COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Significance of the highest occupied Kohn-Sham eigenvalue"

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With more explanation than usual and without appeal to Janak's theorem, we review the statement and proof of the ionization potential theorems for the exact Kohn-Sham density-functional theory of a many-electron system: (1) For any average electron number N between the integers $Z-1$ and Z, and thus for $N \rightarrow Z$ from below, the highest occupied or partly occupied Kohn-Sham orbital energy is minus the ionization energy of the Z-electron system. (2) For $Z-1 < N < Z$, the exact Kohn-Sham effective potential $v_s(\mathbf{r})$ tends to zero as $|\mathbf{r}| \rightarrow \infty$. We then argue that an objection to these theorems. [L. Kleinman, Phys. Rev. B **56**, 12 042 (1997)] overlooks a crucial step in the proof of theorem (2): The asymptotic exponential decay of the exact electron density of the Z-electron system is controlled by the exact ionization energy, but the decay of an approximate density is *not* controlled by the approximate ionization energy. We review relevant evidence from the numerical construction of the exact Kohn-Sham potential. In particular, we point out a model two-electron problem for which the ionization potential theorems are exactly confirmed. Finally, we comment on related issues: the self-interaction correction, the discontinuity of the exact Kohn-Sham potential as N passes through the integer Z, and the generalized sum rule on the exchange-correlation hole. [S0163-1829(98)04403-8]

I. INTRODUCTION

Kohn-Sham density functional theory[1-4] is a formally exact way to find the ground-state energy and density of a many-electron system by solving a self-consistent one-electron Schrödinger equation. In practice, the density functional for the exchange-correlation energy must be approximated, and approximate Kohn-Sham calculations are a mainstay of modern electronic structure theory in both condensed matter physics and quantum chemistry.

Perdew, Parr, Levy, and Balduz[5] (PPLB) showed that the highest-occupied exact Kohn-Sham orbital energy (for all electron numbers N between the integers $Z-1$ and Z) is minus the ionization energy of the Z-electron system. The ensemble constrained search of Ref. 5 implicitly fixes the constant $\lim_{|\mathbf{r}| \rightarrow \infty} \delta E_{\text{xc}} / \delta n(\mathbf{r})$. Later Levy, Perdew, and Sahni[6] (LPS) showed that this limit of the exact exchange-correlation potential vanishes for $Z-1 < N < Z$, and thus for $N \rightarrow Z$ from below. These "ionization potential theorems" have been challenged in a recent article by Kleinman.[7]

Our comment on Kleinman's article begins with a review of the ionization potential theorems and their proofs (Sec. II). These proofs were originally presented separately and briefly in Refs. 5 and 6. They appear together in Ref. 8, a conference proceedings article which also addresses other related issues. In Sec. III, we examine Kleinman's critique, and show that it

overlooks a crucial step in the proof of Ref. 6. In Sec. IV, we review numerical evidence for and against the ionization potential theorems. Section V reviews the related ideas of self-interaction correction, derivative discontinuity, and exchange-correlation sum rule. Appendix B presents an exactly-solved model two-electron problem for which the ionization potential theorems are exactly confirmed.

II. IONIZATION-POTENTIAL THEOREMS AND PROOFS

In the original density-functional theory[1,9,10] based upon many-electron wave functions, the electron number

$$N = \int d^3 r \, n(\mathbf{r}) \tag{1}$$

is a fixed integer. As a result, functional derivatives $\delta F / \delta n(\mathbf{r})$, which satisfy the equation

$$\delta F[n] = \int d^3 r \, \frac{\delta F}{\delta n(\mathbf{r})} \, \delta n(\mathbf{r}) \tag{2}$$

for infinitesimal density changes $\delta n(\mathbf{r})$, are only defined to within an arbitrary additive constant. Reference 5 extended the domain of density-functional theory to noninteger electron number N, for two reasons: (1) to ensure that all functional derivatives, and hence all potentials, are completely

defined, and (2) to describe an open system which can exchange electrons with its environment. In an open system, the electron number can fluctuate between integers, and its time or ensemble average need not be an integer. For most electronic systems,[5,8] this extension is nothing more than an explicit display of the zero-temperature limit of Mermin's finite-temperature density-functional theory[11] within the grand canonical ensemble.

