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Reformulation of density functional theory for N-representable densities and the resolution of the v-representability problem

A. Gonis [a,*], X.-G. Zhang [b], M. Däne [a], G.M. Stocks [c], D.M. Nicholson [d]

[a] Physical and Life Sciences, Lawrence Livermore National Laboratory, PO Box 808, L-372, Livermore, CA 94551, United States
[b] Department of Physics and the Quantum Theory Project, University of Florida, Gainesville, FL 32611, United States
[c] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[d] Department of Physics, University of North Carolina Asheville, Asheville, NC 28804 , United States

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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 proof of existence of a mathematical procedure that determines whether a density is v-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 v-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. Numerical results for one-dimensional non-interacting systems illustrate the formalism. Some direct formal and practical implications of the present reformulation of DFT are also discussed.

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

$$E_v[n] = \int v(\mathbf{r})\boldsymbol{n}(\mathbf{r}\, \mathrm{d}\mathbf{r}) + \langle \Psi_{\mathrm{GS}}|\hat{T}^N + \hat{U}^N|\Psi_{\mathrm{GS}}\rangle, \tag{1}$$

where $\Psi_{\mathrm{GS}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \Psi_{\mathrm{GS}}(\mathbf{r}_{(N)})$ 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 is everywhere non-negative, normalized to an integer, N, and satisfies the so-called kinetic energy condition

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

The minimum value of $E_v[n]$ 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

$$\langle \Psi_{\mathrm{GS}}|\hat{T}^N + \hat{U}^N|\Psi_{\mathrm{GS}}\rangle = F_{\mathrm{HK}}[n], \tag{3}$$

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 v-representable, i.e., are derived from the solution of a Schrödinger equation corresponding to a given potential (other forms of v-representability, such as ensemble v-representability can be defined but not considered here). We confine the discussion to pure-state v-representability and refer to the condition simply as v-rep. As is well-known [2,4], however, the v-rep condition introduces a serious difficulty in the theory, known as the v-representability problem. Namely, given an arbitrary density

* Corresponding author.
E-mail address: gonis1@llnl.gov (A. Gonis).

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the present form of the theory provides no mathematical procedure that can determine whether or not it is v-rep.

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

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

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, $\frac{\delta F_{HK}[n]}{\delta n(\mathbf{r})}$, defined through the procedure [2] (where the test function, $\phi(\mathbf{r})$, is arbitrary):

$$\lim_{\epsilon\to 0}\frac{F_{HK}[n+\epsilon\phi(\mathbf{r})]-F_{HK}[n]}{\epsilon} = \int\frac{\delta F_{HK}[n]}{\delta n(\mathbf{r})}\phi(\mathbf{r})\,d\mathbf{r}, \tag{5}$$

at a given density hinges on the evaluation of the Hohenberg and Kohn functional, $F_{HK}[n+\delta n]$, 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, $n(\mathbf{r}) \to n(\mathbf{r})+\epsilon\phi(\mathbf{r})$, where $\phi(\mathbf{r})$ is arbitrary (within common caveats of smoothness and integrability), and $\epsilon \to 0$. 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, $F_{HK}[n]$ 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 $\epsilon\to 0$). Second, the perceived need to obtain the potential through the functional derivative in (5) requires the knowledge of the value of $F_{HK}[n]$ 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, $E_{N,v}[w]=E^{HK}_{N,v}[n[w]]$, where $E^{HK}_{N,v}[n[w]]$ 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 of functionals of potential defining 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 $F_{HK}[n]$. 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 $F_{HK}[n]$ 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 $F_{HK}[n]$. 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, at the formal level, 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 a formulation at the same level of conceptual rigor as the constrained search of the existence of such a procedure.

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 inter-particle 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

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

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 expected to yield an energy (expectation) value. Instead, it provides a method of parametric differentiation of any functional of densities