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Reformulation of Density Functional Theory for N -Representable Densities and the Resolution of the ν -Representability Problem

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Abstract

Density functional theory for the case of general, N -representable densities is reformulated in terms of density functional derivatives of expectation values of operators evaluated with wave functions leading to a density, making no reference to the concept of potential. The developments provide a complete solution of the ν -representability problem by establishing a mathematical procedure that determines whether a density is ν -representable and in the case of an affirmative answer determines the potential (within an additive constant) as a derivative with respect to the density of a constrained search functional. It also establishes the existence of an energy functional of the density that, for ν -representable densities, assumes its minimum value at the density describing the ground state of an interacting many-particle system. The theorems of Hohenberg and Kohn emerge as special cases of the formalism.

Keywords: A. ν -representability, B. density functional theory, C. functional derivative, D. constrained search

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1. Introduction

The theorems of Hohenberg and Kohn [1–3] ushered in density functional theory (DFT), a paradigm in quantum mechanics geared towards the solution of the electronic structure problem defined, for our purposes, as the determination of the quantum states of an interacting system of N -electrons in condensed matter. The theorems are developed with respect to the static ground state of an interacting system. The First Theorem shows that the density determines the potential, $v(\mathbf{r})$, acting on an interacting N -particle system as a unique (within an additive constant) functional of the density. The Second Theorem establishes the existence of an energy functional of the density,

$$E_\nu[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \langle \Psi_{\text{GS}} | \hat{T}^N + \hat{U}^N | \Psi_{\text{GS}} \rangle, \quad (1)$$

where $\Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Psi_{\text{GS}}(\mathbf{r}_{(N)})$ is the wave function of the ground state of an interacting N -particle system evolving under the action of an external potential, $v(\mathbf{r})$. The operators, \hat{T}^N and \hat{U}^N , denote, respectively, the kinetic energy and inter-particle interaction of the interacting system. We consider a function of coordinates to be a *density* if it's everywhere non-negative, normalized to an integer, N , and satisfies the so-called kinetic energy condition,

$$\int [\nabla_{\mathbf{r}} \sqrt{n(\mathbf{r})}]^2 d\mathbf{r} < \infty. \quad (2)$$

The minimum value of $E_\nu[n]$ occurs at the exact density of the ground state of an interacting system where it equals the energy of the system's ground state.

The expectation value,

$$\langle \Psi_{\text{GS}} | \hat{T}^N + \hat{U}^N | \Psi_{\text{GS}} \rangle = F_{\text{HK}}[n], \quad (3)$$

is the Hohenberg and Kohn functional that is determined through knowledge of the density alone being independent of the potential, and is hence referred to as a universal functional of the density.

By construction, the theorems are applicable to densities that are pure-state ν -representable, i.e., are derived from the solution of a Schrödinger equation corresponding to a given potential (other forms of ν -representability, such as ensemble ν -representability can be defined but not considered here). We confine the discussion to pure-state ν -representability and refer to the condition simply as ν -rep. As is well known [2, 4], however, the ν -rep condition introduces a serious difficulty in the theory, known as the ν -representability problem. Namely, given an arbitrary density the present form of the theory provides no mathematical procedure that can determine whether or not it is ν -rep.

The main difficulty presented by $F_{\text{HK}}[n]$ springs from the fact that the set of ν -rep densities is unknown, (given a density it cannot be ascertained as to whether or not it is ν -rep), and consequently, $F_{\text{HK}}[n]$ is ill-defined [5] (the basic formulation of the ν -rep problem). An additional difficulty arises because the set of ν -rep densities is not differentially dense, i.e, there exist densities that do not come from a potential [6–10] of an interacting

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(or non-interacting) system. If one ignored these difficulties, the potential would be obtained from the relation,

$$\frac{\delta F_{\text{HK}}[n]}{\delta n(\mathbf{r})} = -v(\mathbf{r}), \quad (4)$$

modulo an arbitrary constant (that leaves the density unchanged). This relation is generally accepted as to arise from the minimum property of the energy functional, Eq. (1), at the density of the ground state of the system (characterized by $v(\mathbf{r})$).

In the conventional interpretation of functional differentiation, the functional derivative, $\frac{\delta F_{\text{HK}}[n]}{\delta n(\mathbf{r})}$, defined through the procedure [2] (where the test function, $\phi(\mathbf{r})$, is arbitrary),

$$\begin{aligned} & \lim_{\epsilon \rightarrow 0} \frac{F_{\text{HK}}[n + \epsilon\phi(\mathbf{r})] - F_{\text{HK}}[n]}{\epsilon} \\ &= \int \frac{\delta F_{\text{HK}}[n]}{\delta n(\mathbf{r})} \phi(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (5)$$

at a given density hinges on the evaluation of the Hohenberg and Kohn functional, $F_{\text{HK}}[n + \delta n]$, at densities that differ infinitesimally from $n(\mathbf{r})$. This requires that the density, $n(\mathbf{r}) + \delta n(\mathbf{r})$, be v -rep, a serious difficulty since the set of v -rep densities is not known, as well as requiring the existence of a small dense neighborhood around the density in which the densities are v -rep. Assuming such a neighborhood for any density, it can be readily shown that *all* densities are v -rep in contradiction to known facts to the contrary [2, 6, 7]. (A direct proof of the impossibility of differentiating over the domain of v -rep densities is given near the end of this paper.)