Let Z be an integer, and consider average electron number N in the range $Z-1 < N < Z$. Generalize the constrained-search[10] definition of the universal density functional $F[n]$ to

$$F[n] \equiv \min_{\Gamma \to n} \langle \hat{T} + \hat{V}_{ee} \rangle_\Gamma. \qquad (3)$$

In Eq. (3), $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic and electron-electron repulsion operators. Γ is an ensemble or statistical mixture of a $(Z-1)$-electron pure state Ψ_{Z-1} with probability $1-\omega$, and a Z-electron pure state Ψ_Z with probability ω, where $0 < \omega < 1$. The pure states must be antisymmetric under exchange of a pair of electrons. For each Ψ_M ($M=Z-1$ or Z), define a density

$$n_M(\mathbf{r}) = \langle \Psi_M | \hat{n}(\mathbf{r}) | \Psi_M \rangle, \qquad (4)$$

so that

$$\langle \hat{n}(r) \rangle_\Gamma = (1-\omega) n_{Z-1}(\mathbf{r}) + \omega n_Z(\mathbf{r}), \qquad (5)$$

$$\langle \hat{N} \rangle_\Gamma = (1-\omega)(Z-1) + \omega Z = Z-1+\omega = N. \qquad (6)$$

Equation (3) can then be rewritten as

$$F[n] = \min\{(1-\omega)\langle \Psi_{Z-1} | \hat{T} + \hat{V}_{ee} | \Psi_{Z-1} \rangle + \omega \langle \Psi_Z | \hat{T} + \hat{V}_{ee} | \Psi_Z \rangle\}, \qquad (7)$$

where the minimum is taken over all pairs Ψ_{Z-1} and Ψ_Z such that $(1-\omega) n_{Z-1}(\mathbf{r}) + \omega n_Z(\mathbf{r}) = n(\mathbf{r})$.

We now establish the density-functional variational principle. For a given electron number N and external potential $v(\mathbf{r})$, define the ground-ensemble energy

$$E_N^g = \min_{\Gamma \to N} \left\langle \hat{T} + \hat{V}_{ee} + \int d^3r \, \hat{n}(\mathbf{r}) v(\mathbf{r}) \right\rangle_\Gamma, \qquad (8)$$

and define the ground-ensemble density $n_N^g(\mathbf{r})$ as the density of the minimizing ensemble Γ. The minimization of Eq. (8) can be done in two steps: first over all ensembles Γ yielding a given density $n(\mathbf{r})$, then over all densities $n(\mathbf{r})$ integrating to N, whence

$$E_N^g = \min_{n \to N} \left\{ F[n] + \int d^3r \, n(\mathbf{r}) v(\mathbf{r}) \right\} = (1-\omega) E_{Z-1}^g + \omega E_Z^g, \qquad (9)$$

$$n_N^g(\mathbf{r}) = (1-\omega) n_{Z-1}^g(\mathbf{r}) + \omega n_Z^g(\mathbf{r}). \qquad (10)$$

The Euler equation for the minimization of Eq. (9) is $\delta[F[n] + \int d^3r \, n(\mathbf{r}) v(\mathbf{r}) - \mu N] = 0$ or

$$\frac{\delta F}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu, \qquad (11)$$

where $\mu = \partial E_N^g / \partial N$ is the Lagrange multiplier for the constraint of constant N. (Since the Lagrange multiplier is always the derivative with respect to the constraint, we do not need Janak's theorem.[12]) Also Appendix A arrives at $\mu = \partial E_N^g / \partial N$ by a different route for those who are unfamiliar with Lagrange multipliers.

Now consider a fictitious noninteracting ($\hat{V}_{ee} = 0$) system of electrons with the same density $n(\mathbf{r})$ as above. By analogy with Eq. (3), we define the noninteracting kinetic energy

$$T_s[n] \equiv \min_{\Gamma \to n} \langle \hat{T} \rangle_\Gamma. \qquad (12)$$

Define the Hartree self-repulsion of the electron density as

$$U[n] = \tfrac{1}{2} \int d^3r \int d^3r' \, n(\mathbf{r}) n(\mathbf{r}') / |\mathbf{r}' - \mathbf{r}|, \qquad (13)$$

and the exchange-correlation energy E_{xc} by

$$F[n] = T_s[n] + U[n] + E_{\text{xc}}[n]. \qquad (14)$$

The Euler equation (11) can then be written as

$$\frac{\delta T_s}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = \mu, \qquad (15)$$

where

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}, \qquad (16)$$

and $\delta U / \delta n(\mathbf{r}) = \int d^3r' \, n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$. Equation (15) is the Euler equation for a system of noninteracting electrons moving in an external potential $v_s(\mathbf{r})$, the Kohn-Sham effective potential, which holds them at density $n(\mathbf{r})$. The Kohn-Sham spin orbitals $\psi_i(\mathbf{r})$ are self-consistent solutions of the Kohn-Sham equations

$$[-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \qquad (17)$$

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \qquad (18)$$

where $f_1 = 1$ for $\epsilon_i < \epsilon_Z(i < Z)$, 0 for $\epsilon_i > \epsilon_Z(i > Z)$, and ω for $\epsilon_i = \epsilon_Z(i = Z)$. Then $T_s[n] = \Sigma_i f_i \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle$.

