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# Hellmann-Feynman, virial, and scaling requisites for the exact universal density functionals. Shape of the correlation potential and diamagnetic susceptibility for atoms

Mel Levy
*Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118*

John P. Perdew
*Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118*

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By the Hellmann-Feynman theorem, the density $n(\mathbf{r})$ of many electrons in the presence of external potential $v(\mathbf{r})$ obeys the relationships $\int d^3r\, n(\mathbf{r})\nabla v(\mathbf{r})=\mathbf{0}$ and $\int d^3r\, n(\mathbf{r})\mathbf{r}\times\nabla v(\mathbf{r})=\mathbf{0}$. By the virial theorem, the interacting kinetic and electron-electron repulsion expectation values obey $2T[n]+V_{ee}[n]=-\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta T/\delta n(\mathbf{r})+\delta V_{ee}/\delta n(\mathbf{r})]$. The exchange energy functional $E_x[n]$ and potential $v_x([n];\mathbf{r})\equiv\delta E_x/\delta n(\mathbf{r})$ must satisfy $E_x[n]+\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_x([n];\mathbf{r})=0$, while the correlation energy and potential must satisfy $E_c[n]+\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r})<0$. Somewhat counterintuitively, it is *not true* that $T[n_\gamma]=\gamma^2 T[n]$ and $V_{ee}[n_\gamma]=\gamma V_{ee}[n]$, where $n_\gamma(\mathbf{r})\equiv\gamma^3 n(\gamma\mathbf{r})$ is a scaled density with scale factor $\gamma\neq 1$. In fact, it is *impossible* to partition the exact Hohenberg-Kohn functional into a piece that scales as $\gamma^2$ and a piece that scales as $\gamma$, even if complete freedom with the partitioning is allowed. Instead there are universal scaling *inequalities.* For instance, $T[n_\gamma]+V_{ee}[n_\gamma]<\gamma^2 T[n]+\gamma V_{ee}[n]$ and $T[n_\gamma]+\gamma V_{ee}[n_\gamma]>\gamma^2(T[n]+V_{ee}[n])$, and consequent inequalities involving $E_c[n]$. All the above virial and scaling requisites are universal in that they are *independent* of external potential and they must hold for arbitrary proper $n$. In addition, for the ground-state energy ($E$) and $n$ of any atom or molecule at its equilibrium nuclear configuration, there is the *inequality* $E<-T_s[n]$, where $T_s$ is the noninteracting kinetic energy. In the closed-shell tight-binding limit, the correlation potential obeys $\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r})=0$, and so cannot be a monotonic function of $r$ for an atom in this limit. Further, $(\partial/\partial\gamma)E_c[n_\gamma]\,|_{\gamma=1}=E_c[n]+T_c[n]=-\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r})$, which implies that the exact $E_c$ should be fairly insensitive to scaling. With the help of the *ionization-potential theorem,* it is argued that the exact $v_c([n];\mathbf{r})$ in an atom often has a positive part. Common approximations to the correlation potential are examined for their effects upon the highest occupied Kohn-Sham orbital energy and the density moment $\langle r^2\rangle$, and these effects are found to be related. Further improvements needed in the approximate correlation potentials are relatively large, but not nearly so large as those recently suggested for the atoms Ne, Ar, Kr, and Xe: The discrepancy between theoretical values of $\langle r^2\rangle$ from Hartree-Fock or configuration-interaction calculations, and experimental values from measured diamagnetic susceptibilities, is tentatively resolved in favor of theory.

## I. INTRODUCTION AND SUMMARY

An important simplification of the many-particle ground-state problem is proffered by density-functional theory,[1,2] in which the basic variational object is the density $n(\mathbf{r})$ instead of the many-particle wave function. In the Kohn-Sham[2] version of density-functional theory, an exact-in-principle self-consistent-field formalism often applied to electronic systems, the only approximation required in practice is the functional dependence $E_{\text{xc}}[n]$ of the exchange-correlation energy upon the density. To find accurate forms of $E_{\text{xc}}[n]$ constitutes an active area of research. Accordingly, in this work we will derive conditions upon $E_{\text{xc}}[n]$ and $n(\mathbf{r})$ within the *exact* density-functional theory from the Hellmann-Feynman[3] and virial[3] theorems. Then we will apply some of these relationships, and others, to argue for the nonmonotonic and positive behavior of the exact correlation potential in an atom.[4–6] (Of course, there have already been many applications of the Hellman-Feynman and virial theorems to density-functional theory, such as Refs. 7–19.)

In Sec. II we apply the Hellmann-Feynman theorem to show that

$$\int d^3r\, n(\mathbf{r})\nabla v(\mathbf{r})=\mathbf{0}\ , \tag{1}$$

$$\int d^3r\, n(\mathbf{r})\mathbf{r}\times\nabla v(\mathbf{r})=\mathbf{0}\ , \tag{2}$$

where $v(\mathbf{r})$ is the external potential acting on the particles. Equations (1) and (2), which correspond, respectively, to the static-equilibrium conditions of "no net external force" and "no net external torque" on the density, seem rather obvious, although we have not encountered them in the literature. They are also quite general: From their derivation, it will be clear that Eqs. (1) and (2) apply for

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any choice of particle statistics or interparticle interactions and for any stationary-state density $n(\mathbf{r})$ (not just the ground state). Equations (1) and (2) are useful constraints upon any attempt to model the density $n(\mathbf{r})$, given the external potential $v(\mathbf{r})$. Such attempts arise in the analysis of x-ray diffraction data[20] and also in the construction of trial densities for use in the Hohenberg-Kohn[1] variational principle.

In Sec. III we apply the virial theorem to generalize, to arbitrary coupling constant and external potential, the result of Averill and Painter[16] for Coulomb potentials. We also modify slightly their original result to now give for any proper trial density $n(\mathbf{r})$, *independent* of external potential,

$$E_{xc}[n]+\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_{xc}([n];\mathbf{r})=-T_c[n]<0\ . \tag{3}$$

We have added the inequality in Eq. (3) and noted that $T_c[n]=T_{xc}[n]$, where

$$T_c[n]=T[n]-T_s[n]>0\ . \tag{4}$$

Here $v_{xc}([n];\mathbf{r})=\delta E_{xc}/\delta n(\mathbf{r})$ is the exchange-correlation potential of the exact Kohn-Sham theory, and $T[n]$ and $T_s[n]$ are the kinetic energies of density $n(\mathbf{r})$ for interacting and noninteracting electrons, respectively, so that by definition of density-functional correlation energy, $T_c[n]$ is the correlation contribution to the kinetic energy. Also by definition of the density-functional exchange energy, the exchange contribution to the kinetic energy, $T_x[n]$, is always zero. We further find that for the exchange energy functional $E_x[n]$,

$$E_x[n]+\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_x([n];\mathbf{r})=0\ . \tag{5}$$

Subtraction of Eq. (5) from Eq. (3) yields

$$E_c[n]+\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r})=-T_c[n]<0\ . \tag{6}$$

It is important to note that Eqs. (3)—(6) apply even when $n$ is not the ground-state density for the *actual* external potential of interest.

The unique features of Eqs. (3)—(6), and the other virial and scaling conditions to be derived, stem from the fact that the conditions apply to the exact universal functionals and that the conditions themselves are universal—that is, they are independent of external potentials, as stated above. Hence, we may use the relations to test the universal functionals with *arbitrary* $n(\mathbf{r})$. We do not have to know for what external potential is our trial $n(\mathbf{r})$ a ground-state density or an optimum density within a given model.

In Sec. IV, we discuss the local density approximation[2] and compare the correlation contributions to $T[n]$ and $E_{xc}[n]$ for the electron gas of uniform density.

The correlation potential $v_c([n];\mathbf{r})$ predicted for an atom by the local density approximation is always negative and increases monotonically with distance from the nucleus. However, recently Smith *et al.*,[4] Almbladh and Pedroza,[5] and Laufer and Krieger[6] have constructed the exact correlation potential in a few-electron atom. They find that $v_c([n];\mathbf{r})$ is nonmonotonic and positive at large distance from the nucleus. In Sec. V, we explain the nonmonotonic behavior by showing that, to leading order ($e^4$) in the electronic charge $e$,

$$\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r})=0\ . \tag{7}$$

Thus, $v_c([n];\mathbf{r})$ *cannot* be a monotonic function of $r$ in strongly bound closed-shell atoms for which an expansion of $v_c$ in powers of $e^2$ is rapidly convergent.

In addition, we argue for the positive part of the correlation potential by an appeal to the *ionization potential theorem*[21–23]

$$\epsilon_{\max}^{\mathrm{KS}}=-I\ , \tag{8}$$

where $\epsilon_{\max}^{\mathrm{KS}}$ is the exact Kohn-Sham energy eigenvalue for the highest occupied orbital, and $I$ is the first ionization potential. We compare $\epsilon_{\max}^{\mathrm{KS}}$ within the exchange-only approximation to measured values of $-I$ and find that the former is more negative than the latter for many atoms. From this, we conclude that the expectation value of the exact correlation potential $v_c([n];\mathbf{r})$ over the highest occupied orbital is often positive.

