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Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion

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A perturbation theory is developed for the correlation energy $E_c[n]$, of a *finite*-density system, with respect to the *coupling constant* α which multiplies the electron-electron repulsion operator in $H^\alpha=\hat{T}+\alpha\hat{V}_{ee}+\sum_i v_\alpha(\mathbf{r}_i)$. The external potential v_α is constrained to keep the gound-state density n fixed for all $\alpha\geq 0$. v_α is given completely in terms of functional derivatives at *full charge* ($\alpha=1$), from which $E_c[n_\lambda]=e_{c,2}[n]+\lambda^{-1}e_{c,3}[n]+\lambda^{-2}e_{c,4}[n]+\cdots$, where each $e_{c,j}[n]$ is expressed in terms of integrals involving *Kohn-Sham determinants.* Here, $n_\lambda(x,y,x)=\lambda^3 n(\lambda x,\lambda y,\lambda z)$ and $\lambda=\alpha^{-1}$. The identification of $\lim_{\lambda\to\infty}E_c[n_\lambda]$, which is a high-density limit, as the *second-order* energy $e_{c,2}[n]$ allows one to compute bounds upon $\lim_{\lambda\to\infty}E_c[n_\lambda]$; the bounds imply that $\lim_{\lambda\to\infty}E_c[n_\lambda]\simeq E_c[n]$ for a large class of small atoms and molecules, and suggest that $\lim_{\lambda\to\infty}E_c[n_\lambda]$ should be of the same order of magnitude as $E_c[n]$ in *finite* insulators and semiconductors. Approximations to $E_c[n]$ should reflect all this. In contrast, perhaps the well-known overbinding of the local-density approximation (LDA) in molecules and solids is due, in part, to the fact that the LDA correlation energy is too sensitive to a coordinate scaling of n. Indeed, the LDA for $E_c[n_\lambda]$ diverges when $\lambda\to\infty$ because of the presence of the $-\ln(\lambda)$ term in the Gell-Mann and Brueckner high-density expression for the correlation energy, per particle, of a homogeneous density, which is infinite. In a sense, the derived perturbation expansion transforms the Gell-Mann and Brueckner expression into one that applies specifically to an inhomogeneous density which integrates to a finite number of electrons.

I. INTRODUCTION AND SUMMARY

The construction and continued improvement of accurate density functionals for the exchange-correlation energy are essential for high-quality Kohn-Sham calculations of electronic structures. Knowledge of conditions and relations fulfilled by the unknown exact exchange-correlation-energy functional is valuable because approximate functionals could then be made to satisfy the conditions. With this in mind, a perturbation theory is developed here for arbitrary *finite* systems, including molecules and finite solids. (Previous density-functional perturbation expositions have most often focused upon infinite systems.) We expand the correlation energy with respect to a *coupling constant* α which turns on the electron-density repulsion in

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

where N is the number of electrons, $\hat{T}=-\frac{1}{2}\sum_i\nabla_i^2$, $\hat{V}_{ee}=\sum_i\sum_{j>i}|\mathbf{r}_i-\mathbf{r}_j|^{-1}$, and where v_α is the local external potential which is constrained to keep n, the ground-state density of H^α, *fixed* for all $\alpha\geq 0$.

Coordinate scaling has recently provided constraints upon the exchange-correlation function.[1-12] By using coordinate scaling in this paper, we shall here be able to partition H^α into a form which is particularly suitable for a perturbation expansion, because coordinate scaling allows us to express v_α completely in terms of functional derivatives at *full charge*, $\alpha=1$, as follows:

$$v_\alpha([n];\mathbf{r})=v_0([n];\mathbf{r})-\alpha\left\{u([n];\mathbf{r})+v_x([n];\mathbf{r})+\alpha\frac{\delta E_c[n_\lambda]}{\delta n(\mathbf{r})}\right\},\quad \lambda=\alpha^{-1}\ . \tag{2}$$

In Eq. (2), $n_\lambda(x,y,z)=\lambda^3 n(\lambda x,\lambda y,\lambda z)$, v_0 is the noninteracting Kohn-Sham effective potential, $u([n];\mathbf{r})=\int n(\mathbf{r}')d^3r'/|\mathbf{r}'-\mathbf{r}|$, and $v_x([n];\mathbf{r})=\delta E_x/\delta n(\mathbf{r})$ is the exchange potential, where E_x is the exchange energy. The corresponding zero-order Hamiltonian, implied by Eqs. (1) and (2), is $H^0=\hat{T}+\sum_i v_0([n];\mathbf{r}_i)$.

By employing Eqs. (1) and (2), the resultant perturbation expressions shall allow us to express $E_c[n_\lambda]$ in terms of expectation values involving the Kohn-Sham orbitals. These expectation values may then be used to test various approximations to the correlation energy, the correlation potential, and the exchange potential. In particular,

$$E_c[n_\lambda]=e_{c,2}[n]+\lambda^{-1}e_{c,3}[n]+\lambda^{-2}e_{c,4}[n]+\cdots \tag{3}$$

so that, for instance, an explicit expression for a high-density limit, $\lim_{\lambda\to\infty}E_c[n_\lambda]$, arises as the following *second-order* result:

$$\lim_{\lambda\to\infty}E_c[n_\lambda]=e_{c,2}[n]=\sum_{k=1}^{\infty}\frac{\left|\left\langle\Psi^0\left|\hat{V}_{ee}-\sum_{i=1}^{N}[u(\mathbf{r}_i)+v_x(\mathbf{r}_i)]\right|\Psi_k^0\right\rangle\right|^2}{E^0-E_k^0}\ . \tag{4}$$

In Eq. (4), Ψ^0 is the noninteracting Kohn-Sham ground state, and the Ψ_K^0 are the excited Kohn-Sham wave functions (determinants of Kohn-Sham orbitals) of the H^0 that yields n. E^0 and E_K^0 are the corresponding total noninteracting energies of the Kohn-Sham determinants.

We shall also reveal a relation similar to Eq. (4) for a correlation energy functional, ${}^{\mathrm{HF}}E_c[n]$, which is defined with respect to a Hartree-Fock wave function, and whose functional derivative is intended to be added onto a Hartree-Fock calculation as part of the iteration process to self-consistency.

In the case of the local-density approximation, the correlation energy for $\lambda\to\infty$ diverges,[7] as $-\ln\lambda$, because the Gell-Mann and Brueckner contribution to the correlation energy per particle, of a homogeneous electron gas, goes as $-\ln(n^{1/3})$ in the high-density limit.[13] In contrast to the local-density approximation result, $\lim_{\lambda\to\infty}E_c[n_\lambda]$ was earlier shown[5,9,10] to be a bounded negative constant. Here the value of this constant is given through Eq. (4). Therefore, by Eq. (4) the quality of any correlation energy functional and of the accompanying exchange potential can be tested by evaluating and comparing both sides of Eq. (4) for arbitrary densities. In a sense, Eqs. (3) and (4) convert the Gell-Mann and Brueckner expression into one that applies specifically to an inhomogeneous density which integrates to a finite number of electrons.

