

Extrema of the density functional for the energy: Excited states from the ground-state theory

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Although every stationary-state density $n_i(\mathbf{r})$ of a many-particle system is not an extremum of the ground-state density functional $E_v[n]$, every extremum of $E_v[n]$ [i.e., every solution of the Euler equation $\delta E_v/\delta n(\mathbf{r})=\lambda$] is a stationary-state density $n_i(\mathbf{r})$. Always, $E_v[n_i]\leq E_i$, where E_i is the lowest stationary-state energy for density $n_i(\mathbf{r})$; the equality holds if and only if $n_i(\mathbf{r})$ is an extremum of $E_v[n]$. The extrema lying above the absolute minimum are excited-state densities which fail to be pure-state v -representable. Surprisingly, infinitesimal number-conserving density variations $\delta n(\mathbf{r})$ about an extremum $n(\mathbf{r})$ do not lead to energy variations δE_v of order $(\delta n)^2$ when $\delta n(\mathbf{r})/n^{1/2}(\mathbf{r})$ fails to be square-integrable; in fact, variations δE_v of order $|\delta n|$ about the ground state are exemplified by the recently discovered "derivative discontinuities of the energy." This unconventional behavior of $E_v[n]$ may be traced in part to an asymptotic divergence of $\delta^2 E_v/\delta n(\mathbf{r})\delta n(\mathbf{r}')$. Conditions are presented under which a self-consistent solution of the Kohn-Sham single-particle problem represents an extremum of $E_v[n]$. The multiplets of the ground-state orbital configuration of the carbon atom are examined. The local-density and Langreth-Mehl approximations are found to yield a remarkably accurate account of the degeneracy of the various ground-state densities for this system, but no estimate of the multiplet splitting is obtained. Finally, aspects of v -representability are discussed, with emphasis on the iron atom.

I. INTRODUCTION AND SUMMARY

Density-functional theory¹⁻⁹ is a standard approach to the structure of many-electron systems, such as atoms, molecules, and solids. The fundamental variable of this exact-in-principle variational theory is the density $n(\mathbf{r})$, instead of the many-particle wave function $\Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)$ or its hierarchy of Green's functions.

"One of the most important and controversial questions in density-functional theory concerns the extent to which excited states can be studied by these methods."⁸ The original Hohenberg-Kohn-Sham theory^{1,2} is formally exact for the density $n(\mathbf{r})$ and energy E of the ground state for N identical nonrelativistic particles in the presence of external potential $v(\mathbf{r})$. Extensions have been made to the lowest-energy stationary state of a given symmetry,¹⁰⁻¹³ to Theophilou's¹⁴ subspace of the M lowest-energy eigenvalues,¹²⁻¹⁶ and to arbitrary individual bound states.^{12,16,17} However, these extensions search for minima of specially-defined density functionals different from the ground-state functional $E_v[n]$. It is only for the ground-state functional, thus far, that practical approximations of increasing sophistication^{2,18-20} have been developed.

In this work, we will use the constrained-search definition²¹ of the ground-state functional $E_v[n]$ to provide the needed connection between densities and wave functions. We consider the *extrema* of $E_v[n]$, i.e., the solutions of the Euler-Lagrange equation:

$$\delta E_v/\delta n(\mathbf{r})=\lambda. \quad (1)$$

In Sec. III, we show that every extremum of $E_v[n]$ represents the density $n_i(\mathbf{r})$ and energy E_i of a stationary state. The absolute minima represent the ground states, and the extrema lying above the minimum represent a subset of the excited states. For excited-state densities $n_i(\mathbf{r})$ outside this subset, the ground-state functional provides a lower bound on the energy. Always,

$$E_v[n_i]\leq E_i. \quad (2)$$

We shall discuss the precise condition under which a stationary-state density is an extremum of $E_v[n]$. We find that the extrema of $E_v[n]$ above the minimum fall outside the set of pure-state v -representable densities. (A pure-state v -representable density is²¹ a ground-state density for *some* choice of external potential.)

It might be expected that any number-conserving density variation about an extremum,

$$\delta n(\mathbf{r})=\epsilon f(\mathbf{r}) \quad (3)$$

[where ϵ is a positive infinitesimal, the shape function f is continuous and differentiable, and $\int d^3r f(\mathbf{r})=0$], should give rise to an energy variation $\delta E_v[n]$ of order ϵ^2 . This is so for the large class of "conventional" density variations, i.e., those associated via the constrained search with wave-function variations of order ϵ . However, we show in Sec. IV that, surprisingly, there is also a large class of "unconventional" density variations (including those where both the initial and final densities are pure-state v -representable), for which $\delta E_v[n]$ may be of order $|\epsilon|$. We find that the variation (3) about density $n(\mathbf{r})$ is uncon-

ventional if the function

$$f(\mathbf{r})/n^{1/2}(\mathbf{r}) \quad (4)$$

fails to be square-integrable. The "derivative discontinuities"^{22,23} in the energy of an open system as a function of its time-averaged particle number are shown to arise from unconventional density variations about the ground state of the combined system (open system plus reservoir).

Realistic, practical, density-functional calculations are performed by solving the Kohn-Sham² self-consistent single-particle equations. We discuss these equations in Sec. V, and argue that the density and kinetic energy should be constructed from a noninteracting-system wave function which is not necessarily either a single Slater determinant or even a noninteracting ground state. Only a few of the solutions of the Kohn-Sham equations represent extrema of $E_v[n]$. We discuss how to recognize these meaningful solutions, which include in particular all those where the Kohn-Sham noninteracting wave function is a noninteracting ground state. (In earlier work,²²⁻²⁶ we have already discussed the extent to which the orbital energy eigenvalues of the exact Kohn-Sham equations for the ground state may be interpreted as exact excitation energies.)

