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Expectation values in density-functional theory, and kinetic contribution to the exchange-correlation energy

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Bauer's expression for the *difference* between the expectation values of an arbitrary quantum-mechanical operator with the physical interacting ground-state wave function and its corresponding noninteracting Kohn-Sham wave function is obtained here by a very simple and general derivation via the constrained-search formulation of density-functional theory. Our proof does not require v-representability or a coupling-constant integration. We show that the following expression of Bass for the *kinetic* part of the exact exchange-correlation energy $E_{\text{xc}}[n]$: $T_{\text{xc}}[n]=a_0\,\partial E_{\text{xc}}[n]/\partial a_0$, where $a_0=\hbar^2/me^2$ is the Bohr radius, can also be derived by a constrained-search proof and is equivalent to the following expression of Levy and Perdew: $T_{\text{xc}}[n]=(\partial E_{\text{xc}}[n_\lambda]/\partial\lambda)|_{\lambda=1}-E_{\text{xc}}[n]$, where $n_\lambda(x,y,z)=\lambda^3 n(\lambda x,\lambda y,\lambda z)$. When an *approximate* E_{xc} is employed, the two expressions will yield the same result for the corresponding T_{xc} if certain coordinate scaling relations, involving the electronic charge, are satisfied. Moreover, the Levy-Perdew relation has the advantage that it is applied at full electronic charge (e) and full electronic mass (m). Corresponding relations are also exhibited for the correlation hole. We discuss the high- and low-density limits of T_{xc}, generalize our results to spin-density functional theory, and present numerical estimates of T_{xc} for atoms, evaluated within the local spin density, gradient expansion, and generalized gradient approximations.

I. INTRODUCTION

Today, most applications of density-functional theory[1] are performed by using the Kohn-Sham formalism.[2] Therefore it is of interest to know the *difference*

$$\langle {}^0\Psi^{1,1}_{[n]}|\hat{A}|{}^0\Psi^{1,1}_{[n]}\rangle-\langle {}^0\Psi^{1,0}_{[n]}|\hat{A}|{}^0\Psi^{1,0}_{[n]}\rangle\ , \tag{1}$$

where $\hat{A}$ is an arbitrary quantum-mechanical operator, ${}^0\Psi^{1,1}_{[n]}$ is the exact Hohenberg-Kohn[3] interacting ground-state wave function for electron density n, and ${}^0\Psi^{1,0}_{[n]}$ is the corresponding Kohn-Sham[2] noninteracting wave function. Bauer[4] obtained this "difference" by introducing a special effective potential in the Kohn-Sham Hamiltonian and by using the coupling-constant integration approach[5-7] at fixed n.[6,7] In this paper we derive the difference within the constrained-search formulation[8] of density-functional theory, in a very simple way, without reference to any effective potential or to any coupling-constant integration. Furthermore, our derivation is more general because it does not require the assumption of v-representability.[8]

Bass[9] used Bauer's relation for the above-introduced difference to deduce an expression for the kinetic part of the exchange-correlation energy, T_{xc}. We will demonstrate here that Bass's expression for T_{xc} is equivalent to the one of Levy and Perdew,[10] and at the very end of Sec. II, we shall derive Bass's expression in essentially two steps by constrained-search theory, without recourse to Bauer's relation.

II. THEORY

Let us employ the constrained-search representation and define ${}^\gamma\Psi^{\alpha,\beta}_{[n]}$ as that wave function which minimizes $\langle \alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}\rangle$ and yields the density n:

$$\langle {}^\gamma\Psi^{\alpha,\beta}_{[n]}|\alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}|{}^\gamma\Psi^{\alpha,\beta}_{[n]}\rangle = \min_{\Psi\to n}\langle\Psi|\alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}|\Psi\rangle\ , \tag{2}$$

where $\hat{T}$ and $\hat{V}_{ee}$ are the operators for the kinetic and electron-electron repulsion energies, respectively, and $\hat{A}$ is an arbitrary general quantum-mechanical operator. ($\hat{A}$ is *not* generally assumed to be a one-body multiplicative external potential.) It follows then that ${}^0\Psi^{1,1}_{[n]}$ is the familiar interacting Hohenberg-Kohn wave function[3] and ${}^{0}\Psi^{1,0}_{[n]}$ is the familiar noninteracting Kohn-Sham wave function.[2] In anticipation of Bauer's result,[4] we shall define the exchange and correlation energies with γ included. To make the definition more general, we also include α and β. Namely,