The evaluation of all terms on the right-hand side in Eq. (4) with any Kohn-Sham program should be straightforward except for the terms containing the electron-electron repulsion operator. The latter lead to four center integrals whose evaluation, however, are of course well known from Hartree-Fock programs. The infinite sum on the right side in Eq. (4) has to be truncated in any real calculation, but because all terms of the sum are negative at least an upper bound for $\lim_{\lambda\to\infty}E_c[n_\lambda]$ is obtained.

The left side of Eq. (4), $\lim_{\lambda\to\infty}E_c[n_\lambda]$, is especially easily accessible for practically any approximate energy functional under consideration by the following recipe resulting from appropriate coordinate transformations. (See, for example, Refs. 9 and 10.) In the original unscaled functional, the density n is replaced by $\lambda^3 n$, any occurring ∇ is replaced by $\lambda\nabla$, and the functional as a whole is multiplied by λ^{-3}. The limit $\lambda\to\infty$ is performed for the functional $E_c[n_\lambda]$ obtained in this way. So, for example, for the following[14] very simple approximate correlation energy functional,

$$\tilde{E}_c[n]=\int d\mathbf{r}\frac{an+b|\nabla n|/n^{1/3}}{c+d|\nabla n|/(n/2)^{4/3}+(3/4\pi n)^{1/2}}\ , \tag{5}$$

the corresponding scaled functional, by the above prescription, is then

$$\tilde{E}_c[n_\lambda]=\int d\mathbf{r}\frac{an+b|\nabla n|/n^{1/3}}{c+d|\nabla n/(n/2)^{4/3}+\lambda^{-1}(3/4\pi n)^{1/3}}\ , \tag{6a}$$

so that

$$\lim_{\lambda\to\infty}\tilde{E}_c[n_\lambda]=\int d\mathbf{r}\frac{an+b|\nabla n|/n^{1/3}}{c+d|\nabla n|/(n/2)^{4/3}} \tag{6b}$$

is obtained.

When atoms combine to form molecules and certain solids, the density contracts. Hence, since a uniform scaling contracts the density when $\lambda>1$, perhaps the well-known overbinding of the local-density approximation is due, in part, to the fact that the correlation energy in the local-density approximation changes too radically as λ is increased past unity. In fact, for the density of small atoms and molecules (under, say, 40 electrons) $E_c[n_\lambda]$ should be *extremely insensitive*, in general, to a scaling all the way from $\lambda=1$ to $\lambda=\infty$. Indeed, from Eq. (4) we estimate that, generally, $\lim_{\lambda\to\infty}E_c[n_\lambda]$ should differ in relatively small systems from $E_c[n]$ by no more than about 10%. This estimate is based upon the fact that the perturbation and the orbitals on the right-hand side of Eq. (4) reveals that $\lim_{\lambda\to\infty}E_c[n_\lambda]$ should be relatively close to that second-order correlation energy for which the Hartree-Fock Hamiltonian is the zero-order Hamiltonian, and there are published data[15] for the latter. (It is well-known that the Kohn-Sham determinant is close to the Hartree-Fock determinant in small and moderately sized atoms.)

For *finite* solids, including clusters consisting of several unit cells of a solid, Eq. (4) informs us that $\lim_{\lambda\to\infty}|E_c[n_\lambda]-E_c[n]|$ is bounded. The value should generally be much smaller for insulators and semiconductors than for metals, because the noninteracting excitation energies, $E_K^0-E^0$, which appear in the denominators of the perturbation terms *beyond* second order in the expansion for $E_c[n]$, should be larger in insulators and semiconductors, due to the presence of the band gaps. Consequently, the second-order term should dominate in insulators and semiconductors, and Eq. (4) gives $\lim_{\lambda\to\infty}E_c[n_\lambda]$ as a second-order term. Hence, we feel that $\lim_{\lambda\to\infty}E_c[n_\lambda]$ should quite safely be of the same order of magnitude as $E_c[n]$ for insulators and semiconductors. Approximations for E_c should be constructed to reflect this.

As shall be reviewed, the correlation energy $E_c[n_\lambda]$ of the scaled density n_λ is connected to the correlation energy $E_c^\alpha[n]$ of the unscaled density n, where in the latter case, the electron-electron interaction is turned on and off by multiplication by a factor $\alpha=1/\lambda$. For $\alpha=0$ ($\alpha=1$) the electron-electron interaction is absent (fully present).[3,4,11] This means that the limit of strong scaling (high λ) which results in a high-density limit is connected to the limit of weak electron-electron interaction, i.e., the noninteracting limit, for the unscaled density.

By investigating the Taylor series of $E_c^\alpha[n]$ with respect to α, which is assumed to exist, Eq. (4) is derived here by showing that the limit $\lim_{\lambda\to\infty}E_c[n_\lambda]$ is connected to the first term of the Taylor series. The higher-order terms of $E_c^\alpha[n]$ are shown to be expressible by higher-order perturbation terms. Finally, a formula given in Ref. 1 for the kinetic contribution to E_c or its approximations is extended which allows the division of $E_c^\alpha[n]$ or its approximations into a kinetic part and an electron-electron repulsion part,[1] and a Taylor series for each part is presented.

Before deriving the relations mentioned above, the various kinds of correlation energies that will be used are defined thoroughly and the accompanying Kohn-Sham and Hartree-Fock equations are given.

II. CORRELATION ENERGIES AND ACCOMPANYING KOHN-SHAN AND HARTREE-FOCK EQUATIONS

The correlation energy $E_c[n]$ in density-functional theory is usually defined, according to the constrained search formulation, by

$$E_c[n]=[\langle\Psi|\hat{T}|\Psi\rangle-\langle\Psi^0|\hat{T}|\Psi^0\rangle]+[\langle\Psi|\hat{V}_{ee}|\Psi\rangle-\langle\Psi^0|\hat{V}_{ee}|\Psi^0\rangle]\ , \tag{7}$$

with $\hat{T}$ being the kinetic-energy operator. In Eq. (7), Ψ and Ψ^0 are those wave functions that yield the density n and minimize $\langle\hat{T}+\hat{V}_{ee}\rangle$ and $\langle\hat{T}\rangle$, respectively. More generally, a correlation energy $E_c^\alpha[n]$ is defined by[3,4,11]

$$E_c^\alpha[n]=[\langle\Psi^\alpha|\hat{T}|\Psi^\alpha\rangle-\langle\Psi^0|\hat{T}|\Psi^0\rangle]+\alpha[\langle\Psi^\alpha|\hat{V}_{ee}|\Psi^\alpha\rangle-\langle\Psi^0|\hat{V}_{ee}|\Psi^0\rangle]\ . \tag{8}$$