Recently, Englert and Schwinger,[24] and independently Cole and Toigo,[25] have observed that the density moment $\langle r^2\rangle$ for Ne, Ar, Kr, and Xe, calculated within the Hartree-Fock or related density-functional approximations, is about 10% too large in comparison with values deduced from measured diamagnetic susceptibilities. Along with Vosko and Wilk,[26] we disbelieve that the exact correlation potential can have such a huge effect upon $\langle r^2\rangle$, when approximate correlation potentials have only a small effect. Using alternative "exact" values for $\langle r^2\rangle$ from configuration-interaction calculations, we find that the effect of the exact correlation potential upon $\langle r^2\rangle$ is indeed small and can be related simply to its effect upon $\epsilon_{\max}^{\mathrm{KS}}$.

Szasz, Berrios-Pagan, and McGinn[27] analyzed in detail the scaling properties of the various kinetic and electron-electron repulsion functionals within the Thomas-Fermi and extended Thomas-Fermi models. What are the scaling properties, though, for the exact interacting kinetic functional $T[n]$ and the exact electron repulsion functional $V_{ee}[n]$? Well, as shown in Sec. VI, it is *not* true in the exact limit that $T[n_\gamma]=\gamma^2T[n]$ and $V_{ee}[n_\gamma]=\gamma V_{ee}[n]$, where $n_\gamma(\mathbf{r})\equiv\gamma^3n(\gamma\mathbf{r})$ and $\gamma\neq1$ is a scale factor. In contrast, the equalities hold[27] in Thomas-Fermi and in various familiar extended Thomas-Fermi approximations for $T[n]$ and $V_{ee}[n]$. In fact, we shall prove that it is *impossible* to partition the exact Hohenberg-Kohn universal functional, $Q[n]$, into two parts that scale as $\gamma^2$ and $\gamma$.

Finally, in Sec. VII the inequalities of Sec. VI are exploited to derive necessary scaling requisites for $E_c[n]$, $E_x[n]$, and $T_s[n]$. For instance, we shall obtain strict correlation inequalities for $\gamma\neq1$ such as Eqs. (106), (109), and (112). We also show that the local density approximation,[2] with common choices for its electron-gas correlation-energy input, obeys these inequalities.

## II. DENSITY-POTENTIAL RELATIONSHIPS FROM THE HELLMANN-FEYNMAN THEOREM

Given a Hamiltonian $\hat{H}_\lambda$ depending upon a parameter $\lambda$, consider the eigenvalue problem $\hat{H}_\lambda\Psi_\lambda=E_\lambda\Psi_\lambda$,

$\langle \Psi_\lambda | \Psi_\lambda \rangle = 1$. The Hellmann-Feynman theorem[3] asserts that

$$\frac{d}{d\lambda} E_\lambda = \left\langle \Psi_\lambda \left| \frac{\partial}{\partial\lambda} \hat{H}_\lambda \right| \Psi_\lambda \right\rangle . \tag{9}$$

In this section we deal with a Hamiltonian of the form

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v_\lambda(\mathbf{r}_i) , \tag{10}$$

for $N$ identical particles of any statistics, with any choice for the kinetic energy $\hat{T}$ and interparticle interaction $\hat{V}_{ee}$ and any local external potential $v_\lambda(\mathbf{r})$. Then

$$\frac{d}{d\lambda} E_\lambda = \int d^3r \, n_\lambda(\mathbf{r}) \frac{d}{d\lambda} v_\lambda(\mathbf{r}) . \tag{11}$$

First, let $v_\lambda(\mathbf{r}) = v(\mathbf{r} + \lambda\hat{\mathbf{u}}) = v(\mathbf{r}) + \lambda\hat{\mathbf{u}}\cdot\nabla v(\mathbf{r}) + \cdots$, where $\hat{\mathbf{u}}$ is any unit vector. By the homogeneity of space, $dE_\lambda/d\lambda = 0$, so Eq. (11) implies Eq. (1). Next, let $v_\lambda(\mathbf{r}) = v(\mathbf{r} + \lambda\mathbf{r}\times\hat{\mathbf{u}}) = v(\mathbf{r}) + \lambda(\mathbf{r}\times\hat{\mathbf{u}})\cdot\nabla v(\mathbf{r}) + \cdots$ . By the isotropy of space, $dE_\lambda/d\lambda = 0$, so Eq. (11) becomes

$$\int d^3r \, n(\mathbf{r})(\mathbf{r}\times\hat{\mathbf{u}})\cdot\nabla v(\mathbf{r}) = 0 . \tag{12}$$

From the identity $(\mathbf{a}\times\mathbf{b})\cdot\mathbf{c} = -\mathbf{b}\cdot(\mathbf{a}\times\mathbf{c})$, we derive Eq. (2) from Eq. (12).

If $n(\mathbf{r})$ is the ground-state density for external potential $v(\mathbf{r})$, then Eqs. (1) and (2) are clearly differential forms for the minimum principle

$$\int d^3r \, n(\mathbf{r}) v(\mathbf{r}) = \min_\lambda \left\{ \int d^3r \, n(\mathbf{r}) v_\lambda(\mathbf{r}) \right\} , \tag{13}$$

where each $v_\lambda(\mathbf{r})$ in Eq. (13) results from a translation or rotation of $v(\mathbf{r})$. By the Hohenberg-Kohn[1] theorems, the required minimum is absolute and unique.

For electronic systems, the external potential $v(\mathbf{r})$ may, but need not, arise from Coulomb attraction of the electrons toward nuclei. Recent interest[28] has focused on the extent to which the electron density in a molecule is just a function of the bare nuclear potential. We observe that this choice, $n(\mathbf{r}) = F(v(\mathbf{r}))$, naturally satisfies Eqs. (1) and (2).

## III. THE EXCHANGE-CORRELATION FUNCTIONAL AND THE VIRIAL THEOREM

The work of Sham[7] suggests that the virial theorem is obeyed in exact exchange-only density-functional theory and shows that the virial theorem is obeyed in the local density approximation to this exchange-only theory. (Sham[7] also noted that the result applies to $X\alpha$ theory.) However, the exact correlation energy functional $E_c[n]$ contains a kinetic contribution. This fact complicates the virial conditions which are to be derived for $E_{xc}[n]$ in this section.

The Hohenberg-Kohn universal functional $Q_\lambda[n]$ is defined within an extended domain via the constrained-search formulation[29,30] as follows:

$$Q_\lambda[n] = \langle \Psi_\lambda | (\hat{T} + \lambda\hat{V}_{ee}) | \Psi_\lambda \rangle , \tag{14}$$

where $\Psi_\lambda = \Psi_\lambda[n]$ is that antisymmetric $N$-electron function which yields $n(\mathbf{r})$ and minimizes $\langle (\hat{T} + \lambda\hat{V}_{ee}) \rangle$. The minimum always exists as shown by Lieb.[31] Therefore, unless prevented by certain unusual situations described by Englisch and Englisch,[32] it has been shown that $\Psi_\lambda$ turns out to be an eigenstate of a Hamiltonian of the form[33]

$$\hat{H}_\lambda = \hat{T} + \lambda\hat{V}_{ee} + \hat{V}_\lambda , \tag{15}$$

with

$$\hat{T} = \sum_{i=1}^{N} -\tfrac{1}{2}\nabla_i^2 , \tag{16}$$

$$\hat{V}_{ee} = \tfrac{1}{2} \sum_i \sum_{j\,(\neq i)} e^2 |\mathbf{r}_i - \mathbf{r}_j|^{-1} , \tag{17}$$

$$\hat{V}_\lambda = \sum_{i=1}^{N} v_\lambda(\mathbf{r}_i) , \tag{18}$$

where $\lambda$ is a coupling constant.[10,12-14] Hence we have

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda , \tag{19}$$

where $E_\lambda$ does not have to be the ground-level energy[34] of $\hat{H}_\lambda$.

The coupling constant $\lambda$ is equal to unity for real electrons and is equal to zero for noninteracting electrons. Following the adiabatic connection orientation[12-14] between interacting and noninteracting systems, our trial $n(\mathbf{r})$ is held constant[12,13] while the interaction is turned off: $\langle \hat{n}(\mathbf{r}) \rangle_\lambda = n(\mathbf{r})$ (independent of $\lambda$), where we have denoted the expectation value of operator $\hat{O}$ by

$$\langle \hat{O} \rangle_\lambda = \langle \Psi_\lambda | \hat{O} | \Psi_\lambda \rangle . \tag{20}$$

When no subscript is shown it shall be meant that $\lambda = 1$.

