PHYSICAL REVIEW A VOLUME 43, NUMBER 9 1 MAY 1991

Density-functional exchange correlation through coordinate scaling in adiabatic connection and correlation hole

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(Received 6 July 1990; revised manuscript received 19 October 1990)

The exact exchange-correlation functional $E_{\rm xc}[n]$ must be approximated in density-functional theory for the computation of electronic properties. By the coupling-constant integration (adiabatic-connection) formula we know that $E_{\rm xc}[n]=\int_0^1(V_{ee}^{\alpha}[n]-U[n])d\alpha$, where $V_{ee}^{\alpha}[n]$ is the electron-electron repulsion energy of $\Psi_n^{\min,\alpha}$, which is that wave function that yields the density n and minimizes $\langle \hat{T}+\alpha\hat{V}_{ee}\rangle$. Here α is the coupling constant. Consequently, knowledge of the behavior of $V_{ee}^{\alpha}[n]$ as a function of α ensures knowledge of $E_{\rm xc}[n]$. With this in mind and for the purpose of approximating $E_{\rm xc}$, it was previously established that $(\partial V_{ee}^{\alpha}/\partial\alpha)\leq 0$. The present paper reveals that $V_{ee}^{\alpha}[n]=\alpha V_{ee}^{1}[n_{1/\alpha}]$, where $n_\beta(x,y,z)=\beta^3 n(\beta x,\beta y,\beta z)$, and where β is a coordinate scale factor. In other words, knowledge of $V_{ee}^{1}[n]$ implies knowledge of $V_{ee}^{\alpha}[n]$ for *all* α. Alternatively, knowledge of $V_{ee}^{\alpha}[n]$ for some *small* α implies knowledge of all of the $V_{ee}^{\alpha}[n]$. In any case, any viable approximation to $V_{ee}^{\alpha}[n]$ should be made to satisfy the above displayed equality. Analogous conclusions hold for the second-order density matrix, the pair-correlation function, the exchange-correlation hole, and the correlation component of the exchange-correlation hole, etc. For example, $\rho_{\rm xc}([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)=\alpha^3\rho_{\rm xc}([n_{1/\alpha},1];\,\alpha\mathbf{r}_1,\alpha\mathbf{r}_2)$, where $\rho_{\rm xc}([n,\alpha];\,\mathbf{r}_1,\mathbf{r}_2)$ is the exact exchange-correlation hole of $\Psi_n^{\min,\alpha}$. (A corresponding expression holds for the correlation hole alone.) Further, when n belongs to a noninteracting ground state that is nondegenerate, then $\lim_{\alpha\to 0}V_{ee}^{\alpha}[n]=A[n]+f_n(\alpha)B[n]+\cdots$, where $f_n(\alpha)$ must vanish at least as rapidly as α, and $\lim_{\lambda\to\infty}E_c[n_\lambda]>-\infty$, where $E_c[n]=E_{\rm xc}[n]-\lim_{\gamma\to\infty}\gamma^{-1}E_{\rm xc}[n_\gamma]$, and where E_c is a familiar exact density-functional "correlation energy." In contrast, in the local-density approximation and in certain nonlocal approximations, $f_n(\alpha)$ is replaced by a function that goes as $\alpha[\ln(\alpha^{-1})]$, $\alpha\to 0$, and E_c is replaced by a functional that is *unbounded* as $\lambda\to\infty$. Further, $\lim_{\lambda\to\infty}E_{\rm xc}[n_\lambda^x]>-\infty$ and $\lim_{\lambda\to\infty}E_x[n_\lambda^x]>-\infty$, which are also not generally satisfied by common approximations. Here $n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z)$ and E_x is a familiar exact density-functional "exchange energy." Finally, comparison is made between E_c and the traditional quantum-mechanical correlation energy, which is expressed exactly as a functional of the Hartree-Fock density.

I. INTRODUCTION

Hohenberg-Kohn-Sham density-functional theory[1–4] constitutes a dramatic simplification of the many-electron problem for the study of electronic properties. Only the three-dimensional electron density $n(\mathbf{r})$ need be employed, independent of the size of the system. One simply minimizes the energy functional $E[n]$ to obtain the ground-state energy. However, the exact exchange-correlation $E_{\rm xc}[n]$ component of $E[n]$ must be approximated. It is the purpose of this paper to show that coordinate scaling provides a powerful tool for understanding fundamental aspects of $E_{\rm xc}$ that were not previously known in connection with the coupling-constant integration (adiabatic connection) formulas[5–8] of Harris and Jones, Langreth and Perdew, and Gunnarsson and Lundqvist. This paper derives exact coordinate scaling conditions involving $E_{\rm xc}$ and its correlation component. Approximations to these functionals should be constructed to satisfy these conditions because coordinate scaling requirements help to dictate the *form* of $E_{\rm xc}$. Most commonly employed approximations to $E_{\rm xc}$ do not presently satisfy all the coordinate scaling requirements presented within.

Following is the adiabatic connection (or coupling-constant integration) formula,[5–8] which involves only the diagonal part of the second-order density matrix (pair probability density), and which has served as a marvelous exact formal expression for $E_{\rm xc}$,

$$E_{\rm xc}[n]=\int_0^1(V_{ee}^{\alpha}[n]-U[n])d\alpha\ , \qquad (1)$$

where $V_{ee}^{\alpha}[n]$ is the electron-electron repulsion energy functional associated with $\langle \hat{\mathbf{T}}+\alpha\hat{\mathbf{V}}_{ee}\rangle$, and where $U[n]$ is the classical electron-electron repulsion functional which is, of course, known exactly and is given by

$$U[n]=\tfrac{1}{2}\int\int n(\mathbf{r}_1)n(\mathbf{r}_2)|\mathbf{r}_1-\mathbf{r}_2|^{-1}d^3r_1d^3r_2\ .$$

In the above formula the density is held *fixed* in the integrand as the *coupling constant* α is varied from 0 to 1. Hence, Eq. (1) is the form of the coupling-constant integration formula of Langreth-Perdew[6] and Gunnarsson-Lundqvist.[7] (The density is not held fixed in the earlier formula of Harris and Jones.[5]) In Eq. (1), it is $V_{ee}^{\alpha}[n]$ that must be approximated. Accordingly, this paper reveals exact properties of $V_{ee}^{\alpha}[n]$ as a function of α. Now, it is already known[9] that $V_{ee}^{\alpha}[n]$ is monotonically decreasing with increasing α. Here through the asymptotic coordinate scaling study of E_c in Sec. II, it shall be shown that

$$\lim_{\alpha\to 0} V_{ee}^{\alpha}[n]=A[n]+f(\alpha)B[n]+\cdots , \tag{2}$$

where $f(\alpha)$ must vanish at least as fast as α. (In contrast, it shall be seen that the local-density approximation and certain nonlocal approximations, as well, take the form $A'[n]+\alpha\ln(\alpha^{-1})B'[n]$, as $\alpha\to 0$.) Moreover, the work of Levy and Perdew[9] implies that

$$V_{ee}^{\alpha}[n]=\alpha V_{ee}^{1}[n_{1/\alpha}] , \tag{3}$$

where n_β is defined by

$$n_\beta(\mathbf{r})=n_\beta(x,y,z)=\beta^3 n(\beta x,\beta y,\beta z) ,$$

and where $n_\beta(\mathbf{r})$ is a uniformly scaled electron density with β as a coordinate scale factor. Hence, Eq. (3) reveals the surprising fact that knowledge of $V_{ee}^{1}[n]$, the universal repulsion functional for $\alpha=1$, is sufficient to know E_{xc}. Alternatively, knowledge of $V_{ee}^{\alpha}[n]$ for some *small* α implies knowledge of all of the $V_{ee}^{\alpha}[n]$ and therefore knowledge of E_{xc}. Hence, knowledge of the universal $V_{ee}^{\alpha}[n]$ for some *small* fixed α is all that is necessary in principle for solution to the many-body problem, and an appropriate perturbation treatment might be applicable.