Here Ψ^α yields the density n and minimizes $\langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle$; see Ref. 2. The correlation energy $E_c^1[n]$ and the wave function Ψ^1, of course, are identical with $E_c[n]$ and Ψ of definition (7). Next we define the functionals $F^\alpha[n]$, $T_c^\alpha[n]$, and $V_c^\alpha[n]$ as follows:

$$F^\alpha[n]=\langle\Psi^\alpha|\hat{T}+\alpha\hat{V}_{ee}|\Psi^\alpha\rangle\ , \tag{9}$$

$$T_c^\alpha[n]=\langle\Psi^\alpha|\hat{T}|\Psi^\alpha\rangle-\langle\Psi^0|\hat{T}|\Psi^0\rangle\ , \tag{10}$$

$$V_c^\alpha[n]=\langle\Psi^\alpha|\hat{V}_{ee}|\Psi^\alpha\rangle-\langle\Psi^0|\hat{V}_{ee}|\Psi^0\rangle\ . \tag{11}$$

The functional $F^\alpha[n]$ is a generalization of the Hohenberg-Kohn functional[16,17] in the constrained search formulation[8] of density-functional theory. (Compare the F^α here with the one in Ref. 2.) $T_c^\alpha[n]$ and $\alpha V_c^\alpha[n]$ are the kinetic and the electron-electron repulsion parts of the correlation energy $E_c^\alpha[n]$. From the definition it follows immediately that

$$E_c^\alpha[n]=F^\alpha[n]-F^0[n]-\alpha U[n]-\alpha E_x[n] \tag{12}$$

or

$$E_c^\alpha[n]=T_c^\alpha[n]+\alpha V_c^\alpha[n]\ , \tag{13}$$

with $U[n]=\frac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'[n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]$ and $E_x[n]=\langle\Psi^0|\hat{V}_{ee}|\Psi^0\rangle-U[n]$.

To obtain a definition of the correlation energy ${}^{\rm HF}E_c^\alpha[n]$ which is related to a Hartree-Fock wave function, first the functional ${}^{\rm HF}F^\alpha[n]$ is defined by

$${}^{\rm HF}F^\alpha[n]=\langle{}^{\rm HF}\Psi^\alpha|\hat{T}+\alpha\hat{V}_{ee}|{}^{\rm HF}\Psi^\alpha\rangle\ , \tag{14}$$

where ${}^{\rm HF}\Psi^\alpha$ is that single determinant which yields n and minimizes $\langle\hat{T}+\alpha\hat{V}_{ee}\rangle$. By starting with $F^\alpha[n]$, the correlation energy is

$$\begin{aligned}{}^{\rm HF}E_c^\alpha[n]&=F^\alpha[n]-{}^{\rm HF}F^\alpha[n]\\&=[\langle\Psi^\alpha|\hat{T}|\Psi^\alpha\rangle-\langle{}^{\rm HF}\Psi^\alpha|\hat{T}|{}^{\rm HF}\Psi^\alpha\rangle]\\&\quad+\alpha[\langle\Psi^\alpha|\hat{V}_{ee}|\Psi^\alpha\rangle-\langle{}^{\rm HF}\Psi^\alpha|\hat{V}_{ee}|{}^{\rm HF}\Psi^\alpha\rangle]\end{aligned} \tag{15}$$

and a difference energy is defined by

$$\begin{aligned}D^\alpha[n]&={}^{\rm HF}F^\alpha[n]-F^0[n]-\alpha U[n]-\alpha E_x[n]\\&=[\langle{}^{\rm HF}\Psi^\alpha|\hat{T}|{}^{\rm HF}\Psi^\alpha\rangle-\langle\Psi^0|\hat{T}|\Psi^0\rangle]\\&\quad+\alpha[\langle{}^{\rm HF}\Psi^\alpha|\hat{V}_{ee}|{}^{\rm HF}\Psi^\alpha\rangle-\langle\Psi^0|\hat{V}_{ee}|\Psi^0\rangle]\ .\end{aligned} \tag{16}$$

Similarly, as in Eqs. (10) and (11), ${}^{\rm HF}E_c^\alpha[n]$ and $D^\alpha[n]$ can be divided into kinetic and an electron-electron repulsion parts, ${}^{\rm HF}T_c^\alpha[n]$, ${}^{\rm HF}V_c^\alpha[n]$, and ${}^{D}T^\alpha[n]$, ${}^{D}V^\alpha[n]$, respectively. As easily seen from the definitions, the following equations are valid:

$$E_c^\alpha[n]={}^{\rm HF}E_c^\alpha[n]+D^\alpha[n]\ , \tag{17}$$

$$T_c^\alpha[n]={}^{\rm HF}T_c^\alpha[n]+{}^{D}T^\alpha[n]\ , \tag{18}$$

$$V_c^\alpha[n]={}^{\rm HF}V_c^\alpha[n]+{}^{D}T^\alpha[n]\ . \tag{19}$$

Next assume that the wave function Ψ in Eq. (7) is the ground state of

$$H=\hat{T}+\hat{V}_{ee}+\sum_{i=1}^{N}v(\mathbf{r}_i)\ , \tag{20a}$$

where

$$H\Psi=E\Psi \tag{20b}$$

with v being some local, (multiplicative) external potential (for an atom, a molecule, or a solid, v is generated by the nuclei). With the functionals and wave functions defined above, the ground-state energy E in Eq. (20b) can be expressed in the following ways:

$$E=\langle\Psi^{\alpha}|\hat{T}+\alpha\hat{V}_{ee}|\Psi^{\alpha}\rangle+\int d\mathbf{r}\,v(\mathbf{r})n(\mathbf{r})+[F^{1}[n]-F^{\alpha}[n]] \tag{21a}$$

or

$$E=\langle{}^{\mathrm{HF}}\Psi^{\alpha}|\hat{T}+\alpha\hat{V}_{ee}|{}^{\mathrm{HF}}\Psi^{\alpha}\rangle+\int d\mathbf{r}\,v(\mathbf{r})n(\mathbf{r})+[F^{1}[n]-{}^{\mathrm{HF}}F^{\alpha}[n]]\ . \tag{21b}$$