The considerations of Sec. V suggest that the multiplet splitting of a ground-state orbital configuration might provide a real, nontrivial example of excited states obtainable from the exact ground-state functional. We examine this question more closely for the $(2p)^2$ configuration of the carbon atom in Sec. VI. However, the best estimates we have for the densities of some of the excited simultaneous eigenstates of \hat{H} , \hat{L}^2 , \hat{S}^2 , \hat{L}_z , and \hat{S}_z are identical to various ground-state densities, and so the ground-state functional $E_v[n]$ assigns the ground-state energy to these excited states. We also find that the local-density² and Langreth-Mehl²⁰ approximations for exchange and correlation, unlike the local-*spin*-density approximation, yield a remarkably accurate account of the degeneracy of the various ground-state densities.

For a physical many-electron system, with interacting electrons and a Coulombic external potential, we have found no clearcut example of an extremum of $E_v[n]$ lying above its absolute minimum. It is an open question to what extent such situations arise. However, such situations do unquestionably arise for interacting electrons with *some* choice of external potential, as discussed at the end of Sec. III.

For the model noninteracting system of Sec. II, we also find extrema of $E_v[n]$ lying above the minimum. This model illustrates several other points of our work, including the inequality of Eq. (2) as well as conventional and unconventional density variations.

II. AN ILLUSTRATION

Consider the simple system of two noninteracting electrons bound to a Coulombic external potential $v(r) = -1/r$. For this system, the exact ground-state functional is known explicitly:

$$\begin{aligned} E_v[n] &= \int d^3r n^{1/2} \left(-\frac{1}{2} \nabla^2 \right) n^{1/2} - \int d^3r n/r \\ &= \int d^3r |\nabla n|^2 / 8n - \int d^3r n/r. \end{aligned} \quad (5)$$

The Euler-Lagrange equation (1) may be written simply as

$$\left[-\frac{1}{2} \nabla^2 - \frac{1}{r} \right] n^{1/2}(\mathbf{r}) = \lambda n^{1/2}(\mathbf{r}). \quad (6)$$

Its solutions are those densities which can be generated by *double* occupation of a hydrogenic orbital, such as,

$$\psi_{1s}(\mathbf{r}) = \pi^{-1/2} e^{-r} \quad (\epsilon_{1s} = -\frac{1}{2}) \quad (7)$$

or

$$\psi_{2s}(\mathbf{r}) = (8\pi)^{-1/2} (1-r/2) e^{-r/2} \quad (\epsilon_{2s} = -\frac{1}{8}). \quad (8)$$

Thus, the $(1s)^2$ and $(2s)^2$ densities are extrema of the ground-state functional, while the $(1s)^1(2s)^1$ density is not.

Consider two paths along which the density may be continuously deformed, as a function of the parameter y , from the $(1s)^2$ density at $y=0$ to the $(1s)^1(2s)^1$ density at $y=0.5$, and then to the $(2s)^2$ density at $y=1$. As an example of an unconventional path, take

$$n(\mathbf{r}) = 2(1-y) |\psi_{1s}(\mathbf{r})|^2 + 2y |\psi_{2s}(\mathbf{r})|^2. \quad (9)$$

As a conventional path, choose

$$\begin{aligned} n(r) &= 2(1-y) \frac{A}{\pi} \left[1 - \frac{\alpha r}{2} \right]^2 e^{-2r} \\ &\quad + 2y \frac{B}{8\pi} \left[1 - \frac{r}{2} \right]^2 e^{-\beta r}, \end{aligned} \quad (10)$$

where

$$\alpha = 2y \left(y - \frac{1}{2} \right), \quad (11)$$

$$\beta = 1 + 2 \left(y - \frac{1}{2} \right) (y - 1), \quad (12)$$

$$A = \left(1 - \frac{3}{2} \alpha + \frac{3}{4} \alpha^2 \right)^{-1}, \quad (13)$$

$$B = \beta^3 \left[1 - \frac{3}{\beta} + \frac{3}{\beta^2} \right]^{-1}. \quad (14)$$

Figure 1 shows $E_v[n]$ of Eq. (5) versus y along each density path. The crosses indicate the true stationary-state energies for this system. Note that $E_v[n]$ equals the true stationary-state energy E_i for the $(1s)^2$ and $(2s)^2$ densities, which are extrema of $E_v[n]$. For the $(1s)^1(2s)^1$ density, which is not an extremum, $E_v[n]$ provides only a lower bound, as asserted by Eq. (2). Similarly, for the density of $(1s)^1(2p_z)^1$ (the lowest-energy stationary state of symmetry $L=1$; not included in Fig. 1), we find that $E_v[n]$ equals -0.746 a.u., which lies below the stationary-state energy of -0.625 a.u.

Return to Fig. 1. Along the conventional path of Eq. (10), $E_v[n]$ goes flat at its $(1s)^2$ and $(2s)^2$ extrema, but this conventional behavior is *not* found along the unconventional path of Eq. (9). The condition of Eq. (4) shows that the density path of Eq. (9) yields unconventional density variations around the $(1s)^2$ ($y=0$) and $(2s)^2$ ($y=1$)

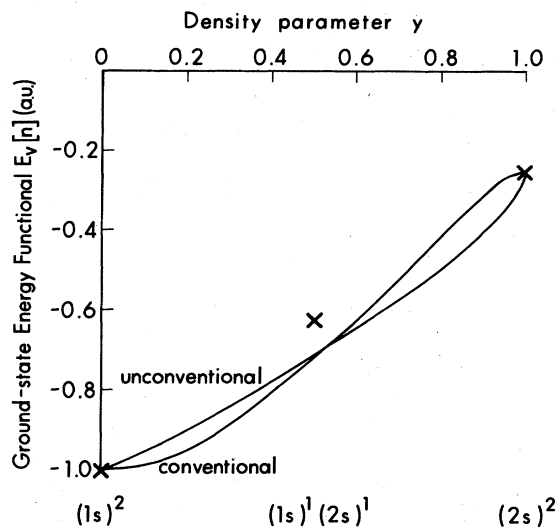


FIG. 1. Exact ground-state energy functional $E_v[n]$ of Eq. (5) for two noninteracting electrons bound to the potential $v(\mathbf{r}) = -1/r$, evaluated as a function of the parameter y along the unconventional density path of Eq. (9) and the conventional path of Eq. (10). Crosses indicate the true stationary-state energies and densities for the configurations $(1s)^2$ ($\epsilon_{1s} + \epsilon_{1s} = -1$ a.u.), $(1s)^1(2s)^1$ ($\epsilon_{1s} + \epsilon_{2s} = -0.625$ a.u.), and $(2s)^2$ ($\epsilon_{2s} + \epsilon_{2s} = -0.25$ a.u.).

densities: Around $y=0$, the function $f(\mathbf{r})/n^{1/2}(\mathbf{r})$ equals $(|\psi_{2s}|^2 - |\psi_{1s}|^2)/\psi_{1s}$, which diverges as r^2 when $r \rightarrow \infty$. Around $y=1$, the function $f(\mathbf{r})/n^{1/2}(\mathbf{r})$ equals $(|\psi_{1s}|^2 - |\psi_{2s}|^2)/\psi_{2s}$, which diverges as $|1 - r/2|^{-1}$ when $r \rightarrow 2$.