The potential $v = v_1$ might or might not turn out to be our actual external potential of interest. In any case, for each value of $\lambda$ the corresponding energy is

$$E_\lambda = \langle \hat{H}_\lambda \rangle_\lambda = \langle \hat{T} \rangle_\lambda + \lambda \langle \hat{V}_{ee} \rangle_\lambda + \int d^3r \, n(\mathbf{r}) v_\lambda(\mathbf{r}) , \tag{21}$$

or, in terms of density-functional notation,

$$\begin{aligned} E_\lambda &= \int d^3r \, n(\mathbf{r}) v_\lambda(\mathbf{r}) + Q_\lambda[n] \\ &= \int d^3r \, n(\mathbf{r}) v_\lambda(\mathbf{r}) + T_\lambda[n] + \lambda V_{ee\lambda}[n] . \end{aligned} \tag{22}$$

Next, from Eq. (22)

$$\mu_\lambda = \delta E_\lambda / \delta n(\mathbf{r}) = v_\lambda(\mathbf{r}) + \delta Q_\lambda / \delta n(\mathbf{r}) , \tag{23}$$

where $\mu_\lambda$ is the chemical potential;[35] it is the negative of the ionization energy[21] or the negative of the electron affinity[21] depending upon the direction in which the functional derivatives are taken. Also, in taking $\delta Q_\lambda/\delta n(\mathbf{r})$, we have implicitly employed the definition of $Q[n]$ for fractional electron number.[21]

Multiply Eq. (23) by $n(\mathbf{r})$ and integrate:

$$N\mu_\lambda = \int d^3r \, n(\mathbf{r}) v_\lambda(\mathbf{r}) + \int d^3r \, n(\mathbf{r}) \delta Q_\lambda / \delta n(\mathbf{r}) . \tag{24}$$

Then subtract Eq. (24) from Eq. (22) to obtain

$$E_\lambda = \mu_\lambda N - \int d^3r \, n(\mathbf{r}) \delta Q_\lambda / \delta n(\mathbf{r}) + Q_\lambda[n] , \tag{25}$$

which interestingly gives the energy of a given $n$ without explicit use of the external potential with which $n$ is associated; knowledge of $\mu_\lambda$ is required, though.[36] In any case, for our present purposes let us now operate on Eq. (23) with $\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla$. This gives

$$\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_\lambda(\mathbf{r}) = -\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta Q_\lambda/\delta n(\mathbf{r})] \; . \tag{26}$$

Next, for each value of $\lambda$, the virial theorem[3] asserts that

$$\begin{aligned}2\langle \hat{T}\rangle_\lambda &= \left\langle \sum_{i=1}^{N} \mathbf{r}_i\cdot\nabla_i(\lambda\hat{V}_{ee}+\hat{V}_\lambda)\right\rangle_\lambda \\ &= -\lambda\langle \hat{V}_{ee}\rangle_\lambda + \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_\lambda(\mathbf{r}) \; .\end{aligned} \tag{27}$$

Finally, add Eqs. (26) and (27) to obtain our initial universal virial relation:

$$Q_\lambda[n]+T_\lambda[n] = -\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta Q_\lambda/\delta n(\mathbf{r})] \; . \tag{28}$$

Further, partition $Q_\lambda[n]$ and set $\lambda=1$. Obtain

$$\begin{aligned}2T[n] &+ \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta T/\delta n(\mathbf{r})] \\ &= -V_{ee}[n] - \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta V_e/\delta n(\mathbf{r})] \; ,\end{aligned} \tag{29}$$

which is a generalization, to arbitrary $n$, of Eq. (23) of Bartolotti and Parr.[10] Equations (28) and (29) are the first known relations to connect the purely kinetic piece of $Q[n]$ with the purely electron-electron repulsion piece of $Q[n]$ for arbitrary $n$. These relationships should help to improve the existing direct $T[n]$ and $V_{ee}[n]$ functionals.

Most practical calculations at present are performed within Kohn-Sham theory.[2] Within this theory the exact exchange-correlation functional $E_{\mathrm{xc}}^{\lambda}[n]$ may be implicitly defined by the equation

$$E_\lambda = \langle \hat{T}\rangle_0 + \int d^3r\, n(\mathbf{r})v_\lambda(\mathbf{r}) + \lambda U[n] + \lambda E_{\mathrm{xc}}^{\lambda}[n] \; , \tag{30}$$

where

$$U[n] = \frac{e^2}{2}\int d^3r \int d^3r'\, n(\mathbf{r})n(\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1} \tag{31}$$

is the classical Coulomb repulsion. In other words,

$$E_{\mathrm{xc}}^{\lambda}[n] = E_x[n] + E_c^{\lambda}[n] \tag{32}$$

with

$$E_x[n] = \langle \Psi_0 |\, \hat{V}_{ee}\, | \Psi_0\rangle - U[n] \tag{33}$$

and

$$\begin{aligned}E_c^{\lambda}[n] &= \langle \Psi_\lambda |\, \hat{V}_{ee}\, | \Psi_\lambda\rangle - \langle \Psi_0 |\, \hat{V}_{ee}\, | \Psi_0\rangle \\ &\quad + \lambda^{-1}(\langle \Psi_\lambda |\, \hat{T}\, | \Psi_\lambda\rangle - \langle \Psi_0 |\, \hat{T}\, | \Psi_0\rangle) \; .\end{aligned} \tag{34}$$

Note that, by definition, $E_x$ is independent of $\lambda$.

Let us now follow the path of Averill and Painter.[16] Equate Eqs. (21) and (30). We find

$$\lambda\langle \hat{V}_{ee}\rangle_\lambda = \lambda U[n] + \lambda E_{\mathrm{xc}}^{\lambda}[n] - (\langle \hat{T}\rangle_\lambda - \langle \hat{T}\rangle_0) \; . \tag{35}$$

Substitution of (35) into (27) yields the equation

$$\begin{aligned}2\langle \hat{T}\rangle_\lambda &= \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_\lambda(\mathbf{r}) - \lambda U[n] \\ &\quad - \lambda E_{\mathrm{xc}}^{\lambda}[n] + \langle \hat{T}\rangle_\lambda - \langle \hat{T}\rangle_0 \; .\end{aligned} \tag{36}$$

For $\lambda=0$, (36) reduces to

$$2\langle \hat{T}\rangle_0 = \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_0(\mathbf{r}) \; . \tag{37}$$

Now subtract (37) from (36), and solve for $\langle \hat{T}\rangle_\lambda - \langle \hat{T}\rangle_0$:

$$\begin{aligned}\langle \hat{T}\rangle_\lambda - \langle \hat{T}\rangle_0 &= \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[v_\lambda(\mathbf{r}) - v_0(\mathbf{r})] \\ &\quad - \lambda U[n] - \lambda E_{\mathrm{xc}}^{\lambda}[n] \; .\end{aligned} \tag{38}$$

Within the exact Kohn-Sham theory, the effective potential for noninteracting electrons is[2]

$$\begin{aligned}v_0(\mathbf{r}) &= v_\lambda(\mathbf{r}) + \lambda e^2 \int d^3r'\, n(\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1} \\ &\quad + \lambda\, \delta E_{\mathrm{xc}}^{\lambda}/\delta n(\mathbf{r}) \; ,\end{aligned} \tag{39}$$

so Eqs. (38) and (39) yield our major result of Eq. (3):

$$\begin{aligned}-\lambda E_{\mathrm{xc}}^{\lambda}[n] &- \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\lambda\, \delta E_{\mathrm{xc}}^{\lambda}/\delta n(\mathbf{r})] \\ &= \langle \hat{T}\rangle_\lambda - \langle \hat{T}\rangle_0 \geq 0 \; .\end{aligned} \tag{40}$$

Note that $v_\lambda$ has dropped out so that only the universal functionals remain. Also, in Eq. (40) the classical Coulomb contributions have canceled out, leading to the equality on the left, while the kinetic inequality on the right has been derived in earlier work.[17,30,37,38]

As a first consequence of Eq. (40), Eq. (35) can be rewritten as

$$\begin{aligned}\langle \hat{V}_{ee}\rangle_\lambda &= U[n] + 2E_{\mathrm{xc}}^{\lambda}[n] \\ &\quad + \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta E_{\mathrm{xc}}^{\lambda}/\delta n(\mathbf{r})] \; ,\end{aligned} \tag{41}$$

which defines the density functional for $\langle \hat{V}_{ee}\rangle_\lambda$. In the noninteracting ($\lambda=0$) limit, $E_{\mathrm{xc}}^{\lambda}[n]$ reduces to the exchange energy $E_x[n]$, so (41) becomes

$$\langle \hat{V}_{ee}\rangle_0 = U[n] + 2E_x[n] + \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta E_x/\delta n(\mathbf{r})] \; . \tag{42}$$

Moreover, by Eq. (33)

$$\langle \hat{V}_{ee}\rangle_0 = U[n] + E_x[n] \; . \tag{43}$$

Equate (42) and (43) to derive Eq. (5). Further, Eq. (40) becomes

$$\begin{aligned}-\lambda E_c^{\lambda}[n] &- \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\lambda\, \delta E_c^{\lambda}/\delta n(\mathbf{r})] \\ &= \langle \hat{T}\rangle_\lambda - \langle \hat{T}\rangle_0 \geq 0 \; .\end{aligned} \tag{44}$$

With the help of Eq. (5), we can write Eq. (41) more transparently as

$$\begin{aligned}\langle \hat{V}_{ee}\rangle_\lambda &= U[n] + E_{\mathrm{xc}}^{\lambda}[n] + E_c^{\lambda}[n] \\ &\quad + \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla[\delta E_c^{\lambda}/\delta n(\mathbf{r})]\end{aligned} \tag{45}$$

or, with $\lambda=1$,

$$\begin{aligned}V_{ee}[n] &= U[n] + E_{\mathrm{xc}}[n] + E_c[n] \\ &\quad + \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r}) \; .\end{aligned} \tag{46}$$

Good configuration-interaction wave-function calculations and computer programs are presently available for the determination of $V_{ee}[n]$ for small- to medium-sized atoms and molecules. The $V_{ee}[n]$ so determined may now, via Eq. (46), be used to test the validity of an approximate $E_x[n]$ and $E_c[n]$.