An additional problem exists in the performance of functional differentiation. Conventional functional differentiation requires that the domain of the functional, say the set of densities, $\{n(\mathbf{r})\}$, with a given normalization, N , contains all variations of the form, $n(\mathbf{r}) \rightarrow n(\mathbf{r}) + \epsilon\phi(\mathbf{r})$, where $\phi(\mathbf{r})$ is arbitrary (within common caveats of smoothness and integrability), and $\epsilon \rightarrow 0$. It is certainly not true that the set of v -representable densities possess this property. Unfortunately, neither does the set of *all* densities as arbitrary variations may break the requirement of integral normalization.

At least two more difficulties must be mentioned in attempting the performance of the derivative: First, $F_{\text{HK}}[n]$ is defined in terms of an expectation value with respect to the wave function of a pure state (possibly the solution of a Schrödinger equation) and hence with respect to densities with integral normalization, a condition that may fail in the mathematical process of functional differentiation that is based on the use [2] of an arbitrary test function, $\phi(\mathbf{r})$, (such that $\delta n(\mathbf{r}) = \epsilon\phi(\mathbf{r})$, with $\epsilon \rightarrow 0$). Second, the perceived need to obtain the potential through the functional derivative in (5) requires the knowledge of the value of $F_{\text{HK}}[n]$ at densities other than the one in question, and thus stands in contradiction to the First Theorem [1] specifying that the potential is given through knowledge of the density alone. The requirement that the test function be arbitrary causes further difficulties. A density must be non-negative but for arbitrary functions $\phi(\mathbf{r})$ it is possible that $n(\mathbf{r}) + \epsilon\phi(\mathbf{r}) < 0$. Guarding against the appearance of a negative density compromises the arbitrariness requirement on the test function.

A formal solution to the v -representability problem has been sought in terms of potential functional theory [4]. Here, for N -particle systems, one introduces functionals of potential, $E_{N,v}[w] = E_{N,v}^{\text{HK}}[n[w]]$, where $E_{N,v}^{\text{HK}}[n[w]]$ is the Hohenberg and Kohn energy functional for $v(\mathbf{r})$, usually denoted by the symbol, $E_v[n]$, evaluated at the v -rep density, $n(\mathbf{r})$, corresponding to potential, $w(\mathbf{r})$. The stationary points (minima) of $E_{N,v}[w]$ occur at the potentials, $w(\mathbf{r}) = v(\mathbf{r}) + c$, associated with the minima of the Hohenberg and Kohn functional at the v -representable densities corresponding to $v(\mathbf{r})$. The optimized effective potential (OEP) method [11–15] requires this theory as its mathematical justification. Potential functional theory relies on the concept that functionals of potential define a space that is the dual of that of density functional theory. For such a concept to be valid one must have some way of excluding densities that are not v -representable from the space of the densities.

The introduction of the concept of N -representability [2, 7, 16], referred to as N -rep, namely that all densities can be obtained from antisymmetric, N -particle wave functions, established the rigorous foundation of a functional that, when the density is v -representable, leads to $F_{\text{HK}}[n]$. In other words, the set of v -representable densities is a subset of all densities, each of which leads to a well-defined functional, $F[n]$. Hence, the set $F_{\text{HK}}[n]$ is a subset of functionals each of which is well defined, so that the subset is well-defined. N -representability and the constrained search establish existence but provide no means of determination, identification or construction of $F_{\text{HK}}[n]$. Neither does N -representability resolve the difficulties with respect to normalization in the performance of functional differentiation.

The v -representability problem would be convincingly solved through the development of a rigorous mathematical procedure that could determine whether or not the density is v -representable. For this to materialize, density functional theory must be formulated entirely based on the density, without reference to a potential. This paper provides such a formulation.

The remainder of the paper takes the following form. The generalization of the Hohenberg and Kohn theorems to general, N -representable densities is presented in the following section. Then, we show how the density and corresponding wave function can be determined given the derivative with respect to the density of a functional of the density determined as the minimum expectation value of the sum of the kinetic and interparticle potential operators. A discussion of the formal developments in the paper is given in the final section.