III. GROUND-STATE FUNCTIONAL $E_v[n]$ AND ITS EXTREMA

We consider a system of N identical fermions (electrons) with Hamiltonian

$$\hat{H}_v = \hat{T} + \hat{V}_{e-e} + \sum_{k=1}^N v(\mathbf{r}_k) = \hat{T} + \hat{V}_{e-e} + \int d^3r v(\mathbf{r})\hat{n}(\mathbf{r}). \quad (15)$$

Here, \hat{T} is the kinetic energy, \hat{V}_{e-e} is the electron-electron interaction, $\hat{n}(\mathbf{r}) = \sum_{k=1}^N \delta(\mathbf{r} - \mathbf{r}_k)$ is the density operator, and $v(\mathbf{r})$ is an external potential. By a wave function Ψ we shall mean a normalized, antisymmetric function of the coordinates and spins $(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)$. We define the universal density functional:²¹

$$Q[n] = \min_{\Psi} \{ \langle \Psi | (\hat{T} + \hat{V}_{e-e}) | \Psi \rangle | \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = n(\mathbf{r}) \}, \quad (16)$$

which searches over all wave functions Ψ constrained to have density $n(\mathbf{r})$, and finds the minimum expectation value of $\hat{T} + \hat{V}_{e-e}$. It has been proved²⁷ that the minimum of Eq. (16) exists. Let $\Psi\{n\}$ be any one of the one or more wave functions which "deliver the minimum for density $n(\mathbf{r})$ " in the constrained search of Eq. (16). Then,

$$Q[n] = \langle \Psi\{n\} | (\hat{T} + \hat{V}_{e-e}) | \Psi\{n\} \rangle. \quad (17)$$

We also define the ground-state density functional for the energy,

$$E_v[n] = Q[n] + \int d^3r v(\mathbf{r})n(\mathbf{r}) = \langle \Psi\{n\} | \hat{H}_v | \Psi\{n\} \rangle. \quad (18)$$

While the original Hohenberg-Kohn¹ functional was defined only on the domain of v -representable densities, the functionals (16) and (18) are defined on the larger, better-understood domain of densities constructed from any wave function.²¹

Now consider the stationary-state problem for Hamiltonian \hat{H}_v ,

$$\hat{H}_v \Psi_i = E_i \Psi_i, \quad (19)$$

with E_0 as the ground-state energy or lowest eigenvalue. From the usual variational principle of quantum mechanics,

$$\begin{aligned} E_0 &= \min_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle \} \\ &= \min_n \min_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle | \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = n(\mathbf{r}) \} \\ &= \min_n \{ E_v[n] \}. \end{aligned} \quad (20)$$

Thus, the absolute minimum of the functional $E_v[n]$ is the ground-state energy, and the minimizing densities are the ground-state densities. Degeneracies pose no problem.²¹

The ground-state functional $E_v[n]$ immediately provides a lower bound on the stationary-state energies of a given density. Let $n_i(\mathbf{r})$ be the density of stationary state Ψ_i with energy E_i . Then,

$$\begin{aligned} E_i &= \langle \Psi_i | \hat{H}_v | \Psi_i \rangle \geq \min_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle | \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \\ &= n_i(\mathbf{r}) \}, \end{aligned} \quad (21)$$

or

$$E_i \geq E_v[n_i]. \quad (22)$$

The equality in Eq. (22) holds if and only if Ψ_i delivers the minimum for its own density n_i in the constrained search of Eq. (16), i.e., if and only if Ψ_i equals one of the $\Psi\{n_i\}$.

Consider the problem of extremizing $E_v[n]$ subject to the constraint $\int d^3r n(\mathbf{r}) = N$. Introduce the Lagrange multiplier λ , and find

$$\delta \left[E_v[n] - \lambda \int d^3r n(\mathbf{r}) \right] = 0 \quad (23)$$

in any infinitesimal density variation $\delta n(\mathbf{r})$ such that $|\delta n(\mathbf{r})| \ll n(\mathbf{r})$ everywhere. Functional Taylor expansion now implies the Euler-Lagrange equation (1). This highly nonlinear equation may have multiple solutions for the extrema of $E_v[n]$. The absolute minima are ground-state solutions, for which the Lagrange multiplier λ equals the chemical potential μ .

By a familiar theorem of quantum mechanics, every stationary state Ψ_i is an extremum of $\langle \Psi | \hat{H}_v | \Psi \rangle$. But

every stationary-state density $n_i(\mathbf{r})$ is not an extremum of $E_v[n]$. If Ψ_i does not deliver the minimum for its own density n_i in the search of Eq. (16), then $E_v[n]$ in the vicinity of n_i knows nothing about Ψ_i . However, if Ψ_i does deliver the minimum for its own density n_i , then conventional number-conserving variations (in the sense of Sec. IV) of $n(\mathbf{r})$ about $n_i(\mathbf{r})$ amount to variations of Ψ about Ψ_i , and for these variations,

$$\delta E_v[n] = \delta \langle \Psi | \hat{H}_v | \Psi \rangle = 0. \quad (24)$$

Conversely, every extremum of $E_v[n]$ is a stationary-state density, and the value of $E_v[n]$ at this extremum is the lowest stationary-state energy of that density. To see this, let $\tilde{n}(\mathbf{r})$ be an extremum of $E_v[n]$, and let $\Psi\{\tilde{n}\}$ be a wave function which delivers the minimum for density \tilde{n} in the search of Eq. (16). Then, the expectation value $\langle \Psi | \hat{H}_v | \Psi \rangle$ is extremal for variations of Ψ about $\Psi\{\tilde{n}\}$, whether or not these variations change the density. It follows that $\Psi\{\tilde{n}\}$ must be a stationary state. Thus, $\tilde{n}(\mathbf{r})$ is a stationary-state density, and $E_v[\tilde{n}] = \langle \Psi\{\tilde{n}\} | \hat{H}_v | \Psi\{\tilde{n}\} \rangle$ is the lowest stationary-state energy of that density.