$$ {}^{\gamma}E^{\alpha,\beta}_{x}[n]=\langle {}^{\gamma}\Psi^{\alpha,0}_{[n]}|\beta\hat{V}_{ee}|{}^{\gamma}\Psi^{\alpha,0}_{[n]}\rangle-\beta U[n] \ , \tag{3} $$

$$ \begin{aligned} {}^{\gamma}E^{\alpha,\beta}_{c}[n]=&\langle {}^{\gamma}\Psi^{\alpha,\beta}_{[n]}|\alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}|{}^{\gamma}\Psi^{\alpha,\beta}_{[n]}\rangle \\ &-\langle {}^{\gamma}\Psi^{\alpha,0}_{[n]}|\alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}|{}^{\gamma}\Psi^{\alpha,0}_{[n]}\rangle \ , \end{aligned} \tag{4} $$

with

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

so that the total exchange-correlation energy ${}^{\gamma}E^{\alpha,\beta}_{\rm xc}[n]\equiv{}^{\gamma}E^{\alpha,\beta}_{x}[n]+{}^{\gamma}E^{\alpha,\beta}_{c}[n]$ is

$$ \begin{aligned} {}^{\gamma}E^{\alpha,\beta}_{\rm xc}[n]=&\langle {}^{\gamma}\Psi^{\alpha,\beta}_{[n]}|\alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}|{}^{\gamma}\Psi^{\alpha,\beta}_{[n]}\rangle \\ &-\langle {}^{\gamma}\Psi^{\alpha,0}_{[n]}|\alpha\hat{T}+\gamma\hat{A}|{}^{\gamma}\Psi^{\alpha,0}_{[n]}\rangle-\beta U[n] \ . \end{aligned} \tag{5} $$

The factors α and β may be considered to change the inverse of the mass and the square of the charge of the electron.

We now assert that Bauer's relation[4] is obtained as a direct consequence of Eq. (5) by utilization of the fact that ${}^{\gamma}\Psi^{\alpha,\beta}_{[n]}$ is defined via the *minimization* in Eq. (2). In other words, the definition of ${}^{\gamma}\Psi^{\alpha,\beta}_{[n]}$ as an optimizing wave function implies its stationary character:

$$ \frac{\partial}{\partial\omega}\langle {}^{\omega}\Psi^{\alpha,\beta}_{[n]}|\alpha\hat{T}+\beta\hat{V}_{ee}+\gamma\hat{A}|{}^{\omega}\Psi^{\alpha,\beta}_{[n]}\rangle|_{\omega=\gamma}=0 \ , \tag{6} $$

so that

$$ \frac{\partial}{\partial\gamma}{}^{\gamma}E^{\alpha,\beta}_{\rm xc}[n]=\langle {}^{\gamma}\Psi^{\alpha,\beta}_{[n]}|\hat{A}|{}^{\gamma}\Psi^{\alpha,\beta}_{[n]}\rangle-\langle {}^{\gamma}\Psi^{\alpha,0}_{[n]}|\hat{A}|{}^{\gamma}\Psi^{\alpha,0}_{[n]}\rangle \ , \tag{7} $$

which means

$$ \begin{aligned} \frac{\partial}{\partial\gamma}{}^{\gamma}E^{\alpha,\beta}_{\rm xc}[n]|_{\gamma=0}=&\langle {}^{0}\Psi^{\alpha,\beta}_{[n]}|\hat{A}|{}^{0}\Psi^{\alpha,\beta}_{[n]}\rangle \\ &-\langle {}^{0}\Psi^{\alpha,0}_{[n]}|\hat{A}|{}^{0}\Psi^{\alpha,0}_{[n]}\rangle \ . \end{aligned} \tag{8} $$

Equation (8), for $\alpha=\beta=1$, is Bauer's relation, our desired result.

