authors started to view the KS wave function as a legitimate object both for qualitative and quantitative purposes. For example, it is quite common to use wave functions built from Kohn-Sham orbitals in quantum Monte Carlo simulations where the nodal shape and connectivity is crucial to obtain accurate results. This is not a real issue in quantum Monte Carlo simulations since the fixed node energy is a rigorous upper bound to the exact ground state regardless of the origin of the wave function that is employed to define the nodes.

More problematic, however, could be the use of the KS orbitals and wave function for interpretive purposes in DFT

itself or to compute properties other than the energy and the density, since there is no guarantee that the wave function would be even close to the exact one. However, an often used justification on the use of the KS orbitals and wave function as if they possess physical meaning is that, after all, they come from a one-electron potential where exchange and correlation effects have been introduced and, furthermore, they are able to generate the exact density. On the other hand, the HF wave function does not include correlation effects and its generated density is not the exact one, but HF wave functions and orbitals are routinely used to interpret experimental results. As Reboredo and Kent[22] recently remarked. the success of DFT has led to its use "beyond its formal scope and unfortunately tempted some to believe that if we had the exact ground state density functional we would only need to solve noninteracting problems even for properties not related to the ground state energy and density."

Given the above discussion on the nodal surfaces of the beryllium atom and the two nodal domains conjecture it is easy to see that the KS wave function, as the HF one, *always* has features not present in the exact ground state wave function. Suppose we have the exact exchange-correlation functional. In this case the Kohn-Sham equations would generate the orbitals, exact solutions of a noninteracting four-electron system, that give the exact ground state energy and the exact density of the beryllium atom. However, since the KS wave function is written as a determinant, it will necessarily have at least two independent nodal surfaces and at least four nodal domains. This argument extends to all systems where the conjecture proves to be true, including possibly all nondegenerate ground states of atoms and molecules. Even if we knew the exact Kohn-Sham exchange-correlation potential, in all these cases we would obtain the exact ground state energy and density but a wave function fundamentally different from the exact one. For this reason its use for more than qualitative purposes should be viewed with caution since there is no guarantee that expectation values other than the density will be close to the exact ones.

As explained above this paradox is only apparent since, strictly speaking, there is no wave function in DFT, and the Hohenberg-Kohn theorem relates the energy directly to the density. The wave function in the Kohn-Sham scheme is only an intermediate tool to generate the density and is not guaranteed to be close to the exact one. This agrees with the conclusions of Reboredo and Kent,[22] studying a model system, that the popular expectation that the DFT solution has good nodal surfaces is not valid in general.

A number of reviews on perspective and current challenges of DFT theory have appeared recently[23–25] but in none of these is mentioned the fact that the KS wave function, written as a single determinant, is fundamentally different than the exact wave function due to its wrong nodal structure, even if one has the exact functional. This is an explicit and clear example why any attempt to use the KS wave function to compute properties other than the energy and density cannot be theoretically justified. Interestingly a few papers have appeared in the DFT literature[26,27] suggesting the use of multideterminant wave functions in DFT. In this case the DFT wave function would have, at least in principle, the correct nodal topology.

C. Feynman and Cohen backflow wave function

In many field of physics the fermionic system of interest is usually described at first order using some kind of one-particle approximation, i.e., a single determinant wave function built from single-particle orbitals. It can be either the result of a HF calculation, a DFT description with some approximate functional [e.g., Becke three-parameter Lee-Yang-Parr (B3LYP)], or it can come from some other single-particle theory.

A popular approach to improve the variational freedom of the wave function, suggested by Feynman and Cohen[28] in a study of liquid helium, is to use the so called backflow transformation. The coordinates $\mathbf{R}$ of the particles in the determinant are replaced by the transformed collective coordinates $\mathbf{X}(\mathbf{R})$, where the new coordinates $\mathbf{X}_i$ are related to the old electronic coordinates $\mathbf{R}_i$ through

$$\mathbf{X}_i(\mathbf{R}) = \mathbf{R}_i + \xi(\mathbf{R}), \qquad (5)$$

where $\xi(\mathbf{R})$ is the backflow displacement for particle i possibly containing some variational parameter.