2. Hohenberg and Kohn Theorems for N -representable Densities

The main result of the paper is a generalization of the Hohenberg and Kohn theorems in terms of general densities without the condition that they are derived from a potential. The generalization is based on the concept of *parametric differentiation* leading to the determination of *rates of change* [17] with respect to the density of expectation values of operators in terms of wave functions that lead to a density. Now, the arbitrary test

function of conventional functional differentiation is replaced by a Dirac delta function leading to the definition,

$$\frac{\delta F[n]}{\delta n(\mathbf{r}')} = \lim_{\epsilon \rightarrow 0} \frac{F[n(\mathbf{r}) + \epsilon \delta(\mathbf{r} - \mathbf{r}')] - F[n(\mathbf{r})]}{\epsilon} \quad (6)$$

The Dirac delta function is not a proper function. Therefore $n(\mathbf{r}) + \epsilon \delta(\mathbf{r} - \mathbf{r}')$ does not represent a proper charge density that yields an energy expectation value. Instead, it provides a method of parametric differentiation of any functional of densities through the properties of the delta function using the density n only (and the associated wave functions, if appropriate) [17]. This procedure bypasses the difficulties with conventional functional derivatives when applied to functionals of the density, and allows derivatives with respect to the density of any wave function that leads to the density, and any expectation value of operators with respect to such wave functions. Parametric differentiation, in turn, can be justified based on the work of Cioslowski [18–20], showing that every antisymmetric wave function that leads to a density possesses well-defined and unique derivatives *at the density* obtained through the parametric differentiation with respect to the density of *all* wave functions that lead to the density. The general expression of the explicit form of that derivative is given in Cioslowski [18–20] (for a summary, see the appendix).

Let $\hat{O} = \hat{T}^N + \hat{U}^N$, and denote the *parametric* derivative with respect to the density of the expectation value, $\langle \Psi | \hat{T}^N + \hat{U}^N | \Psi \rangle$, with the symbol, $-q_\Psi(\mathbf{r})$,

$$\frac{\delta \langle \Psi | \hat{T}^N + \hat{U}^N | \Psi \rangle}{\delta n(\mathbf{r})} = -q_\Psi(\mathbf{r}). \quad (7)$$

Conventionally, a constant, c , is added to $q_\Psi(\mathbf{r})$ to indicate the fact that for ν -rep densities, the density remains unaffected by a uniform change in the potential. This constant is suppressed in subsequent discussion.

Cioslowski [18] has shown how to construct the set of all antisymmetric, N -particle wave functions that lead to a density. Corresponding to each such wave function, construct the quantity,

$$E_\Psi = \int q_\Psi(\mathbf{r})n(\mathbf{r})d(\mathbf{r}) + \langle \Psi | \hat{T}^N + \hat{U}^N | \Psi \rangle, \quad (8)$$

and, confining derivatives only to first order with respect to the density, note the identity,

$$\frac{\delta E_\Psi}{\delta n(\mathbf{r})} = 0. \quad (9)$$

Now, among all E_Ψ choose the lowest in value.

In the absence of degeneracy (assumed throughout), the quantity, E_Ψ , is a minimum if and only if for any wave function, $\Psi' \neq \Psi$, that leads to the density, we have,

$$\langle \Psi' | q_\Psi + \hat{T}^N + \hat{U}^N | \Psi' \rangle > E_\Psi. \quad (10)$$

The existence of a minimum follows from the assumption that the search over the wave functions leading to a density is exhaustive, and that the derivative of any wave function with respect to the density is well-defined [19, 20].

We now prove the Generalized First Theorem of Hohenberg and Kohn: *The parametric derivative, $q_\Psi(\mathbf{r})$, leading to the minimum value of $E_\Psi[n]$ is a unique (within an arbitrary additive constant) functional of the density.*

In other words, for a given density, there exists only a single minimum among the E_Ψ that determines the parametric derivative, $q_\Psi(\mathbf{r})$, uniquely within an additive constant.

Consider the functional, $\{E_\Psi\}[n]$, consisting of the set of all E_Ψ obtained for a given density, $n(\mathbf{r})$, and consider the minimum value of the set. We show that the minimum leads to a parametric derivative that is a unique (within an additive constant) functional of the density. A schematic representation of this form of the theorem is shown in Fig. 1.