The self-consistent equations (17) and (18) result, with a fractional occupation number *only* at $i = Z$, because by equations (12) and (15) $n(\mathbf{r})$ is simultaneously the ground-ensemble density whose noninteracting energy is

$$E_N^{sg} = (1-\omega) E_{Z-1}^{sg} + \omega E_Z^{sg}, \qquad (19)$$

where E_M^{sg} is the total ground-state energy (sum of occupied orbital energies) of that M-electron noninteracting system whose external potential is $v_s(\mathbf{r})$, with $M = Z-1$ or $M = Z$.

By construction the chemical potentials, μ, for the noninteracting and interacting systems of the same density $n(\mathbf{r})$ are the same. Further, by Eqs. (15) and (19) we have

$$\mu = \frac{\partial E_N^{sg}}{\partial N} = \frac{\partial E_N^{sg}}{\partial \omega} = E_Z^{sg} - E_{Z-1}^{sg} = \epsilon_Z, \qquad (19a)$$

and by Eqs. (9) and (11) we have

$$\mu = \frac{\partial E_N^g}{\partial N} = \frac{\partial E_N^g}{\partial \omega} = E_Z^g - E_{Z-1}^g = -I_Z, \qquad (19b)$$

where the derivatives are taken at fixed $v_s(\mathbf{r})$ and $v(\mathbf{r})$, respectively. Consequently, by Eqs. (19a) and (19b), our desired result is obtained:

$$\epsilon_Z = -I_Z \quad (Z-1 < N < Z). \qquad (19c)$$

Thus through a somewhat different route than previously employed[5] and without use of Janak's theorem, we have confirmed that the exact highest-occupied Kohn-Sham eigenvalue is minus the ionization energy of the Z-electron system. Since Eq. (19c) holds for all N between $Z-1$ and Z, it also holds in the limit $N \to Z$ from below, for which the calculations described in Sec. IV are carried out.

We pause to review the interacting and noninteracting ensembles we have constructed. We are given an external potential $v(\mathbf{r})$ and an average electron number N in the range $Z-1 < N < Z$. The interacting ground ensemble is simply a mixture of the ground states of the $(Z-1)$ electron system (with probability $1-\omega$) and of the Z-electron system (with probability ω). Thus $n_N^g(\mathbf{r})$, E_N^g, and $F[n_N^g]$ vary linearly with N, although the individual components of F [Eq. (14)] do not. The noninteracting or Kohn-Sham ensemble is a mixture of the ground states for $(Z-1)$ and Z noninteracting electrons in the presence of the external potential $v_s(\mathbf{r})$, which of course depends upon $v(\mathbf{r})$ and varies with N. The Kohn-Sham potential $v_s(\mathbf{r})$ is chosen so that the ground-ensemble density of the noninteracting electrons is the same as that of the interacting electrons.

LPS (Ref. 6) arrived at

$$\lim_{|\mathbf{r}| \to \infty} v_s(\mathbf{r}) = 0 \quad (Z-1 < N < Z) \qquad (20)$$

within the exact Kohn-Sham theory by proving conclusively that the asymptotic decay of the exact electron density of the Z-electron system is

$$n(\mathbf{r}) \sim \exp[-2\sqrt{2I_Z}|\mathbf{r}|] \qquad (21)$$

when the external potential $v(\mathbf{r})$ vanishes as $|\mathbf{r}| \to \infty$. The proof depends upon the fact that, as one electron coordinate of the Z-electron ground-state wave function tends to infinity, the remaining electrons collapse to the $(Z-1)$-electron ground state (if it is accessible by symmetry). For a numerical demonstration of this collapse, see Ref. 13.

Since typically $I_Z < I_{Z-1}$, Eq. (21) describes the asymptotic decay of the ensemble density of Eq. (10). The Kohn-Sham noninteracting ensemble density has by construction the same density $n(\mathbf{r})$, and clearly

$$|\mathbf{r}| \to \infty: \quad n(\mathbf{r}) \sim \exp\{-2\sqrt{2[-\epsilon_Z + v_s(\infty)]}|\mathbf{r}|\}. \qquad (22)$$

Comparison of Eqs. (19c), (21), and (22) leads immediately to Eq. (20). The theorem (21) and its associated conclusions were derived independently in a different way by Almbladh and von Barth.[14]

Theorem (21) was also deduced in an unpublished technical report[15] and by Katriel and Davidson.[16] However, as discussed in the beginning of the paragraph containing Eq. (21) of LPS,[6] LPS bypassed the need for a conjecture concerning the S matrix in Ref. 16 and the need for a certain suspect assumption, involving the decay of an infinite series of exponentials, that was employed in Refs. 14, 15, and 16. Not yet having the definitive proof of LPS at hand, PPLB played it conservatively and gave the right-hand side of Eq. (20) here as a non-negative number, by considering the corresponding asymptotic inequality in Ref. 17 as well as the asymptotic equality in Refs. 15 and 16.