From Eqs. (21a) and (21b), Kohn-Sham- and Hartree-Fock-like equations for the wave functions Ψ^{α} and ${}^{\mathrm{HF}}\Psi^{\alpha}$ can be derived: Start with

$$\begin{aligned}H^{\alpha}&=\hat{T}+\alpha\hat{V}_{ee}+\sum_{i=1}^{n}\left[v(\mathbf{r}_i)+\frac{\delta(F^{1}[n]-F^{\alpha}[n])}{\delta n(\mathbf{r}_i)}\right]\\&=\hat{T}+\alpha\hat{V}_{ee}+\sum_{i=1}^{N}\left[v(\mathbf{r}_i)+(1-\alpha)u(\mathbf{r}_i)+(1-\alpha)v_x(\mathbf{r}_i)+\frac{\delta E_c^{1}[n]}{\delta n(\mathbf{r}_i)}-\frac{\delta E_c^{\alpha}[n]}{\delta n(\mathbf{r}_i)}\right]\ ,\end{aligned} \tag{22a}$$

where

$$\begin{aligned}&H^{\alpha}\Psi^{\alpha}=E^{\alpha}\Psi^{\alpha}\ ,\\&H^{1}=H,\quad \Psi^{1}=\Psi,\quad E^{1}=E\ ,\end{aligned} \tag{22b}$$

so that

$$\begin{aligned}{}^{\mathrm{HF}}H^{\alpha}&=\hat{T}+\alpha\,{}^{\mathrm{HF}}\hat{v}_x+\sum_{i=1}^{N}\left[\alpha u(\mathbf{r}_i)+v(\mathbf{r}_i)+\frac{\delta(F^{1}[n]-{}^{\mathrm{HF}}F^{\alpha}[n])}{\delta n(\mathbf{r}_i)}\right]\\&=\hat{T}+\alpha\,{}^{\mathrm{HF}}\hat{v}_x+\sum_{i=1}^{N}\left[u(\mathbf{r}_i)+v(\mathbf{r}_i)+(1-\alpha)v_x(\mathbf{r}_i)+\frac{\delta E_c^{1}[n]}{\delta n(\mathbf{r}_i)}-\frac{\delta D^{\alpha}[n]}{\delta n(\mathbf{r}_i)}\right]\end{aligned} \tag{23a}$$

and

$${}^{\mathrm{HF}}H^{\alpha}\,{}^{\mathrm{HF}}\Psi^{\alpha}={}^{\mathrm{HF}}E^{\alpha}\,{}^{\mathrm{HF}}\Psi^{\alpha}\ . \tag{23b}$$

Here ${}^{\mathrm{HF}}v_x$ is the nonlocal Hartree-Fock exchange operator. It is important to note that the eigenfunctions Ψ^{α} and ${}^{\mathrm{HF}}\Psi^{\alpha}$ yield the same density n. Also, Eq. (22) becomes the usual many-electron Hamiltonian, Eq. (20), if $\alpha=1$ and becomes the standard Kohn-Sham equation if $\alpha=0$, because $E_c^{\alpha}[n]$, and therewith $\delta E_c^{\alpha}[n]/\delta n$, vanishes for $\alpha\to 0$. Equations (23), for $\alpha=1$, represents a modified HF equation, that in contrast to the usual HF equation allows, in principle, the calculation of the exact ground-state density and, via Eq. (21b), of the exact ground-state energy E of the considered system. Furthermore, the eigenvalue of the highest occupied orbital of ${}^{\mathrm{HF}}\Psi^{1}$ turns out to be the negative of the exact ionization energy of H. For a detailed discussion of Eq. (23), with $\alpha=1$, see Refs. 9, 10, and 18–21. For $\alpha=0$, Eq. (23b) becomes identical to the standard Kohn-Sham equations, i.e., Eq. (22b) with $\alpha=0$, if, as we will do in this paper, only nondegenerate ground states are considered and the Kohn-Sham wave function Ψ^{0} is therefore a single determinant function like the HF wave function.

III. PERTURBATION THEORY EXPRESSION FOR $E_c[n_\lambda]$ AND ${}^{\mathrm{HF}}E_c[n_\lambda]$

The Hamiltonian operators and wave functions obtained in the foregoing section are now used to derive Eq. (1). The starting point is the following relation between the correlation energies $E_c[n_\lambda]$ and $E_c^{\alpha}[n]$, $\alpha=\lambda^{-1}$, which has been obtained in Refs. 3 and 4 from the development in Refs. 1 and 2:

$$E_c[n_\lambda]=\lambda^{2}E_c^{1/\lambda}[n]=(1/\alpha^{2})E_c^{\alpha}[n]\ . \tag{24}$$

Next, the definition, Eq. (8), of the correlation energy $E_c^{\alpha}[n]$ is used:

$$\begin{aligned}E_c[n_\lambda]&=(1/\alpha^{2})[\langle\Psi^{\alpha}|\hat{T}+\alpha\hat{V}_{ee}|\Psi^{\alpha}\rangle-\langle\Psi^{0}|\hat{T}+\alpha\hat{V}_{ee}|\Psi^{0}\rangle] &\text{(25a)}\\&=(1/\alpha^{2})[\langle\Psi^{\alpha}|H^{\alpha}|\Psi^{\alpha}\rangle-\langle\Psi^{0}|H^{\alpha}|\Psi^{0}\rangle] &\text{(25b)}\\&=(1/\alpha^{2})[E^{\alpha}-E^{0}-\langle\Psi^{0}|H^{\alpha}-H^{0}|\Psi^{0}\rangle]\ . &\text{(25c)}\end{aligned}$$

To obtain Eq. (25b) the fact that the wave functions Ψ^{α} and Ψ^{0} both yield density n is employed. For the application of perturbation theory, the Hamiltonian H^{α} is partitioned with the help of Eqs. (12) and (22) according to

$$\begin{aligned}H^{\alpha}&=H^{0}+\alpha\hat{V}_{ee}+\sum_{i=1}^{N}\left[\frac{\delta(F^{1}[n]-F^{\alpha}[n])}{\delta n(\mathbf{r}_i)}-\frac{\delta(F^{1}[n]-F^{0}[n])}{\delta n(\mathbf{r}_i)}\right]\\&=H^{0}+\alpha\hat{V}_{ee}-\sum_{i=1}^{N}\frac{\delta(F^{\alpha}[n]-F^{0}[n])}{\delta n(\mathbf{r}_i)}\\&=H^{0}+\alpha\hat{V}_{ee}+\sum_{i=1}^{N}\left[-\alpha u(r_i)-\alpha v_x(\mathbf{r}_i)-\frac{\delta E_c^{\alpha}[n]}{\delta n(\mathbf{r}_i)}\right]\\&=H^{0}+\alpha\left\{\hat{V}_{ee}+\sum_{i=1}^{N}\left[-u(r_i)-v_x(\mathbf{r}_i)-\alpha\frac{\delta E_c[n_{1/\alpha}]}{\delta n(\mathbf{r}_i)}\right]\right\},\end{aligned}\tag{26a}$$

where H^0 is the unperturbed Hamiltonian and the second part of the right side is considered as perturbation. Equation (24) has been used again for the last term in Eq. (26a).