Proof: Consider two antisymmetric wave functions, Ψ and Ψ' , both leading to $n(\mathbf{r})$ and to the same minimum value of the functional in (8), but with $q_\Psi(\mathbf{r}) \neq q_{\Psi'}(\mathbf{r}) + c$. Because the parametric derivative of the quantity, $\int q_\Psi(\mathbf{r})n(\mathbf{r})d(\mathbf{r}) + \langle \Psi' | \hat{T}^N + \hat{U}^N | \Psi' \rangle$, with respect to $n(\mathbf{r})$ is non-zero, we have the inequality,

$$\begin{aligned} E_\Psi[n] &< \langle \Psi' | q_\Psi(\mathbf{r}) + \hat{T}^N + \hat{U}^N | \Psi' \rangle \\ &= \langle \Psi' | q_{\Psi'}(\mathbf{r}) + \hat{T}^N + \hat{U}^N | \Psi' \rangle \\ &+ \int [q_\Psi(\mathbf{r}) - q_{\Psi'}(\mathbf{r})]n(\mathbf{r})d\mathbf{r} \\ &= E_{\Psi'}[n] + \int [q_\Psi(\mathbf{r}) - q_{\Psi'}(\mathbf{r})]n(\mathbf{r})d\mathbf{r}, \end{aligned} \quad (11)$$

since $E_\Psi[n] = E_{\Psi'}[n]$. Interchanging the roles of the primed and unprimed wave functions, and adding the corresponding expressions, we obtain the contradiction (*reductio ad absurdum*),

$$E_\Psi[n] + E_{\Psi'}[n] < E_\Psi[n] + E_{\Psi'}[n]. \quad (12)$$

It follows that there cannot be two different parametric derivatives, $q_\Psi(\mathbf{r})$, leading to the same minimum value of the expression in (8), so that $q_\Psi(\mathbf{r})$ is a unique functional of the density. As above we can write the functional in (8) in the form, $E_{q[n]}[n]$. For ν -representable densities, this notation corresponds to the conventional one, $E_\nu[n]$.

Clearly, in order to interpret this result in terms of the uniqueness of the potential associated with a ground-state density, one must first provide proof [21] that two potentials that differ by more than a constant, $v'(\mathbf{r}) \neq v(\mathbf{r}) + c$, cannot lead to the same ground-state density, $n'(\mathbf{r}) \neq n(\mathbf{r})$.

For ν -representable densities, the results just established prove that the density of the ground state of a potential determines uniquely the potential (within an additive constant) thus regaining the first of the theorems of Hohenberg and Kohn. However, the theorem emerges as a special case for ν -rep densities of the general result that a density determines uniquely (within an arbitrary constant) the parametric derivative of a functional that is uniquely defined by the density.

Generalized Second Theorem: The functional $E_{q[n]}[n]$ assumes its minimum value for the density that leads to $q[n](\mathbf{r})$ where, $\frac{\delta E_{q[n]}[n]}{\delta n(\mathbf{r})} = 0$.

Proof: Let there be two wave functions, $\Psi(\mathbf{r}_{(N)}) \rightarrow n(\mathbf{r})$ and $\Psi'(\mathbf{r}_{(N)}) \rightarrow n'(\mathbf{r})$, leading to $q_\Psi(\mathbf{r}) \neq q_{\Psi'}(\mathbf{r}) + c$ such that the

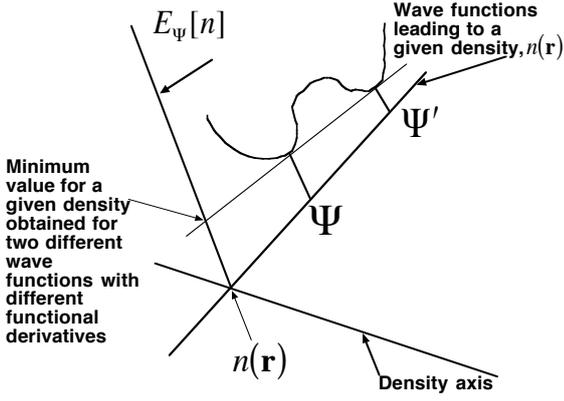


Figure 1: Two wave functions leading to the same density and minimizing $E_{\Psi}[n]$, as discussed in the text.

parametric derivatives of $E_{q[n]}[n]$ and $E_{q[n']}[n']$ at their respective arguments vanish identically. We have,

$$\begin{aligned} E_{q[n]}[n'] &= \langle \Psi' | q_{\Psi} + \hat{T}^N + \hat{U}^N | \Psi' \rangle \\ &= \int q_{\Psi}(\mathbf{r}) n'(\mathbf{r}) d\mathbf{r} + \langle \Psi' | \hat{T}^N + \hat{U}^N | \Psi' \rangle, \end{aligned} \quad (13)$$

so that,

$$\begin{aligned} \frac{\delta E_{q[n]}[n']}{\delta n'(\mathbf{r})} &= q_{\Psi}(\mathbf{r}) + \frac{\delta \langle \Psi' | \hat{T}^N + \hat{U}^N | \Psi' \rangle}{\delta n'(\mathbf{r})} \\ &= q_{\Psi}(\mathbf{r}) - q_{\Psi'}(\mathbf{r}) \neq 0. \end{aligned} \quad (14)$$

Noting that the non-vanishing of the derivative at a point indicates that the functional at that point is above its minimum completes the proof.

