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Hohenberg-Kohn theorem including electron spin

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The Hohenberg-Kohn theorem is generalized to the case of a *finite* system of N electrons in external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and magnetostatic $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ fields in which the interaction of the latter with both the orbital and spin angular momentum is considered. For a nondegenerate ground state a bijective relationship is proved between the gauge invariant density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$ and the potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$. The possible many-to-one relationship between the potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and the wave function is explicitly accounted for in the proof. With the knowledge that the basic variables are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, and explicitly employing the bijectivity between $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$, the further extension to N-representable densities and degenerate states is achieved via a Percus-Levy-Lieb constrained-search proof. A $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$-functional theory is developed. Finally, a Slater determinant of equidensity orbitals which reproduces a given $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ is constructed.

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I. INTRODUCTION

The concept of a basic variable of quantum mechanics plays the key role in a host of theories of electronic structure developed and applied over the past half century. For the definition of a basic variable, consider a system of N electrons in an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, with $v(\mathbf{r})$ a scalar potential. The Hamiltonian $\hat{H}$ of this system (in atomic units $e = \hbar = m = 1$ employed throughout) is

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}, \tag{1}$$

where the operators are the kinetic $\hat{T} = \frac{1}{2}\sum_k \hat{\mathbf{p}}_k^2$, the momentum $\hat{\mathbf{p}}_k = -i\boldsymbol{\nabla}_{\mathbf{r}_k}$, the electron-interaction $\hat{U} = \frac{1}{2}\sum_{\ell,k} 1/|\mathbf{r}_\ell - \mathbf{r}_k|$, and external $\hat{V} = \sum_k v(\mathbf{r}_k)$. A basic variable is defined [1,2] as a gauge invariant property of the system that uniquely determines the Hamiltonian $\hat{H}$, and thereby via the solution Ψ of the Schrödinger equation $\hat{H}\Psi = E\Psi$, *all* the properties of the system. This path from the basic variable to the wave function Ψ emanates from the Hohenberg-Kohn (HK) theorem [3]. For the electronic system defined by the Hamiltonian of Eq. (1), the basic variable is the nondegenerate ground state density $\rho(\mathbf{r})$ which is the expectation value of the density operator $\hat{\rho}(\mathbf{r}) = \sum_k \delta(\mathbf{r}_k - \mathbf{r})$.

The manner by which this conclusion is arrived at is via a two-step proof. In the first, Map C, it is proved that there is a bijective or *one-to-one* relationship between the external potential $v(\mathbf{r})$ and the nondegenerate ground state wave function Ψ. In the second, Map D, then employing the conclusion of Map C, it is proved that that there is a bijective relationship between the Ψ and the ground state density $\rho(\mathbf{r})$. Hence knowledge of the density $\rho(\mathbf{r})$ uniquely determines the external potential $v(\mathbf{r})$ to within a constant, and therefore the external potential operator $\hat{V}$. Since the kinetic $\hat{T}$ and electron-interaction $\hat{U}$ operators of the electrons are assumed known, the Hamiltonian $\hat{H}$ is uniquely determined. The proof is for v-representable densities. It is the proof of bijectivity between $\rho(\mathbf{r})$ and $v(\mathbf{r})$ that establishes the density $\rho(\mathbf{r})$ as the basic variable.

A second basic variable identified in the literature [4] is the density $\rho^e(\mathbf{r})$ of the lowest nondegenerate excited state of a given symmetry for the system defined by the Hamiltonian of Eq. (1). The Gunnarsson-Lundqvist theorem [4,5] also proves, in a manner analogous to the HK theorem, the bijectivity between $\rho^e(\mathbf{r})$ and the external potential $v(\mathbf{r})$. The proof, once again, is for v-representable densities. For such an excited but noninteracting v-representable density $\rho^e(\mathbf{r})$, it has been shown [5] by example that the potential $v(\mathbf{r})$ is unique.

Knowledge of what constitutes a basic variable then lays the foundation to an approach to electronic structure based solely on that property. Thus, for example, knowledge that the ground state density $\rho(\mathbf{r})$ is a basic variable leads to (a) HK density functional theory [3] (DFT) and (b) local effective potential theories such as Kohn-Sham (KS) [6] and quantal [7,8] density functional theories. In these latter theories, one constructs model systems of noninteracting fermions or bosons with the same density as that of the interacting system. This in turn has led to the development of various scaling laws and integral sum rules [9] for the unknown energy functionals of the density of HK and KS DFT.