At this point, we have derived everything needed for a comment on Ref. 7. We note, however, that there are other implications of these arguments, which are drawn out in Refs. 5, 6, and 8, and Sec. V.

III. REBUTTAL OF FORMAL OBJECTIONS TO THE IONIZATION POTENTIAL THEOREMS

Our first reading of Ref. 7 suggested to us that Kleinman was questioning the validity of Janak's theorem[12] for ensembles with noninteger particle number. Although he does not, and although the theorem is in fact valid, we have here improved the intelligibility of our argument, and made it simpler, by deriving Eqs. (19c) and (20) without it.

An important part of Kleinman's objection[7] to Eqs. (19c) and (20) is the assertion that the same derivation can be given for approximate density functionals, for which the conclusions clearly do not follow.

Any approximate density functional $F^{\text{approx}}[n]$ has a direct extension from integer to noninteger electron number, which may differ from the extension of Eq. (7). For example, the local density approximation[1] for exchange and correlation,

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3r \, n(\mathbf{r}) \epsilon_{\text{xc}}(n(\mathbf{r})), \qquad (23)$$

can be evaluated directly for any $n(\mathbf{r})$, whether it integrates to an integer or not, and can lead to a highly nonlinear N dependence of the total energy for $Z-1 < N < Z$ (see Fig. 5 of Ref. 8) which is completely different from the exact behavior of Eq. (9). Much (but not all) of the spurious nonlinearity disappears in self-interaction-free[18] approximations such as the optimized effective potential (OEP) method of Refs. 19 and 20, an exact-exchange-only implementation of Kohn-Sham theory.[21] As support for the preceding sentence, see for example Figs. 8 and 9 of Ref. 20, or Fig. 5 of Ref. 8.

Kleinman[7] is not referring to these direct extensions of approximate functionals, but to an analog of Eqs. (7) and (9):

$$F^{\text{approx}}[n] \equiv \min\{(1-\omega)F^{\text{approx}}[n_{Z-1}] + \omega F^{\text{approx}}[n_Z]\}, \qquad (24)$$

where the minimum is taken over all pairs $n_{Z-1}(\mathbf{r})$ and $n_Z(\mathbf{r})$, such that $(1-\omega)n_{Z-1}(\mathbf{r}) + \omega n_Z(\mathbf{r}) = n(\mathbf{r})$. (Note

that, even when the evaluation of $F^{\text{approx}}[n_M]$ for integer M is trivial, the evaluations of $F^{\text{approx}}[n]$ for non-integer N and of its functional derivative are not.) Then

$$E_N^{g,\text{approx}} = \min_{n \to N} \left\{ F^{\text{approx}}[n] + \int d^3r \; n(\mathbf{r})v(\mathbf{r}) \right\}$$

$$= (1-\omega)E_{Z-1}^{g,\text{approx}} + \omega E_Z^{g,\text{approx}}, \qquad (25)$$

and

$$\epsilon_Z^{\text{approx}} = \partial E_N^{g,\text{approx}}/\partial\omega = -I_Z^{\text{approx}} (Z-1 < N < Z). \quad (26)$$

So far as we can see, Eq. (26) is a valid conclusion. However, it *cannot* be used to conclude that $v_s^{\text{approx}}(\infty) = 0$ for $Z-1 < N < Z$ because there is no analog of Eq. (21) for approximate functionals, i.e., the ensemble density

$$n^{g,\text{approx}}(\mathbf{r}) = (1-\omega)n_{Z-1}^{g,\text{approx}}(\mathbf{r}) + \omega n_Z^{g,\text{approx}}(\mathbf{r}) \quad (27)$$

does *not* decay with an exponent controlled by I_Z^{approx} (except possibly in special cases like the metallic surface). For an approximate functional, the crucial link between the asymptotic density decay and the ionization energy is missing.