## IV. THE LOCAL-DENSITY APPROXIMATION AND THE VIRIAL THEOREM

The popular local-density approximation[2] (LDA) for the exchange-correlation energy is

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n]=\int d^3r\, n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r}))\;, \tag{47}$$

where $\epsilon_{\mathrm{xc}}(n)$ is the exchange-correlation energy per particle of a uniform electron gas of density $n$. The corresponding exchange-correlation potential is

$$v_{\mathrm{xc}}^{\mathrm{LDA}}([n];\mathbf{r})=\mu_{\mathrm{xc}}(n(\mathbf{r}))\;, \tag{48}$$

$$\mu_{\mathrm{xc}}(n)=\frac{d}{dn}[n\epsilon_{\mathrm{xc}}(n)]\;. \tag{49}$$

The LDA is valid in the limit of slowly varying density $n(\mathbf{r})$.

Equations (3)—(6) are valid in particular for all slowly varying densities $n(\mathbf{r})$. We now repeat the work of Averill and Painter,[16] but in slightly greater detail. Consider the equality in Eq. (6) applied to such a slowly varying density, and observe that

$$\begin{aligned}\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla\mu_c(n(\mathbf{r}))&\\ =\int d^3r\{(\mathbf{r}\cdot\nabla)[n(\mathbf{r})\mu_c(n(\mathbf{r}))]&-\mu_c(n(\mathbf{r}))\mathbf{r}\cdot\nabla n(\mathbf{r})\}\\ =\int d^3(\mathbf{r}\cdot\nabla)\{n(\mathbf{r})[\mu_c(n(\mathbf{r}))&-\epsilon_c(n(\mathbf{r}))]\}\\ =-3\int d^3r\, n(\mathbf{r})[\mu_c(n(\mathbf{r}))&-\epsilon_c(n(\mathbf{r}))]\;,\end{aligned} \tag{50}$$

where the last step involves integration by parts. Thus the left-hand side of (6) becomes

$$\int d^3r\, n(\mathbf{r})[4\epsilon_c(n(\mathbf{r}))-3\mu_c(n(\mathbf{r}))]\;, \tag{51}$$

while the right-hand side of (6) becomes

$$-\int d^3r\, n(\mathbf{r})t_c(n(\mathbf{r}))\;, \tag{52}$$

where $t_c(n)$ is the correlation contribution to the kinetic energy per particle in a uniform electron gas of density $n$. By equating (51) and (52), we find that

$$t_c(n)=3\mu_c(n)-4\epsilon_c(n)\;, \tag{53}$$

a result derived earlier by Williams and von Barth.[19] The corresponding relationship for exchange is $0=3\mu_x(n)-4\epsilon_x(n)$. By running this argument in reverse, one can show[16] that the LDA obeys Eqs. (5) and (6) even for densities that are not slowly varying over space.

Table I shows $\epsilon_c$, $\mu_c$, and $t_c$ as functions of the density parameter $r_s$, where (in atomic units)

$$n=(4\pi r_s^3/3)^{-1}\;. \tag{54}$$

In this table, $\epsilon_c$ and $\mu_c$ were computed from a parametrization[39] of the Ceperley-Alder[40] numerical results for $\epsilon_c(n)$. The ratio $t_c/(-\epsilon_c)$, which is roughly 0.5 in the metallic range $2\le r_s\le 6$, tends to 1 in the high-density limit and to 0 in the low-density limit, a result which can also be derived analytically.

TABLE I. Ceperley-Alder correlation energy $\epsilon_c$ and correlation potential $\mu_c$ for a uniform electron gas, as parametrized in Ref. 39, and the correlation contribution $t_c$ of Eq. (53) to the kinetic energy per electron. $r_s$ is the density parameter of Eq. (54). (Atomic units.)

| $r_s$ | $\epsilon_c$ | $\mu_c$ | $t_c$ |
|---|---|---|---|
| 0.01 | −0.191 | −0.202 | 0.161 |
| 0.1 | −0.121 | −0.131 | 0.092 |
| 1 | −0.060 | −0.067 | 0.038 |
| 2 | −0.045 | −0.052 | 0.025 |
| 4 | −0.032 | −0.038 | 0.015 |
| 6 | −0.026 | −0.031 | 0.011 |
| 10 | −0.019 | −0.023 | 0.007 |
| 100 | −0.003 | −0.004 | 0.001 |

## V. NONMONOTONIC AND POSITIVE BEHAVIOR OF THE CORRELATION POTENTIAL IN AN ATOM: DIAMAGNETIC SUSCEPTIBILITY

In an atom the electron density $n(\mathbf{r})$ is a monotonic[41,42] function of the distance $r$ from the nucleus, and hence the LDA correlation potential $\mu_c(n(\mathbf{r}))$ is an everywhere-negative, monotonically increasing function of $r$. Recently, however, there have been several constructions[4–6] of the *exact* correlation potential $v_c([n];\mathbf{r})$ in a few-electron atom such as He, Li, or Be. These constructions all start with the "exact" electron density $n(\mathbf{r})$ for the atom and infer therefrom the exact Kohn-Sham potential needed to produce this density in a system of noninteracting electrons. The exact correlation potential so constructed is not monotonic and in fact is often positive at large values of $r$.

We will now show that the correlation potential *cannot* be monotonic in a tightly bound closed-shell atom. To this end, differentiate Eq. (30) with respect to $\lambda$, and evaluate the left-hand side with the help of the Hellmann-Feynman theorem (9):

$$\begin{aligned}\langle\hat{V}_{ee}\rangle_\lambda+\int d^3r\, n(\mathbf{r})\frac{d}{d\lambda}v_\lambda(\mathbf{r})&\\ =\int d^3r\, n(\mathbf{r})\frac{d}{d\lambda}v_\lambda(\mathbf{r})&+U[n]+E_{\mathrm{xc}}^\lambda[n]+\lambda\frac{\partial E_c^\lambda[n]}{\partial\lambda}\;.\end{aligned} \tag{55}$$

For $\langle\hat{V}_{ee}\rangle_\lambda$ in Eq. (55), substitute the right-hand side of Eq. (45), and find

$$\lambda\frac{dE_c^\lambda[n]}{d\lambda}=E_c^\lambda[n]+\int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla\left[\frac{\delta E_c^\lambda}{\delta n(\mathbf{r})}\right]\;. \tag{56}$$

In a tightly bound closed-shell atom, where the correlation energy can be computed to leading order in perturbation theory, we expect to find $E_c^\lambda[n]$ proportional to $\lambda$, and in this situation Eq. (7) follows from Eq. (56). Combination of Eq. (7) with Eq. (6) then yields

$$T_c[n]=-E_c[n]\;. \tag{57}$$

TABLE II. Approximate validity of Eq. (57). Relationship between $-E_c[n]$ and $T_c[n]=T[n]-T_s[n]$ for two-electron atoms. Data obtained from Table II in Ref. 5. (Units are eV.)

| Atom | $-E_c[n]$ | $T_c[n]$ |
|---|---|---|
| $H^-$ | 0.75 | 0.8 |
| He | 1.12 | 1.0 |
| $Li^+$ | 1.16 | 1.1 |
| $Be^{2+}$ | 1.19 | 1.1 |

Since the density $n(\mathbf{r})$ is everywhere positive, the exact correlation potential $v_c([n];\mathbf{r})$ in a tightly bound closed-shell atom, which satisfies Eq. (7), *cannot* be a monotonic function of $r$. More generally, when the correlation contributions are expanded in powers of $e^2$, the leading or $e^4$ pieces will satisfy Eqs. (7) and (57).