With the knowledge that the basic variable is the nondegenerate ground state density $\rho(\mathbf{r})$, it is then possible [10] via the constrained-search proof of Percus-Levy-Lieb (PLL) [11] to extend the domain to N-representable densities, while also extending the arguments to include degenerate ground states. This path from the density $\rho(\mathbf{r})$ to the ground state wave function Ψ requires a constrained search over all antisymmetric functions Ψ_ρ that lead to the ground state density $\rho(\mathbf{r})$. The wave function Ψ is that which minimizes the expectation of the operators $\hat{T} + \hat{U}$. [The same remarks are valid for the density $\rho^e(\mathbf{r})$.] We note that the PLL proof is possible [10] only with prior knowledge of the property that constitutes the basic variable. The basic variable in turn

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is determined *solely* by the proof of bijectivity between it and the external potential. The path from the density $\rho(\mathbf{r})$ to Ψ via the proof of bijectivity is thus more fundamental than that of the constrained search. The PLL proof thus has little meaning for arbitrarily chosen properties [12], or those considered basic variables via proofs that ignore the relationship between the external potentials and the ground state wave function Ψ. An attribute of the constrained-search proof is that it is explicitly independent of the external potential. However, there is an implicit dependence on the external potential as knowledge of the density $\rho(\mathbf{r})$ uniquely determines $v(\mathbf{r})$ via HK. In this manner the HK theorem of bijectivity provides a deeper perspective to the proof via the constrained search.

In our recent work [1,2], we have considered the case of the presence of both an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and magnetostatic field $\mathbf{B}(\mathbf{r}) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r})$, with $\mathbf{A}(\mathbf{r})$ the vector potential. The Hamiltonian, when the interaction of the magnetic field is only with the orbital angular momentum, is then

$$\hat{H} = \frac{1}{2}\sum_k \left[\hat{\mathbf{p}}_k + \frac{1}{c}\mathbf{A}(\mathbf{r}_k)\right]^2 + \hat{U} + \hat{V}. \tag{2}$$

This Hamiltonian can be rewritten as

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}_A, \tag{3}$$

where the total external potential operator $\hat{V}_A$ is

$$\hat{V}_A = \hat{V} + \frac{1}{c}\int \hat{\mathbf{j}}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int \hat{\rho}(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}, \tag{4}$$

with $\hat{\mathbf{j}}(\mathbf{r})$ the physical current density operator:

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}), \tag{5}$$

where the paramagnetic $\hat{\mathbf{j}}_p(\mathbf{r})$ and diamagnetic $\hat{\mathbf{j}}_d(\mathbf{r})$ component operators are defined as

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2}\sum_k [\hat{\mathbf{p}}_k \delta(\mathbf{r}_k - \mathbf{r}) + \delta(\mathbf{r}_k - \mathbf{r})\hat{\mathbf{p}}_k(\mathbf{r})], \tag{6}$$

$$\hat{\mathbf{j}}_d(\mathbf{r}) = \hat{\rho}(\mathbf{r})\mathbf{A}(\mathbf{r})/c. \tag{7}$$

The solution Ψ of the corresponding Schrödinger equation $\hat{H}\Psi = E\Psi$ then leads to the energy E which is the expectation of the Hamiltonian $\hat{H}$:

$$E = T + E_{ee} + V_A, \tag{8}$$

where T and E_{ee} are the kinetic and electron-interaction energies being the expectation value of the respective operators, and the total external potential energy V_A is

$$V_A = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}, \tag{9}$$

with $\mathbf{j}(\mathbf{r})$ the physical current density being the expectation of the corresponding operator.

For the system defined by the Hamiltonian of Eq. (2), we have proved [1,2] that the basic variables are the gauge invariant nondegenerate ground state density $\rho(\mathbf{r})$ and the *physical* current density $\mathbf{j}(\mathbf{r})$. We arrived at this conclusion by proving for the nondegenerate ground state a bijective relationship between $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$. Knowledge of the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ then uniquely determines the potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ to within a constant and the gradient of a scalar function. As the energy $\hat{T}$ and electron-interaction $\hat{U}$ operators are known, so is the Hamiltonian $\hat{H}$. The solution Ψ of the Schrödinger equation then leads to *all* the properties of the system. This then constitutes a third example of properties that are basic variables. The proof of bijectivity in this case differs fundamentally from that of the original HK theorem. Whereas, in the HK $[\mathbf{B}(\mathbf{r}) = 0]$ case, the relationship between the external potential $v(\mathbf{r})$ and the wave function Ψ is proven to be *one-to-one*, for the $\mathbf{B}(\mathbf{r}) \neq 0$ case the relationship between the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function Ψ can be *many-to-one* [13] and even *infinite-to-one* [14]. Hence, in this case there is no equivalent of the Map C, and consequently the original proof of HK cannot be extended. Our proof of bijectivity between $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ explicitly accounts for the many-to-one relationship between $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and Ψ.