The functional $E_v[n]$ of Eqs. (16) and (18) is *not*²⁷ convex, and this fact makes it possible to find excited states from the ground-state functional in an interacting system. If $E_v[n]$ were convex, we would have

$$E_v[n_i + x(n_0 - n_i)] \leq E_v[n_i] + x(E_v[n_0] - E_v[n_i]), \quad (25)$$

where $0 \leq x \leq 1$. Then, for $E_v[n_i] > E_v[n_0]$, any small ($x \ll 1$) admixture of ground-state density $n_0(\mathbf{r})$ into the excited state density $n_i(\mathbf{r})$ would lower $E_v[n]$ linearly with x (or even faster). In an interacting system (where all excited-state densities are expected to be nodeless), this admixture would be a conventional density variation, so $n_i(\mathbf{r})$ could not be an extremum of $E_v[n]$.

When the pure-state search of Eqs. (16) and (18) is extended^{22,27-29} to a search over ensembles $\hat{\Gamma}$, the resulting functionals

$$Q'[n] = \min_{\hat{\Gamma}} \{ \text{Tr}[\hat{\Gamma}(\hat{T} + \hat{V}_{e-e})] | \text{Tr}[\hat{\Gamma}\hat{n}(\mathbf{r})] = n(\mathbf{r}) \}, \quad (26)$$

$$E'_v[n] = Q'[n] + \int d^3r v(\mathbf{r})n(\mathbf{r}), \quad (27)$$

are²⁷ convex, and $E'_v[n]$ has no extremum lying above its minimum. Since $E_v[n]$ and $E'_v[n]$ coincide²⁹ on the set of pure-state v -representable densities,^{12,21,30} we conclude that any extrema of $E_v[n]$ which lie above the minimum fall outside that set.

Many densities^{13,21,27} fail to be pure-state v -representable. We assume that the functional derivative $\delta E_v/\delta n(\mathbf{r})$ exists for these densities, although so far existence of the derivative has been proved³¹ only for v -

representable densities. We close this section by establishing the existence of extrema of $E_v[n]$ lying above the minimum, for certain choices of external potential $v(\mathbf{r})$ and for arbitrary electron-electron coupling constant g in the range $0 \leq g \leq 1$. In the following discussion, g is regarded as a fixed constant equal to 1 for real electrons and 0 for noninteracting electrons.

First, consider the problem of finding $\Psi\{\tilde{n}\}$, a wave function which minimizes $\langle \Psi | (\hat{T} + g\hat{V}_{e-e}) | \Psi \rangle$ subject to the constraints $\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = \tilde{n}(\mathbf{r})$ (a given density) and $\langle \Psi | \Psi \rangle = 1$. Upon introduction of Lagrange multipliers $w(\{\tilde{n}\}; \mathbf{r})$ and $E\{\tilde{n}\}$, it is found,³² unless prevented by the kind of non- v -representability exhibited by Englisch and Englisch,¹³ that $\Psi\{\tilde{n}\}$ satisfies the eigenvalue equation,

$$\left[\hat{T} + g\hat{V}_{e-e} + \sum_{k=1}^N w(\{\tilde{n}\}; \mathbf{r}_k) \right] \Psi\{\tilde{n}\} = E\{\tilde{n}\} \Psi\{\tilde{n}\}. \quad (28)$$

Next, let the given density $\tilde{n}(\mathbf{r})$ be constructed as a special convex sum of degenerate ground-state densities for Hamiltonian $\hat{T} + g\hat{V}_{e-e} + \sum_k v(\mathbf{r}_k)$, with some choice of potential v' . By a previous theorem,^{27,29} \tilde{n} is not pure-state v -representable. Consequently, $\Psi\{\tilde{n}\}$ is not a ground state for any Hamiltonian of the form $\hat{T} + g\hat{V}_{e-e} + \sum_k v(\mathbf{r}_k)$. Instead, by Eq. (28), $\Psi\{\tilde{n}\}$ is an excited-state for Hamiltonian $\hat{T} + g\hat{V}_{e-e} + \sum_k v(\mathbf{r}_k)$, when $v(\mathbf{r})$ is chosen to be $w(\{\tilde{n}\}; \mathbf{r})$. Moreover, by the theorems proved earlier in this section, \tilde{n} is an extremum of

$$E_v[n] \equiv \langle \Psi\{n\} | (\hat{T} + g\hat{V}_{e-e}) | \Psi\{n\} \rangle + \int d^3r v(\mathbf{r})n(\mathbf{r}),$$

which is the desired result.