Examples of studies using this approach are numerous and include both finite and infinite systems.[29,30] Let us consider a system with N_α and N_β electrons, both greater than 1. Before the transformation the wave function has at least two independent nodal surfaces, with at least four nodal domains. One surface depends only on the coordinates of α electrons while the other depends on the coordinates of the β electrons. After the backflow transformation the wave function $\Psi_{BF} = |\mathbf{X}(\mathbf{R})|_\alpha |\mathbf{X}(\mathbf{R})|_\beta$ is still a product of two determinants. The difference now is that each determinant depends on all coordinates. However, since each determinant is, by definition, antisymmetric, it must have at least one node. Since the backflow transformation is continuous the topology of the nodal domains is not changed by a backflow transformation. This means that, even with infinite flexibility in the backflow transformation, convergence to the exact wave function and exact energy is never reached. This does not prevent the nodal set of the backflow wave function to be better than the single determinant nodes since now they depend on all the coordinates, as in the exact wave function. However, in order to converge to the exact nodes it is first necessary to establish the correct number of nodal domains, and only at that point the backflow transformation can converge to the exact wave function.

A number of different ways to write a wave function with the correct, at least in principle, number of nodes is available, the more common being the configuration interaction method. A CI wave function, with a few well chosen determinants, seems to be able to reduce the number of nodal regions to two, as we saw for the beryllium atom, although a general proof is still lacking. A number of other functional forms have been investigated in recent years, including Pfaffians[31] and geminals.[32]

The above discussion rigorously applies to finite systems. For infinite systems, a solid for example, one is interested in the total energy *per particle*, and while for a given cell size it is still true that a single determinant from a single-particle theory gives a number of nodal domains greater than 2, and so cannot converge to the exact wave function and total energy, it is still open to question if the energy per particle could, at least in principle, converge to the exact value.

D. Excited states

In all the above discussions we have considered a generic fermionic ground state. It is interesting to speculate, along the same line of arguments, in which cases a single-determinant wave function *might* give the correct description of the nodal topology.

Let us considered a spin-polarized system of N electrons. For example, this might be an excited state (of different symmetry than the ground state) of an atom or a molecule. Since all electrons have the same spin, the Slater determinant factorizes into a spin part and only a single determinant (α, for example) is left. In principle this functional form is able to describe the correct topology of the nodal structure, with a single node that divides the whole configuration space in two equivalent regions. How this could be achieved in practice is still open to investigation, but Mitas and co-workers[5,9] showed that there are cases where this is indeed possible. It is interesting to note that in this case the two nodal domains conjecture does not prevent convergence to the exact node.

A similar argument applies when we have $N-1$ α electrons ($N > 2$) and one β electron. The atomic case $N = 3$ corresponds to the lithium atom ground state while for larger N it can represent excited states. The HF and KS wave functions are products of a Slater determinant of order $N - 1$, with at least two nodal domains, and a β determinant composed by a single orbital. If this is the $1s$ orbital, positive everywhere, we fall into the previous case where this wave function can, in principle, describe the correct nodal topology.

In the generic case of $N-M$ α electrons and M β electrons ($M > 1$) a spin-space determinant factorizes into a product of two determinants, composed by independent variables, and as discussed in a previous section, the wave function has the wrong number of nodal domains.

IV. CONCLUSIONS

After illustrating the two nodal domains conjecture we showed that it has interesting ramifications and nontrivial implications in different fields of physics. Although it is well known that the DFT wave function in the Kohn-Sham formulation is only a tool to generate the density, we were able to precisely show the structural differences with respect to the exact wave function of the real interacting system and point out that these differences persist even if the exact exchange-correlation functional is available. For this reason any attempt to use the KS wave function to compute properties other than the energy and density cannot be theoretically justified. We pointed out that the popular way to improve the quality of a wave function using a backflow transformation cannot converge to the exact value, even in principle, unless one starts from a wave function with the already correct number of nodal domains. We remarked on the connections between the two nodal domains conjecture and the related phenomenon of nodal avoided crossings and pointed out that this is not related to electronic correlation by explicitly examining the nodes of a doubly excited state of the noninteracting helium atom. Finally we speculated in which cases a single determinant could in principle give a qualitatively correct description of the nodes for excited states. We hope our analysis will stimulate further investigations on nodes in different fields of physics.