Equations (7) and (8) remain valid if the familiar *noninteracting* Kohn-Sham wave function ${}^{0}\Psi^{1,0}_{[n]}$ is employed, at *all* γ, instead of ${}^{\gamma}\Psi^{\alpha,0}_{[n]}$ in the definition of ${}^{\gamma}E^{\alpha,\beta}_{\rm xc}[n]$. If ${}^{0}\Psi^{1,0}_{[n]}$ is employed instead of ${}^{\gamma}\Psi^{\alpha,0}_{[n]}$ in Eqs. (3)–(5), then ${}^{0}\Psi^{1,0}_{[n]}$ replaces ${}^{\gamma}\Psi^{\alpha,0}_{[n]}$ on the right-hand-side of Eq. (7). In any case, the right-hand side of Eq. (8) is the same at $\alpha=1$ regardless which of the two definitions for the Kohn-Sham wave function is used, even though $\partial{}^{\gamma}E^{\alpha,\beta}_{\rm xc}[n]/\partial\gamma$ depends upon our choice at values of γ other than zero. We have chosen ${}^{\gamma}\Psi^{\alpha,0}_{[n]}$ for our original definition of the Kohn-Sham wave function because ${}^{\gamma}\Psi^{\alpha,0}_{[n]}$ is the one which is implied in Bauer's work through his particular use of the coupling-constant integration. The equivalence of our ${}^{\gamma}E^{1,1}_{\rm xc}$ according to Eq. (5) and Bauer's definition is demonstrated in Appendix A.

By using Eq. (8) and setting $\hat{A}=\hat{T}$, we quickly obtain the following expression for the kinetic part of the exchange-correlation energy:

$$ T_{\rm xc}[n]=\frac{\partial}{\partial\gamma}{}^{\gamma}E^{1,1}_{\rm xc}[n]|_{\gamma=0} \tag{9a} $$

or

$$ T_{\rm xc}[n]=\frac{\partial}{\partial\gamma}{}^{\gamma}E^{1,1}_{c}[n]|_{\gamma=0} \ , \tag{9b} $$

where $T_{\rm xc}[n]$ is defined by

$$ T_{\rm xc}[n]\equiv\langle {}^{0}\Psi^{1,1}_{[n]}|\hat{T}|{}^{0}\Psi^{1,1}_{[n]}\rangle-\langle {}^{0}\Psi^{1,0}_{[n]}|\hat{T}|{}^{0}\Psi^{1,0}_{[n]}\rangle \ . \tag{10} $$

Equation (9b) follows from Eq. (9a), because in the special case of $\hat{A}=\hat{T}$, the wave functions ${}^{\gamma}\Psi^{1,0}$ and ${}^{0}\Psi^{1,0}$ are identical and therefore the exchange part ${}^{\gamma}E^{1,1}_{x}[n]$ [Eq. (3)], of ${}^{\gamma}E^{1,1}_{\rm xc}[n]$ [Eq. (5)] is independent of γ. Equation (9a) is equivalent to the equation of Bass,[9] as demonstrated shortly.

To derive Eq. (9) directly via the constrained-search formulation of density-functional theory, without reference to Bauer's relation, we exploit the fact that ${}^{\gamma}\Psi^{\alpha,\beta}_{[n]}$ is defined by a minimization in Eq. (2) to obtain

$$ \frac{\partial}{\partial\alpha'}\langle {}^{0}\Psi^{\alpha',1}_{[n]}|\alpha\hat{T}+\hat{V}_{ee}|{}^{0}\Psi^{\alpha',1}_{[n]}\rangle|_{\alpha'=\alpha}=0 \ , \tag{11} $$

so that the differentiation of Eq. (5) with respect to α, at $\gamma=0$ and $\beta=1$, leads to

$$ \begin{aligned} \left.\frac{\partial\,{}^{0}E^{\alpha,1}_{\rm xc}[n]}{\partial\alpha}\right|_{\alpha=1}&=\langle {}^{0}\Psi^{1,1}_{[n]}|\hat{T}|{}^{0}\Psi^{1,1}_{[n]}\rangle-\langle {}^{0}\Psi^{1,0}_{[n]}|\hat{T}|{}^{0}\Psi^{1,0}_{[n]}\rangle \\ &=T_{\rm xc}[n] \ . \end{aligned} \tag{12} $$

Next, the insertion of the identity

$$ \begin{aligned} \left.\frac{\partial\,{}^{0}E^{\alpha,1}_{\rm xc}[n]}{\partial\alpha}\right|_{\alpha=1}&=\left.\frac{\partial\,{}^{0}E^{1+\gamma,1}_{\rm xc}[n]}{\partial\gamma}\right|_{\gamma=0} \\ &=\left.\frac{\partial\,{}^{\gamma}E^{1,1}_{\rm xc}[n]}{\partial\gamma}\right|_{\gamma=0} \ , \end{aligned} \tag{13} $$

which is valid for $\hat{A}=\hat{T}$, into Eq. (12) gives Eq. (9a).