Previously, Vignale *et al.* [15] have claimed that the basic variables are the ground state density $\rho(\mathbf{r})$ and the gauge variant paramagnetic current density $\mathbf{j}_p(\mathbf{r})$. It is known [13] that $\{\rho(\mathbf{r}),\mathbf{j}_p(\mathbf{r})\}$ cannot uniquely determine the potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$. Thus the arguments for $\{\rho(\mathbf{r}),\mathbf{j}_p(\mathbf{r})\}$ being the basic variables are based on solely a Map D type proof presupposing [1,2,16] the existence of a Map C. However, as noted above, there is no Map C in this case. Hence the many-to-one relationship between $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and Ψ is not accounted for in these arguments. As a significant consequence, knowledge of $\{\rho(\mathbf{r}),\mathbf{j}_p(\mathbf{r})\}$ cannot determine uniquely $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ since $\mathbf{j}(\mathbf{r})$ depends on $\mathbf{A}(\mathbf{r})$ and there could be an infinite number of $\mathbf{A}(\mathbf{r})$. However, a current density functional theory based on treating $\{\rho(\mathbf{r}),\mathbf{j}_p(\mathbf{r})\}$ as the variables has been developed and applied [15–17].

For completeness, we note that the use of $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ as the basic variables was due to Ghosh and Dhara [18] and Diener [19]. The former employ these variables without proving the bijective relationship between $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$. The latter employs a solely Map D type argument, and hence also does not account for the many-to-one relationship between $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and Ψ.

In the present work, we extend the HK theorem further to the case where the Hamiltonian [20] includes the interaction of the magnetic field with both the orbital angular momentum and electron spin. Hence we determine the gauge invariant properties which constitute the basic variables for a *finite* system of N electrons each with spin angular momentum $\mathbf{s}$ in the presence of both an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and magnetostatic field $\mathbf{B}(\mathbf{r}) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r})$. In a manner analogous to, but by a proof which differs from the original HK theorem, we prove that the basic variables are once again the ground state density $\rho(\mathbf{r})$ and the physical current density $\mathbf{j}(\mathbf{r})$. In other words, we prove that for the nondegenerate ground state, there is a bijective relationship between the basic variables $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$. Hence knowledge of $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ uniquely determines the Hamiltonian $\hat{H}$, and thereby via the solution Ψ of the Schrödinger equation, all the properties of the system. With the knowledge that $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ are the basic variables, we (a) construct a $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ functional theory, (b) provide a corresponding PLL constrained-search proof which then reduces the v-representability constraint to one of N-representability while generalizing the proof to degenerate states, and (c) construct a Slater determinant of equidensity orthonormal orbitals which reproduces a given $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$.

We conclude the Introduction by summarizing the order in which the various proofs fit together. The order [10] is the following. (a) The one-to-one relationship between the external potentials and the basic variables must first be derived. This proof establishes what properties constitute the basic variables. As the basic variables, which in the present case are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, uniquely determine the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$, the Hamiltonian is known and thus so are the wave functions for both the ground and excited states. (b) With the knowledge of what the basic variables are, a constrained-search proof extending the domain to N-representable and degenerate ground states can then be constructed. (c) The above, in turn, establishes that there exists a ground state wave function for any $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ pair. The three steps also establish the existence of a practical wave function constrained search. We reiterate that the constrained search [12] over arbitrarily chosen properties is inappropriate.

II. PROOF OF BIJECTIVITY BETWEEN $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ AND $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$

When the interaction of the magnetic field $\mathbf{B}(\mathbf{r})$ with both the orbital and spin angular momentum is considered, the Hamiltonian $\hat{H}$, due originally to Pauli and which can be derived [20] from Schrödinger theory with the correct gyromagnetic ratio of 2 via an appropriate choice of kinetic energy operator for spin $\frac{1}{2}$ particles, is

$$\hat{H} = \frac{1}{2}\sum_k \left[\hat{\mathbf{p}}_k + \frac{1}{c}\mathbf{A}(\mathbf{r}_k)\right]^2 + \hat{U} + \hat{V} + \frac{1}{c}\sum_k \mathbf{B}(\mathbf{r}_k)\cdot\mathbf{s}_k, \tag{10}$$

where $\mathbf{s}_k$ is the electron spin angular momentum operator. For *finite* systems this Hamiltonian may be written as in Eq. (3), but in this case the physical current density operator $\hat{\mathbf{j}}(\mathbf{r})$ is defined as