Before proceeding at this moment it is worthwhile to further investigate the Hamiltonian H^{α} of (26a) by writing it in the form

$$\begin{aligned}H^{\alpha}&=\hat{T}+\alpha\hat{V}_{ee}+\sum_{i=1}^{N}[v_0(\mathbf{r}_i)-\alpha u(\mathbf{r}_i)-\alpha v_x(\mathbf{r}_i)-\alpha^2\delta E_c[n_{1/\alpha}]/\delta n(\mathbf{r}_i)]\\&=\hat{T}+\alpha\hat{V}_{ee}+\sum_{i=1}^{N}v_{\alpha}(\mathbf{r}_i)\ ,\end{aligned}\tag{26b}$$

with

$$v_{\alpha}(\mathbf{r})=v_0(\mathbf{r})-\alpha u(\mathbf{r})-\alpha v_x(\mathbf{r})-\alpha^2\delta E_c[n_{1/\alpha}]/\delta n(\mathbf{r})\ ,\tag{26c}$$

where v_0 is the Kohn-Sham potential which is, within an additive constant, $-\delta F^0[n]/\delta n(\mathbf{r})$. The Hamiltonian H^{α} is the one belonging to the well-known coupling-constant procedure[21–24] and v_{α} is the corresponding external potential. Equation (26b) is remarkable because the coupling-constant external potential v_{α}, for all $\alpha\geq 0$, is expressed entirely in terms of the functional deviations at full charge, $\alpha=1$. Merely the scaled density $n_{1/\alpha}$ is involved. [Note that Eqs. (26b) and (26c) are restatements of Eqs. (1) and (2).]

By continuing from Eq. (26a), the energy can be expanded as

$$E^{\alpha}=E_{(0)}+\alpha E^{\alpha}_{(1)}+\alpha^2E^{\alpha}_{(s)}+\alpha^3E^{\alpha}_{(3)}+\cdots\tag{27}$$

with $E_{(0)}=E^0$,

$$E_{(1)}=\left\langle\Psi^0\left|\hat{V}_{ee}-\sum_{i=1}^{N}\left[u(\mathbf{r}_i)+v_x(\mathbf{r}_i)+\alpha\frac{\delta E_c[n_{1/\alpha}]}{\delta n(\mathbf{r}_i)}\right]\right|\Psi^0\right\rangle .$$

If Eq. (27) for E^{α} is substituted into Eq. (25), the first two terms of E^{α} are canceled and the correlation energy for the scaled density n_{λ} is obtained as the following series:

$$\begin{aligned}E_c[n_{\lambda}]&=E^{\alpha}_{(2)}+\alpha E^{\alpha}_{(3)}+\cdots\\&=\sum_{k=1}^{\infty}\frac{\left|\left\langle\Psi^0\left|\hat{V}_{ee}-\sum_{i=1}^{N}\left[u(r_i)+v_x(\mathbf{r}_i)+\alpha\frac{\delta E_c[n_{\lambda}]}{\delta n(\mathbf{r}_i)}\right]\right|\Psi^0_k\right\rangle\right|^2}{E^0-E^0_k}+\alpha E^{\alpha}_{(3)}+\cdots\ ;\ \alpha=\lambda^{-1}\ .\end{aligned}\tag{28}$$

Here Ψ^0_k is the kth excited eigenfunction of the Kohn-Sham Hamiltonian H^0 with eigenvalue E^0_k. For the limit $\lambda\rightarrow\infty$, corresponding to $\alpha\rightarrow 0$, Eq. (4) follows when one employs the fact that $\lim_{\lambda\rightarrow\infty}E_c[n_{\lambda}]$ is a constant, as shown in Refs. 5, 9, and 10, and therefore the part in the right-hand side of Eq. (28) that is connected to the correlation energy vanishes.

There is a small difficulty with the way the perturbation theory has been applied. In Eq. (27) the factor α has been used as a parameter to turn on and off the perturbation $(\hat{V}_{ee}-\sum_{i=1}^{N}\{u(r_i)+v_x(\mathbf{r}_i)+\alpha\delta E_c[n_{\lambda}]/\delta n(\mathbf{r}_i)\})$. However, in contrast to standard Rayleigh-Schrödinger perturbation theory the perturbation itself here is dependent on the parameter α. To justify the application of Rayleigh-Schrödinger perturbation theory, one can consider the expression $\alpha(\hat{V}_{ee}-\sum_{i=1}^{N}\{u(\mathbf{r}_i)+v_x(\mathbf{r}_i)+\beta\delta E_c[n_{1/\beta}]/\delta n(\mathbf{r}_i)\})$ as the perturbation. The energy is first expanded in terms of α at fixed β. Then β is set equal to α. Alternatively, in the next section the α-dependent part of the perturbation in Eq. (28) is expanded in a Taylor series in α and an appropriate modification of Rayleigh-Schrödinger perturbation theory is applied.

The derivation of the analogous perturbation theory expression for the correlation energy ${}^{\mathrm{HF}}E_c[n_{\lambda}]$ is done in a similar way. Corresponding to Eq. (25), ${}^{\mathrm{HF}}E_c[n_{\lambda}]$ can be written as

$$
\begin{aligned}
{}^{\mathrm{HF}}E_c[n_\lambda] &= (1/\alpha^2)[\langle \Psi^\alpha | \hat{T} + \alpha \hat{V}_{ee} | \Psi^\alpha \rangle - \langle {}^{\mathrm{HF}}\Psi^\alpha | \hat{T} + \alpha \hat{V}_{ee} | {}^{\mathrm{HF}}\Psi_\alpha \rangle] \\
&= (1/\alpha^2)[\langle \Psi^\alpha | H^\alpha | \Psi^\alpha \rangle - \langle {}^{\mathrm{HF}}\Psi^\alpha | H^\alpha | {}^{\mathrm{HF}}\psi^\alpha \rangle] \\
&= (1/\alpha^2)[E^\alpha - {}^{\mathrm{HF}}E^\alpha - \langle {}^{\mathrm{HF}}\Psi^\alpha | H^\alpha - {}^{\mathrm{HF}}H^\alpha | {}^{\mathrm{HP}}\Psi^\alpha \rangle] \, .
\end{aligned}
\tag{29}
$$