IV. CONVENTIONAL AND UNCONVENTIONAL DENSITY VARIATIONS

Second- or higher-order functional derivatives of $E_v[n]$ can diverge in certain regions of space, leading to peculiar behavior of $E_v[n]$ under the unconventional density variations discussed below. Consider, for example, the second functional derivative. The quantity $-\delta^2 E_v/\delta n(\mathbf{r})\delta n(\mathbf{r}')$ plays the role of an inverse density response function,³² i.e., the integral

$$\delta v(\mathbf{r}) = - \int d^3r' \frac{\delta^2 E_v}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \delta n(\mathbf{r}'), \quad (29)$$

is the change of external potential needed to produce a given infinitesimal, number-conserving variation $\delta n(\mathbf{r}')$ in the stationary-state density. Since an electron which wanders far out into the exponentially decaying density tail of a closed system has only noninteracting kinetic energy,²⁵ we find that for $|\mathbf{r}| \rightarrow \infty$ or $|\mathbf{r}'| \rightarrow \infty$,

$$\begin{aligned} \frac{\delta^2 E_v}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} &\rightarrow \frac{\delta^2}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \int d^3r'' n^{1/2}(\mathbf{r}'') \left(-\frac{1}{2} \nabla_{\mathbf{r}''}^2 \right) n^{1/2}(\mathbf{r}'') \\ &= \frac{1}{4} \{ \delta(\mathbf{r} - \mathbf{r}') n^{-3/2}(\mathbf{r}) \nabla^2 n^{1/2}(\mathbf{r}) - n^{-1/2}(\mathbf{r}) \nabla^2 [n^{-1/2}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')] \}, \quad (30) \end{aligned}$$

which diverges exponentially as n^{-1} .

Here, we consider infinitesimal density variations $n(\mathbf{r}) \rightarrow n(\mathbf{r}) + \delta n(\mathbf{r})$, with $\delta n(\mathbf{r}) = \epsilon f(\mathbf{r})$ of the form of Eq. (3). The mere fact that $\delta n(\mathbf{r})$ is infinitesimal is not sufficient to establish that $|\delta n(\mathbf{r})| \ll n(\mathbf{r})$ for all \mathbf{r} . However, if $|f(\mathbf{r})|/n(\mathbf{r})$ is bounded, then the inequality is established. For this kind of density variation, $E_v[n]$ presumably has a convergent functional Taylor expansion:

$$\begin{aligned} E_v[n + \delta n] &= E_v[n] + \int d^3r \frac{\delta E_v}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) \\ &+ \frac{1}{2} \int d^3r \int d^3r' \frac{\delta^2 E_v}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \delta n(\mathbf{r}) \delta n(\mathbf{r}') \\ &+ \dots \end{aligned} \quad (31)$$

If $n(\mathbf{r})$ is an extremum of $E_v[n]$, i.e., a solution of Eq. (1), then the corresponding energy variation δE_v is clearly of order ϵ^2 .

More generally, we know from Sec. III that a number-conserving density variation of order ϵ about an extremum $n(\mathbf{r})$ of $E_v[n]$ will lead to an energy variation δE_v of order ϵ^2 if $\delta n(\mathbf{r})$ is associated by the constrained search of Eq. (16) with a wave-function variation $\delta \Psi\{n\}$ of order ϵ , i.e., if $\delta n(\mathbf{r})$ is a "conventional" density variation.

We now derive a necessary condition which every conventional variation $\delta n(\mathbf{r})$ must satisfy. Let $n(\mathbf{r})$ be associated by the constrained search with Ψ , so that

$$\begin{aligned} n(\mathbf{r}_1) &= N \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_2 \dots d^3r_N |\Psi(1, 2, \dots, N)|^2 \\ &\equiv N \int |\Psi|^2. \end{aligned} \quad (32)$$

Let $\delta n(\mathbf{r}) = \epsilon f(\mathbf{r})$ be associated by the constrained search with the wave-function variation $\epsilon \chi$, where χ is a normalized, antisymmetric function of the space-spin coordinates $(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)$, so that

$$\delta n(\mathbf{r}_1) = \epsilon N \int 2 \operatorname{Re} \Psi^* \chi. \quad (33)$$

Following Levy, Perdew, and Sahni,²⁵ write

$$\Psi(1, 2, \dots, N) = N^{-1/2} n^{1/2}(\mathbf{r}_1) \Phi(1, 2, \dots, N), \quad (34)$$

where Φ depends parametrically on \mathbf{r}_1 and σ_1 , Φ is antisymmetric in space-spin coordinates $(\mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N)$, and

$$\int |\Phi|^2 = 1. \quad (35)$$

Rewrite Eq. (33) as

$$\delta n(\mathbf{r}_1)/n^{1/2}(\mathbf{r}_1) = 2\epsilon N^{1/2} \operatorname{Re} \int \Phi^* \chi. \quad (36)$$

From Eq. (36), obtain the inequality

$$|\delta n(\mathbf{r}_1)|/n^{1/2}(\mathbf{r}_1) \leq 2\epsilon N^{1/2} \left| \int \Phi^* \chi \right|. \quad (37)$$

Apply the Cauchy-Schwarz inequality to the right-hand side of Eq. (37), and find

$$|\delta n(\mathbf{r}_1)|/n^{1/2}(\mathbf{r}_1) \leq 2\epsilon \left[\int |\Phi|^2 \right]^{1/2} \left[N \int |\chi|^2 \right]^{1/2}. \quad (38)$$

With the help of Eqs. (3) and (35), recast Eq. (38) as

$$|f(\mathbf{r})|/n^{1/2}(\mathbf{r}) \leq 2n_\chi^{1/2}(\mathbf{r}), \quad (39)$$

where $n_\chi(\mathbf{r})$ is the density of wave function χ . Since $n_\chi^{1/2}(\mathbf{r})$ must be square-integrable, we conclude that, for a conventional density variation with the form of Eq. (3), $f(\mathbf{r})/n^{1/2}(\mathbf{r})$ must be square-integrable.

As a particular example, consider a density variation $\delta n(\mathbf{r}) = \epsilon f(\mathbf{r})$, which meets the sufficient condition for conventionality, $|\delta n(\mathbf{r})|/n(\mathbf{r}) \ll 1$ for all \mathbf{r} or $|f(\mathbf{r})|/n(\mathbf{r})$ bounded. For this variation, $|f(\mathbf{r})|/n^{1/2}(\mathbf{r})$ equals the product of $n^{1/2}(\mathbf{r})$ with a bounded function, so $f(\mathbf{r})/n^{1/2}(\mathbf{r})$ is manifestly square-integrable. On the other hand, there are conventional density variations $\epsilon f(\mathbf{r})$ which satisfy the necessary condition that $f(\mathbf{r})/n^{1/2}(\mathbf{r})$ be square-integrable but not the sufficient condition that $|f(\mathbf{r})|/n(\mathbf{r})$ be bounded; an example is provided by the conventional path of Eq. (10) away from the ground-state density ($y=0$).