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}) + \hat{\mathbf{j}}_m(\mathbf{r}), \tag{11}$$

with the magnetization $\hat{\mathbf{j}}_m(\mathbf{r})$ current density operator defined as

$$\hat{\mathbf{j}}_m(\mathbf{r}) = c\nabla\times\hat{\mathbf{m}}(\mathbf{r}), \tag{12}$$

where $\hat{\mathbf{m}}(\mathbf{r}) = -\frac{1}{c}\sum_k \mathbf{s}_k\delta(\mathbf{r}_k-\mathbf{r})$ is the local magnetization density operator. The corresponding Schrödinger equation is $\hat{H}\Psi = E\Psi$ with the expression for the energy being the same as in Eqs. (8) and (9). In this case the relationship between the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function Ψ is also *many-to-one*. This physical fact must, once again, be accounted for in any proof of bijectivity.

Our proof of the bijectivity between $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ is for the system in a nondegenerate ground state. Let us assume there exists another set of external potentials $\{v'(\mathbf{r}),\mathbf{A}'(\mathbf{r})\}$ with Hamiltonian $\hat{H}'$ and ground state wave function $\Psi'(\mathbf{X})$ that also generate the ground state densities $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ as obtained for the Hamiltonian of Eq. (10). We prove this cannot be for the following three possible cases.

A. Case I

In this case the $v'(\mathbf{r})$ differs from $v(\mathbf{r})$ by more than a constant C: $v'(\mathbf{r}) \neq v(\mathbf{r}) + C$, and $\mathbf{A}'(\mathbf{r})$ differs from $\mathbf{A}(\mathbf{r})$ by more than the gradient of a scalar function $\chi(\mathbf{r})$: $\mathbf{A}'(\mathbf{r}) \neq \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$. (The proof is along the lines of our prior work [1,2].) Assume that $\Psi \neq \Psi'$. Then according to the variational principle for the energy

$$E = \langle\Psi|\hat{H}|\Psi\rangle \;<\; \langle\Psi'|\hat{H}|\Psi'\rangle. \tag{13}$$

Now we may write

$$\begin{aligned}\langle\Psi'|\hat{H}|\Psi'\rangle = E' &+ \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r} \\ &+ \frac{1}{c}\int \mathbf{j}(\mathbf{r})\cdot[\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r})]d\mathbf{r} \\ &- \frac{1}{2c^2}\int \rho(\mathbf{r})[\mathbf{A}^2(\mathbf{r}) - \mathbf{A}'^2(\mathbf{r})]d\mathbf{r},\end{aligned} \tag{14}$$

where

$$\begin{aligned}E' = \langle\Psi'|\hat{T} + \hat{U} + \hat{V}' &+ \frac{1}{c}\int \hat{\mathbf{j}}(\mathbf{r})\cdot\mathbf{A}'(\mathbf{r})d\mathbf{r} \\ &- \frac{1}{2c^2}\int \hat{\rho}(\mathbf{r})\mathbf{A}'^2(\mathbf{r})d\mathbf{r}|\Psi'\rangle.\end{aligned} \tag{15}$$

On assuming the inequality obtained by substituting Eq. (14) into Eq. (13) to the inequality obtained by interchanging the primed and unprimed quantities, one obtains the contradiction

$$E + E' < E + E'. \tag{16}$$

Therefore, $\Psi = \Psi'$. This means that the ground state density, and the paramagnetic and magnetization current densities obtained from Ψ and Ψ', are the same:

$$\rho(\mathbf{r})|_\Psi = \rho'(\mathbf{r})|_{\Psi'}, \quad \mathbf{j}_p(\mathbf{r})|_\Psi = \mathbf{j}'_p(\mathbf{r})|_{\Psi'}, \quad \mathbf{j}_m(\mathbf{r})|_\Psi = \mathbf{j}'_m(\mathbf{r})|_{\Psi'}. \tag{17}$$