To be specific, we consider the exchange-only OEP approximation of Refs. 19, 20, and 7. For the Z-electron system, we can construct an OEP Kohn-Sham potential which goes to zero (by arbitrary choice) at infinity. By Koopmans' theorem, the highest occupied orbital energy differs by Δ, a negative electronic relaxation energy ($\Delta = -0.05$ hartree for the Ar atom) from minus the OEP ionization energy. But this potential can and does differ by the additive constant Δ from the limit (as $N \to Z$ from below) of

$$v(\mathbf{r}) + \frac{\delta U}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}^{\text{approx}}}{\delta n(\mathbf{r})} \qquad (28)$$

of Eq. (24), whose highest occupied Kohn-Sham eigenvalue is minus the OEP ionization energy according to Eq. (26). Kleinman does grant that the potential of Eq. (28) might differ from zero in the limit $|\mathbf{r}| \to \infty$, but says that then ''the result would be of little utility,'' as indeed it is.

We stress again that Eq. (24) is not the direct extension [e.g., Eq. (23) for LDA] of a density-functional approximation to noninteger electron number. One can construct systems in which the exact ground-state wave function places noninteger electron number on each of two or more separated subsystems, e.g., ''stretched H_2^+'' of Sec. V. This situation is[8] energetically equivalent to one in which each of the subsystems is described by an exact ensemble. But, if we apply a density-functional approximation like LDA to the combined system, the result will be energetically equivalent to one in which each subsystem is described by the direct extension of this approximation to noninteger electron number, and not by Eq. (24).

In Ref. 7, Kleinman also defines two (nonstandard) Hartree energies, his Eqs. (11) and (12), which are equal at $\omega = 1$. He shows that the partial derivative of the first with respect to ω differs from that of the second with respect to ω at $\omega = 1$. We do not see any implication of this result for the derivation of PPLB (our Ref. 5), or *a fortiori* for our present derivation.

PPLB provided the uniquely correct extension of the exact total energy from $N = Z$ to $Z-1 < N < Z$, and thus of the sum of the Hartree and exchange-correlation energies. While there is no such unique extension of the Hartree or exchange-correlation energies separately, we believe that our choice is the most natural one. However, careful consideration of Kleinman's argument does help to explain why self-interaction free approximations like his Eq. (12) can mimic the straight line behavior of the exact total energy for $Z-1 < N < Z$.

By Eq. (9), the total energy of the interacting system is a minimum with respect to arbitrary density variations $\delta n(\mathbf{r})$ which conserve the number N of electrons ($\delta\omega = 0$). This condition leads to Eq. (11), and hence to the Kohn-Sham equations. Eqs. (16) and (17) of Ref. 7 are not correct, because the normalized orbitals are to be varied freely at fixed N. Only *after* minimization with respect to orbitals do we obtain Eqs. (9) and (10).

In summary, we do not find any formal argument in Ref. 7 which casts doubt upon our Eqs. (19c) and (20). We turn to the numerical evidence in the following section.

IV. NUMERICAL EVIDENCE FOR THE IONIZATION POTENTIAL THEOREMS

When we first wrote Refs. 5 and 6, little was known about the exact Kohn-Sham potentials for real electronic systems. Since then, many authors[14,22–36] have constructed essentially exact Kohn-Sham potentials for small atoms and molecules by various numerical methods, starting from accurate correlated ground-state electron densities. Because these potentials are constructed to vanish at infinity, all this work can be regarded as an investigation of the limit $N \to Z$ from below, where Z is the integer electron number of the atom or molecule.

The earliest reference (Ref. 22) in our list assumed, and was consistent with, the ionization potential theorems. Many of the more recent works do not assume the ionization potential theorems of Eqs. (19c) and (20), and so provide a direct numerical test of these theorems. In none of these articles do we find a challenge to the truth of the theorems.

Kleinman[7] observes that Ref. 25 finds some numerical discrepancies between the highest-occupied eigenvalues [calculated under the assumption of Eq. (20)] and minus the ionization energies. These discrepancies are extremely small for the light atoms, but for the Ar atom $\epsilon_{3p} = -0.55$ hartree is somewhat different from $-I = -0.58$ hartree. However, the authors of Ref. 25 ''expect more accurate ionization potentials will be found when higher quality densities are used as the reference.'' The problem is that the reference densities are found by variational means such as the method of configuration interaction, and the total energy is not sensitive to the asymptotic decay of the density into the vacuum.

For the small molecules LiH, BH, and HF (Table I of Ref. 33) or H_2O and HF (Table 2 of Ref. 32), the ionization potential theorems are obeyed with remarkable accuracy. In Appendix B, we discuss a model two-electron problem for which these theorems are exactly confirmed.