As a fact which was tacitly used for the derivation of the inequality in Eq. (96) of Ref. 9 and for the generation of the right-hand-side of Eq. (97) in Ref. 9, Eq. (85) in Ref. 9 dictates that

$$V_{ee}^{\alpha}[n_\alpha]=\alpha V_{ee}^{1}[n] .$$

Equation (3) in the present paper follows from the above equation by replacing $n(x,y,z)$ by

$$n_{1/\alpha}(x,y,z)=\alpha^{-3}n(\alpha^{-1}x,\alpha^{-1}y,\alpha^{-1}z)$$

on both sides of the equation. (See also Ref. 10 for related coordinate scaling considerations.)

Consistent with Eq. (3), it will be shown that the exact exchange-correlation hole satisfies

$$\rho_{\text{xc}}([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)=\alpha^3\rho_{\text{xc}}([n_{1/\alpha},1];\alpha\mathbf{r}_1,\alpha\mathbf{r}_2) , \tag{4}$$

where $\rho_{\text{xc}}([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)$ is the exchange-correlation hole associated with $\langle\hat{\mathbf{T}}+\alpha\hat{\mathbf{V}}_{ee}\rangle$. Moreover, this paper also reveals limiting coordinate scaling properties of $E_{\text{xc}}[n]$. For instance,

$$\lim_{\lambda\to\infty}\left(E_{\text{xc}}[n_\lambda]-\lim_{\gamma\to\infty}\gamma^{-1}E_{\text{xc}}[n_{\lambda\gamma}]\right)>-\infty . \tag{5}$$

In contrast, the local-density approximation (LDA) to E_{xc} does not satisfy Eq. (5) because the LDA is unbounded as $\lambda\to\infty$.

Part of the appeal of coordinate scaling is the fact that it is often quite easy to observe immediately how a functional behaves upon coordinate scaling. It turns out that one often just has to divide the functional by λ^3 and within the integrand, one just has to replace n by $\lambda^3 n$, ∇ by $\lambda\nabla$, and $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$ by $\lambda|\mathbf{r}_1-\mathbf{r}_2|^{-1}$, etc. For example, $\int(|\nabla n|^2/n^{4/3})d\mathbf{r}$ becomes $\lambda\int(|\nabla n|^2/n^{4/3})d\mathbf{r}$ when n is replaced by n_λ. This result arises because

$$\begin{aligned}\int[|\nabla n|^2/n^{4/3}]d\mathbf{r}&=\int[|\nabla(\lambda\mathbf{r})n(\lambda\mathbf{r})|^2/n(\lambda\mathbf{r})^{4/3}]d^3(\lambda r)\\&=\int[|\lambda^{-1}\nabla(\mathbf{r})n(\lambda\mathbf{r})|^2/n(\lambda\mathbf{r})^{4/3}]\lambda^3 d^3r .\end{aligned}$$

For another example, $\int n(|\nabla n|n^{-4/3}+n^{-1/3})^{-1}d\mathbf{r}$ simply becomes $\int n(|\nabla n|n^{-4/3}+\lambda^{-1}n^{-1/3})^{-1}d^3r$ when n is replaced by n_λ.

It shall be convenient to partition E_{xc} as $E_{\text{xc}}=E_x+E_c$ and first focus upon the E_c component, where E_x shall be called an "exchange energy functional" and E_c shall be called a "correlation energy functional." The results for E_c will then be added to what is already known about E_x to deduce vital properties of the whole of E_{xc}. Here E_x signifies a particular definition for exchange energy and E_c signifies a particular definition for correlation energy, but given the definition for E_{xc}, it will become apparent during the course of this paper that the conclusions for E_{xc} will be *independent* of the working definitions of exchange and correlation. I shall employ that partitioning of E_{xc} which best facilitates proof of the coordinate scaling theorems for the whole E_{xc}. For this purpose, E_x shall be defined in Sec. II such that E_x is that part of E_{xc} with the simple homogeneous coordinate scaling. In other words,[9]

$$E_x[n_\lambda]=\lambda E_x[n] \tag{6}$$

so that $E_c[n]$ shall be defined in Sec. II as that component of E_{xc} with the complicated scaling, and it is thus the E_c component upon which I shall concentrate. Equation (6) enables one to project out the E_c component from E_{xc}. In any case, as shall be discussed later, the correlation energy in this paper and the traditional quantum-mechanical correlation energy (which is expressed exactly in terms of the Hartree-Fock density) yield very similar numerical values for many systems, because E_x here is defined to be the exchange energy of the Kohn-Sham determinant which is often close to the Hartree-Fock determinant with the same density.

This paper concerns finite densities, but there is no limit to the number of electrons provided that the density is integrable. Also, this paper shall restrict itself to those trial n's, for the interacting problem, which simultaneously arise from those single determinants which are nondegenerate groundstates for noninteracting Hamiltonians. Situations stemming from various degeneracies are planned to be discussed in a future paper.

II. CORRELATION ENERGY FUNCTIONAL

The correlation energy E_c, which is negative, is defined here and is often defined in density-functional theory[11] by[5,9,12,13]

$$E_c[n]=\langle\Psi_n^{\min}|\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}|\Psi_n^{\min}\rangle-\langle\Phi_n^{\min}|\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle , \tag{7a}$$

$$E_c[n]=V_{ee}[n]-E_x[n]-U[n]+T_c[n]\ . \tag{7b}$$

with

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

and

$$\hat{\mathbf{V}}_{ee}=\sum_{i}\sum_{j>i}|\mathbf{r}_i-\mathbf{r}_j|^{-1}\ ,$$

$$\begin{aligned}V_{ee}[n]&=\langle\Psi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Psi_n^{\min}\rangle\ ,\\ T[n]&=\langle\Psi_n^{\min}|\hat{\mathbf{T}}|\Psi_n^{\min}\rangle\ ,\end{aligned} \tag{8}$$

$$\begin{aligned}E_x[n]&=\langle\Phi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle-U[n]\ ,\\ T_s[n]&=\langle\Phi_n^{\min}|\hat{\mathbf{T}}|\Phi_n^{\min}\rangle\ ,\end{aligned} \tag{9}$$

$$T_c[n]=T[n]-T_s[n]\ , \tag{10}$$

so that[9]

$$T_c[n]=-E_c[n]+\left[\frac{\partial E_c[n_\gamma]}{\partial\gamma}\right]_{\gamma=1}\geq 0\ . \tag{11}$$

Consistent with the constrained-search formulation[14] of density-functional theory, $\Phi_n^{\min}$ is defined[15] as that antisymmetric wave function which yields n and minimizes $\langle\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}\rangle$, and $\Phi_n^{\min}$ is defined[16,17] as that antisymmetric wave function which yields n and minimizes just $\langle\hat{\mathbf{T}}\rangle$. The minima always exist.[18] When $\Psi_n^{\min}$ is the nondegenerate ground-state wave function of an interacting Hamiltonian, then $\Psi_n^{\min}$ is the original Hohenberg-Kohn interacting wave function.[15] Likewise, when $\Phi_n^{\min}$ is the nondegenerate ground-state wave function of a noninteracting Hamiltonian, then $\Phi_n^{\min}$ is the original Kohn-Sham single determinant,[17] and the present paper shall restrict itself to this situation. The work of Levy for interacting systems in Ref. 15 follows in the spirit of the work of Percus for noninteracting systems in Ref. 16.