However, the physical current density as determined from Ψ and Ψ' is not the same:

$$\mathbf{j}(\mathbf{r})|_\Psi \neq \mathbf{j}'(\mathbf{r})|_{\Psi'}. \tag{18}$$

The reason for this is that the physical current density operator $\hat{\mathbf{j}}(\mathbf{r})$ depends upon the vector potential via its diamagnetic component $\hat{\mathbf{j}}_d(\mathbf{r})$, and $\mathbf{A}(\mathbf{r})$ and $\mathbf{A}'(\mathbf{r})$ differ by more than a gauge transformation. This proves that the original assumption that there exists a $\{v'(\mathbf{r}),\mathbf{A}'(\mathbf{r})\}$ that also generates the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ is incorrect. Therefore, there exists only one set of $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ that generate the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. We have therefore proved the bijective relationship

$$\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\} \longleftrightarrow \{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}. \tag{19}$$

B. Case II

We next consider the case when $v'(\mathbf{r}) = v(\mathbf{r})$ but $\mathbf{A}'(\mathbf{r}) \neq \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$. The proof of the bijectivity of Eq. (19) in this instance is the same as that of Case I with the exception that the second term on the right-hand side of Eq. (14) is absent.

C. Case III

Here we consider $v'(\mathbf{r}) \neq v(\mathbf{r}) + C$ but $\mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$. By absorbing the gauge function $\chi(\mathbf{r})$ into the phase of the wave function $\Psi'(\mathbf{X})$ we have that $\mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r})$. Therefore, the expression for the physical kinetic energy operator $\hat{T}_A = \frac{1}{2}\sum_k(\hat{p}_k + \frac{\mathbf{A}(\mathbf{r}_k)}{c})^2$ is the same in the Hamiltonian $\hat{H}$ and $\hat{H}'$. The two Hamiltonians differ only in their external potential operators $\hat{V}$ and $\hat{V}'$. This is akin to the original HK [3] situation $[\mathbf{B}(\mathbf{r}) = 0]$ where the kinetic $\hat{T}$ and electron-interaction $\hat{U}$ operators are assumed known and it is proved that $\rho(\mathbf{r}) \neq \rho'(\mathbf{r})$ (Map D) so that $\rho(\mathbf{r})$ uniquely determines $v(\mathbf{r})$ to within a constant C. In the present case with $\hat{T}_A$ and $\hat{U}$ known, the original HK proof can be employed to show that $\rho(\mathbf{r}) \neq \rho'(\mathbf{r})$. This is in contradiction to the original assumption that there exists a second set of external potentials that generate the same density $\rho(\mathbf{r})$. Thus the bijectivity of Eq. (19) is once again proved.

Knowledge of the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ then uniquely determines the Hamiltonian $\hat{H}$ with the scalar potential determined to within a constant and the vector potential to within the gradient of a scalar function. The solution Ψ of the Schrödinger equation then determines all the properties of the system. Therefore, the basic variables in the presence of a magnetostatic field when its interaction with both the orbital and spin angular momentum are considered are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. Thus the wave function $\Psi(\mathbf{X})$ is a functional of the gauge invariant properties $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. By performing a density and physical current density preserving unitary or gauge transformation, it is seen that the wave function must also be a functional of a gauge function $\alpha(\mathbf{R})$. It is the presence of the gauge function $\alpha(\mathbf{R})$ that ensures the wave function when written as a functional $\Psi[\rho(\mathbf{r}),\mathbf{j}(\mathbf{r}),\alpha(\mathbf{R})]$ is gauge variant. As the physical system remains unchanged in a unitary transformation, the choice of gauge function is arbitrary, and one may choose $\alpha(\mathbf{R}) = 0$.

For completeness, we note that in the literature [21–23] it is thought that the basic variables for the Hamiltonian of Eq. (10) are the ground state density $\rho(\mathbf{r})$, the magnetization density $\mathbf{m}(\mathbf{r})$, and the gauge variant paramagnetic current density $\mathbf{j}_p(\mathbf{r})$. Once again, there is no proof of any bijective relationship between these properties and the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$. In spin density functional theory [13] (SDFT), the Hamiltonian of the corresponding interacting system does not include the interaction of the magnetic field with the orbital angular momentum. It includes only the interaction of the magnetic field with the electron spin. In SDFT the basic variables are thought to be the ground state density $\rho(\mathbf{r})$ and the magnetization density $\mathbf{m}(\mathbf{r})$. However, no proof exists of the bijectivity between these properties and the external potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ because the relationship between the potentials $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ and Ψ is many-to-one. Hence there exists a solely Map D type proof [13], as well as a constrained-search proof [24,25] following the assumption that $\{\rho(\mathbf{r}),\mathbf{m}(\mathbf{r})\}$ are the basic variables. Again, based on the assumption that the basic variables are $\{\rho(\mathbf{r}),\mathbf{m}(\mathbf{r})\}$, there also exists a "potential functional" theory [26] as well as a Legendre transform approach [27] to SDFT. We address SDFT in a future publication.

