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Variational theorems for the single-particle probability density and density matrix in momentum space

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The existence of Hohenberg-Kohn–like density-functional theorems in momentum space is demonstrated. Invoking principles employed by Levy to construct universal variational density and density-matrix functionals in position space, it is found that (1) there exists a universal variational functional for the one-electron reduced density matrix in momentum space, and (2) for any given external potential, there exists a proper variational functional for the one-electron momentum-space probability density.

I. INTRODUCTION

In a recent paper,[1] Levy provided a unifying theoretical framework for many density-functional studies undertaken in the spirit of the theorems of Hohenberg and Kohn.[2] He there presented universal variational functionals of the electron density and first-order density matrix in position space. Our purpose here is to investigate extension of those considerations to the corresponding momentum-space quantities.

II. COORDINATE SPACE FUNCTIONALS

Consider the Hamiltonian for N electrons in the presence of a local external potential $\hat{v}$:

$$\hat{H}=\hat{T}+\hat{V}_{ee}+\sum_{i=1}^{N}\hat{v}(i)\equiv\hat{T}+\hat{V}_{ee}+\hat{U}\,, \tag{1}$$

where $\hat{T}$ is the kinetic-energy operator and $\hat{V}_{ee}$ the electron-electron repulsion operator. In position space, $\hat{v}$ is a single-particle scalar operator, while evaluation of $\langle\hat{T}\rangle$ requires knowledge of the single-particle density matrix. The forms of $\hat{T}$ and $\hat{V}_{ee}$ are given once N is specified, whereas $\hat{v}$ is specific to a particular system.

Hohenberg and Kohn proved that to within an additive constant, $\hat{v}$ is a unique functional of $\rho_{GS}(\vec{r})$, the ground-state electron density for the system of interest. Thus $\rho_{GS}(\vec{r})$ determines the full N-electron ground state since it fixes $\hat{H}$. They then introduced a functional of ρ,

$$F[\rho]\equiv\langle\Psi_\rho|\hat{T}+\hat{V}_{ee}|\Psi_\rho\rangle\,, \tag{2}$$

where Ψ_ρ is the antisymmetric N-electron wave function which (1) yields $\rho(\vec{r})$ as its electron density and (2) is the ground-state eigenfunction of the Hamiltonian arising from the external potential fixed by the given $\rho(\vec{r})$ [not necessarily equal to $\hat{v}(\vec{r})$] for the system under study. This functional is "universal" in the sense that it is valid for any N [itself a simple functional of $\rho(\vec{r})$] and any "v-representable"[3] ρ, that is, any ρ associated with the ground state of some v. The Hohenberg-Kohn variational theorem states that the energy functional

$$E_{HK}[\rho]\equiv\int\hat{v}(\vec{r})\,d\vec{r}+F[\rho] \tag{3}$$

has its minimum at E_{GS}, the correct N-electron ground-state energy when $\rho=\rho_{GS}$, and provides an upper bound to E_{GS} otherwise, so long as the class of ρ functions is restricted to be normalized to N and v-representable.

Levy[1] presented a universal variational density functional free of the encumbrance of the v-representability condition

$$Q[\rho]=\min\langle\Psi_\rho|\hat{T}+\hat{V}_{ee}|\Psi_\rho\rangle\,, \tag{4}$$

where $Q[\rho]$ searches all antisymmetric functions of N position and spin coordinates Ψ_ρ which yield the given ρ and provides the minimum expectation value of $\hat{T}+\hat{V}_{ee}$. Since $Q[\rho]$ is valid for any N-representable[4] ρ and since the kinetic and electron repulsion operators are defined once

$$N=\int\rho(\vec{r})d\vec{r} \tag{5}$$

is specified, it is a universal functional. Further, by invoking the variational theorem for wave functions, Levy shows that

$$E_L[\rho]\equiv\int\hat{v}(\vec{r})\rho(\vec{r})d\vec{r}+Q[\rho] \tag{6}$$

yields an upper bound to the ground-state energy for a given $\hat{v}$ and yields the ground-state energy if provided with the ground-state density. As a result, the ground-state wave function is fixed by the ground-state density via $Q[\rho]$ even if the external potential giving rise to Ψ is not given. For our purposes, the key step was to partition the energy into a portion given immediately by ρ, namely,

$$\langle \hat{U} \rangle = \int \hat{v}(\vec{r})\rho(\vec{r})\, d\vec{r}\,, \tag{7}$$

and to define a proper functional of ρ which minimizes the remaining portion of the energy.