From the vantage point of the present discussion, we can see that the "derivative discontinuities of the energy"^{22,23,26} arise from unconventional density variations. In earlier work,²² it was found that the ground-state energy E of an open electronic system, as a function of its time-averaged electron number N , is a linkage of straight-line segments with possible slope discontinuities at integer values of N . Thus, for N between the integers $J-1$ and J ,

$$E(N) = (N - J + 1)E(J) + (J - N)E(J - 1). \quad (40)$$

The first derivation of Eq. (40) was based on an ensemble description for the open system.²² Equation (40) was used to explain (within density-functional theory) why separated subsystems have integer electron numbers in the ground-state of the combined system,^{22,33} to reveal the physical content of the exact Kohn-Sham orbital energies,^{22,23} and to discover the discontinuity of the exchange-correlation potential²² which is responsible for the difference^{23,26} between the true band gap in an insulator and the gap in the exact Kohn-Sham band structure.

Consider an open system (S) very far from, but free to exchange electrons with, an electron reservoir (R). The open system and its reservoir together comprise a combined system ($C = S + R$) with K electrons. Suppose that the ground state of C localizes J electrons in S , and the remaining $K - J$ in R . Take a number-conserving density variation about this ground state, which makes the electron number N in S slightly less than J but otherwise minimizes the energy. The constrained search of Eq. (16) associates²⁶ with the final density a wave function for C :

$$\begin{aligned} \Psi_C &= \hat{A} [(N - J + 1)^{1/2} \Psi_S(1, \dots, J) \Psi_R(J + 1, \dots, K) \\ &+ (J - N)^{1/2} \Psi_S(1, \dots, J - 1) \Psi_R(J, \dots, K)], \end{aligned} \quad (41)$$

where $\Psi_S(1, \dots, M)$ is the M -electron ground state for S and $\Psi_R(M + 1, \dots, K)$ is the $(K - M)$ -electron ground state for R . \hat{A} is an operator which antisymmetrizes and normalizes. The corresponding final energy for S is Eq. (40), and the final density for C is

$$n(N; \mathbf{r}) = (N - J + 1)n(J; \mathbf{r}) + (J - N)n(J - 1; \mathbf{r}), \quad (42)$$

where $n(M; \mathbf{r})$ equals the density of C when M electrons are in S .

Let $\epsilon = J - N$ be infinitesimal. The density variation of Eq. (42) about the ground-state density $n(J; \mathbf{r})$ is

$$\delta n(\mathbf{r}) = \epsilon [n(J-1; \mathbf{r}) - n(J; \mathbf{r})]. \quad (43)$$

But the associated wave-function variation of Eq. (41) is of order $\epsilon^{1/2}$, not ϵ . It follows that $\delta n(\mathbf{r})$ is not a conventional density variation. The corresponding energy variation is of order $|\epsilon|$, not ϵ^2 . Thus, the discontinuity in the derivative dE/dN at $N=J$ arises from an unconventional density variation within the combined system.

V. SELF-CONSISTENT SINGLE-PARTICLE EQUATIONS

Several versions^{12,19,31,34} of the Kohn-Sham procedure² involve a constrained search.²¹ The one¹² we discuss here seems best suited to the quest for excited states from the ground-state theory.

If the electron-electron repulsion \hat{V}_{e-e} is switched off, the constrained-search functional $Q[n]$ of Eq. (16) reduces to the kinetic-energy functional^{12,27,29}

$$T_s[n] = \min_{\Psi} \{ \langle \Psi | \hat{T} | \Psi \rangle \mid \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = n(\mathbf{r}) \}. \quad (44)$$

We also define the Hartree repulsion functional as

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|, \quad (45)$$

and the exchange-correlation energy functional as

$$E_{xc}[n] = Q[n] - (T_s[n] + U[n]). \quad (46)$$

The Euler equation (1) for the extrema of $E_v[n]$ may be written as

$$\frac{\delta T_s}{\delta n(\mathbf{r})} + v_s([n]; \mathbf{r}) = \lambda, \quad (47)$$

where

$$v_s([n]; \mathbf{r}) = v(\mathbf{r}) + \int d^3r' n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + \delta E_{xc}/\delta n(\mathbf{r}). \quad (48)$$

Let $\tilde{n}(\mathbf{r})$ be a density which extremizes $E_v[n]$. By Eq. (47), $\tilde{n}(\mathbf{r})$ also extremizes

$$\begin{aligned} T_s[n] + \int d^3r n(\mathbf{r})v_s([\tilde{n}]; \mathbf{r}) \\ = \min_{\Psi} \left\{ \left\langle \Psi \left| \left[\hat{T} + \sum_k v_s([\tilde{n}]; \mathbf{r}_k) \right] \right| \Psi \right\rangle \mid \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = n(\mathbf{r}) \right\}, \end{aligned} \quad (49)$$

the ground-state functional for *noninteracting* electrons in the presence of the effective potential $v_s([\tilde{n}]; \mathbf{r})$. By the discussion of Sec. III, $\tilde{n}(\mathbf{r})$ must be a stationary-state density for this noninteracting system.

For noninteracting electrons in the presence of an external potential $v_s(\mathbf{r})$, the stationary states Ψ_i^s and energies E_i^s may be constructed as follows: First solve the one-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \psi_\alpha(\mathbf{r}) = \epsilon_\alpha \psi_\alpha(\mathbf{r}) \quad (50)$$

for the orbitals $\psi_\alpha(\mathbf{r})$ and orbital energies ϵ_α . Then, the Ψ_i^s are either single Slater determinants constructed from these orbitals, with E_i^s equal to the sum of the orbital energies, or linear combinations of several degenerate Slater determinants. [In alternative versions of the Kohn-Sham method, the search in Eq. (44) may be extended from wave functions to ensembles,^{19,31} or restricted to single Slater determinants.^{12,27,34}]

A self-consistent solution of the Kohn-Sham equations (48) and (50) is a stationary state Ψ_i^s for noninteracting electrons in the presence of external potential $v_s([n_i^s]; \mathbf{r})$. The density $n_i^s(\mathbf{r}) = \langle \Psi_i^s | \hat{n}(\mathbf{r}) | \Psi_i^s \rangle$ may be constructed by the standard rules³⁵ for evaluating the matrix element of a one-electron operator between Slater determinants. Every density which extremizes $E_v[n]$ may be constructed from such a self-consistent solution. However, every self-consistent solution does not yield a density which extremizes $E_v[n]$. [For example, in the model of Sec. II, the $(1s)^2$, $(1s)^1(2s)^1$, and $(2s)^2$ determinants are *all* solutions of the Kohn-Sham equations.]