III. DENSITY AND PHYSICAL CURRENT DENSITY FUNCTIONAL THEORY

We next construct a $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ functional theory. The ground state energy written as a functional is

$$E[N,v,\mathbf{A}] = E[\rho,\mathbf{j}] = \langle\Psi[\rho,\mathbf{j}]|\hat{H}|\Psi[\rho,\mathbf{j}]\rangle = F[\rho,\mathbf{j}] + \int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int\mathbf{j}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int\rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}, \quad (20)$$

where the universal internal energy functional $F[\rho,\mathbf{j}] = \langle\Psi[\rho,\mathbf{j}]|\hat{T} + \hat{U}|\Psi[\rho,\mathbf{j}]\rangle$. From the variational principle for the energy

$$E[\rho',\mathbf{j}'] > E[\rho,\mathbf{j}] \text{ for } \{\rho',\mathbf{j}'\} \neq \{\rho,\mathbf{j}\}, \quad (21)$$

$$E[\rho',\mathbf{j}'] = E[\rho,\mathbf{j}] \text{ for } \{\rho',\mathbf{j}'\} = \{\rho,\mathbf{j}\}. \quad (22)$$

The Euler equations for $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ are

$$\left.\frac{\delta E[\rho,\mathbf{j}]}{\delta\rho(\mathbf{r})}\right|_{\mathbf{j}(\mathbf{r})} = 0, \quad \left.\frac{\delta E[\rho,\mathbf{j}]}{\delta\mathbf{j}(\mathbf{r})}\right|_{\rho(\mathbf{r})} = 0, \quad (23)$$

and these must be solved self-consistently with the constraints

$$\int\rho(\mathbf{r})d\mathbf{r} = N, \quad \nabla\cdot\mathbf{j}(\mathbf{r}) = 0. \quad (24)$$

The variations of $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ are $\{v,\mathbf{A}\}$-representable.

Note that the equations for this $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ functional theory reduce to those where the interaction of the magnetic field with the electron spin is ignored [1,2]. The latter set of equations in turn reduce to HK DFT in the absence of a magnetic field.

IV. PERCUS-LEVY-LIEB CONSTRAINED-SEARCH PROOF

Having established that the basic variables are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, it is then [10] possible to construct the Percus-Levy-Lieb [11] (PLL) constrained-search path from knowledge of the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ to the ground state wave function Ψ and thereby to the Hamiltonian $\hat{H}$. Suppose there exist antisymmetric functions $\Psi_{\rho,\mathbf{j}}$ that all lead to the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. Then, from the variational principle

$$\langle\Psi_{\rho,\mathbf{j}}|\hat{H}|\Psi_{\rho,\mathbf{j}}\rangle \geqslant \langle\Psi|\hat{H}|\Psi\rangle = E. \quad (25)$$

On employing the expression of Eq. (8) for the energy, Eq. (25) for the known $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and therefore (via the bijectivity) *fixed* $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ reduces to

$$\langle\Psi_{\rho,\mathbf{j}}|\hat{T} + \hat{U}|\Psi_{\rho,\mathbf{j}}\rangle \geqslant \langle\Psi|\hat{T} + \hat{U}|\Psi\rangle\ . \quad (26)$$

Thus, for fixed $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$, of all antisymmetric functions $\Psi_{\rho,\mathbf{j}}$ that give rise to $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, the true wave function Ψ is that which minimizes the expectation value of the operators $\hat{T} + \hat{U}$. (The $\Psi_{\rho,\mathbf{j}}$ give rise to rigorous upper bounds to the ground state energy.) Since Ψ cannot be an eigenfunction of more than one $\hat{H}$ with a multiplicative scalar potential and vector potential, it follows that $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ once again determine $\hat{H}$ to within an additive constant and the gradient of a scalar function. The PLL path from $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ to the Hamiltonian $\hat{H}$ is then

$$\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\} \longrightarrow \Psi \longrightarrow \hat{H}. \tag{27}$$

Suppose next that there exist different Ψ that satisfy the constrained-search minimization of Eq. (26). Then each of these minimizing functions must give the same expectation value of $\hat{H}$ or equivalently the same ground state energy. Thus, each Ψ is a degenerate wave function of $\hat{H}$, and each corresponding $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ will determine $\hat{H}$ uniquely. The constrained-search proof is thus extendable to degenerate states.