The E_c defined in Eq. (7) is consistent with the desired partitioning of E_{xc} into E_x and E_c, as described in Sec. I, so that *all* the complicated scaling is incorporated into E_c. Here E_x is the exchange energy of the Kohn-Sham determinant. Hence E_x satisfies the *simple* scaling in Eq. (6). A different partitioning of E_{xc} would not necessarily yield an E_x with simple scaling. For example, simple scaling for E_x would not result if a Hartree-Fock determinant were to replace $\Phi_n^{\min}$ in Eq. (9).

There has been exciting progress recently[13,19–28] in the generation of encouraging nonlocal approximations to E_c. To help in the continuing evolution of accurate approximations, this paper reveals limiting coordinate scaling requirements that are satisfied by the exact E_c, and this paper also reveals a coordinate scaling equality for the correlation hole because these requirements help dictate the form of the functional. It shall be proved that E_c is, surprisingly, *bounded* asymptotically upon coordinate scaling. The new limiting relations, for an *arbitrary* trial inhomogeneous electron density $n(\mathbf{r})$, with the restrictions described in Sec. I, are the bounded asymptotic condition

$$\lim_{\lambda\to\infty}E_c[n_\lambda]>-\infty \tag{12}$$

and

$$\lim_{\lambda\to 0}\lambda^{-1}E_c[n_\lambda]=-b[n]\ , \tag{13}$$

$$0<\left[\frac{\partial E_c[n_\gamma]}{\partial\gamma}\right]_{\gamma=1}-2E_c[n]\leq b[n]\leq U[n]+E_x[n]<U[n]\ . \tag{14}$$

Equation (12) is not satisfied by the LDA, which is unbounded as $\lambda\to\infty$, when applied to finite densities. The LDA goes as $-\ln\lambda$ at high λ, from the Gell-Mann and Bruecker high-density formula.[29] This is not surprising because the LDA is derived for and is thus exact for uniform densities, which must be infinite, while our coordinate scaling requisites are derived for and are thus exact for densities which integrate to a finite number of electrons. Unlike a uniform density, a finite density has a surface which vanishes as $\mathbf{r}\to\infty$. It is the presence of this surface which is responsible, in part, for Eq. (12).

Equations (12) and (13) are proved by combining the adiabatic connection[5–8] with coordinate scaling.[9] Define $\Psi_n^{\min,\alpha}$ as that antisymmetric wave function which yields n and minimizes $\langle\hat{\mathbf{T}}+\alpha\hat{\mathbf{V}}_{ee}\rangle$. Clearly then, $\Psi_n^{\min,1}=\Psi_n^{\min}$ and also $\Psi_n^{\min,0}=\Phi_n^{\min}$. Now, as first proved by Levy and Perdew,[9] and as later confirmed with an alternative proof by Levy, Yang, and Parr,[10] since $\Psi_{n^{\min,\alpha}}$ yields n and minimizes $\langle\hat{\mathbf{T}}+\alpha\hat{\mathbf{V}}_{ee}\rangle$, then $\lambda^{3N/2}\Psi_n^{\min,\alpha}(\lambda\mathbf{r}_1,\ldots,\lambda\mathbf{r}_N)$ yields n_λ and minimizes $\langle\hat{\mathbf{T}}+\lambda\alpha\hat{\mathbf{V}}_{ee}\rangle$. (Note the presence of λ in the latter expectation value.) Hence, $\lambda^{3N/2}\Psi_N^{\min,\alpha}(\lambda\mathbf{r}_1,\ldots,\lambda\mathbf{r}_N)$ yields n_λ and minimizes $\langle\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}\rangle$ when $\lambda=\alpha^{-1}$. In other words,

$$\Psi_{n_\lambda}^{\min}(\mathbf{r},\ldots,\mathbf{r}_N)=\lambda^{3N/2}\Psi_n^{\min,\alpha}(\lambda\mathbf{r}_1,\ldots,\lambda\mathbf{r}_N)\quad\lambda=\alpha^{-1} \tag{15}$$

or

$$\Psi_n^{\min,\alpha}(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\alpha^{3N/2}\Psi_{n_\lambda}^{\min}(\alpha\mathbf{r}_1,\ldots,\alpha\mathbf{r}_N)\quad\lambda=\alpha^{-1}\ . \tag{16}$$

Also, since $\Phi_n^{\min}$ yields n and minimizes just $\langle\hat{\mathbf{T}}\rangle$, it means that[9] $\lambda^{3n/2}\Phi_n^{\min}(\lambda\mathbf{r}_1,\ldots,\lambda\mathbf{r}_N)$ yields n_λ and minimizes just $\langle\hat{\mathbf{T}}\rangle$. In other words,

$$\Phi_{n_\lambda}^{\min}(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\lambda^{3N/2}\Phi_n^{\min}(\lambda\mathbf{r}_1,\ldots,\lambda\mathbf{r}_N)\ . \tag{17}$$

Equation (7) implies

$$\begin{aligned}E_c[n_\lambda]=&\langle\Psi_{n_\lambda}^{\min}|\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}|\Psi_{n_\lambda}^{\min}\rangle\\ &-\langle\Phi_{n_\lambda}^{\min}|\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}|\Phi_{n_\lambda}^{\min}\rangle\ .\end{aligned}$$

Now substitute expressions (15) and (17) into the above equation for $E_c[n_\lambda]$ to obtain

$$\begin{aligned}E_c[n_\lambda]=&\lambda^2(\langle\Psi_n^{\min,\alpha}|\hat{\mathbf{T}}|\Psi_n^{\min,\alpha}\rangle-\langle\Phi_n^{\min}|\hat{\mathbf{T}}|\Phi_n^{\min}\rangle)\\ &+\lambda(\langle\Psi_n^{\min,\alpha}|\hat{\mathbf{V}}_{ee}|\Psi_n^{\min,\alpha}\rangle\\ &-\langle\Phi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle)\ ,\end{aligned} \tag{18}$$

where it has been taken into consideration that $\hat{\mathbf{V}}_{ee}$ is homogeneous of degree -1 and T is homogeneous of degree -2 with respect to the scale factor λ. Equation (18) exhibits the *formal scaling essence* of E_c from which Eqs. (12) and (13) are derived.

To obtain Eq. (13), use

$$\langle \Psi_n^{\min,\alpha} | \hat{\mathbf{T}} | \Psi_n^{\min,\alpha} \rangle \geq \langle \Phi_n^{\min} | \hat{\mathbf{T}} | \Phi_n^{\min} \rangle \tag{19}$$

with Eq. (18) to arrive at

$$\lambda^{-1} E_c[n_\lambda] \geq \langle \Psi_n^{\min,\alpha} | \hat{\mathbf{V}}_{ee} | \Psi_n^{\min,\alpha} \rangle - \langle \Phi_n^{\min} | \hat{\mathbf{V}}_{ee} | \Phi_n^{\min} \rangle \ , \tag{20}$$

which with $\langle \Psi^{\min,\alpha} | \hat{\mathbf{V}}_{ee} | \Psi^{\min,\alpha} > \geq 0$ gives

$$\lambda^{-1} E_c[n_\lambda] \geq -\langle \Phi_n^{\min} | \hat{\mathbf{V}}_{ee} | \Phi_n^{\min} \rangle \ . \tag{21}$$

Equation (21), in turn, yields the upper bounds to $b[n]$ in Eq. (14) upon employment of Eq. (9). The lower bounds to $b[n]$ in Eq. (14) are obtained from[9] $T[n_\lambda] + V_{ee}[n_\lambda] \leq \lambda^2 T[n] + \lambda V_{ee}$ with Eqs. (7)–(11) and with[9]

$$T_s[n_\lambda] = \lambda T_s[n] \ . \tag{22}$$

The condition $\lim_{\lambda\to\infty} \lambda^{-1} E_c[n_\lambda] = 0$, which is weaker than condition (12), comes about directly from Eq. (18). Just employ the fact that $\lim_{\lambda\to\infty} \lambda^{-1} E_c[n_\lambda] \leq 0$, by the definition of $E_c[n]$, and the fact that the presence of the non-negative λ^2 term implies $\lim_{\lambda\to\infty} \lambda^{-1} E_c[n_\lambda] \geq 0$.