By using Eqs. (15) and (23), the Hamiltonian H^α is split again, but now ${}^{\mathrm{HF}}H^\alpha$ is considered as the unperturbed part:

$$
\begin{aligned}
H^\alpha &= {}^{\mathrm{HF}}H^\alpha + \alpha \hat{V}_{ee} - \alpha\, {}^{\mathrm{HF}}\hat{v}_x + \sum_{i=1}^{N} \left[-\alpha u(\mathbf{r}_i) + \frac{\delta(F^1[n] - F^\alpha[n])}{\delta n(\mathbf{r}_i)} - \frac{\delta(F^1[n] - {}^{\mathrm{HF}}F^\alpha[n])}{\delta n(\mathbf{r}_i)} \right] \\
&= {}^{\mathrm{HF}}H^\alpha + \alpha \hat{V}_{ee} - \alpha\, {}^{\mathrm{HF}}v_x + \sum_{i=1}^{N} \left[-\alpha u(\mathbf{r}_i) - \frac{\delta\, {}^{\mathrm{HF}}E_c^\alpha[n]}{\delta n(\mathbf{r}_i)} \right] \\
&= {}^{\mathrm{HF}}H^\alpha + \alpha \hat{V}_{ee} - \alpha\, {}^{\mathrm{HF}}\hat{v}_x + \sum_{i=1}^{N} \left[-\alpha u(\mathbf{r}_i) - \frac{\delta\, {}^{\mathrm{HF}}E_c^\alpha[n]}{\delta n(\mathbf{r}_i)} \right] \\
&= {}^{\mathrm{HF}}H^\alpha + \alpha \left\{ \hat{V}_{ee} - {}^{\mathrm{HF}}\hat{v}_x + \sum_{i=1}^{N} \left[-u(\mathbf{r}_i) - \alpha \frac{\delta\, {}^{\mathrm{HF}}E_c[n_{1/\alpha}]}{\delta n(\mathbf{r}_i)} \right] \right\} .
\end{aligned}
\tag{30}
$$

After writing the energy ${}^{\mathrm{HF}}E^\alpha$ as

$$
\begin{aligned}
&{}^{\mathrm{HF}}E^\alpha[n] = {}^{\mathrm{HF}}E_{(0)} + \alpha\, {}^{\mathrm{HF}}E^\alpha_{(1)} + \alpha^2\, {}^{\mathrm{HF}}E^\alpha_{(2)} + \alpha^3\, {}^{\mathrm{HF}}E^\alpha_{(3)} + {}^{\mathrm{HF}}E^\alpha_{(0)} = {}^{\mathrm{HF}}E^\alpha \, , \\
&{}^{\mathrm{HF}}E^\alpha_{(1)} = \left\langle {}^{\mathrm{HF}}\Psi^\alpha \middle| \hat{V}_{ee} - {}^{\mathrm{HF}}\hat{v}_x + \sum_{i=1}^{N} \left[-u(\mathbf{r}_i) - \alpha \frac{\delta\, {}^{\mathrm{HF}}E_c[n_{1/\alpha}]}{\delta n(\mathbf{r}_i)} \right] \middle| {}^{\mathrm{HF}}\Psi^\alpha \right\rangle ,
\end{aligned}
\tag{31}
$$

the correlation energy ${}^{\mathrm{HF}}E_c[n_\lambda]$ can finally be expressed as

$$
\begin{aligned}
{}^{\mathrm{HF}}E_c[n_\lambda] &= {}^{\mathrm{HF}}E^\alpha_{(2)} + \alpha\, {}^{\mathrm{HF}}E^\alpha_{(3)} + \cdots \\
&= \sum_{k=1}^{\infty} \frac{\left| \left\langle {}^{\mathrm{HF}}\Psi^\alpha \middle| \hat{V}_{ee} - {}^{\mathrm{HF}}\hat{v}_x + \sum_{i=1}^{\infty} \left[-u(\mathbf{r}_i) - \alpha \frac{\delta\, {}^{\mathrm{HF}}E_c[n_\lambda]}{\delta n(\mathbf{r}_i)} \right] \middle| {}^{\mathrm{HF}}\Psi^\alpha_k \right\rangle \right|^2}{{}^{\mathrm{HF}}E^\alpha - {}^{\mathrm{HF}}E^\alpha_k} + \alpha\, {}^{\mathrm{HF}}E_{(3)} + \cdots \, .
\end{aligned}
\tag{32}
$$

In Eq. (32), ${}^{\mathrm{HF}}\Psi^\alpha_k$ is the kth excited eigenfunction of the Hamiltonian ${}^{\mathrm{HF}}H^\alpha$ with eigenvalue ${}^{\mathrm{HF}}E^\alpha_k$. By performing the limit $\lambda \to \infty$, one obtains

$$
\lim_{\lambda \to \infty} {}^{\mathrm{HF}}E_c[n_\lambda] = \sum_{u=1}^{\infty} \frac{\left| \left\langle \Psi^0 \middle| \hat{V}_{ee} - {}^{\mathrm{HF}}\hat{v}_x - \sum_{i=1}^{N} u(\mathbf{r}_i) \middle| \Psi^0_k \right\rangle \right|^2}{E^0 - E^0_k} \, . \tag{33}
$$

Equation (33) employs

$$
\lim_{\alpha \to 0} {}^{\mathrm{HF}}\Psi^\alpha_k = \Psi^0_k \tag{34a}
$$

$$
{}^{\mathrm{HF}}E^0_k = E^0_k \tag{34b}
$$

which follows from Eqs. (22) and (23), for $\alpha \to 0$. Notice that the limit $\lambda \to \infty$ for ${}^{\mathrm{HF}}E_c[n_\lambda]$, by Eq. (33), is expressed entirely in terms of the usual Kohn-Sham wave functions. However, the operator ${}^{\mathrm{HF}}\hat{v}_x$ is a nonlocal exchange operator built of Kohn-Sham orbitals.

IV. TAYLOR SERIES OF $E_c^\alpha[n]$, $T_c^\alpha[n]$, and $V_c^\alpha[n]$

For the further investigation of Eq. (25) the behavior of the correlation energy $E_c^\alpha[n]$ and its parts $T_c^\alpha[n]$ and $V_c^\alpha[n]$ with α has to be inspected. This is done by investigating the Taylor series, with respect to α, of $E_c^\alpha[n]$, $T_c^\alpha[n]$, and $V_c^\alpha[n]$ that are assumed to exist near $\alpha = 0$. The equality

$$
\frac{\partial T_c^\alpha[n]}{\partial \alpha} = -\alpha \frac{\partial V_c^\alpha[n]}{\partial \alpha} \tag{35}
$$

is a differential counterpart and a slightly more general formulation of the well-known adiabatic connection (coupling constant integration) formula.[22,25] The Taylor series for $V_c^\alpha[n]$,

$$
V_c^\alpha[n] = \sum_{j=1}^{\infty} v_{c,j}[n] \alpha^j \, , \tag{36}
$$

has no zero-order term because $V_c^\alpha[n]$ is zero for $\alpha = 0$ by definition. With the generalized adiabatic connection formula (35), the Taylor series for $T_c^\alpha[n]$ is determined by