The right-hand side of Eq. (26) is the universal functional $F[\rho,\mathbf{j}]$ which was originally defined for $\{v,\mathbf{A}\}$-representable $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. The constrained-search path shows that the functional $F[\rho,\mathbf{j}]$ is in fact defined for N-representable $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. The functional is also valid for degenerate states. Hence the functional $F[\rho,\mathbf{j}]$ may be defined as

$$F[\rho,\mathbf{j}] = \min_{\Psi_{\rho,j}\to\rho,\mathbf{j}} \langle \Psi_{\rho,\mathbf{j}}|\hat{T}+\hat{U}|\Psi_{\rho,\mathbf{j}}\rangle. \tag{28}$$

Searching over all N-representable $\Psi_{\rho,\mathbf{j}}$ that lead to the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, the functional $F[\rho,\mathbf{j}]$ delivers the minimum of the expectation value $\langle \hat{T}+\hat{U}\rangle$.

Employing the definition of the functional $F[\rho,\mathbf{j}]$ of Eq. (28), it follows that the energy functional $E[\rho,\mathbf{j}]$ of Eq. (20) assumes its minimum for the ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. From the variational principle, the ground state energy

$$E = \min_{\Psi}\langle \Psi|\hat{H}|\Psi\rangle, \tag{29}$$

where the search is over all N-particle antisymmetric functions. This search can be constrained and broken into two consecutive minima:

$$E = \min_{\rho,\mathbf{j}}\Big\{\min_{\Psi_{\rho,j}\to\rho,\mathbf{j}}\langle\Psi_{\rho,\mathbf{j}}|\hat{H}|\Psi_{\rho,\mathbf{j}}\rangle\Big\}, \tag{30}$$

$$= \min_{\rho,\mathbf{j}}\Big\{\min_{\Psi_{\rho,j}\to\rho,\mathbf{j}}\langle\Psi_{\rho,\mathbf{j}}|\hat{T}+\hat{U}+\int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int\hat{\mathbf{j}}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int\hat{\rho}(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}|\Psi\rangle\Big\}, \tag{31}$$

$$= \min_{\rho,\mathbf{j}}\Big\{F[\rho,\mathbf{j}] + \int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int\mathbf{j}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int\rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}\Big\}, \tag{32}$$

$$= \min_{\rho,\mathbf{j}} E[\rho,\mathbf{j}]. \tag{33}$$

The inner minimization is constrained to all antisymmetric $\Psi_{\rho,\mathbf{j}}$ that lead to well-behaved $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, whereas the outer minimization is a search over all $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. In these searches, the $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$ remain fixed. This proves that the ground state energy may be obtained from the functional $E[\rho,\mathbf{j}]$ by searching over all N-representable $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$.

V. CONSTRUCTION OF SLATER DETERMINANT TO REPRODUCE A GIVEN $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$

In this section we construct equidensity orthonormal orbitals $\phi_k(\mathbf{r})$ whose Slater determinant reproduces a given ground state $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, and where the current density $\mathbf{j}(\mathbf{r})$ is the sum of its paramagnetic $\mathbf{j}_p(\mathbf{r})$, diamagnetic $\mathbf{j}_d(\mathbf{r})$, and magnetization $\mathbf{j}_m(\mathbf{r})$ components. This is in the spirit of the Harriman [28] construction. As knowledge of $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ uniquely determines $\{v,\mathbf{A}\}$, the diamagnetic $\mathbf{j}_d(\mathbf{r})$ current density component is known. The magnetization current density $\mathbf{j}_m(\mathbf{r})$ arises from the $(1/c)\sum_k \mathbf{B}(\mathbf{r}_k)\cdot\mathbf{s}_k$ term of the Hamiltonian Eq. (10). Since, $\mathbf{A}(\mathbf{r})$ is known, so is the field $\mathbf{B}(\mathbf{r})$ and therefore $\mathbf{j}_m(\mathbf{r})$ is known. Another way to arrive at this conclusion is the following. If the orbitals $\phi_k(\mathbf{r})$ are constructed such that they reproduce the paramagnetic $\mathbf{j}_p(\mathbf{r})$ component, then knowledge of $\mathbf{j}(\mathbf{r})$,$\mathbf{j}_p(\mathbf{r})$, and $\mathbf{j}_d(\mathbf{r})$ uniquely determines $\mathbf{j}_m(\mathbf{r})$.