Condition (12) also arises from Eq. (18). Define $\hat{\mathbf{H}}_s$ to be the noninteracting system for which $\Phi_n^{\min}$ is the ground state, where

$$\hat{\mathbf{H}}_s = \hat{\mathbf{T}} + \sum_i v_s(\mathbf{r}_i) \ , \tag{23}$$

and where v_s is a local-multiplicative potential (the Kohn-Sham potential). Then since $\Psi_n^{\min,\alpha}$ and $\Phi_n^{\min}$ have the same density, n, Eq. (18) becomes

$$E_c[n_\lambda] = \lambda^2 (\langle \Psi_n^{\min,\alpha} | \hat{\mathbf{H}}_s | \Psi_n^{\min,\alpha} \rangle - \langle \Phi_n^{\min} | \hat{\mathbf{H}}_s | \Phi_n^{\min} \rangle) + \lambda (\langle \Psi_n^{\min,\alpha} | \hat{\mathbf{V}}_{ee} | \Psi_n^{\min,\alpha} \rangle - \langle \Psi_n^{\min} | \hat{\mathbf{V}}_{ee} | \Psi_n^{\min} \rangle) \ . \tag{24}$$

Next, expand $\Psi_n^{\min,\alpha}$ in terms of the eigenstates of $\hat{\mathbf{H}}_s$. Couple terms in the expansion whose coefficients decay alike as $\alpha \to 0$ to obtain

$$\Psi_n^{\min,\alpha} = \sum_{i=0}^{\infty} C_i^\alpha \Phi_i^\alpha \ , \tag{25}$$

where $\Phi_0^\alpha = \Phi_n^{\min}$ because $\Psi_n^{\min,0} = \Phi_n^{\min}$, with $\langle \Phi_i^\alpha | \Phi_j^\alpha \rangle = \delta_{ij}$, $\sum_i |C_i^\alpha|^2 = 1$, $C_0^0 = 1$, $C_i^0 = 0$ for $i > 0$, and $\lim_{\alpha \to o} (C_j^\alpha / C_i^\alpha) = 0$ with $j > i$. (Note that each Φ_i^α may be a linear combination of more than one eigenstate of $\hat{\mathbf{H}}_s$ and each eigenstate within Φ_i^α is different from each eigenstate within Φ_j^α, $i \neq j$.) In the limit $\lambda \to \infty$, Eq. (24) becomes

$$\begin{aligned}\lim_{\lambda\to\infty} E_c[n_\lambda] = {} & \lambda^2 |C_1^\alpha|^2 (\langle \Phi_1^\alpha | \hat{\mathbf{H}}_s | \Phi_1^\alpha \rangle - \langle \Phi_n^{\min} | \hat{\mathbf{H}}_s | \Phi_n^{\min} \rangle) \\ & + \lambda [|C_1^\alpha|^2 (\langle \Phi_1^\alpha | \hat{\mathbf{V}}_{ee} | \Phi_1^\alpha \rangle - \langle \Phi_n^{\min} | \hat{\mathbf{V}}_{ee} | \Phi_n^{\min} \rangle) \\ & + (C_1^\alpha)^* (C_0^\alpha) \langle \Phi_1^\alpha | V_{ee} | \Phi_0^\alpha \rangle + (C_0^\alpha)^* (C_1^\alpha) \langle \Phi_0^\alpha | V_{ee} | \Phi_1^\alpha \rangle] + \cdots \ . \end{aligned} \tag{26}$$

Now, it should be clear, as $\alpha \to 0$, that C_1^α in Eq. (26) must decay to zero at least as fast as α (or λ^{-1}). Otherwise, by virtue of

$$(\langle \Phi_1^\alpha | \hat{\mathbf{H}}_s | \Phi_1^\alpha \rangle - \langle \Phi_n^{\min} | \hat{\mathbf{H}}_s | \Phi_n^{\min} \rangle) > 0$$

we would have $\lim_{\lambda\to\infty} E_c[n_\lambda] = +\infty$, in violation of the condition that $E_c[n_\lambda] \leq 0$ which stems from the definition of E_c. Finally, since $\lim_{\lambda\to\infty} |\lambda C_1^\alpha| < \infty$, Eq. (12) follows because the negative $\hat{\mathbf{V}}_{ee}$ component of Eq. (26) is thereby kept bounded as $\lambda \to \infty$. In essence, a proof by contradiction has been employed.

For a common and important situation we have additional knowledge about the bound on $\lim_{\lambda\to\infty} E_c[n_\lambda]$. Consider $\hat{\mathbf{H}}_s^\alpha = \hat{\mathbf{H}}_s + \alpha \hat{\mathbf{V}}_{ee}$. Call E_s^α the ground-state energy of $\hat{\mathbf{H}}_s^\alpha$. Now express E_s^α in the form of the perturbation expansion $E_s^\alpha = \sum_{i=0}^{\infty} \alpha^i \varepsilon_i$. By focusing upon the $\alpha \to 0$ limit, it is straightforward to prove that[30]

$$\lim_{\lambda\to\infty} E_c[n_\lambda] \geq \varepsilon_2$$

when the perturbation expansion has a nonzero radius of convergence. The constant ε_2 is already known for some densities. For example, $\varepsilon_2 = -0.16$ a.u. when n is the two-electron ground-state density of

$$\hat{\mathbf{H}}_s = \hat{\mathbf{T}} - \sum_{i=1}^{2} r_i^{-1} \ .$$

At large λ (small α), $\Psi_n^{\min,\alpha}$ may be expanded in powers of α when $\Psi_n^{\min,\alpha}$ is analytic about $\alpha = 0$. When this expansion is valid, the substitution of $\Psi_n^{\min,\alpha}$ into Eq. (18) yields the following power series for $E_c[n_\lambda]$ which is applicable for large λ,

$$E_c[n_\lambda] = D[n] + \lambda^{-1} D_1[n] + \lambda^{-2} D_2[n] + \cdots \ . \tag{27}$$

We have recently imposed conditions (11), (12), and (13) to help arrive at the following very simple nonlocal formula for approximating E_c for spin-paired systems[28]:

$$\tilde{E}_c[n]=\int(an+b|\nabla n|n^{-1/3})\times(c+d|\nabla n|n^{-4/3}+n^{-1/3})^{-1}d\mathbf{r}\;, \tag{28}$$

so that

$$\tilde{E}_c[n_\lambda]=\int(an+b|\nabla n|n^{-1/3})\times(c+d|\nabla n|n^{-4/3}+\lambda^{-1}n^{-1/3})^{-1}d\mathbf{r}\;,$$

where $a=-1.2067$, $b=0.0967$, $c=5.8043$, and $d=3.6558$. $\tilde{E}_c$ yields competitive results. For example, it gives, in atomic units, -0.042, -0.095, -0.383, -0.444, and -0.787 for the He, Be, Ne, Mg, and Ar atoms. The corresponding exact results are estimated to be -0.042, -0.094, -0.387, -0.444, and -0.787.