Table II reveals that Eq. 57 applies well when $n$ is a ground-state density for a two-electron atom. More generally, if $n$ is the ground-state density for any atom, then

$$\langle \hat{H} \rangle = -T[n] \ . \tag{58}$$

Equation (58) may be rearranged to read

$$E_c[n]+T_c[n] = -\langle \Psi_0[n] | \hat{H} | \Psi_0[n] \rangle - \langle \Psi_0[n] | \hat{T} | \Psi_0[n] \rangle \tag{59}$$

(where $\Psi_\lambda[n]$ was defined following Eq. (14)) or construed as[30]

$$\langle \hat{H} \rangle < -T_s[n] \tag{60}$$

because $T_c[n]>0$. Now, if the true ground-state density $n(\mathbf{r})$ were identical to the self-consistent density $n_0(\mathbf{r})$ predicted for the system by the exact exchange-only Kohn-Sham formalism,[43,44] then the right-hand side of Eq. (59) would vanish because $\Psi_0[n_0]$ obeys[45] $\langle \Psi_0[n_0] | \hat{H} | \Psi_0[n_0] \rangle = -\langle \Psi_0[n_0] | \hat{T} | \Psi_0[n_0] \rangle$. Equation (57) would thereby follow. Consequently, the extent to which $E_c[n]+T_c[n] = -\int d^3r\, n\mathbf{r}\cdot\nabla v_c$ in Eq. (6) deviates from zero is a measure of the effect of correlation upon the density of the system. In many atoms, $\langle \Psi_0[n] | \hat{T} | \Psi_0[n] \rangle$ may be slightly greater[46] than $\langle \Psi_0[n_0] | \hat{T} | \Psi_0[n_0] \rangle$ (by about $|E_c|/6$), making $E_c[n] + T_c[n]$ slightly negative (or $\int d^3r\, n\mathbf{r}\cdot\nabla v_c$ slightly positive).

The remarks of the preceding paragraph apply as well in molecules, solids, the electron gas, etc., if the self-repulsion of the positive background is included in $\hat{H}$ and the equilibrium background configuration is attained.

As shown earlier, Eqs. (57) and (7) are exact when $\langle \hat{V}_{ee} \rangle_\lambda$ is linear in $\lambda$ from $\lambda=0$ to $\lambda=1$. To see this in integrated form, start with[12,13]

$$E_x[n]+E_c[n] = \int_0^1 d\lambda \langle \hat{V}_{ee} \rangle_\lambda - U[n] \ . \tag{61}$$

When $\langle \hat{V}_{ee} \rangle_\lambda$ is linear in $\lambda$, the trapezoid rule for integration applies and Eq. (61) becomes

$$E_x[n]+E_c[n] = \tfrac{1}{2}\langle \hat{V}_{ee} \rangle + \tfrac{1}{2}\langle \hat{V}_{ee} \rangle_0 - U[n] \ . \tag{62}$$

Finally, employment of Eq. (35) with Eq. (62) gives Eq. (57) with Eq. (7).

From all the above arguments, it is expected that $\langle V_{ee} \rangle_\lambda$ will be closely linear in $\lambda$ when $n(\mathbf{r})$ is compact. In any case, $\langle \hat{V}_{ee} \rangle_\lambda$ is always monotonically decreasing with increasing $\lambda$. To show this, designate $\lambda > \lambda'$ and obtain by the variational theorem

$$\langle \Psi_{\lambda'} | \hat{H}_\lambda | \Psi_{\lambda'} \rangle > \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \tag{63}$$

and

$$\langle \Psi_\lambda | \hat{H}_{\lambda'} | \Psi_\lambda \rangle > \langle \Psi_{\lambda'} | \hat{H}_{\lambda'} | \Psi_{\lambda'} \rangle \ . \tag{64}$$

On the left-hand side of Eq. (63), set $\hat{H}_\lambda = \hat{H}_{\lambda'} + (\lambda-\lambda')\hat{V}_{ee} + \hat{V}_\lambda - \hat{V}_{\lambda'}$. On the left-hand side of Eq. (64), set $\hat{H}_{\lambda'} = \hat{H}_\lambda + (\lambda'-\lambda)\hat{V}_{ee} + \hat{V}_{\lambda'} - \hat{V}_\lambda$. Then add Eqs. (63) and (64). The result is

$$(\lambda-\lambda')(\langle \hat{V}_{ee} \rangle_{\lambda'} - \langle \hat{V}_{ee} \rangle_\lambda) > 0 \ , \tag{65}$$

which proves the monotonicity.

Equation (56), which incidentally may be integrated between two $\lambda$'s, is most intriguing in that it is an equality involving just the correlation energy functional on both sides of the equation. Hence, the satisfaction of this equation and Eqs. (5) and (6), for all $n$ and $\lambda$, might provide nice tests for various $E_x$ and $E_c$ functionals that are beyond the local-density approximation.

Finally, we argue that in many atoms there is a region of space in which the correlation potential is positive. We appeal to the *ionization-potential theorem*[21–23] of Eq. (8), which asserts that the exact Kohn-Sham energy eigenvalue $\epsilon_{\max}^{KS}$ for the highest occupied orbital equals minus the first ionization potential $I$ of the system. Note well that, within an exact Kohn-Sham treatment of exchange *and* correlation, there is no "relaxation correction" to Eq. (8).

Table III shows $\epsilon_{\max}^{KS}$ for the helium atom, with and without correlation, in the exact Kohn-Sham theory and in various approximations. For two-electron systems, the exchange-only Kohn-Sham theory (KS-$X$) is identical to Hartree-Fock theory (HF). (More generally,[43,44] KS-$X$ constructs the optimum local potential which minimizes $\langle \hat{H} \rangle$ over Slater determinants, while HF constructs the optimum nonlocal potential.) Note that for helium the KS-$X$ eigenvalue $\epsilon_{\max}^{KS-X}$ is too negative in comparison with the measured[47] value of $-I$. Hence, a *positive* expectation value of the exact correlation potential $v_c([n];\mathbf{r})$, over the density of the $1s$ orbital, is needed to satisfy Eq. (8).

Table III also shows the results of several approximations of increasing sophistication: the local-density approximation,[2] the self-interaction correction[39] (SIC) to the LDA, and the combination of exact exchange with the Langreth-Mehl[48] approximation for correlation. All of these approximations incorrectly produce *negative* expectation values of the approximated correlation potential.

For many other neutral atoms of the Periodic Table, the exchange-only eigenvalue[44,49] $\epsilon_{\max}^{KS-X}$ is again too negative in comparison with the measured value[47] of $-I$, as shown in Table IV.

TABLE III. Highest occupied Kohn-Sham orbital energy $\epsilon_{\max}^{\mathrm{KS}}$ for the helium atom, in some common approximations and in the exact theory. $X$, exchange only; XC, exchange and correlation; LDA, local-density approximation; SIC, self-interaction correction to LDA; LMC, Langreth-Mehl approximation ($f=0.15$) for correlation. (Atomic units.)

| Scheme | | $\epsilon_{\max}^{\mathrm{KS}}$ |
|---|---|---|
| LDA | $X$ | $-0.517$ |
| | XC | $-0.570$ |
| SIC | $X$ | $-0.918$ |
| | XC | $-0.948$ |
| Exact $X+$ LMC | XC | $-0.96$[a] |
| Exact | $X$ | $-0.918$ |
| | XC | $-0.904$[b] |

[a] Reference 48.

[b] $-I$ from Ref. 47.

The same result is found for positive ions, as indicated for the two-electron isoelectronic series in Table V. In this table we have defined the Kohn-Sham exchange-only relaxation correction

$$\Sigma_{\mathrm{KS}-X}=E_{\mathrm{KS}-X}\,|_{N=2}-E_{\mathrm{KS}-X}\,|_{N=1}-\epsilon_{\max}^{\mathrm{KS}-X}\,|_{N=2} \qquad (66)$$

and the correlation energy[50] difference

$$\Delta E_c=E_c\,|_{N=2}-E_c\,|_{N=1}=E_c\,|_{N=2}\ , \qquad (67)$$

so that

$$\epsilon_{\max}^{\mathrm{KS}-X}\,|_{N=2}+\Sigma_{\mathrm{KS}-X}+\Delta E_c=-I\ . \qquad (68)$$

$\Sigma_{\mathrm{KS}-X}$ and $\Delta E_c$ show some tendency to cancel, but the cancellation is imperfect and the sum $\Sigma_{\mathrm{KS}+X}+\Delta E_c$ is always positive. In the large-$Z$ limit for two-electron ions, the quantity

$$\Sigma_{\mathrm{KS}-X}+\Delta E_c=\int d^3r\frac{n(\mathbf{r})}{2}v_c([n];\mathbf{r}) \qquad (69)$$

approaches a well-defined *positive* limit $\approx 0.01$ a.u.