$$
T_c^\alpha[n] = \sum_{j=2}^{\infty} t_{c,j}[n] \alpha^j = \sum_{j=2}^{\infty} -\frac{j-1}{j} v_{c,j-1}[n] \alpha^j \tag{37}
$$

with

$$
t_{c,j}[n] = -\frac{j-1}{j} v_{c,j-1}[n] \, . \tag{38}
$$

In the Taylor series for $T_c[n]$, not only is the zero-order term missing but also the one of first order. This is consistent with the fact that the wave function Ψ^α, with $\alpha=0$, minimizes $\langle \hat{T} \rangle$. From Eqs. (13), (36), and (37) the Taylor series of $E_c^\alpha[n]$ follows immediately:

$$E_c^\alpha[n]=\sum_{j=2}^{\infty} e_{c,j}[n]\alpha^j=\sum_{j=2}^{\infty}\frac{1}{j}v_{c,j-1}[n]\alpha^j \tag{39a}$$

$$=\sum_{j=2}^{\infty}-\frac{1}{j-1}t_{c,j}[n]\alpha^j\ , \tag{39b}$$

with

$$e_{c,j}[n]=\frac{1}{j}v_{c,j-1}[n]=-\frac{1}{j-1}t_{c,j}[n]\ . \tag{40}$$

It is now possible to use perturbation theory in a somewhat different way than in the previous section to derive expression (4) for $\lim_{\lambda\to\infty}E_c[n_\lambda]$. By inserting Eq. (39) into Eq. (26) for the Hamiltonian H^α and by performing the functional derivative for each term of the Taylor series (39) separately, one obtains

$$H^\alpha=H^0+\alpha\left[\hat{V}_{ee}+\sum_{i=1}^{N}[-u(\mathbf{r}_j)-v_x(\mathbf{r}_i)]\right] -\sum_{j=2}^{\infty}\left[\frac{\alpha^j}{j}\sum_{i=1}^{N}\frac{\delta v_{c,j-1}[n]}{\delta n(\mathbf{r}_i)}\right]\ . \tag{41}$$

By writing the Hamiltonian H^α as in Eq. (41) the order of the different terms in α becomes clear. In particular, it is shown that the contributions to the terms related to the correlation energy are of second and higher order in α. Next, the energy E^α can be expanded:

$$E^\alpha=E_{(0)}+\alpha E_{(1)}+\alpha^2E_{(2)}+\cdots\ . \tag{42}$$

Equation (42) is in accordance with a modified form of Rayleigh-Schrödinger perturbation theory that is appropriate for a perturbation that has terms of higher order in α. In contrast to Eq. (27) in the foregoing section, the energy terms in Eq. (42) are not dependent on α. The expressions here for $E_{(0)}$, $E_{(1)}$, and $E_{(2)}$ are

$$\begin{aligned} E_{(0)}&=E^0\ ,\\ E_{(1)}&=\left\langle\Psi^0\left|\hat{V}_{ee}+\sum_{i=1}^{N}[-u(\mathbf{r}_i)]\right|\Psi^0\right\rangle\ , \end{aligned} \tag{43}$$

$$E_{(2)}=\sum_{k=1}^{\infty}\frac{\left|\left\langle\Psi^0\left|\hat{V}_{ee}+\sum_{i=1}^{N}[-u(\mathbf{r}_i)-v_x(\mathbf{r}_i)]\right|\Psi_k^0\right\rangle\right|^2}{E^0-E_k^0} -\left\langle\Psi^0\left|\sum_{i=1}^{N}\frac{1}{2}\frac{\delta v_{c,1}[n]}{\delta n(\mathbf{r}_i)}\right|\Psi^0\right\rangle\ . \tag{44}$$

For the scaled correlation energy, $E_c[n_\lambda]$, by using Eqs. (25), (43), and (44), one obtains

$$\begin{aligned} E_c[n_\lambda]&=(1/\alpha^2)[\langle\Psi^\alpha|H^\alpha|\Psi^\alpha\rangle-\langle\Psi^0|H^\alpha|\Psi^0\rangle]\\ &=(1/\alpha^2)\left[E^\alpha-E^0-\alpha E_{(1)}+\sum_{j=2}^{\infty}\alpha^j\left\langle\Psi^0\left|\sum_{i=1}^{N}\frac{1}{j}\frac{\delta v_{c,i-1}[n]}{\delta n(\mathbf{r}_i)}\right|\Psi^0\right\rangle\right]\\ &=\sum_{k=1}^{\infty}\frac{\left|\left\langle\Psi^0\left|\hat{V}_{ee}+\sum_{i=1}^{\infty}[-u(\mathbf{r}_i)-v_x(\mathbf{r}_i)]\right|\Psi_k^0\right\rangle\right|^2}{E^0-E_k^0}+\sum_{j=3}^{\infty}\alpha^{j-2}\left[E_{(j)}+\left\langle\Psi^0\left|\sum_{i=1}^{N}\frac{1}{j}\frac{\delta v_{c,i-1}[n]}{\delta n(\mathbf{r}_i)}\right|\Psi^0\right\rangle\right]\\ &=\sum_{k=1}^{\infty}\frac{\left|\left\langle\Psi^0\left|\hat{V}_{ee}+\sum_{i=1}^{\infty}[-u(\mathbf{r}_i)-v_x(\mathbf{r}_i)]\right|\Psi_k^0\right\rangle\right|^2}{E^0-E_k^0}+O(\lambda^{-1})\ . \end{aligned} \tag{45}$$

In the limit of $\alpha=0,\lambda\to\infty$, the correlation energy $E_c[n_\lambda]$ becomes identical to the right side of Eq. (4) which was derived in the previous section. Further, the modified adiabatic connection formula (35) and the Taylor series (36), (37), and (39), for $E_c^\alpha[n]$, $T_c^\alpha[n]$, and $V_c^\alpha[n]$, can be used to achieve more insight into the meaning of the limit $\lim_{\lambda\to\infty}E_c^\alpha[n]$. By starting with Eq. (13), the relations named above lead to

$$\begin{aligned} \lim_{\lambda\to\infty}E_c[n_\lambda]&=\lim_{\alpha\to0}(1/\alpha^2)E_c^\alpha[n]=\frac{v_{c,1}[n]}{2}\\ &=-t_{c,2}[n]=e_{c,2}[n] \end{aligned} \tag{46}$$

or equivalently to

$$\begin{aligned} \lim_{\lambda\to\infty}E_c[n_\lambda]&=\lim_{\alpha\to0}(1/\alpha^2)E_c^\alpha[n]\\ &=\frac{1}{2}\frac{\partial V_c^\alpha[n]}{\partial\alpha}\bigg|_{\alpha=0}=-\frac{1}{2}\frac{\partial^2T_c^\alpha[n]}{\partial\alpha^2}\bigg|_{\alpha=0}\ . \end{aligned} \tag{47}$$