The equivalence of Eq. (12), and therewith of Eq. (9a), with Bass's equation for $T_{\rm xc}$ becomes clear if one explicitly writes

$$ (\alpha a_0)(-\tfrac{1}{2}e^2)\sum_i\nabla_i^2 $$

for $\alpha\hat{T}$ (with a_0 as the Bohr radius and e as the charge of the electron). The chain rule then leads to

$$ \left.\frac{\partial\,{}^{0}E^{\alpha,1}_{\rm xc}[n]}{\partial\alpha}\right|_{\alpha=1}=a_0\frac{\partial\,{}^{0}E^{1,1}_{\rm xc}[n]}{\partial a_0}=T_{\rm xc}[n] \ . \tag{14} $$

The rightmost equality in Eq. (14) constitutes Bass's equation. Again, the fact has been used that ${}^{\gamma}\Psi^{\alpha,\beta}_{[n]}$ is defined by a minimization [Eq. (2)].

We now show that Eq. (9) is equivalent to and follows from the Levy-Perdew relation for $T_{\rm xc}$, which is

$$T_{\mathrm{xc}}[n]=\left.\frac{\partial\,{}^{0}E_{c}^{1,1}[n_{\lambda}]}{\partial\lambda}\right|_{\lambda=1}-{}^{0}E_{c}^{1,1}[n] \tag{15a}$$

or

$$T_{\mathrm{xc}}[n]=\left.\frac{\partial\,{}^{0}E_{\mathrm{xc}}^{1,1}[n_{\lambda}]}{\partial\lambda}\right|_{\lambda=1}-{}^{0}E_{\mathrm{xc}}^{1,1}[n]\ , \tag{15b}$$

where

$$n_{\lambda}(x,y,z)=\lambda^{3}n(\lambda x,\lambda y,\lambda z)\ . \tag{16}$$

(Equation (15a) implies Eq. (15b) because[10] ${}^{0}E_{x}^{1,1}[n_{\lambda}]=\lambda\,{}^{0}E_{x}^{1,1}[n]$.) For the proof of the equivalence of Eqs. (9) and (15), observe that

$${}^{0}\Psi_{[n]}^{1,\lambda^{-1}}={}^{0}\Psi_{[n]}^{\lambda,1}\ , \tag{17}$$

which leads, according to Eq. (4), to

$${}^{0}E_{c}^{1,\lambda^{-1}}[n]=\lambda^{-1}\,{}^{0}E_{c}^{\lambda,1}[n]\ . \tag{18}$$

Next, the combination of Eq. (18) with the following coordinate scaling relation of Levy and Perdew[11,12] and Yang,[13]

$${}^{0}E_{c}^{1,\lambda^{-1}}[n]=\lambda^{-2}\,{}^{0}E_{c}^{1,1}[n_{\lambda}]\ , \tag{19}$$

gives

$${}^{0}E_{c}^{1,1}[n_{\lambda}]=\lambda\,{}^{0}E_{c}^{\lambda,1}[n]\ . \tag{20}$$

Finally, the combination of Eq. (20) with Eq. (15a) yields

$$T_{\mathrm{xc}}[n]=\left.\frac{\partial\,{}^{0}E_{c}^{\lambda,1}[n]}{\partial\lambda}\right|_{\lambda=1} \tag{21a}$$

or

$$T_{\mathrm{xc}}[n]=\left.\frac{\partial\,{}^{0}E_{\mathrm{xc}}^{\lambda,1}[n]}{\partial\lambda}\right|_{\lambda=1}\ , \tag{21b}$$

which is the same as Eq. (12) and therewith equivalent to Eqs. (9) and (14). Equation (21b) follows from Eq. (21a), because ${}^{0}\Psi^{\lambda,0}$ is equal to ${}^{0}\Psi^{1,0}$ for all λ ($\lambda>0$) and therefore ${}^{0}E_{x}^{\lambda,1}[n]$ [Eq. (3)] is independent of λ. Note, by the way, that Eq. (21a) is equivalent to

$$T_{\mathrm{xc}}[n]={}^{0}E_{c}^{1,1}[n]-\frac{\partial}{\partial\beta}\,{}^{0}E_{c}^{1,\beta}[n]\big|_{\beta=1}\ , \tag{22}$$

which follows directly from the minimizing nature of ${}^{0}\Psi^{1,\beta}$ [Eq. (2)] and from the definitions (4) and (10). Equation (22) is distinguished from Eqs. (12) and (21a) by the fact that the coefficient β, belonging to $\beta\hat{V}_{ee}$, is varied in Eq. (22), while the coefficient α, belonging to $\alpha\hat{T}$, is varied in Eq. (12) or varied as λ in Eq. (21a). By replacing ${}^{0}E_{c}^{1,1}[n]$ and ${}^{0}E_{c}^{1,\beta}[n]$ by ${}^{0}E_{\mathrm{xc}}^{1,1}[n]$ and ${}^{0}E_{\mathrm{xc}}^{1,\beta}[n]$, respectively, in Eq. (22), a relation equivalent to Eq. (21b) is obtained.