Given a self-consistent solution Ψ_i^s of the Kohn-Sham equations, how can we tell if its density $n_i^s(\mathbf{r}) = \langle \Psi_i^s | \hat{n}(\mathbf{r}) | \Psi_i^s \rangle$ and kinetic energy $\langle \Psi_i^s | \hat{T} | \Psi_i^s \rangle$ are those of an extremum of $E_v[n]$? From the discussion of Sec. III, the necessary and sufficient condition is that Ψ_i^s must deliver the minimum for its own density $n_i^s(\mathbf{r})$ in the constrained search of Eq. (44). Every self-consistent solution Ψ_i^s which satisfies this condition provides the density and (via $E_v[n]$) the energy of a stationary state Ψ_i of the interacting system. Moreover, there is likely an adiabatic connection^{10,36-39} between Ψ_i^s and Ψ_i , neither of which need be ground states. To see this adiabatic connection, simply take Eq. (28) from $g=1$ to $g=0$, at fixed $\tilde{n} = n_i$. Observe that $\Psi\{n_i\}$ is transformed from Ψ_i at $g=1$ to Ψ_i^s at $g=0$. Adiabatic connection favors the practical computability^{38,39} of the exchange-correlation energy $E_{xc}[n]$.

Suppose the density of a particular Kohn-Sham self-consistent solution is noninteracting pure-state v -representable (i.e., it is the ground-state density for *some* system of noninteracting electrons). Then, the necessary and sufficient condition of the preceding paragraph is that the occupation numbers of the Kohn-Sham orbitals must obey ground-state Fermi statistics, with all orbitals occupied for $\epsilon_\alpha < \mu$ and empty for $\epsilon_\alpha > \mu$. In general, if a Kohn-Sham self-consistent solution obeys ground-state Fermi statistics, then it provides the density and (via $E_v[n]$) the energy of a stationary state of the interacting system.

In some cases, e.g., the iron atom,^{19,40,41} there may be *no* self-consistent solution of the Kohn-Sham equations which obeys ground-state Fermi statistics. In other cases, there may be *several* self-consistent solutions which obey ground-state Fermi statistics. The latter situation might arise, for example, when the ground state is degenerate. Thus, in our search for excited states from the ground-state functional, we turn in Sec. VI to the multiplets derived from a degenerate ground-state orbital configuration.

The exact ground-level density of the iron atom is, by

definition, interacting ensemble v -representable.²⁹ As implied in the above paragraph, however, this density is not expected to be simultaneously noninteracting pure-state v -representable. Nevertheless, by an earlier argument,¹² this density is expected to be noninteracting ensemble v -representable. Hence, in a Kohn-Sham approach, this density can be constructed either with fractional occupation numbers obeying Fermi statistics, or with integer occupation numbers in violation thereof. With the latter choice, the holes lying below occupied orbitals should be few.

To show how interacting ensemble v -representability leads to noninteracting ensemble v -representability, we shall follow Ref. 12 where we started with the following slight generalization of Eq. (4.5) from Lieb:²⁷

$$\sup_w \left\{ E_g(w) - \int d\mathbf{r} w(\mathbf{r})n(\mathbf{r}) \right\} \\ = \inf_{\hat{\Gamma}} \{ \text{Tr}(\hat{\Gamma}\hat{G}) \mid \text{Tr}[\hat{\Gamma}\hat{n}(\mathbf{r})] = n(\mathbf{r}) \}. \quad (51)$$

In the above equation $\hat{G} = \hat{T} + g\hat{V}_{e-e}$, where $n(\mathbf{r})$ is, say, the interacting ground-level iron density of interest, and where $E_g(w)$ is the ground-level energy for Hamiltonian $\hat{H}_g^w = \sum_{i=1}^N w(\mathbf{r}_i) + \hat{T} + g\hat{V}_{e-e}$. With $g=1$, $\bar{w}_g = -Zr^{-1}$, and $Z=26$, where \bar{w}_g is the maximizing w on the left-hand side of Eq. (51) for a given g . The search for the infimum on the right-hand side of Eq. (51) includes all those ensembles $\hat{\Gamma}$ which yield $n(\mathbf{r})$. Also, it has been shown²⁷ that the infimum is always a minimum.

Now, at fixed iron $n(\mathbf{r})$, gradually let $g \rightarrow 0$ in Eq. (51). There should be no reason to believe that the presence of a maximizing w would suddenly disappear between $g=1$ and $g=0$. Accordingly, call \bar{w}_0 the maximizing w at $g=0$. Equation (51) then becomes¹²

$$E_0(\bar{w}_0) - \int d\mathbf{r} \bar{w}_0(\mathbf{r})n(\mathbf{r}) \\ = \min_{\hat{\Gamma}} \{ \text{Tr}(\hat{\Gamma}\hat{G}) \mid \text{Tr}[\hat{\Gamma}\hat{n}(\mathbf{r})] = n(\mathbf{r}) \} \quad (52)$$

or, upon rearrangement

$$E_0(\bar{w}_0) = \min_{\hat{\Gamma}} \left\{ \text{Tr} \left[\hat{\Gamma} \left[\hat{G} + \sum_{i=1}^N \bar{w}_0(\mathbf{r}_i) \right] \right] \mid \text{Tr}[\hat{\Gamma}\hat{n}(\mathbf{r})] = n(\mathbf{r}) \right\}. \quad (53)$$

The equality in Eq. (53) dictates that $n(\mathbf{r})$ is noninteracting ensemble v -representable.