Nonuniform scaling was recently introduced into density-functional theory.[31] Here I now reveal the following new limiting nonuniform coordinate scaling relations:

$$\lim_{\lambda\to\infty}E_c[n_\lambda^x]\ge-\tfrac{1}{2}\int\int\frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{[(y_1-y_2)^2+(z_1-z_2)^2]^{1/2}}d^3r_1d^3r_2\;, \tag{29}$$

$$\lim_{\lambda\to\infty}\lambda^{-1}E_c[n_{\lambda\lambda}^{xy}]>-\infty\;, \tag{30}$$

$$\lim_{\lambda\to 0}E_c[n_\lambda^x]>-\infty\;, \tag{31}$$

$$\lim_{\lambda\to 0}\lambda^{-1}E_c[n_{\lambda\lambda}^{xy}]\ge-\tfrac{1}{2}\int\int\frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{[(x_1-x_2)^2+(y_1-y_2)^2]^{1/2}}d^3r_1d^3r_2\;, \tag{32}$$

where $n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z)$ and $n_{\lambda\lambda}^{xy}(x,y,z)=\lambda^2n(\lambda x,\lambda y,z)$.

Equations (29)–(32) are easily derived. For this purpose note that $V_{ee}[n_\lambda^x]\ge 0$, $E_x[n_\lambda^x]\le 0$, and[9,32] $T_c[n_\lambda^x]\ge 0$, with corresponding equations for $n_{\lambda\lambda}^{xy}$. Next, the substitution of these inequalities into Eq. (7) gives

$$E_c[n_\lambda^x]\ge-U[n_\lambda^x] \tag{33}$$

and

$$E_c[n_{\lambda\lambda}^{xy}]\ge-U[n_{\lambda\lambda}^{xy}] \tag{34}$$

which lead to Eqs. (29–(32). In contrast, the LDA violates conditions (29) and (32) because the LDA gives $-\infty$ for both limits. Most other common approximations to E_c also violate these conditions.

It is common for density-functional investigations to approximate the correlation hole.[27] With this in mind, the remainder of this section shall concern coordinate scaling properties of the exact correlation hole. Consistent with our definition of E_c, the second-order density matrix of $\Psi_n^{\min,\alpha}$, $\Gamma_{n,\alpha}(r_1'r_2'|r_1r_2)$, is conveniently partitioned in density-functional theory as[27]

$$\Gamma_{n,\alpha}=\Gamma_n^{\text{KS}}+\Gamma_{n,\alpha}^c\;, \tag{35}$$

where Γ_n^{KS} is the second-order density matrix of $\Phi_n^{\min}$, which is independent of α, and $\Gamma_{n,\alpha}^c$ is thus the correlation contribution to $\Gamma_{n,\alpha}$. E_c is obtained from the correlation hole, ρ_c because $\rho_c[n,\alpha]$, the correlation hole of $\Psi_n^{\min,\alpha}$, is related to $\Gamma_{n,\alpha}^c$ by

$$\rho_c([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)=2\Gamma_{n,\alpha}^c(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)/n(\mathbf{r}_1)\;, \tag{36}$$

so that by the form of the adiabatic connection[5-8] of Langreth-Perdew[6] and Gunnarsson-Lundquist,[7]

$$E_c[n]=\tfrac{1}{2}\int r_{12}^{-1}n(\mathbf{r}_1)\bar{\rho}_c([n];\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2 \tag{37}$$

where

$$\bar{\rho}_c([n];\mathbf{r}_1,\mathbf{r}_2)=\int_0^1\rho_c([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)d\alpha\;. \tag{38}$$

From Eqs. (37) and (38), it is clear that $\rho_c([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)$ is the *unknown* that has to be modeled to obtain $E_c[n]$, and a vast literature exists on this subject. With this in mind, it is already known, of course, that Eq. (35) implies[27]

$$\int\rho_c([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)d^3r_2=0\;, \tag{39}$$

for arbitrary n and arbitrary α, because both $\Gamma_{n,\alpha}$ and Γ_n^{KS} yielded n.

As constraints for approximations, *new* coordinate scaling equalities shall now be revealed involving the exact $\rho_c[n,\alpha]$. Perhaps the most important new equality is[33]

$$\rho_c([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)=\alpha^3\rho_c([n_{1/\alpha},1];\alpha\mathbf{r}_1,\alpha\mathbf{r}_2)\;. \tag{40}$$

This coordinate scaling equality for the correlation hole arises by integrating Eq. (16) over the coordinates of electrons 3 to N. With the latter expression, Eq. (37) becomes

$$E_c[n]=\tfrac{1}{2}\int_0^1\alpha\int r_{12}^{-1}n_{1/\alpha}(\mathbf{r}_1)\times\rho_c([n_{1/\alpha},1];\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2d\alpha \tag{41}$$

so only knowledge of correlation holes with coupling constants of unity are needed. Further, from Eqs. (35) and (40) and from the definition of $\Phi_n^{\min}$, it follows that

$$\lim_{\alpha\to 0}\alpha^3\rho_c([n_{1/\alpha},1];\alpha\mathbf{r}_1,\alpha\mathbf{r}_2)=0\;. \tag{42}$$

Also Ref. 9 implies that $\alpha\int r_{12}^{-1}n_{1/\alpha}(\mathbf{r}_1)\rho_c([n_{1/\alpha},1];\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2$ is never positive, decreases monotonically with increasing α, satisfies

$$\lim_{\alpha\to\infty}\alpha\int r_{12}^{-1}n_{1/\alpha}(\mathbf{r}_1)\rho_c([n_{1/\alpha},1];\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2\ge-U[n]-E_x[n]\ge-U[n]\;, \tag{43}$$

and thus must decrease to a finite negative constant.

To quickly illustrate the use of Eq. (40), consider

$$\rho_c^{\text{Becke}}([n,\alpha];r,s)=a\alpha(s-z)nF/(1+\alpha z)\;,$$

which is the spherically averaged hole function, for two electrons, which is proposed in the pertinent work of

Becke.[27] Here, a is a constant, F is a "damping" function, and z is a correlation "length" given by $z = n^{m}$+nonlocal terms. Now, Eq. (40) is satisfied by ρ_c^{Becke} only if $m = -\frac{1}{3}$, which supports with rigor the value obtained by Becke through a more qualitative argument.

It should be noted that the development leading to Eqs. (15) and (16) implies the following generalization to Eq. (40):

$$\rho_c([n,\alpha];\mathbf{r}_1,\mathbf{r}_2)=\beta^{-3}\rho_c([n_\beta,\alpha\beta];\beta^{-1}\mathbf{r}_1,\beta^{-1}\mathbf{r}_2)\ , \tag{44}$$

where β is not necessarily equal to α^{-1}. In fact, as α is varied from 0 to 1 in Eq. (38), it may actually be desirable to make $\alpha\beta = w$, where w is some *small* fixed constant such that $0 < w \ll 1$. In other words, knowledge of the *universal* hole for some *small* fixed coupling constant w is all that is necessary for solution to the many-body problem.

III. EXCHANGE AND EXCHANGE-CORRELATION FUNCTIONALS

For the whole exchange-correlation hole, Eq. (16) implies Eq. (4). The latter equation would be used in the adiabatic connection formula for E_{xc}; simply replace $\rho_c[n_{1/\alpha},1]$ and $E_c[n]$ in Eq. (41) by $\rho_{\mathrm{xc}}[n_{1/\alpha},1]$ and $E_{\mathrm{xc}}[n]$. Further, any approximation to E_{xc} should be made to satisfy Eq. (5).