TABLE IV. Highest occupied orbital energy $\epsilon_{\max}$ for neutral atoms. HF, Hartree-Fock (Ref. 49); KS-$X$, Kohn-Sham exchange-only (Ref. 44). $-I$ is minus the measured first ionization potential from Ref. 47. (Atomic units.) The asterisk indicates those atoms for which $\epsilon_{\max}^{\mathrm{KS}-X}<-I$.

| Atom | $\epsilon_{\max}^{\mathrm{HF}}$ | $\epsilon_{\max}^{\mathrm{KS}-X}$ | $-I$ |
|---|---|---|---|
| *He | $-0.918$ | $-0.918$ | $-0.904$ |
| Li | $-0.196$ | $-0.196$ | $-0.198$ |
| Be | $-0.309$ | $-0.308$ | $-0.343$ |
| *B | $-0.310$ | $-0.310$ | $-0.305$ |
| *C | $-0.433$ | $-0.431$ | $-0.414$ |
| *N | $-0.568$ | $-0.563$ | $-0.534$ |
| *O | $-0.632$ | $-0.629$ | $-0.500$ |
| *F | $-0.730$ | $-0.725$ | $-0.640$ |
| *Ne | $-0.850$ | $-0.846$ | $-0.793$ |
| Na | $-0.182$ | $-0.182$ | $-0.189$ |
| Mg | $-0.253$ | $-0.252$ | $-0.281$ |
| Al | $-0.210$ | $-0.209$ | $-0.220$ |
| Si | $-0.297$ | $-0.296$ | $-0.300$ |
| *P | $-0.392$ | $-0.387$ | $-0.385$ |
| *S | $-0.437$ | $-0.437$ | $-0.381$ |
| *Cl | $-0.506$ | $-0.500$ | $-0.477$ |
| *Ar | $-0.591$ | $-0.585$ | $-0.579$ |

Information about the electron density in an atom is conveniently expressed by the density moments

$$\langle r^m\rangle=\int d^3r\,n(r)r^m\ . \qquad (70)$$

It is well known that the Hartree-Fock and related approximations predict extremely accurate values for $\langle r^{-1}\rangle$. For instance, see the data for $\langle r^{-1}\rangle$ in Ref. 51. However, Englert and Schwinger[24] have recently observed that Hartree-Fock[52] values of $\langle r^2\rangle$ are 5% to 13% too large in the atoms Ar, Kr, and Xe, in comparison with values determined from measured diamagnetic susceptibilities[53] $\chi$ via the equation

$$\chi=-\frac{e^2}{6mc^2}\langle r^2\rangle\ . \qquad (71)$$

Cole and Toigo[25] have independently observed the same $\sim$10% discrepancy in Ne ($\langle r^2\rangle_{\mathrm{HF}}=9.37$, $\langle r^2\rangle_{\mathrm{expt}}=8.51$). Equation (71) is a direct consequence of the Hellmann-Feynman theorem and seems unimpeachable.

The large discrepancy between Hartree-Fock and "measured" values for $\langle r^2\rangle$ for a number of atoms was discussed earlier by Vosko and Wilk.[26] In the case of the Ne atom, they quote a best theoretical value of $\langle r^2\rangle=9.45$ from a configuration-interaction calculation[54] (150 configurations) which was specifically designed to uncover the correlation effects upon the density. We are thus left with two *very* different candidates for the "exact" value of $\langle r^2\rangle$ in Ne. Like Vosko and Wilk,[26] we choose to believe the theoretical value.

The discrepancy between theoretical and experimental values of $\langle r^2\rangle$ in the noble-gas atoms demands at least an attempt at resolution. Table VI compares the relativistic Hartree-Fock values of Desclaux[55] to the measured values of Barter, Meisenheimer, and Stevenson,[56] "the last very important work regarding the infrequent measurements of gas susceptibilities."[57] The theoretical values for Ne, Ar, Kr, and Xe are all 6.5% larger than the measured values and fall outside the quoted experimental error bars. However, the measured value for Ar was not found directly; it was constructed as an average of older measurements and

TABLE V. Kohn-Sham exchange-only relaxation correction $\Sigma_{\mathrm{KS}-X}$ of Eq. (66), and the correlation energy difference $\Delta E_c$ of Eq. (67), for two-electron ions of nuclear charge $Z$. This table has been constructed from Hartree-Fock data of Ref. 49 and from the $1/Z$ expansion for the total energy of Ref. 50. (Atomic units.)

| $Z$ | $\epsilon_{\max}^{\mathrm{KS}-X}$ | $\Sigma_{\mathrm{KS}-X}$ | $\Delta E_c$ |
|---|---|---|---|
| 2 | $-0.918$ | 0.056 | $-0.042$ |
| 10 | $-43.917$ | 0.056 | $-0.046$ |
| 18 | $-150.917$ | 0.056 | $-0.046$ |
| 36 | $-625.667$ | 0.056 | $-0.046$ |

TABLE VI. Theoretical (relativistic Hartree-Fock) and experimental (diamagnetic susceptibility) values for the density moment $\langle r^2 \rangle$ in the rare-gas atoms. (Atomic units.) Relativistic effects shrink $\langle r^2 \rangle$ by about 2% in Xe.

| Atom | Theory[a] | Expt.[b] | Ratio |
|---|---|---|---|
| He | 2.37 | 2.55 ±0.10 | 0.93 ±0.03 |
| Ne | 9.36 | 8.79 ±0.18 | 1.065 ±0.02 |
| Ar | 25.97 | (24.39)±0.19 | (1.065)±0.01 |
| Kr | 39.10 | 36.62 ±0.5 | 1.068 ±0.01 |
| Xe | 61.20 | 57.4 ±0.9 | 1.066 ±0.02 |

[a] Reference 55.

[b] Reference 56.

TABLE VII. Density moments $\langle r^m \rangle$ of Eq. (70) for the neon atom, in some common approximations and in the exact theory. $X$, exchange only; XC, exchange and correlation; LDA, local-density approximation; SIC, self-interaction correction to LDA; HF, Hartree-Fock; LMC, Langreth-Mehl approximation ($f=0.15$) for correlation. (Atomic units.)

| Scheme | | $\langle r^{-1} \rangle$ | $\langle r^2 \rangle$ |
|---|---|---|---|
| LDA | $X$ | 30.95 | 10.04 |
| | XC | 31.00 | 9.85 |
| SIC | $X$ | 31.15 | 9.51 |
| | XC | 31.17 | 9.43 |
| HF | $X$ | 31.11[a] | 9.37[a] |
| Exact $X+$LMC | XC | 31.15[c] | 9.22[c] |
| Exact | $X$ | 31.10[b] | 9.40[b] |
| | XC | 31.11[d] | 9.45[e] |

[a] Reference 52.

[b] Reference 48.

[c] Reference 58.

[d] Reference 51.

[e] Reference 26.

was used to calibrate the instrument. It appears that a recalibration might vindicate the theoretical calculations for Ne, Ar, Kr, and Xe.

Table VII shows exact and approximate values for $\langle r^{-1} \rangle$ and $\langle r^2 \rangle$ in the neon atom. The LDA,[2] SIC,[39] and Langreth-Mehl[48,58] approximations to the correlation potential *reduce* the calculated value of $\langle r^2 \rangle$ by 1% or 2%, while the exact correlation potential *increases* $\langle r^2 \rangle$ by about 0.5%.

Vosko and Wilk[26] have displayed the difference between the exact and Hartree-Fock densities for the atoms He, Be, Ne, and Mg, as well as the exact and Hartree-Fock values for $\langle r^2 \rangle$. We make the following observation which relates their results to our results of Table IV for the exact and Hartree-Fock values of $\epsilon_{\max}$. In the atoms He or Ne, where the Hartree-Fock value of $\epsilon_{\max}$ is too negative in comparison with $-I$, the Hartree-Fock density is too small at large $r$, as is its value for $\langle r^2 \rangle$. In the atoms Be or Mg, where the Hartree-Fock value of $\epsilon_{\max}$ is not negative enough, the Hartree-Fock density is too large at large $r$, as is its value for $\langle r^2 \rangle$. This relationship might have been expected, since $\epsilon_{\max}$ controls the long-range exponential decay[6,21-23] of the density.

As a final observation in this section, it can be seen from Table VII that improvements to the LDA *reduce* $\langle r^2 \rangle$ in an atom. Just the opposite effect was predicted by Puska, Nieminen, and Manninen,[59] who argued as follows: Within the LDA, the effective potential decays exponentially at large $r$, whereas the exact Kohn-Sham potential decays as $-r^{-1}$. Thus, improving on the LDA would relax $n(r)$ outwards, making $\langle r^2 \rangle$ larger. This interesting argument is almost correct; what it overlooks is the fact that the LDA effective potential is also in error at small $r$, where its error is approximately a positive constant. This "constant" can be regarded either as a self-interaction error[39] or as a consequence of averaging over the derivative discontinuity[21] of $E_{\mathrm{xc}}[n]$.