VI. MULTIPLETS PROBLEM FOR THE CARBON ATOM

Here, we consider the multiplets problem for the ground-state orbital configuration $(2p)^2$ of the carbon atom. This problem has been discussed in detail by von Barth,⁴² and we will draw heavily on his analysis for the discussion at hand.

von Barth⁴² solved the Kohn-Sham equations for a spherically-symmetric, spin-unpolarized density. This procedure gave a set of Kohn-Sham orbitals which were used to construct single Slater determinants for the configuration $(1s)^2(2s)^2(2p)^2$, or linear combinations of such determinants, which were simultaneous eigenstates of the total angular momentum and total spin operators \hat{L}^2 , \hat{L}_z , \hat{S}^2 , and \hat{S}_z . The spin-up and spin-down densities of these noninteracting wave functions are shown in Table I. All these noninteracting wave functions have the same expectation values for the kinetic energy and for the electron-nuclear attraction energy. von Barth⁴² then evaluated the Hartree repulsion of Eq. (45), and the exchange-correlation energy in the local-spin-density (LSD) approximation.^{2,43}

$$E_{xc}^{\text{LSD}}[n_1, n_1] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n_1(\mathbf{r}), n_1(\mathbf{r})), \quad (54)$$

where $\epsilon_{xc}(n_1, n_1)$ is the exchange-correlation energy per particle in an electron gas with uniform spin densities n_1 and n_1 . von Barth found (Table I) that LSD produced a large, unphysical splitting among ground-state densities which should be degenerate.

With the same carbon atom densities used by von

TABLE I. Multiplets of the carbon atom in its ground-state orbital configuration $(2p)^2$. All deviations Δ are taken with respect to the spherical, spin-unpolarized 1S state rather than the ground state 3P . E_i is the measured stationary-state energy. The fourth column tells whether a given eigenstate of \hat{L}^2 , \hat{S}^2 , \hat{L}_z , and \hat{S}_z , with eigenvalues $L(L+1)$, $S(S+1)$, M_L , and M_S , respectively, derives from a single determinant in the noninteracting limit. In the fifth and sixth columns, $P_2 = (3 \cos^2 \theta - 1)/2$. $E_v[n]$ is the ground-state density functional, $U[n]$ is the Hartree repulsion, and $\Delta E_v = \Delta U + \Delta E_{xc}$. Most entries, including the local-spin-density (LSD) results, were taken from Tables I, II, and III of Ref. 42. The local-density (LD) and Langreth-Mehl (LM) results were calculated here. (All energies are units of eV.)

Multiplet	ΔE_i	$ L, S; M_L, M_S\rangle$	Single determinant?	Valence-electron spin density		ΔU	ΔE_v^{LSD}	ΔE_v^{LD}	ΔE_v^{LM}
				$\rho_1/\rho(r)$	$\rho_1/\rho(r)$				
3P	-2.68	$ 1, 1; 1, 1\rangle$	yes	$2 + P_2$	0	0.13	-1.24	0.05	0.04
		$ 1, 1; 0, 1\rangle$	yes	$2 - 2P_2$	0	0.50	-1.25	0.16	0.10
		$ 1, 1; 1, 0\rangle$	no	$1 + \frac{1}{2}P_2$	$1 + \frac{1}{2}P_2$	0.13	0.05	0.05	0.04
1D	-1.42	$ 1, 1; 0, 0\rangle$	no	$1 - P_2$	$1 - P_2$	0.50	0.16	0.16	0.10
		$ 2, 0; 2, 0\rangle$	yes	$1 - P_2$	$1 - P_2$	0.50	0.16	0.16	0.10
		$ 2, 0; 1, 0\rangle$	no	$1 + \frac{1}{2}P_2$	$1 + \frac{1}{2}P_2$	0.13	0.05	0.05	0.04
1S	0.00	$ 2, 0; 0, 0\rangle$	no	$1 + P_2$	$1 + P_2$	0.50	0.18	0.18	0.13
		$ 0, 0; 0, 0\rangle$	no	1	1	0.00	0.00	0.00	0.00

Barth, we have calculated the exchange-correlation energy in the local-density (LD) approximation:^{2,43}

$$E_{xc}^{LD}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(\frac{1}{2}n(\mathbf{r}), \frac{1}{2}n(\mathbf{r})), \quad (55)$$

and in the Langreth-Mehl (LM) approximation²⁰ (based upon wave-vector analysis of the density-gradient expansion):⁴⁴

$$E_{xc}^{LM}[n] = E_{xc}^{LD}[n] + 0.002144 \int d^3r \frac{|\nabla n|^2}{n^{4/3}} (2e^{-F} - \frac{7}{9}), \quad (56)$$

where $F = 0.2618 |\nabla n| / n^{7/6}$. We see in Table I that the LD and LM approximations are remarkably successful in reproducing (within 0.1 eV) the degeneracy of the various ground-state densities, despite correlation-function arguments^{42,45} which suggest that these approximations should be worse for states which do not reduce to single Slater determinants in the noninteracting limit. Moreover, in comparison with the measured multiplet splittings ΔE_i of Table I (several eV), the LD and LM approximations assign about the same energy to all of the ground and excited-state densities in Table I. In some cases, at least, this result is to be expected: Some of the excited-state densities are clearly equal to various ground-state densi-

ties. Also, as pointed out by von Barth,⁴² the spherically symmetric 1S density can be obtained from a certain linear combination of degenerate 1D states, so that the ground-state functional $E_v[n]$ must assign the same energy to both of these excited states.

From Sec. V, we know that any self-consistent solutions of the Kohn-Sham equations for the ground-state orbital configuration of the carbon atom must represent stationary states of the interacting system. But our analysis in the present section seems to suggest that these solutions may all represent ground states of the interacting system.

A practical alternative for the calculation of multiplet splittings is the "sum method"⁴⁵⁻⁴⁸ which is justified by the "density-functional theory of mixed symmetry states."⁴² But then there is the problem that, in principle, the needed density functional is not that of the ground state, as discussed in the Introduction.

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