Finally, the overwhelming numerical confirmation[20] of the OEP Koopmans' theorem[8,20,37] supports the validity of Eq. (21), because the OEP Koopmans' theorem has recently been derived by assuming[37] that Eq. (21) is correct for arbitrary electron-electron repulsion constant, at fixed density. The Koopmans' theorem arises[37] by equating terms that are first order in the coupling constant.

V. SELF-INTERACTION CORRECTION, DERIVATIVE DISCONTINUITY, AND EXCHANGE-CORRELATION SUM RULE

Our work of Ref. 5 was motivated by the self-interaction correction of Ref. 18 (see also Ref. 38), and by an intriguing statement of Slater[39] about the local-density-approximation description of a Na atom and a Cl atom at infinite separation: ''Electronic charge will flow from the Na to the Cl, falling to a lower one-electron energy and producing some positive charge on the Na, negative on the Cl.... This process will have the effect of pushing the energy levels of the Cl upward and lowering those of the Na....''. Since no charge should flow between well-separated neutral atoms in the *exact* Kohn-Sham theory, an explanation for the exact preventative mechanism was needed. This exact mechanism, the derivative discontinuity of the total energy at integer electron number $N=Z$, turned out to very much like the approximate one provided by the self-interaction correction[18,38,40] to the local-density approximation of Eq. (23), and by other self-interaction-free methods such as the exchange-only OEP approximation.[20,40]

To see the derivative discontinuity, generalize Eq. (19b) to

$$\mu = \partial E_N^g / \partial N = \begin{cases} -I_Z = E_Z^g - E_{Z-1}^g & (Z-1<N<Z) \\ -A_Z = E_{Z+1}^g - E_Z^g & (Z<N<Z+1). \end{cases} \quad (29)$$

Equation (29) asserts that the total energy as a function of the average electron number N is a linkage of straight lines with kinks or derivative discontinuities at the integers. Because[5,8] the smallest ionization energy of the Periodic Table is greater than the largest electron affinity, the exact description of any two neutral atoms at large separation (e.g., Na and Cl) is one in which the total energy minimizes at one of these kinks, with an integer number of electrons on each atom and with each atom separately neutral.

For deeper insight, consider Eqs. (11) and (14). Since neither $v(\mathbf{r})$ nor $\delta U / \delta n(\mathbf{r})$ changes discontinuously as N crosses the integer Z, it must be that[5,40,41]

$$\left[\frac{\delta T_s}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right]\bigg|_{N=Z+\delta} - \left[\frac{\delta T_s}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right]\bigg|_{N=Z-\delta}$$
$$= I_Z - A_{Z'} \quad (30)$$

where δ is a positive infinitesimal. The same analysis applied to the Kohn-Sham noninteracting system yields

$$\frac{\delta T_s}{\delta n(\mathbf{r})}\bigg|_{N=Z+\delta} - \frac{\delta T_s}{\delta n(\mathbf{r})}\bigg|_{N=Z-\delta} = \epsilon_{Z+1}(Z) - \epsilon_Z(Z), \quad (31)$$

where $\epsilon_i(Z)$ is the ith Kohn-Sham orbital energy of the Z-electron system. The difference between Eqs. (30) and (31) is the discontinuity of the exact exchange-correlation potential $\delta E_{xc}/\delta n(\mathbf{r})$, which must be positive for an open-shell system in which $\epsilon_{Z+1}(Z) = \epsilon_Z(Z)$.

As N increases through the integer Z, the exact exchange-correlation potential can jump up by an additive positive constant. Then, as N continues to increase above Z, this ''constant'' starts to disappear, first at $|\mathbf{r}| = \infty$ and then at smaller and smaller values of $|\mathbf{r}|$, as shown in Fig. 11 of Ref. 20 or Fig. 4 of Ref. 8.

In a system of two well-separated dissimilar atoms (such as Na and Cl), the exact Kohn-Sham potential shows an extra positive buildup around the more electronegative atom (such as Cl) to prevent the transfer of a fraction of an electron to this more electronegative atom (Ref. 34, and Fig. 7 of Ref. 8).