APPENDIX: PROOF THAT FOUR-ELECTRON ^1S ATOMIC GROUND STATES HAVE ONLY TWO NODAL DOMAINS

According to the tiling theorem,[1] for any ground state fermionic wave function all the nodal domains are equivalent and all are related by permutations. In the four-electron case, this implies that there can be at most four nodal domains, since there are only four permutations that do not interchange spin: two positive permutations, I and $P_{12}P_{34}$, and two negative permutations, P_{12} and P_{34}. The different nodal domains can be labeled with respect to a reference point, $\mathbf{R}^* = (\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4)$, as the set of points that can be reached by a continuous path from the reference point that does not cross a node of Ψ. Any point with $\Psi(\mathbf{R}^*) \neq 0$ can be chosen as a reference point. The tiling theorem tells us that the nodal domain defined with respect to one reference point is equivalent to those defined with respect to another point up to a permutation.

In order to prove that there is only one positive nodal domain it is sufficient to find a reference point $\mathbf{R}^*$ and show that there is a continuous path $\mathbf{R}(t)$, where the wave function is always positive, from $\mathbf{R}^*$ to its doubly permuted image $P_{12}P_{34}\mathbf{R}^*$. The connection between the two negative regions follows by symmetry.

As a reference point we choose a point of the form $\mathbf{R}^* = (\mathbf{R}_1, -\mathbf{R}_1, \mathbf{R}_3, -\mathbf{R}_3)$ where $\mathbf{R}_1$ and $\mathbf{R}_3$ are arbitrary nonzero vectors nonparallel to each other. Since the exact wave function $\Psi(\mathbf{R})$ is a ^1S state it is spherically symmetric, which means that $\Psi(\mathbf{R})$ is invariant with respect to a rotation of all electrons about any axis through the nucleus. We need to find an axis such that with a single rotation the two α electrons exchange positions, and the same happens for the two β electrons. This axis is $\mathbf{R}_1 \times \mathbf{R}_3$, i.e., the axis orthogonal to both $\mathbf{R}_1$ and $\mathbf{R}_3$. A rotation of π around this axis defines a path $\mathbf{R}(t)$ that exchanges electrons 1 and 2 and at the same time 3 and 4, connecting $\mathbf{R}^*$ to $P_{12}P_{34}\mathbf{R}^*$. Since the wave function is invariant with respect to rotation, it is constant along this path. Hence as long as $\Psi(\mathbf{R}^*) \neq 0$, i.e., it is a valid reference point, then there are only two connected nodal domains, a single positive and the symmetric negative region.

To finish the proof we need to show that it is always possible to choose $\mathbf{R}^*$ such that $\Psi(\mathbf{R}^*) \neq 0$. We express the exact wave function using a CI (configuration interaction) expansion $\Psi = \sum_i c_i \varphi_i$, where the first two terms are $\varphi_1 = |1s^2 2s^2|$ and $\varphi_2 = |1s^2 2p^2|$.

As we have already seen, the Hartree-Fock term φ_1 vanishes for any $\mathbf{R}^*$ defined as above. The second term φ_2 has a node of the form

$$[g(r_1)\mathbf{R}_1 - g(r_2)\mathbf{R}_2] \cdot [g(r_3)\mathbf{R}_3 - g(r_4)\mathbf{R}_4] = 0 \qquad (A1)$$

for some positive function g. With the value of $\mathbf{R}^*$ assumed above, φ_2 will vanish only when $\mathbf{R}_1 \cdot \mathbf{R}_3 = 0$. Thus as long as $\mathbf{R}_1$ and $\mathbf{R}_3$ are not orthogonal the sum of the first two CI configurations is not zero, and there is no reason to expect that adding other CI terms will cause $\Psi(\mathbf{R}^*)$ to vanish exactly for all of these points $\mathbf{R}^*$. This completes the proof that the Be atom ground state has only two nodal domains.

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