## VI. SCALING PROPERTIES OF $V_{ee}[n]$ AND $T[n]$

As expressed in Sec. III, the Hohenberg-Kohn universal functional, for $\lambda=1$ in Eq. (14), has been identified as

$$Q[n]=\langle \Psi | (\hat{T}+\hat{V}_{ee}) | \Psi \rangle , \tag{72}$$

where $\Psi$ is that normalized-antisymmetric function which yields $n$ and minimizes $\langle (\hat{T}+\hat{V}_{ee}) \rangle$. The wave function $\Psi$ turns out to be an eigenstate of some Hamiltonian of the form

$$\hat{H}=\hat{T}+\hat{V}_{ee}+\sum_{i=1}^{N} w(\mathbf{r}_i) , \tag{73}$$

where $w$ is a local-multiplicative one-body potential. We have

$$T[n]=\langle \Psi | \hat{T} | \Psi \rangle , \tag{74}$$

$$V_{ee}[n]=\langle \Psi | \hat{V}_{ee} | \Psi \rangle . \tag{75}$$

Now, it is certainly true that

$$\begin{gathered} \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\rightarrow\gamma^3 n(\gamma\mathbf{r}) , \\ \langle \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N) | \hat{T}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) | \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N) \rangle=\gamma^2 T[n] , \end{gathered} \tag{76}$$

and

$$\langle \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N) | \hat{V}_{ee}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) | \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N) \rangle=\gamma V_{ee}[n] , \tag{77}$$

where $\gamma$ is a scale factor. So it *might seem* that

$$T[n_\gamma]=\gamma^2T[n]\,, \tag{78}$$

$$V_{ee}[n_\gamma]=\gamma V_{ee}[n]\,, \tag{79}$$

where $n_\gamma(\mathbf{r})\equiv\gamma^3 n(\gamma\mathbf{r})$ is the scaled density, especially since Eqs. (78) and (79) would give the correct virial relation, $E=-T[n]$, for an atom, etc.[27] But interestingly, both Eqs. (78) and (79) can *never* be *true* in the exact theory, unless, of course, $\gamma=1$, because by the definition of $Q[n]$ as a minimization in Eq. (72), and by the fact that $\gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\neq\Psi_\gamma(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$, it follows immediately, for $\gamma\neq1$, that

$$Q[n_\gamma]\equiv\langle\Psi_\gamma|(\hat{T}+\hat{V}_{ee})|\Psi_\gamma\rangle<\langle\gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)|(\hat{T}+\hat{V}_{ee})|\gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\rangle\,, \tag{80}$$

which gives the *inequality*

$$T[n_\gamma]+V_{ee}[n_\gamma]<\gamma^2T[n]+\gamma V_{ee}[n]\,, \tag{81}$$

where $\Psi_\gamma$ is that normalized-antisymmetric function which yields the scaled density $n_\gamma(\mathbf{r})$ and minimizes $\langle(\hat{T}+\hat{V}_{ee})\rangle$.

To see why

$$\gamma^{3N/2}\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\neq\Psi_\gamma(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \quad (\gamma\neq1)\,, \tag{82}$$

observe that

$$\hat{H}(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)=E\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N) \tag{83}$$

or

$$\left[\gamma^{-2}\hat{T}+\gamma^{-1}\hat{V}_{ee}+\sum_{i=1}^{N}w(\gamma\mathbf{r}_1)\right]\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)=E\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\,, \tag{84}$$

so that

$$\left[\hat{T}+\gamma\hat{V}_{ee}+\sum_{i=1}^{N}\gamma^2w(\gamma\mathbf{r}_i)\right]\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)=(\gamma^2E)\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)\,. \tag{85}$$

Because of the appearance of the factor $\gamma$ in front of $\hat{V}_{ee}$, $\Psi(\gamma\mathbf{r}_1,\gamma\mathbf{r}_2,\ldots,\gamma\mathbf{r}_N)$ cannot be an eigenstate of an $\hat{H}$ of the form of Eq. (73), as required for an equality in Eq. (82).

In summary, thus far we have

$$Q[n_\gamma]=T[n_\gamma]+V_{ee}[n_\gamma]=\gamma^2T[n]+\gamma V_{ee}[n]+G([n];\gamma)\,, \tag{86}$$

where

$$G([n];\gamma)<0 \quad (\gamma\neq1)\,, \tag{87}$$

and

$$G([n];\gamma)=0 \quad (\gamma=1)\,. \tag{88}$$

Since $G$ is maximal at $\gamma=1$,

$$(\partial G/\partial\gamma)_{\gamma=1}=0\,. \tag{89}$$

(It shall always be understood in this paper, of course, that $\gamma>0$.) Also, $G$ shall be identified as the negative of the left-hand side of Eq. (106).

Equations (86) and (89) require

$$\frac{\partial}{\partial\gamma}(T[n_\gamma]+V_{ee}[n_\gamma])_{\gamma=1}=2T[n]+V_{ee}[n]\,. \tag{90}$$

So, even though Eqs. (78) and (79) cannot be both right (and are actually *both wrong* as shown below), these equations do, interestingly, correctly yield Eq. (90) because of Eq. (89).

Thus it is *not* true that

$$Q[n_\gamma]=\gamma^2T[n]+\gamma V_{ee}[n]\,. \tag{91}$$

But, is it possible to find functionals, other than $T[n]$ and $V_{ee}[n]$, say $P[n]$ and $S[n]$, such that $Q[n]\equiv P[n]+S[n]$ with

$$Q[n_\gamma]=\gamma^2P[n]+\gamma S[n]\ ? \tag{92}$$

The answer to the question is *no;* the exact $Q[n]$ can never be partitioned according to Eq. (92). If Eq. (92) were true, then because $n(\mathbf{r})$ is an eigenstate density for some $w$ in Eq. (73), it would follow from

$$\left[\frac{\partial}{\partial\gamma}\left[\int d^3r\,n_\gamma(\mathbf{r})w(\mathbf{r})+Q[n_\gamma]\right]\right]_{\gamma=1}=0 \tag{93}$$

that

$$2P[n]+S[n]=-\left[\frac{\partial}{\partial\gamma}\left[\int d^3r\,n_\gamma(\mathbf{r})w(\mathbf{r})\right]\right]_{\gamma=1}\,. \tag{94}$$

We also have, of course,

$$2T[n]+V_{ee}[n]=-\left[\frac{\partial}{\partial\gamma}\left[\int d^3r\,n_\gamma(\mathbf{r})w(\mathbf{r})\right]\right]_{\gamma=1}\,. \tag{95}$$

Finally, from Eq. (86) and Eq. (92) at $\gamma=1$, and from Eqs. (94) and (95), it would follow that $P[n]=T[n]$ and $S[n]=V_{ee}[n]$. But, since we already proved that Eq. (91) is not true, it then follows that Eq. (92) is not correct. Consequently, when an approximate $Q$ obeys Eq. (92), it means that $Q$ can legitimately approximate only the exchange-only density-functional theory. Significant is the fact, then, that Thomas-Fermi theory,[27] common forms of extended Thomas-Fermi theory,[27] and $X\alpha$ theory[8] all conform to Eq. (92).

Let us now derive the inequalities involving $T[n]$ and $V_{ee}[n]$ with their scaled counterparts. As we shall see, the directions of the derived inequalities change at $\gamma=1$. From Eq. (85), we have for $\gamma\neq1$

$$\langle \Psi_\gamma \,|\, (\hat{T}+\gamma \hat{V}_{ee}) \,|\, \Psi_\gamma \rangle > \langle \gamma^{3N/2}\Psi(\gamma \mathbf{r}_1, \gamma \mathbf{r}_2, \ldots, \gamma \mathbf{r}_N) \,|\, (\hat{T}+\gamma \hat{V}_{ee}) \,|\, \gamma^{3N/2}\Psi(\gamma \mathbf{r}_1, \gamma \mathbf{r}_2, \ldots, \gamma \mathbf{r}_N) \rangle \ , \tag{96}$$

or

$$T[n_\gamma] + \gamma V_{ee}[n_\gamma] > \gamma^2 T[n] + \gamma^2 V_{ee}[n] \ . \tag{97}$$

Combination of Eq. (81) with Eq. (97) gives

$$V_{ee}[n_\gamma] < \gamma V_{ee}[n] \quad (\gamma < 1) \ , \tag{98a}$$

$$V_{ee}[n_\gamma] > \gamma V_{ee}[n] \quad (\gamma > 1) \ ; \tag{98b}$$

$$T[n_\gamma] > \gamma^2 T[n] \quad (\gamma < 1) \tag{99a}$$

$$T[n_\gamma] < \gamma^2 T[n] \quad (\gamma > 1) \ . \tag{99b}$$

Further, combination of Eqs. (98) with Eqs. (99) gives

$$\gamma V_{ee}[n] - V_{ee}[n_\gamma] > \gamma^2 T[n] - T[n_\gamma] \quad (\gamma < 1) \tag{100a}$$

$$\gamma V_{ee}[n] - V_{ee}[n_\gamma] < \gamma^2 T[n] - T[n_\gamma] \quad (\gamma > 1) \ . \tag{100b}$$

Note that Eqs. (100) actually connect kinetic and repulsion functionals.