3. Summary of Density Functional Theory for Ground States

As emerges from this work, density functional theory is a self-contained body of formalism that allows the determination of a wave function corresponding to an observable, the density of a many-particle interacting system's ground state. The methodology accomplishes this task while avoiding the treatment of the corresponding Schrödinger equation. This direct connection, from classical reality to quantum states describing the outcome of measurement, completes the program of quantum mechanics a discipline whose fundamental purpose is the determination of states revealed by and explaining the results of measurement.

The independent variable of the theory is the density and its workhorse is the constrained search. Thus, given a density normalized to N , the theory prescribes the following sequence of formal steps:

1. Generate the set of all antisymmetric, N -particle wave functions that lead to the density.

2. Form the expectation value of the operator, $\hat{T}^N + \hat{U}^N$, with respect to these wave functions.

3. Identify the wave function, $\Psi_0(\mathbf{r}_{(N)})$, that gives the lowest expectation value,

$$F[n] = \langle \Psi_0 | \hat{T}^N + \hat{U}^N | \Psi_0 \rangle. \quad (15)$$

4. Determine the derivative,

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} = -q(\mathbf{r}), \quad (16)$$

5. and construct the Hamiltonian-like expression,

$$\hat{H}^{\text{trial}} = - \sum_{i=1}^N \frac{1}{2} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^N q(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} U(\mathbf{r}_i, \mathbf{r}_j). \quad (17)$$

6. Act on $\Psi_0(\mathbf{r}_{(N)})$ by \hat{H}^{trial} and check the satisfaction of the equality,

$$\hat{H}^{\text{trial}} \Psi_0(\mathbf{r}_{(N)}) = \alpha \Psi_0(\mathbf{r}_{(N)}), \quad (18)$$

for some real α .

7. If the equality fails, the density can be discarded as unphysical, at least with respect to the ground state of a physical system. If it is satisfied, then $q(\mathbf{r})$ is a potential, \hat{H}^{trial} is the corresponding many-particle Hamiltonian, and α is the eigenvalue of the Hamiltonian's ground state.

Steps 1. to 7. constitute a rigorous mathematical procedure that can decide whether or not a density is v -representable thus providing a rigorous solution to the v -representability problem.

It is seen that the density determines *all* properties of the system that may be represented by the density, including the properties of the density itself, in particular whether or not the density is pure ground-state v -representable.

The present formulation allows the definition of density functional theory as a body of work in mathematical physics that leads to a solution of the Schrödinger equation for an interacting, many-particle system (that for a ground state of a potential acting on a system) without the explicit solution of the equation. As is to be shown in future work, it also allows the determination of all eigenstates of a Hamiltonian of an interacting system, as well as the determination of states for time-dependent systems. In short, density functional theory is an alternative methodology to that of the Schrödinger equation for determining the complete electronic structure of interacting systems, and is indeed, the only such method currently known. The verification of this statement is provided through other work (currently in preparation) in which excited states and time-dependent systems are treated within density functional theory, through sole knowledge of the density.

4. Determining the Density

We now inquire as to whether it is possible to determine the density and the corresponding wave function given the parametric derivative, $q(\mathbf{r})$ (suppressing the notation $q[n]$ in favor of q).

Consider the functional, where $q(\mathbf{r})$ corresponds to a density, $n(\mathbf{r})$,

$$E_q[n] = \int q(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n]. \quad (19)$$

In the absence of degeneracies, let the Slater determinant, $\Phi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$, lead to the same density, $n(\mathbf{r})$, and minimize the expectation value of the kinetic energy of a system of N electrons, establishing the functional,

$$\begin{aligned} T_{\text{det}}[n] &= \underbrace{\text{Min}}_{|\Phi\rangle \rightarrow n(\mathbf{r})} \langle \Phi | \hat{T}^N | \Phi^N \rangle \\ &= \langle \Phi_0 | \hat{T}^N | \Phi_0 \rangle. \end{aligned} \quad (20)$$

The density is obtained in terms of $\Phi_0(\mathbf{r}_{(N)})$ by the expression,

$$n(\mathbf{r}) = \sum_j |f_j(\mathbf{r})|^2, \quad (21)$$

where $f_j(\mathbf{r})$ are the single-particle orbitals that enter the construction of the Slater determinant, $\Phi_0(\mathbf{r}_{(N)})$.