Equation (7), $V_{ee}[n_\lambda^x] \ge 0$, $T_c[n_\lambda^x] \ge 0$, and analogous relations for $n_{\lambda\lambda}^{xy}$ dictate that

$$\lim_{\lambda\to\infty} E_{\mathrm{xc}}[n_\lambda^x] \ge -\frac{1}{2}\int\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{[(y_1-y_2)^2+(z_1-z_2)^2]^{1/2}}d^3r_1d^3r_2\ , \tag{45}$$

$$\lim_{\lambda\to\infty} \lambda^{-1}E_{\mathrm{xc}}[n_{\lambda\lambda}^{xy}] > -\infty\ , \tag{46}$$

$$\lim_{\lambda\to 0} E_{\mathrm{xc}}[n_\lambda^x] > -\infty\ , \tag{47}$$

$$\lim_{\lambda\to 0} \lambda^{-1}E_{\mathrm{xc}}[n_{\lambda\lambda}^{xy}] \ge -\frac{1}{2}\int\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{[(x_1-x_2)^2+(y_1-y_2)^2]^{1/2}}d^3r_1d^3r_2\ . \tag{48}$$

Equation (7) also dictates that the right-hand-sides of Eqs. (45)–(48) are lower bounds for the E_x component of E_{xc} because $E_c[n_\lambda^x] \le 0$ and $E_c[n_{\lambda\lambda}^{xy}] \le 0$. Common approximations to E_x generally *violate* conditions (45) and (48).

Assume that one is given a healthy approximation to E_{xc}. Then according to Eqs. (12) and (6) one could project out, for study and analysis, those components which are approximations to E_x and E_c, because for the corresponding exact components,

$$E_x[n] = \lim_{\lambda\to\infty} \lambda^{-1}E_{\mathrm{xc}}[n_\lambda] \tag{49}$$

and thus

$$E_c[n] = E_{\mathrm{xc}}[n] - \lim_{\lambda\to\infty} \lambda^{-1}E_{\mathrm{xc}}[n_\lambda]\ . \tag{50}$$

Hence, since the right-hand sides of Eqs. (49) and (50) contain the whole of E_{xc}, the analysis in the present paper really is *independent of which definition of the correlation energy one chooses.* In other words, I have simply focused upon the coordinate scaling properties of the whole of E_{xc} with emphasis upon the *projection* given by the right-hand-side of Eq. (50).

IV. DIFFERENT DEFINITIONS OF CORRELATION ENERGIES

One should be careful when one compares numerical values for approximations to E_c with the conventional correlational energy as defined at the end of this section. However, as discussed in the following paragraph, the present paper does provide information about a meaningful correlation energy which is meant to be used in conjunction with a Hartree-Fock calculation.

Define E_c^{HF} by[34,35]

$$E_c^{\mathrm{HF}}[n] = \langle \Psi_n^{\min}|\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}|\Psi_n^{\min}\rangle - \langle \Phi_n^{\mathrm{HF}}|\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}|\Phi_n^{\mathrm{HF}}\rangle\ , \tag{51}$$

where Φ_n^{HF} is that single determinant which yields n and minimizes $\langle \hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}\rangle$. Equation (51) was introduced by Baroni and Tuncel[34] and Stoll and Savin.[35] Now, it has previously been shown that when the functional derivative of E_c^{HF} is added to the Fock potential and self-consistency is achieved, then the exact ground-state density n_{GS} is obtained[34] and the highest-occupied orbital energy turns out to be the negative of the *exact*[36] ionization energy. Further, the exact ground-state energy is obtained when $E_c^{\mathrm{HF}}[n_{\mathrm{GS}}]$ is added to the expectation value, via the true interacting Hamiltonian, of the optimum single determinant.[34] With all this in mind, note, from their definitions, that

$$E_c[n] \le E_c^{\mathrm{HF}}[n] \tag{52}$$

when n is pure-state noninteracting v representable. Hence, when the latter situation applies it follows that

$$\lim_{\lambda\to\infty} E_c^{\mathrm{HF}}[n_\lambda] > -\infty\ , \tag{53}$$

and the bounds in Eqs. (29)–(32) also follow for E_c^{HF}.

The conventional quantum-mechanical definition of the correlation energy E_c^{QM}, for let us say an atom, is of course the difference between the true ground-state energy of the nonrelativistic Schrödinger equation for the atom and the Hartree-Fock energy for the atom. From the work of Linderberg and Shull,[37] we know that as the nuclear charge z becomes large, E_c^{QM} either goes to a constant or goes as z, depending upon the number of electrons N in the atom. For instance, for two and ten electrons, E_c^{QM} is bounded from below as $z\to\infty$, while for four electrons, E_c^{QM} is linear in z as $z\to\infty$. (This asymptotic dependence of E_c^{QM} on the number of electrons, as ascertained by Linderberg and Shull, has already been discussed by Perdew, McMullen, and Zunger[38] within the context of density-functional theory.) Now, in view of the Linderberg-Shull results[37] what is "surprising" about the results for $E_c[n]$ in the present paper is how general Eq. (12) is. This bounded condition applies generally to finite systems such as atoms, molecules, and solids. For example, Eq. (12) *applies* for $\lim_{\lambda\to\infty}E_c[n_\lambda^{\text{Be}}]$, where n^{Be} is the ground-state density of the Be atom which has four electrons, even though E_c^{QM} is linear in z at high z for a four-electron atom. Then does not Eq. (12) violate the Linderberg-Shull result? The answer is no for at least two reasons. First, although the density does, of course, become more compact as z becomes large, the density at high z is not simply a scaled Be density. Second, E_c is not the same as E_c^{QM}. How E_c^{QM} depends on high z is determined by whether or not there are degeneracies associated with the bare-nuclear hydrogenic Hamiltonian. But as in the Be atom, one may have degeneracies associated with the bare-nuclear hydrogenic Hamiltonian and no degeneracies associated with the Kohn-Sham noninteracting Hamiltonian. It is the latter Hamiltonian which is of relevance to E_c, and the Kohn-Sham noninteracting Hamiltonian for Be has no ground-level degeneracies.

E_c should often be close in value to the traditional quantum-mechanical correlation energy which, as independently discovered by Harris and Pratt[25] and Levy,[26] may be given exactly in the terms of the Hartree-Fock density. This functional, $E_c^{\text{QM}}[n_v^{\text{HF}}]$, is defined by

$$E_c^{\text{QM}}[n_v^{\text{HF}}]=\langle\Psi_v^{\text{GS}}|\hat{\mathbf{H}}_v|\Psi_v^{\text{GS}}\rangle-\langle\Phi_v^{\text{HF}}|\hat{\mathbf{H}}_v|\Phi_v^{\text{HF}}\rangle\ ,$$

where

$$\hat{\mathbf{H}}_v=\hat{\mathbf{T}}+\hat{\mathbf{V}}_{ee}\sum_{i=1}^{N}v(\mathbf{r}_1)\ ,$$

and where n_v^{HF}, Φ_v^{HF}, and Ψ_v^{GS} are, respectively, for $\hat{\mathbf{H}}_v$, the Hartree-Fock density, the Hartree-Fock wave function, and the exact ground-state wave function. The *exact* ground-state energy is obtained when $E_c^{\text{QM}}[n_v^{\text{HF}}]$ is added to the Hartree-Fock energy for $\hat{\mathbf{H}}_v$. (Incidently, note that the existence of $E_c^{\text{QM}}[n_v^{\text{HF}}]$ implies the existence of $E_c^{\text{QM}}[\Psi_v^{\text{HF}}]$. This latter E_c^{QM} has the same numerical value as $E_c^{\text{QM}}[n_v^{\text{HF}}]$.) Now, from Eq. (7), $E_c[n_v^{\text{HF}}]$ is

$$E_c[n_v^{\text{HF}}]=\langle\Psi_{n_v^{\text{HF}}}^{\min}|\hat{\mathbf{H}}_v|\Psi_{n_v^{\text{HF}}}^{\min}\rangle-\langle\Phi_{n_v^{\text{HF}}}^{\min}\hat{\mathbf{H}}_v|\Phi_{n_v^{\text{HF}}}^{\min}\rangle\ .$$