Following Ghosh and Dhara [29] the orthonormal orbitals $\phi_k(\mathbf{r})$ that reproduce the density $\rho(\mathbf{r})$ and the paramagnetic current density $\mathbf{j}_p(\mathbf{r})$ are

$$\phi_k(\mathbf{r}) = \sqrt{\rho_1(\mathbf{r})}e^{iQ(\mathbf{r})}, \tag{34}$$

where the density normalized to unity is

$$\rho_1(\mathbf{r}) = \rho(\mathbf{r})/N, \tag{35}$$

and where

$$Q(\mathbf{r}) = 2\pi\left(k-\frac{M}{N}\right)q(\mathbf{r}) + s(\mathbf{r}), \tag{36}$$

$$q(\mathbf{r}) = \int^{\mathbf{r}}\rho_1(\mathbf{r}')d\mathbf{r}', \tag{37}$$

$$s(\mathbf{r}) = \int^{\mathbf{r}}\frac{\mathbf{j}_p(\mathbf{r}')}{\rho(\mathbf{r}')}d\mathbf{r}', \tag{38}$$

with

$$\sum_k k = M. \tag{39}$$

Then

$$\sum_k \mathbf{j}_{p,k}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}), \tag{40}$$

where $\mathbf{j}_{p,k}(\mathbf{r}) = \langle\phi_k|\hat{\mathbf{j}}_p(\mathbf{r})|\phi_k\rangle$. The orthonormality condition is

$$\int\phi_k^\star(\mathbf{r})\phi_k(\mathbf{r})d\mathbf{r} = \delta_{kk'} \tag{41}$$

for $k-k'$ differing by integers so that the allowed values of $k=0,\pm 1,\pm 2$, etc. or $k=\pm\frac{1}{2},\pm\frac{3}{2}$, etc. For a discussion of the optimum value of k for a given N that minimizes the kinetic energy, see [30].

Again, with the knowledge that the basic variables are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, wave functions that reproduce these properties may also be determined via the extended constrained-search method [12], or its equivalent formulation [12] in terms of Lieb's Legendre transformation functional.

VI. CONCLUDING REMARKS

The significance of the Hohenberg-Kohn theorem lies in the proof of bijectivity between the nondegenerate ground state density $\rho(\mathbf{r})$, the basic variable, and the external scalar potential $v(\mathbf{r})$. In the present work, we have generalized the HK theorem for finite systems to include electron spin and the interaction of an external magnetostatic field with both the orbital and spin angular momentum. We have proved a bijective relationship between the nondegenerate ground state densities $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and the potentials $\{v,\mathbf{A}\}$. Thus the basic variables for a quantum mechanical system described by the Hamiltonian of Eq. (10) are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$. Here the physical current density $\mathbf{j}(\mathbf{r})$ is the sum of its paramagnetic $\mathbf{j}_p(\mathbf{r})$, diamagnetic $\mathbf{j}_d(\mathbf{r})$, and magnetization $\mathbf{j}_m(\mathbf{r})$ current density components. Our proof explicitly accounts for the possible many-to-one relationship between the potentials $\{v,\mathbf{A}\}$ and the ground state wave function Ψ. As a consequence of the knowledge that the basic variables are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, and explicitly employing the bijectivity between the $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ and $\{v(\mathbf{r}),\mathbf{A}(\mathbf{r})\}$, the generalization to degenerate states and N-representable densities follows via a Percus-Levy-Lieb constrained-search proof. A $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$-functional theory is developed. Finally, a Slater determinant of equidensity orbitals that reproduce a given $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ is constructed.

Knowledge of what properties constitute the basic variables together with the assumption of noninteracting v representability then allows for the construction of model systems of noninteracting fermions or bosons that reproduce these basic variables. Such a unique mapping from the interacting to a model noninteracting particle system is possible only for the correct basic variables. In prior work [31], in which the interaction of the magnetic field with only the orbital angular momentum was considered [1,2] and for which case the basic variables are also $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, we have demonstrated such a mapping via quantal density functional theory (QDFT). There we mapped a ground state of the Hooke's atom in a magnetic field [14] to one of noninteracting fermions also in their ground state reproducing the same $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$.

Having proved that the basic variables are $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$, we are in the process of deriving the corresponding equations of QDFT when the interaction of the magnetic field with both the orbital and spin angular momentum as described by the Hamiltonian of Eq. (10) is considered. Additionally, we are also investigating the construction and application of approximate energy functionals of the variables $\{\rho(\mathbf{r}),\mathbf{j}(\mathbf{r})\}$ to be employed in a KS version of the model system of noninteracting fermions. We note that such functionals do exist in the literature [18].

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