In similar fashion, Levy also defined a universal variational density-matrix functional

$$W[D(x\,|\,x')] \equiv \min \langle \Psi_D \,|\, \hat{V}_{ee} \,|\, \Psi_D \rangle\,, \tag{8}$$

where $D(x\,|\,x')$ is a single-particle N-representable reduced density matrix, or one-density (which may include spin), and $W[D]$ searches all antisymmetric wave functions Ψ_D yielding the given D and provides the minimum value for $\langle \hat{V}_{ee} \rangle$. Again, W will provide a variational bound to E_{GS} since $\langle \hat{V}_{ee} \rangle$ is minimum and $\langle \hat{U} \rangle$ and $\langle \hat{T} \rangle$ are obtained immediately from the given D. Note also that $W[D]$ does not exclude nonlocal or spin-dependent external potentials so long as they remain one-electron operators.

III. MOMENTUM SPACE FUNCTIONALS

These ideas are now carried over to momentum space. We observe that the kinetic and external potential operators exchange roles, with $\hat{T}$ becoming a single-particle scalar operator and evaluation of $\langle \hat{U} \rangle$ requiring the momentum-space density matrix. Thus we may define a variational functional of $\gamma(\vec{p})$, the three-dimensional momentum-space probability density, as follows:

$$G[\gamma] \equiv \min \langle \Psi_\gamma \,|\, \hat{U} + \hat{V}_{ee} \,|\, \Psi_\gamma \rangle\,, \tag{9}$$

where $G[\gamma]$ searches over all antisymmetric functions Ψ_γ of N momentum (and spin) coordinates which yield the given $\gamma(\vec{p})$ and provides the minimum expectation value of $\hat{U} + \hat{V}_{ee}$. In a manner entirely analogous to the proofs for $E_L[\rho]$[1] one can show that for N-representable γ's

$$\int \hat{T}(\vec{p})\gamma(\vec{p})\, d\vec{p} + G[\gamma] \geq E_{GS}\,, \tag{10}$$

where E_{GS} is the ground-state energy of N interacting electrons under $\hat{v}$, and with the equality holding when the ground-state momentum-space probability density $\gamma_{GS}(\vec{p})$ is inserted on the left-hand side. Note, however, that $G[\gamma]$ is *not* a universal functional since it requires that $\hat{v}$ be known. Thus some of the power of the position-space Hohenberg-Kohn and Levy functionals is lost, because a different $G[\gamma]$ must be studied for each physical system.

On the other hand, at the density-matrix level one recovers complete parallelism between the position-space and momentum-space formulations. Since both $\langle \hat{T} \rangle$ and $\langle \hat{U} \rangle$ are immediately accessible given the momentum-space one-density $\Gamma(q\,|\,q')$ (where q specifies the momentum and spin coordinates of a single particle), the appropriate variational functional, defined for N-representable Γ, is

$$\Omega[\Gamma] \equiv \min \langle \Psi_\Gamma \,|\, \hat{V}_{ee} \,|\, \Psi_\Gamma \rangle\,, \tag{11}$$

where $\Omega[\Gamma]$ searches over all antisymmetric N-electron momentum-space wave functions Ψ_Γ which yield the given Γ, and provides the minimum value for $\langle \hat{V}_{ee} \rangle$. Note that unlike $G[\gamma]$, this functional is universal. It could, in fact, have been obtained by Fourier transformation of Levy's density-matrix functional $W[D]$ to momentum space.

IV. CONCLUSIONS

We see then that one is free to proceed with momentum-space density-matrix functional theories, any related orbital theories,[1] and any computations which may be suggested thereby with the knowledge that such developments rest upon a formal groundwork equivalent to that of the corresponding position-space theories. In particular, the universality of $\Omega[\Gamma]$ makes it (as well as $F[\rho]$ and $W[D]$) an excellent focus for the development of approximate theories: A good approximation to it is valid for any number of electrons and any external potential. Although the complete parallelism between position-space and momentum-space density-functional theories is lost because of the form of the Hamiltonian [Eq. (1)] which causes $G[\gamma]$ not to be universal, there does, nevertheless, exist a proper variational functional of the momentum-space probability density for any given external potential. Thus direct variational determination of $\gamma(\vec{p})$ may be contemplated.

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[1] M. Levy, Proc. Natl. Acad. Sci. USA 76, 6062 (1979).

[2] P. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1964).

[3] Term coined by E. G. Larson.

[4] A reduced density matrix is N-representable if it can be obtained from some antisymmetric N-electron wave function. See A. J. Coleman, Rev. Mod. Phys. 35, 668 (1963).