Hence, E_c^{QM} should often be close to E_c because the inequalities

$$\langle\Psi_v^{\text{GS}}|\hat{\mathbf{H}}_v|\Psi_v^{\text{GS}}\rangle\le\langle\Psi_{n_v^{\text{HF}}}^{\min}|\hat{\mathbf{H}}_v|\Psi_{n_v^{\text{HF}}}^{\min}\rangle$$

and

$$\langle\Phi_v^{\text{HF}}|\hat{\mathbf{H}}_v|\Phi_v^{\text{HF}}\rangle\le\langle\Phi_{n_v^{\text{HF}}}^{\min}|\hat{\mathbf{H}}_v|\Psi_{n_v^{\text{HF}}}^{\min}\rangle$$

are often tight and are always partially offsetting in the evaluation of $|E_c^{\text{QM}}-E_c|$.

V. ANALYSIS, SUMMARY, AND CONCLUDING REMARKS

The main implications of this paper can be cast in several different forms. Which form one uses depends upon which orientation one chooses when one employs density-functional theory to help simplify the many-electron problem. Assume that we are interested in the ground-state energy E_{GS} and the ground-state density of the electron-nuclear attraction operator $v_{en}(\mathbf{r})$. Then, of course, by the Hohenberg-Kohn theorem and its generalizations,

$$E_{\text{GS}}=\min_n\left[\int v_{en}(\mathbf{r})n(\mathbf{r})d^3r+F[n]\right]\ , \tag{54}$$

where

$$F[n]=T[n]+V_{ee}[n]\ . \tag{55}$$

Now, the interacting $T[n]$ is never really used. Instead, the simpler noninteracting $T_s[n]$ is employed, and $T_s[n]$ is computed exactly, for present practical calculations, by taking a sum of kinetic energy expectation values involving the Kohn-Sham orbitals. Does this mean that we need, in return, knowledge of something other than $V_{ee}[n]$ to pay a price for the additional simplicity in the kinetic component of $F[n]$? The answer is, surprisingly, no because the formulation in the present paper dictates that

$$F[n]=T_s[n]+\int_0^1\alpha V_{ee}[n_{1/\alpha}]d\alpha\ . \tag{56}$$

Hence, knowledge of the universal $\Gamma_{n,1}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)$, the diagonal part of the second-order density matrix for $\alpha=1$, is all that is needed. Noteworthy then is the fact that Lee and Parr[39] and Valone[40] have very recently studied $V_{ee}[n]$.

Equation (56) arises from the combination of Eq. (3) with

$$F[n]=T_s[n]+\int_0^1V_{ee}^{\alpha}[n]\ . \tag{57}$$

The latter is an alternative way of expressing the adiabatic connection (coupling constant integration) formula which was written in Sec. I with respect to E_{xc}. [See Eq. (1)]. Here,

$$V_{ee}^{\alpha}[n]=\int r_{12}^{-1}\Gamma_{n,\alpha}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)d^3r_1d^3r_2\ . \tag{58}$$

Properties of $V_{ee}^{\alpha}[n]$ have already been ascertained. From Levy and Perdew,[9] we know that

$$\frac{\partial V_{ee}^{\alpha}[n]}{\partial\alpha}\le 0\quad\text{for all }\alpha>0\ , \tag{59}$$

and that

$$\lim_{\alpha\to o}V_{ee}^{\alpha}[n]=\langle\Phi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle\ , \tag{60}$$

which identifies $A[n]$ in Eq. (2) as the right-hand-side of Eq. (60).

As has been emphasized throughout this paper, one naturally works with E_{xc} within the Kohn-Sham procedure[2] where one expresses $F[n]$ as

$$F[n]=T_s[n]+U[n]+E_{\text{xc}}[n]\ . \tag{61}$$

Equation (3) allows us to express Eq. (1) as

$$E_{\text{xc}}[n]=\int_0^1\alpha(V_{ee}[n_{1/\alpha}]-U[n_{1/\alpha}])d\alpha\ , \tag{62}$$

where use has also been made of $U[n_{1/\alpha}]=\alpha^{-1}U[n]$.

Hence, only knowledge of $V_{ee}[n]$, the universal repulsion energy functional corresponding to $\alpha=1$, is necessary to know $E_{\mathrm{xc}}[n]$.

Most often in the literature the "average" of V_{ee}^{α} (from $\alpha=0$ to 1) has been approximated. In particular, we often see in the literature[3,4]

$$E_{\mathrm{xc}}[n]=\bar{V}_{ee}[n]-U[n]\ , \tag{63}$$

where

$$\bar{V}_{ee}[n]=\int\bar{\Gamma}_n(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)r_{12}^{-1}d^3r_1d^3r_2\ , \tag{64}$$

and where the average second-order density matrix $\bar{\Gamma}$ is given by

$$\bar{\Gamma}_n=\int_0^1\Gamma_{n,\alpha}d\alpha\ . \tag{65}$$

In other words it is $\bar{\Gamma}_n(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)$ which is most often approximated. However, in order to ensure that $\bar{\Gamma}_n$ is approximated adequately I feel that it is wise to actually approximate each $\Gamma_{n,\alpha}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)$ by utilizing what are implied in Eqs. (59) and (60) and by utilizing other known properties of $\Gamma_{n,\alpha}$ as a function of α. Other properties of $\Gamma_{n,\alpha}$ include[41]

$$\Gamma_{n,\alpha}(\mathbf{r}_2\mathbf{r}_1|\mathbf{r}_2\mathbf{r}_1)=\Gamma_{n,\alpha}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2) \tag{66}$$

and

$$\left[\frac{2}{N-1}\right]\int\Gamma_{n,\alpha}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)d^3r_2=n(\mathbf{r}_1)\ , \tag{67}$$

$$\left[\frac{2}{N-1}\right]\int\Gamma_{n,\alpha}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)d^3r_1=n(\mathbf{r}_2)\ . \tag{68}$$

It is interesting that the local-density approximation does not satisfy[41] Eq. (66).

It has been a purpose of this paper to reveal key coordinate scaling properties of $\Gamma_{n,\alpha}$. With this in mind, it is now asserted that

$$\Gamma_{n,\alpha}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)=\alpha^6\Gamma_{n_\lambda,1}(\alpha\mathbf{r}_1\alpha\mathbf{r}_2|\alpha\mathbf{r}_1\alpha\mathbf{r}_2) \tag{69}$$

which arises by integrating Eq. (16) over the spatial coordinates of electrons 3 to N and over the spin coordinates of all the electrons. Further, from Ref. 9 we know that

$$\Gamma_{n,0}=\Gamma_n^{\mathrm{KS}} \tag{70}$$

so that $\Gamma_{n,0}$ must possess all the known properties of Γ_n^{KS}. Also, from Ref. 9

$$V_{ee}^{\infty}[n]=\operatorname*{Inf}_{\Gamma\to n}\int\Gamma(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)r_{12}^{-1}d^3r_1d^3r_2\ , \tag{71}$$

where the Γ are n representable. [See Ref. 40 for approximations to the right-hand-side of Eq. (71).]