## VII. SCALING PROPERTIES OF $E_c[n]$, $E_x[n]$, AND $T_s[n]$

Unlike $T[n]$, $T_s[n]$ *does* have the property that[7]

$$T_s[n_\gamma] = \gamma^2 T_s[n] \ , \tag{101}$$

when $n_\gamma(\mathbf{r}) \equiv \gamma^3 n(\gamma \mathbf{r})$ is the scaled density. Further, $E_x[n]$ *does* have the property

$$E_x[n_\gamma] = \gamma E_x[n] \ . \tag{102}$$

This property was suggested without proof in Ref. 7 and corroborated in Ref. 45. We note however that only the Kohn-Sham $E_x$ (as defined in Refs. 43—45) and not the Hartree-Fock $E_x$ has this property. Equations (101) and (102) result from the fact that when a single determinant $\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is an eigenstate of a Hamiltonian of the form of Eq. (73), with $\hat{V}_{ee}$ absent, then $\Phi(\gamma \mathbf{r}_1, \gamma \mathbf{r}_2, \ldots, \gamma r_N)$ is also an eigenstate of the form of Eq. (73), with $\hat{V}_{ee}$ absent. But we now assert that

$$E_c[n_\gamma] \neq \gamma E_c[n] \ , \tag{103}$$

because an equality in Eq. (103) would lead to Eq. (92), in contradiction to the fact that Eq. (92) can never be true. Hence, the existence of a nonzero $G$ in Eq. (86) results essentially from correlation effects as defined for density-functional theory. Accordingly, let us now derive various conditions upon the exact universal correlation functional and its corresponding correlation potential.

From Eqs. (4) and (101), obtain

$$T[n_\gamma] = \gamma^2 T_s[n] + T_c[n_\gamma] \ . \tag{104}$$

Next, insert Eqs. (4), (46), (102), and (104) into Eq. (81) to yield

$$\begin{aligned} &\gamma^2 T_c[n] + 2\gamma E_c[n] + \gamma \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r}) \\ &\quad \geq T_c[n_\gamma] + 2E_c[n_\gamma] + \int d^3r\, n_\gamma(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n_\gamma];\mathbf{r}) \ . \end{aligned} \tag{105}$$

Next, utilize the equality in Eq. (6) to eliminate $T_c[n]$:

$$\begin{aligned} &(2\gamma-\gamma^2)E_c[n] + (\gamma-\gamma^2) \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r}) \\ &\qquad - E_c[n_\gamma] \geq 0 \ , \end{aligned} \tag{106}$$

where the equality in Eq. (106) holds only at $\gamma = 1$, so that the left-hand side of Eq. (106) has a unique minimum at $\gamma = 1$. Note that the negative of the left-hand side of Eq. (106) is the $G$ of Eq. (86). Further, by functional Taylor expansion of $E_c[n_\gamma]$ in powers of $n_\gamma - n$,

$$\frac{\partial}{\partial \gamma} \left[ E_c[n_\gamma] - \int d^3r\, n_\gamma(\mathbf{r}) v_c([n];\mathbf{r}) \right] \Bigg|_{\gamma=1} = 0 \ , \tag{107}$$

which is an equation of interesting symmetry. Alternatively, by a change of variable in Eq. (107),

$$\frac{\partial}{\partial \gamma} E_c[n_\gamma] \Bigg|_{\gamma=1} = - \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r}) \ . \tag{108}$$

From the approximate validity of Eq. (7) for compact closed-shell densities, Eq. (108) reveals that the correlation energies of these densities should *not* be *very sensitive* to their scaling (as is evident in Tables II and V), and approximate $E_c[n]$ should be made to reflect this fact. Namely, $E_c[n_\gamma] \simeq E_c[n]$.

Just as Eq. (81) leads to Eq. (106), Eq. (97) leads to

$$\begin{aligned} &(2\gamma-1)E_c[n_\gamma] + (\gamma-1) \int d^3r\, n_\gamma(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n_\gamma];\mathbf{r}) \\ &\qquad - \gamma^2 E_c[n] \geq 0 \ . \end{aligned} \tag{109}$$

Via the equality in Eq. (6), equivalent forms of Eqs. (106) and (109) may be written, respectively, as

$$\gamma E_c[n] - E_c[n_\gamma] \geq \gamma(1-\gamma) T_c[n] \tag{110}$$

and

$$\gamma^2 E_c[n_\gamma] - \gamma^3 E_c[n] \geq \gamma(\gamma-1) T_c[n_\gamma] \ . \tag{111}$$

Since $T_c[n] > 0$ and $T_c[n_\gamma] > 0$, it follows from Eq. (110) at $\gamma < 1$, and from Eq. (111) at $\gamma > 1$, that

$$E_c[n_\gamma] < \gamma E_c[n] \quad (\gamma < 1) \ , \tag{112a}$$

$$E_c[n_\gamma] > \gamma E_c[n] \quad (\gamma > 1) \ , \tag{112b}$$

which reveal the direction of the inequality in Eq. (103). Next, from Eqs. (99),

$$T_c[n_\gamma] > \gamma^2 T_c[n] \quad (\gamma < 1) \ , \tag{113a}$$

$$T_c[n_\gamma] < \gamma^2 T_c[n] \quad (\gamma > 1) \ , \tag{113b}$$

and substitution of Eq. (6) into Eqs. (113) generates

$$\begin{aligned} &E_c[n_\gamma] + \int d^3r\, n_\gamma(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n_\gamma];\mathbf{r}) \\ &\quad < \gamma^2 E_c[n] + \gamma^2 \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r}) \\ &\qquad\qquad (\gamma < 1) \ , \end{aligned} \tag{114a}$$

$$\begin{aligned} &E_c[n_\gamma] + \int d^3r\, n_\gamma(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n_\gamma];\mathbf{r}) \\ &\quad > \gamma^2 E_c[n] + \gamma^2 \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_c([n];\mathbf{r}) \\ &\qquad\qquad (\gamma > 1) \ . \end{aligned} \tag{114b}$$

It should be noted that for the equations of this section, we have partitioned $E_{xc}$ into $E_c + E_x$. The equations, of course, could have also been written with $E_{xc}$ intact. For instance, with $E_{xc}$ intact, Eqs. (112) become

$$(1-\gamma)E_{xc}[n_\gamma] < (1-\gamma)\gamma E_{xc}[n] \quad (\gamma \neq 1)\ . \tag{115}$$

Finally, it is clear that Eqs. (110)—(113) will be satisfied within the local-density approximation,[2] provided that the electron-gas correlation-energy input obeys the inequalities (for $\gamma \neq 1$)

$$\gamma\epsilon_c(n) - \epsilon_c(\gamma^3 n) - \gamma(1-\gamma)t_c(n) > 0\ , \tag{110$'$}$$

$$\gamma\epsilon_c(\gamma^3 n) - \gamma^2\epsilon_c(n) + (1-\gamma)t_c(\gamma^3 n) > 0\ , \tag{111$'$}$$

$$(1-\gamma)[\gamma\epsilon_c(n) - \epsilon_c(\gamma^3 n)] > 0\ , \tag{112$'$}$$

$$(1-\gamma)[t_c(\gamma^3 n) - \gamma^2 t_c(n)] > 0\ , \tag{113$'$}$$

with $t_c(n)$ given by Eq. (53). These inequalities, as well as the relation $t_c(n) > 0$, were tested with $r_s$ and $r_s/\gamma$ between 0.001 and 3200 for four common parametrizations of $\epsilon_c(n)$: Wigner,[60] Gunnarsson-Lundqvist,[13] random-phase approximation,[42] and Ceperley-Alder.[39] All inequalities were found to be obeyed.

The local-density approximation for the correlation energy does *not* obey the scaling invariance for compact densities predicted by Eqs. (7) and (108). Instead, the LDA correlation energy has a $\ln\gamma$ dependence. For instance, for an atom in the limit of large nuclear charge $Z$ and fixed electron number $N$, the LDA and SIC correlation energies vary as $\ln Z$, while the exact correlation energy varies as $Z^0$ or $Z^1$, depending upon $N$.[61] For all closed-shell and certain open-shell atoms, the exact limiting behavior is $Z^0$.

## VIII. CLOSING REMARKS

The Hellmann-Feynman relations, Eqs. (1) and (2), are necessary requisites that density optimization has in fact been achieved. Further, there are *very few* known equalities or inequalities involving the exact $E_{xc}$ and $v_{xc}$ for arbitrary trial $n$. Accordingly, this paper has introduced a number of rigorous necessary requisites upon $E_{xc}$ and $v_{xc}$, in the form of equalities as in Eqs. (5) and (29) and in the form of inequalities as in Eqs. (6), (106), and (109)—(115). These requisites are satisfied within the local-density approximation. The local-density approximation for $E_c$, however, does not exhibit the required insensitivity to a scaling of $n$, and one should take this into account in the quest for improved exchange-correlation functionals.

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