Continuum approximations to $E_{xc}[n]$, such as the local density approximation (LDA) of Eq. (23) the generalized gradient approximation (GGA) (Refs. 43 and 44), or the Fermi-Amaldi approximation,[45] in their direct extensions [e.g., Eq. (23)] to noninteger electron number, cannot produce the correct derivative discontinuity. In the open-shell case, they average over the discontinuity of Eq. (29), making[41,8,36]

$$\epsilon_Z^{approx}(Z) \approx -\frac{1}{2}(I_Z + A_Z). \quad (32)$$

Continuum approximations typically give good total energies for integer N, but poor total energies for noninteger N. The explanation for both these facts can be found in the generalized sum rule[8] on $n_{xc}(\mathbf{r},\mathbf{r}')$, the density at $\mathbf{r}'$ of the exact exchange-correlation hole around an electron at $\mathbf{r}$. The exchange-correlation energy is half the electrostatic interaction between each electron and its hole:

$$E_{xc}[n] = \frac{1}{2} \int d^3r \int d^3r' \, \frac{n(\mathbf{r})n_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}. \quad (33)$$

In an open system with average electron number N between the integers $Z-1$ and Z, the generalized sum rule for the exact hole is[8]

$$\int d^3r' n_{xc}(\mathbf{r},\mathbf{r}') = -1 + \omega(1-\omega) \int_0^1 d\lambda [n_Z^g(\mathbf{r};\lambda)$$
$$- n_{Z-1}^g(\mathbf{r};\lambda)] / n_N^g(\mathbf{r}), \quad (34)$$

where $\omega = N - (Z-1)$. Here $n_M^g(\mathbf{r};\lambda)$ is the ground-state density for M electrons with scaled interaction $\lambda \hat{V}_{ee}$ and with external potential $v_\lambda(\mathbf{r})$ which holds the N-electron ensemble density fixed at its $\lambda=1$ or fully interacting value; thus $v_{\lambda=1}(\mathbf{r}) = v(\mathbf{r})$ and $v_{\lambda=0}(\mathbf{r}) = v_s(\mathbf{r})$. The exact exchange hole[8] obeys Eq. (34) with $n_M(\mathbf{r};\lambda) \rightarrow n_M(\mathbf{r};0)$. The LDA and GGA holes integrate to -1, which is correct in the integer or nonfluctuating limits $N=Z-1$ and $N=Z$, but not in between [where the correction to -1 in Eq. (34) is typi-

cally positive]. Thus LDA and GGA energies are seriously too negative for the ground state of "stretched H_2^+," [46,38] a system composed of two well-separated protons and one electron, in which the average electron number N is 1/2 for each proton basin. For this problem, neither spin-density generalization nor symmetry breaking can rescue LDA and GGA.

The self-interaction-corrected (SIC) hole of Ref. 18 satisfies a sum rule[8] which is very much like the exact sum rule of Eq. (34), differing from it only in the replacement of $n_M^g(\mathbf{r};\lambda)$ by $n_N^g(\mathbf{r};0)$. However, the SIC method of Ref. 18 is not really a Kohn-Sham method; SIC constructs a different potential for each orbital, and these orbital-dependent potentials always vanish as $|\mathbf{r}|\rightarrow\infty$.

In Eq. (10) of Ref. 7, Kleinman proposes a Hartree energy $U_K[n]$ which differs from the standard one of Eq. (13) by the positive quantity

$$U_K[n]-U[n]=\frac{\omega(1-\omega)}{2}\int d^3r d^3r'$$
$$\times\frac{[n_Z(\mathbf{r})-n_{Z-1}(\mathbf{r})][n_Z(\mathbf{r}')-n_{Z-1}(\mathbf{r}')]}{|\mathbf{r}'-\mathbf{r}|}.$$
(35)

[From $n(\mathbf{r})$, we find ω via Eq. (6), and $v(\mathbf{r})$ via Eq. (11); $n_Z(\mathbf{r})$ and $n_{Z-1}(\mathbf{r})$ are then the Z and $(Z-1)$ electron ground-state densities for external potential $v(\mathbf{r})$.] By our accounting, Eq. (35) is a contribution to $E_{xc}[n]$. Adding it to the LDA of Eq. (23), or to GGA, interestingly produces an exchange-correlation hole which satisfies a sum rule very much like the exact one of Eq. (34), differing from it only in the replacement of $n_M^g(\mathbf{r};\lambda)$ by $n_M^g(\mathbf{r};1)$.

The generalization of Eq. (34) from zero to nonzero temperature, which takes the same mathematical form for fermions, bosons, or classical particles, can be found in Ref. 47.

The exact density functionals $T_s[n]$ and $E_{xc}[n]$ are defined in terms of density-constrained searches over ensembles of antisymmetric wave functions. Thus they already contain information about energy quantization, Fermi statistics, and ensemble weights. The exact functional themselves (and not extraneous constraints, as suggested in Refs. 48 and 49) are responsible for the shell structure and the derivative discontinuities of the ground-state energy.