We denote the parametric derivative of $T_{\text{det}}[n]$ with respect to the density by the symbol $q_\Phi(\mathbf{r})$, so that

$$\frac{\delta T_{\text{det}}[n]}{\delta n(\mathbf{r})} = -q_\Phi(\mathbf{r}) + c. \quad (22)$$

Now, construct the functional,

$$F_s[n] = \langle \Phi_0 | \hat{T}^N + \hat{U}^N | \Phi_0 \rangle, \quad (23)$$

and note that,

$$E_c[n] = F[n] - F_s[n] \leq 0, \quad (24)$$

because $\Phi_0 \neq \Psi_0$. Within the present context, the quantity $E_c[n]$ is referred to as the *correlation energy*. Adding and subtracting $F_s[n]$ to the right-hand side of Eq. (19), we have,

$$E_q[n] = \int q(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F_s[n] + E_c[n]. \quad (25)$$

Setting the parametric derivative of the last expression with respect to the density equal to zero, to signify the presence of a minimum, we obtain the following condition (again suppressing arbitrary constants),

$$\begin{aligned} q_\Phi(\mathbf{r}) &= q_\Psi(\mathbf{r}) + \frac{\delta\{\langle \Phi_0 | \hat{U}^N | \Phi_0 \rangle + E_c[n]\}}{\delta n(\mathbf{r})} \\ &= q_\Psi(\mathbf{r}) + v_C(\mathbf{r}) + \mu_c(\mathbf{r}), \end{aligned} \quad (26)$$

where $v_C(\mathbf{r}) = \frac{\delta\langle \Phi_0 | \hat{U}^N | \Phi_0 \rangle}{\delta n(\mathbf{r})}$ is the *Coulomb potential*, and $\mu_c(\mathbf{r}) = \frac{\delta E_c[n]}{\delta n(\mathbf{r})}$ is the *correlation potential*. Therefore, given the task of obtaining the density and corresponding wave function that lead to the minimum value of the functional in Eq. (19), one searches for the Slater determinant that leads to a parametric derivative satisfying the condition in (26). The implication of these developments to the implementation of DFT based on the Kohn-Sham scheme will be discussed in future work.

4.1. Connection with Initial Formulations

For a given density, $n(\mathbf{r})$, implement the constrained search, identify the wave function (quantum state), $|\Psi_0\rangle$, that minimizes the expectation value of $\hat{T}^N + \hat{U}^N$, construct the derivative, $q_{\Psi_0}(\mathbf{r})$, and check whether or not $|\Psi_0\rangle$ is an eigenstate of the operator, $\hat{q}_{\Psi_0} + \hat{T}^N + \hat{U}^N$, i.e., whether or not it satisfies the equality,

$$\left[\hat{q}_{\Psi_0} + \hat{T}^N + \hat{U}^N \right] = \alpha |\Psi_0\rangle. \quad (27)$$

If it does, then the expression above is a Schrödinger equation for an interacting N -particle system, $q_{\Psi_0}(\mathbf{r})$ is the external scalar potential acting on the system, $|\Psi_0\rangle$ denotes the system's ground state, and α the corresponding ground-state energy. The theorems of Hohenberg and Kohn follow.

With this definition of the potential, we now examine how the conventional functional derivative might be taken for energies that are at minimum. Consider a (parametric) variation of the potential $q_{\Psi_0}(\mathbf{r}) \rightarrow q_{\Psi_0}(\mathbf{r}) + \delta q_{\Psi_0}(\mathbf{r})$. The change in the total energy, which is already minimized with respect to all densities, can be evaluated using the Hellmann-Feynman theorem [22],

$$\delta E_q = E_{q+\delta q} - E_q = \int \delta q_{\Psi_0}(\mathbf{r})n(\mathbf{r})d\mathbf{r}. \quad (28)$$

On the other hand, if the two densities that minimize the total energy for the two potentials are $n(\mathbf{r})$ and $n(\mathbf{r}) + \delta n(\mathbf{r})$ (the latter could be obtained from the former using a perturbation expansion in terms of $\delta q_{\Psi_0}(\mathbf{r})$), we can also write the change in the total energy as,

$$\begin{aligned} \delta E_q &= \int \delta q_{\Psi_0}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\ &+ \int q_{\Psi_0}(\mathbf{r})\delta n(\mathbf{r})d\mathbf{r} + \int \frac{\delta F[n]}{\delta n(\mathbf{r})}\delta n(\mathbf{r})d\mathbf{r}. \end{aligned} \quad (29)$$

These two equations yield,

$$\int \left\{ q_{\Psi_0}(\mathbf{r}) + \frac{\delta F[n]}{\delta n(\mathbf{r})} \right\} \delta n(\mathbf{r})d\mathbf{r} = 0. \quad (30)$$

If $\delta n(\mathbf{r})$ is an arbitrary function (with the constraint $\int \delta n(\mathbf{r})d\mathbf{r} = 0$), then the above equation will lead to Eq. (4). However, $\delta n(\mathbf{r})$ can only take a subset of functions, those that correspond to $\delta q_{\Psi_0}(\mathbf{r})$. It is therefore possible to find at least one function, $g(\mathbf{r}) \neq 0$, that is perpendicular to all allowed $\delta n(\mathbf{r})$,

$$\int g(\mathbf{r})\delta n(\mathbf{r})d\mathbf{r} = 0. \quad (31)$$

Thus, we obtain instead,

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} = -q_{\Psi_0}(\mathbf{r}) + cg(\mathbf{r}), \quad (32)$$

where c is an arbitrary constant. This proves that it is generally not possible to take functional derivatives with only v -representable densities. These developments illustrate the principle that (conventional) functional derivatives can be performed only through arbitrary variations of the independent variable, being blocked over domains constrained by conditions such as v -representability or normalization.