From the perspectives of this paper, Eq. (35) serves as a natural partitioning of $\Gamma_{n,\alpha}$ because Γ_n^{KS} does *not* vary with α and because Γ_n^{KS} exhibits very simple coordinate scaling. Namely,

$$\int r_{12}^{-1}\Gamma_{n_\lambda}^{\mathrm{KS}}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)d^3r_1d^3r_2 =\lambda\int r_{12}^{-1}\Gamma_n^{\mathrm{KS}}(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)d^3r_1d^3r_2\ . \tag{72}$$

[See also Eq. (6).] Hence, it is $\Gamma_{n,\alpha}^c$ which varies with α and possesses the more complicated coordinate scaling. For these reasons, this paper has focused upon $E_c[n]$ and $\Gamma_{n,\alpha}^c$ which are linked by

$$\begin{aligned}E_c[n]&=\int_0^1 r_{12}^{-1}\Gamma_{n,\alpha}^c d^3r_1d^3r_2d\alpha\\ &=\int_0^1 V_{ee}^{c,\alpha}[n]d\alpha\ ,\end{aligned} \tag{73a}$$

where

$$V_{ee}^{c,\alpha}[n]=\int r_{12}^{-1}\Gamma_{n,\alpha}^c d^3r_1d^3r_2\ . \tag{73b}$$

Equations (3), (59), (66), and (69) imply

$$V_{ee}^{c,\alpha}[n]=\alpha V_{ee}^{c,1}[n_{1/\alpha}]\ , \tag{74}$$

$$\frac{\partial V_{ee}^{c,\alpha}[n]}{\partial\alpha}\leq 0\quad\text{all }\alpha\geq 0\ , \tag{75}$$

$$\Gamma_{n,\alpha}^c(\mathbf{r}_2\mathbf{r}_1|\mathbf{r}_2\mathbf{r}_1)=\Gamma_{n,\alpha}^c(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)\ , \tag{76}$$

and

$$\Gamma_{n,\alpha}^c(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)=\alpha^6\Gamma_{n_\lambda,1}^c(\alpha\mathbf{r}_1\alpha\mathbf{r}_2|\alpha\mathbf{r}_1\alpha\mathbf{r}_2)\ . \tag{77}$$

Section II gave analogous equations involving the correlation hole. Equations (73) to (77) are presented here for those who are more familiar with thinking in terms of the second-order density matrix rather than in terms of the correlation hole. In addition, Eqs. (39) and (43) dictate

$$V_{ee}^{c,0}[n]=0\ , \tag{78a}$$

$$V_{ee}^{c,\infty}[n]>-\infty\ . \tag{78b}$$

As an illustration of how one uses the adiabatic connection by starting with a guess for $V_{ee}^{c,\alpha}$, following is perhaps the simplest local form to satisfy the latter two equations and Eqs. (74) and (75):

$$\tilde{V}_{ee}^{c,\alpha}[n]=\int\left[\frac{\alpha n(\mathbf{r})}{a+\alpha bn^{-1/3}(\mathbf{r})}\right]d^3r\ ,$$

where a and b are negative constants. Substitution into Eq. (73) yields

$$\tilde{E}_c[n]=\int d^3r\int_0^1\left[\frac{\alpha n(\mathbf{r})}{a+\alpha bn^{-1/3}(\mathbf{r})}\right]d\alpha\ ,$$

so that

$$\tilde{E}_c[n]=\int d^3r\left[b^{-1}n^{4/3}+ab^{-2}n^{5/3}\ln\left[\frac{a}{a+bn^{-1/3}}\right]\right]\ .$$

Note that $\tilde{E}_c[n_\lambda]$ is bounded from below as λ → ∞ but $\tilde{E}_c[n]$ violates condition (32). Nonlocal components in $V_{ee}^{c,\alpha}$ correct this deficiency.

It has been shown by Stoll and Savin[35] that Eqs. (73) applies for the generation of $E_c^{\mathrm{HF}}[n]$ as defined in Eq. (51). Moreover, it can be shown[42] that Eqs. (74) and (76)–(78) apply for $E_c^{\mathrm{HF}}[n]$. Simply replace Γ_n^{KS} in Eq. (35) with the second-order density matrix of that Hartree-Fock determinant which yields n and minimizes $\langle\hat{\mathbf{T}}+\alpha\hat{\mathbf{V}}_{ee}\rangle$. In addition, Eq. (75) should generally apply when the above replacement for Γ_n^{KS} is made in Eq. (35)

Equation (2) arises from the combination of

$$V_{ee}^{\alpha}[n]=\langle \Phi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle + [\langle \Psi_n^{\min,\alpha}|\hat{\mathbf{V}}_{ee}|\Psi_n^{\min,\alpha}\rangle - \langle \Phi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle]$$

together with Eq. (25) and with the argument following Eq. (25) concerning the behavior of $\Psi_n^{\min,\alpha}$ as $\alpha \to o$. An alternative means of arriving at Eq. (2) employs

$$V_{ee}^{\alpha}[n]=\langle \Phi_n^{\min}|\hat{\mathbf{V}}_{ee}|\Phi_n^{\min}\rangle + \alpha V_{ee}^{c}[n_\lambda] , \tag{79}$$

where from Eq. (11), $V_{ee}^{c}[n]$, the electron-electron repulsion contribution to $E_c[n]$, is given by

$$V_{ee}^{c}[n]=2E_c[n]-\left\{\frac{\partial E_c[n_\lambda]}{\partial \gamma}\right\}_{\gamma=1} , \tag{80}$$

where $V_{ee}^{c}[n]=V_{ee}^{c,1}[n]$. Equation (2) then results from use of Eqs. (12), (79), and (80). [Also, note that the bounds in Eqs. (29)–(32) are applicable for V_{ee}^{c}; simply replace E_c by V_{ee}^{c} in the left-hand-side of each equation.] In contrast to Eq. (2), the local-density approximation to Eq. (2) is

$$\lim_{\alpha \to 0} V_{ee}^{\mathrm{LDA},\alpha}[n]=U[n]+E_x^{\mathrm{LDA}}[n]+\alpha \ln(\alpha^{-1})B'[n] , \tag{81}$$

where E_x^{LDA} is the local-density exchange energy which is proportional to $\int n^{4/3} d^3 r$. Equation (81) stems from

$$V_{ee}^{\mathrm{LDA},\alpha}[n]=U[n]+E_x^{\mathrm{LDA}}[n]+\alpha V_{ee}^{c,\mathrm{LDA}}[n_\lambda] , \tag{82}$$

with the following local-density counterpart to Eq. (80):

$$V_{ee}^{c,\mathrm{LDA}}[n]=2E_c^{\mathrm{LDA}}[n]-\left\{\frac{\partial E_c^{\mathrm{LDA}}[n_\gamma]}{\partial \gamma}\right\}_{\gamma=1} , \tag{83}$$

and with the employment of the fact that $E_c^{\mathrm{LDA}}[n_\lambda]$ goes as $-\log(\lambda)$ as $\lambda \to \infty$.

The last term in Eq. (81) is too negative at low α, which is, perhaps, part of the cause for the fact that the LDA correlation energy is too large in magnitude. Also, when atoms combine to form a molecule, the charge density becomes more compact. Hence, perhaps the well-known LDA overbinding in molecules is due, in part, to the fact that the LDA correlation energy is unbounded as $\lambda \to \infty$. However, on the basis of preliminary calculations[43] it is important to note here that $V_{ee}^{\mathrm{LDA},\alpha}$ appears to *correctly* give $\partial V_{ee}^{\mathrm{LDA},\alpha}/\partial\alpha \le 0$, at least when the Vosko-Wilk-Nusair[29] parametrization for E_c^{LDA} is employed in Eq. (83).

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the valuable suggestions and comments of A. Görling and J. P. Perdew with respect to the limiting coordinate scaling relations.

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