For simplicity, we have presented all arguments and results in the context of density-functional theory, but they carry over directly to spin-density-functional theory.[1-3] Both the density-functional $T_s[n]$ and the spin-density-functional $T_s[n_\uparrow,n_\downarrow]$ for the noninteracting kinetic energy are constructs of the imagination with no exact physical counterpart in real electronic systems, and neither can capture all of the derivative discontinuity of the physical total energy.[41,42]

Finally, it has been observed that the highest-occupied orbital energy equals the negative of the ionization energy, in exact hybrid schemes. The appropriate correlation potential is added to the whole Fock potential,[55] or to a part thereof,[56] and the exact ground-state density is obtained upon self-consistency.

APPENDIX A: DERIVATION OF $\mu=\partial E_N^g \partial N$ THAT DOES NOT EMPLOY THE LAGRANGE MULTIPLIER TECHNIQUE

In Eq. (9) define $E_v[n]$ by

$$E_v[n]=F[n]+\int d^3r\ n(\mathbf{r})\ v(\mathbf{r}),$$
(A1)

and define μ by

$$\mu=\frac{\delta E_v[n]}{\delta n(\mathbf{r})}\bigg|_{n=n_N^g},$$
(A2)

where the derivative is taken at fixed $v(\mathbf{r})$. Next, note that the minimization of $E_v[n]$, at fixed N, dictates that

$$0=\delta E_v[n]=\int d^3r\ \mu\ \delta n(\mathbf{r}),$$
(A3)

for arbitrary infinitesimal variation $\delta n(\mathbf{r})$ about the minimizing density n_N^g, from which it follows the μ is a constant because $\int d^3r\ \delta n(\mathbf{r})=0$. Now consider the infinitesimal variation $\delta n(\mathbf{r})=n_{N+\delta N}^g(\mathbf{r})-n_N^g(\mathbf{r})$, where $n_{N+\delta N}^g(\mathbf{r})$ is the minimizing density for $N+\delta N$ electrons. Since μ has already been identified as a constant, this time we obtain

$$\delta E_v[n]=\int d^3r\ \mu\ \delta n(\mathbf{r})=\mu\int d^3r\ \delta n(\mathbf{r})=\mu\ \delta N,$$
(A4)

where $\delta E_v=E_v[n_{N+\delta N}^g]-E_v[n_N^g]$. Equation (A4) is equivalent to the desired result, $\mu=\partial E_N^g/\partial N$. (See Refs. 3, 4, 50, and 51 for studies that are closely related to this appendix. One crucial difference is that our logical progression here bypasses the use of any Lagrange multiplier.)

APPENDIX B: AN EXACTLY SOLVED TWO-ELECTRON PROBLEM FOR WHICH THE IONIZATION POTENTIAL THEOREMS ARE EXACTLY CONFIRMED

We know only one exactly solved many-electron problem, the "Hooke's atom" or "harmonium," [52-54] in which two electrons repel one another Coulombically and are held together by a harmonic-oscillator external potential

$$v(r)=\tfrac{1}{2}kr^2.$$
(B1)

Laufer and Krieger[53] showed both numerically and analytically that the highest-occupied Kohn-Sham orbital energy $\epsilon_2=\epsilon_1$ for this problem, under the assumption that $\lim_{|\mathbf{r}|\rightarrow\infty}\delta E_{xc}/\delta n(\mathbf{r})=0$, is

$$\epsilon_2=E_2^g-E_1^g$$
(B2)

for all k, in agreement with Eq. (19c). For special values of k, the energies and wave functions are explicit analytic expressions.[54]

Some further discussion is needed here, since $v(r)$ of Eq. (B1) does not satisfy the condition $v(\infty)=0$ used to derive

Eqs. (19c) and (20). We introduce a modified Hooke's atom, depending upon a parameter R, with external potential

$$\widetilde{v}(R,r) = \begin{cases} \frac{1}{2}kr^2 - \frac{1}{2}kR^2 & (r<R) \\ 0 & (r>R). \end{cases} \tag{B3}$$

Clearly, as $R \to \infty$,

$$\widetilde{v}(R,r) \to v(r) - \frac{1}{2}kR^2, \tag{B4}$$

$$\widetilde{E}_Z^g(R) \to E_Z^g - \frac{Z}{2}kR^2, \tag{B5}$$

$$\widetilde{\epsilon}_2(R) \to \epsilon_2 - \frac{1}{2}kR^2, \tag{B6}$$

with corrections that are exponentially small. The modified Hooke's atom obeys the conditions required to derive Eqs. (19c) and (20), so

$$\widetilde{\epsilon}_2(R) = \widetilde{E}_2^g(R) - \widetilde{E}_1^g(R), \tag{B7}$$

for any finite R. Now let $R \to \infty$, and apply Eqs. (B5) and (B6) to (B7); the result is Eq. (B2).

ACKNOWLEDGMENTS

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