5. Discussion

For ν -rep densities, Hohenberg and Kohn's First Theorem establishes a unique functional dependence between the density and the corresponding potential, thus postulating that knowledge of a density, and only knowledge of that density is required in determining the potential. This is the first notion underlying the developments above.

Second, in and of itself the theorem provides no method for determining the potential. Such a method is clearly suggested by Eqs. (4) and (5), only to be realized that the derivative indicated cannot be performed because of the ν -representability problem. Even after that problem has been circumvented, however, through the developments based on N -representability [16], conventional functional differentiation is blocked because of three reasons: The First Theorem disallows consideration of any density other than the one in question in determining the properties of the system (and conventional functional differentiation requires consideration of, in principle, an infinite number of such densities), the wave functions leading to a density are generally not written explicitly in terms of the density, and normalization requirement can be violated in the process of conventional functional differentiation. These seemingly insurmountable barriers are bypassed through the formalism outlined in the paper.

The present formalism reinforces the content of the First Theorem [1] by providing an explicit procedure allowing the determination of the potential through the exclusive knowledge of a density (if it happens to be ν -representable). It is to be noted, however, that the procedure of determining functional derivatives with respect to the density underlying the present formalism is generally applicable to *all* densities, with ν -representable densities occupying no place of prominence. The formalism also preserves the fundamental feature of density functional theory of determining the wave function of the ground state of an interacting many-electron system through the *sole* knowledge of the density, thus fulfilling directly the program of quantum mechanics of determining the states of physical systems corresponding to the results of measurement through sole knowledge of observables (here the ground-state densities) determined through measurement.

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Appendix A. Orbitals and Parametric Derivatives

Cioslowski [18–20] has provided a formal determination of the set $S_{\Psi \rightarrow n}$ of all antisymmetric N -particle wave functions

that lead to a density normalized to N . A general element of $S_{\Psi \rightarrow n}$ is written as a linear superpositions of Slater determinants, (in Einstein summation notation),

$$\Psi(\mathbf{r}_{(N)}) = C_P \Phi_P(\mathbf{r}_{(N)}), \quad C_P C^P = 1, \quad (\text{A.1})$$

where $\Phi_P(\mathbf{r}_{(N)})$ is a Slater determinant of order N constructed from N elements (orbitals), $\psi_j(\mathbf{r})$, that form a complete and orthonormal basis in single-particle, three-dimensional coordinate space. The orbitals, $\psi_j(\mathbf{r})$, are constructed so that the modulus of the wave function, $\Psi(\mathbf{r}_{(N)})$, squared and integrated over all coordinates but one yields the density,

$$\int |\Psi(\mathbf{r}_{(N)})|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N = n(\mathbf{r}_1), \quad (\text{A.2})$$

This property follows from the form of the orbitals (see [18]),

$$\psi_j(\mathbf{r}) = \frac{\sqrt{n(\mathbf{r})} s_j^u \phi_u(\mathbf{r})}{\sqrt{C^P C^Q \Xi_{PQ}^{kl} s_k^u s_l^u \phi_u(\mathbf{r}) \phi_u(\mathbf{r})}}, \quad (\text{A.3})$$

where the functions, $\phi_u(\mathbf{r})$, form a complete but not necessarily orthonormal basis in three-dimensional coordinate space, the matrix, Ξ_{PQ}^{kl} , is defined by the integral over all coordinates but one of two Slater determinants,

$$\begin{aligned} & \int \Phi_Q((\mathbf{r}_{(N)})) \Phi_P(\mathbf{r}_{(N)}) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \\ &= \int \left\{ (-1)^{j+1} \psi_j(\mathbf{r}_1) M_j^Q(\mathbf{r}_2, \dots, \mathbf{r}_N) \right. \\ & \times \left. (-1)^{i+1} \psi_i(\mathbf{r}_1) M_i^P(\mathbf{r}_2, \dots, \mathbf{r}_N) \right\} d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \\ &= \Xi_{QP}^{kl} \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_1) \end{aligned} \quad (\text{A.4})$$

where in the second line we have used the expansion of a determinant along its first row, $M_j^Q(\mathbf{r}_2, \dots, \mathbf{r}_N)$ is the minor of $\psi_j(\mathbf{r}_1)$ in $\Phi_Q((\mathbf{r}_{(N)}))$, and the matrix \underline{s} is defined as the square root of a matrix,

$$\underline{s} = \underline{s}^{-\frac{1}{2}}, \quad (\text{A.5})$$

whose elements are given by the integrals,

$$S_{ij} = \int \frac{n(\mathbf{r}) \phi_i(\mathbf{r}) \phi_j(\mathbf{r})}{[C^P C^Q \Xi_{PQ}^{kl} s_k^u s_l^u \phi_u(\mathbf{r}) \phi_u(\mathbf{r})]} d\mathbf{r}. \quad (\text{A.6})$$