This means that the limit $\alpha=0$ is related to the derivation with respect to α of the kinetic and electron-electron repulsion parts of the correlation energy at $\alpha=0$. In a similar way, the higher-order coefficients $e_{c,j}[n]$, $v_{c,j}[n]$, and $t_{c,j}[n]$ of the Taylor series for $E_c^\alpha[n]$, $V_c^\alpha[n]$, and $T_c^\alpha[n]$ can be expressed by perturbation theory expressions:

$$e_{c,j}[n]=\frac{v_{c,j-1}[n]}{j}=\frac{-t_{c,j}[n]}{j-1}$$

$$=E_{(j)}+\left\langle\Psi^0\left|\sum_{i=1}^{N}\frac{1}{j}\frac{\delta v_{c,j-1}[n]}{\delta n(\mathbf{r}_i)}\right|\Psi^0\right\rangle . \qquad (48)$$

The term $\langle\Psi^0|\sum_{i=1}^{N}\delta v_{c,j-1}[n]/\delta n(\mathbf{r}_i)|\Psi^0\rangle$ in Eq. (48) cancels the $v_{c,j-1}[n]$ dependent term in $E_{(j)}n$. This means that the perturbation theory expression for $V_{c,j-1}[n]$ (corresponding to the ones of $e_{c,j}[n]$ and $t_{c,j}[n]$) contains only functional derivatives of Taylor series coefficients $v_{c,j-2}[n]$ of order $j-2$, or lower (or coefficients $e_{c,j-1}[n]$ or $t_{c,j-1}[n]$ of order $j-1$ or lower.)

To end this section two relations are presented that are not directly related to the foregoing development but which are of some general interest. By differentiating Eq. (13) with respect to α and by using the differential adiabatic connection formula (35), one obtains

$$V_c^{\alpha}[n]=(1/\lambda)V_c[n_\lambda]=2\alpha E_c[n_{1/\alpha}]+\alpha^2\frac{\partial E_c[n_{1/\alpha}]}{\partial\alpha}$$

$$=\frac{2}{\lambda}E_c[n_\lambda]-\frac{\partial E_c[n_\lambda]}{\partial\lambda} \qquad (49)$$

and

$$T_c^{\alpha}[n]=\frac{1}{\lambda^2}T_c[n_\lambda]=-\alpha^2E_c[n_{1/\alpha}]-\alpha^3\frac{\partial E_c[n_{1/\alpha}]}{\partial\alpha}$$

$$=-1/\lambda^2E_c[n_\lambda]+\frac{1}{\lambda}\frac{\partial E_c[n_\lambda]}{\partial\lambda} . \qquad (50)$$

For $\alpha=\lambda=1$, Eqs. (49) and (50) become the relations of Levy and Perdew[1] which allow one to divide any approximate correlation energy functional into its kinetic and electron-electron repulsion part. [See also Eqs. (74) and (80) in Ref. 9 and Eqs. (40A) and (40B) of Ref. 11.] Remember that $E_c[n_\lambda]$, and therewith $\partial E_c[n_\lambda]/\partial\lambda$, can usually be determined easily from the original functional $E_c[n]$, as demonstrated in the Introduction. If, as required, it is valid for the correlation energy belonging to the approximate functional that $\lim_{\lambda\to\infty}E_c[n_\lambda]=\text{const}$, Eqs. (46) and (47) are fulfilled automatically for the kinetic and electron-electron repulsion parts obtained by Eqs. (49) and (50). Together with the relations

$$E_x[n]=\lim_{\lambda\to\infty}\frac{E_{xc}[n_\lambda]}{\lambda} \qquad (51)$$

and

$$E_c[n]=E_{xc}[n]-\lim_{\lambda\to\infty}\frac{E_{xc}[n_\lambda]}{\lambda} , \qquad (52)$$

which have been noted earlier,[9] Eqs. (49) and (50), or their earlier counterparts,[1] make it possible to divide any given exchange-correlation functional by scaling procedures.

V. CLOSING REMARKS

When either $E_c[n]$ or $E_c^{\text{HF}}[n]$ is utilized duirng a self-consistent calculation, where $E_c[n]\leq E_c^{\text{HF}}[n]$, the exact ground-state energy is obtained, the exact ground-state density is obtained, and the highest-occupied orbital energy gives the negative of the exact ionization energy.[20,21] The difference between $E_c[n]$ and $E_c^{\text{HF}}[n]$ is that $E_c[n]$ is employed as part of a complete density-functional calculation, within the Kohn-Sham procedure, for instance, while $E_c^{\text{HF}}[n]$ is to be employed with the Hartree-Fock procedure. The functional derivative of $E_c^{\text{HF}}[n]$ is intended to be added to a Hartree-Fock calculation as part of the iteration process to self-consistency.[18,19,21] Upon self-consistency, the exact ground-state energy is obtained from $\langle{}^{\text{HF}}\Psi^1|H|{}^{\text{HF}}\Psi^1\rangle+E_c^{\text{HF}}[n_{\text{gs}}]$, where ${}^{\text{HF}}\Psi^1$ is that Hartree-Fock determinant which results at self-consistency and yields n_{gs}. Here n_{gs} is the ground-state density of H. (Note that ${}^{\text{HF}}\Psi^1$ is not quite the Hartree-Fock determinant of H and n_{gs} is not quite the Hartree-Fock density of H because of the attachment of the functional derivative of E_c^{HF} to H during the Hartree-Fock self-consistency process. Consequently, $\langle{}^{\text{HF}}\Psi^1|H|{}^{\text{HF}}\Psi^1\rangle$ is above the Hartree-Fock energy of H, although it is close to it.)

Finally, we emphasize that the perturbation expansions allow one to extract a significant amount of information about E_c from *any* single n. For a given n, once the perturbation energies are computed in terms of integrals involving the Kohn-Sham orbitals the $E_{(j)}$ in, say, Eqs. (42) and (45)], then $E_c[n_\lambda]$ is known, from this single set of Kohn-Sham orbitals, for a continuous range of λ's, from $\lambda\to\infty$ to around $\lambda=1$. Therefore, the accuracy of any approximate correlation energy functional could be checked with n_λ, from $\lambda\to\infty$ to about $\lambda=1$, by using a single set of Kohn-Sham orbitals. Moreover, since the integrals in the perturbation expansions contain the exchange and correlation potentials, it also follows that the expansions provide checks on these potentials. The statements in this paragraph apply analogously to $E_c^{\text{HF}}[n]$.

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