The non-linear nature of the transformation, \underline{s} , between the set of functions, $\{\phi_j(\mathbf{r})\}$ and $\{\psi_k\}$, is clear. The existence and convergence of \underline{s} has been demonstrated by Cioslowski [19, 20].

Cioslowski [18] shows that the set of orbitals that form the Slater determinant, $\Phi_0(\mathbf{r}_{(N)})$ take the form,

$$\psi_j(\mathbf{r}) = \frac{\sqrt{n(\mathbf{r})} s_j^u \phi_u(\mathbf{r})}{\sqrt{\langle \phi(\mathbf{r}) | \underline{s}^{-1} | \phi(\mathbf{r}) \rangle}}, \quad (\text{A.7})$$

where,

$$S_{ij} = \int \frac{n(\mathbf{r}) \phi_i(\mathbf{r}) \phi_j(\mathbf{r})}{[\langle \phi(\mathbf{r}) | \underline{s}^{-1} | \phi(\mathbf{r}) \rangle]} d\mathbf{r}. \quad (\text{A.8})$$

In the last two expressions, a vector-matrix notation is used, so that $\langle \phi(\mathbf{r}) | \underline{S}^{-1} | \phi(\mathbf{r}) \rangle = \sum_{kl} \phi_k(\mathbf{r}) [\underline{S}^{-1}]_{kl} \phi_l(\mathbf{r})$.

We now examine the properties of the orbitals defining $\Phi_0(\mathbf{r}_{(N)})$.

Clearly, the set, $\{\phi_j(\mathbf{r})\}$, is arbitrary and hence not a functional of the density. Because of this, the matrix, \underline{S} , whose value depends on $\{\phi_j(\mathbf{r})\}$ is not a functional of the density either, and consequently neither are the orbitals, $\psi_j(\mathbf{r})$. However, the set of orbitals forming $\Phi_0(\mathbf{r})$ is uniquely defined regardless of the choice of $\{\phi_j(\mathbf{r})\}$.

Furthermore, because of the explicit presence of the density in Eq. (A.8), the matrix, \underline{S} , possesses a parametric derivative with respect to the density,

$$\begin{aligned} \frac{\delta \underline{S}}{\delta n(\mathbf{r}')} &= \frac{|\phi(\mathbf{r}')\rangle \langle \phi(\mathbf{r}')|}{\langle \phi(\mathbf{r}') | \underline{S}^{-1} | \phi(\mathbf{r}') \rangle} \\ + \int \frac{n(\mathbf{r}) |\phi(\mathbf{r})\rangle \langle \phi(\mathbf{r})|}{[\langle \phi(\mathbf{r}) | \underline{S}^{-1} | \phi(\mathbf{r}) \rangle]^2} \\ \times \text{Tr} \left[\underline{S}^{-1} |\phi(\mathbf{r})\rangle \langle \phi(\mathbf{r})| \underline{S}^{-1} \frac{\delta \underline{S}}{\delta n(\mathbf{r}')} \right] d\mathbf{r}, \end{aligned} \quad (\text{A.9})$$

an equation to be solved for the derivatives, $\frac{\delta S_{ij}}{\delta n(\mathbf{r})}$ (see [19, 20]). (For a fixed set $\{\phi_j(\mathbf{r})\}$, one can view S_{ij} as a functional of the density, and refer to the paramagnetic derivative as a functional derivative. At the same time, the derivative with respect to the density, $n(\mathbf{r})$, requires no knowledge of \underline{S} for any density other than $n(\mathbf{r})$). This defines the parametric derivative of the basis functions, $\psi_j(\mathbf{r})$, with respect to the density for each choice of auxiliary functions, evaluated at the particular density. Consequently, it defines a unique derivative of any wave function leading to the density that is independent of the choice of auxiliary functions.

To summarize: Each density, $n(\mathbf{r})$, defines its own space of parametric (functional) differentiation of individual orbitals used to construct the antisymmetric, N -particle wave functions, $\Psi(\mathbf{r}_{(N)}; [n])$, that lead to a density. Thus, all orbitals and corresponding wave functions that lead to a density possess uniquely defined parametric derivatives with respect to the density.

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