We conclude this section by noting that Bass's expression for $T_{\mathrm{xc}}[n]$ follows directly from a differentiation of the constrained-search definition for the exchange-correlation energy. Simply define $E_{\mathrm{xc}}^{a_0}[n]$ by

$$\begin{aligned}E_{\mathrm{xc}}^{a_0}[n]=&\langle\Psi_{[n]}^{a_0}|\hat{T}(a_0)+\hat{V}_{ee}|\Psi_{[n]}^{a_0}\rangle\\&-\langle\Phi_{[n]}^{a_0}|\hat{T}(a_0)|\Phi_{[n]}^{a_0}\rangle-U[n]\ ,\end{aligned} \tag{23}$$

where, consistent with Bass,

$$\hat{T}(a_0)=-a_0e^{2}\sum_{i}\tfrac{1}{2}\nabla_i^{2}\ ,$$

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

and, consistent with the constrained-search approach, $\Psi_{[n]}^{a_0}$ minimizes $\langle\hat{T}(a_0)+\hat{V}_{ee}\rangle$ and $\Phi_{[n]}^{a_0}$ minimizes just $\langle\hat{T}(a_0)\rangle$, at fixed n, where a_0 is the Bohr radius. It follows that

$$\begin{aligned}\frac{\partial}{\partial a_0'}[&\langle\Psi_{[n]}^{a_0'}|\hat{T}(a_0)+\hat{V}_{ee}|\Psi_{[n]}^{a_0'}\rangle\\&-\langle\Phi_{[n]}^{a_0'}|\hat{T}(a_0)|\Phi_{[n]}^{a_0'}\rangle]\big|_{a_0'=a_0}=0\ ,\end{aligned} \tag{24}$$

so that

$$\begin{aligned}\frac{\partial E_{\mathrm{xc}}^{a_0}[n]}{\partial a_0}=&\left\langle\Psi_{[n]}^{a_0}\left|\frac{\partial\hat{T}(a_0)}{\partial a_0}\right|\Psi_{[n]}^{a_0}\right\rangle\\&-\left\langle\Phi_{[n]}^{a_0}\left|\frac{\partial\hat{T}(a_0)}{\partial a_0}\right|\Phi_{[n]}^{a_0}\right\rangle\end{aligned} \tag{25}$$

or

$$\begin{aligned}a_0\frac{\partial E_{\mathrm{xc}}^{a_0}[n]}{\partial a_0}&=\langle\Psi_{[n]}^{a_0}|\hat{T}(a_0)|\Psi_{[n]}^{a_0}\rangle-\langle\Phi_{[n]}^{a_0}|\hat{T}(a_0)|\Phi_{[n]}^{a_0}\rangle\\&=T_{\mathrm{xc}}[n]\ ,\end{aligned} \tag{26}$$

which is the relation of Bass.

III. DISCUSSION AND NUMERICAL RESULTS

For practical purposes it is important to point out that the exposition in Sec. II reveals that $T_{\mathrm{xc}}[n]$, obtained from an approximate ${}^{0}E_{c}^{1,1}[n]$, will be the *same* with Eq. (15) as with Eqs. (9), (14), or (22) *provided* that the approximate ${}^{0}E_{c}^{1,1}[n]$ *satisfies* Eqs. (18) and (19), what thus can be considered as a requirement an approximate ${}^{0}E^{1,1}[n]$ has to fulfill. An approximate ${}^{0}E_{c}^{\alpha\beta}[n]$ to a given approximate ${}^{0}E^{1,1}[n]$, as it occurs in Eqs. (18) and (19), is obtained from the approximate ${}^{0}E^{1,1}[n]$ by replacing the inverse of the electron mass ($1/m_e$) by (α/m_e) and the square of the electron charge (e^2) by (βe^2). Further, Eq. (15) has the advantage that it can be employed with an approximate ${}^{0}E_{c}^{1,1}[n]$, which is expressed in atomic units and thus not expressed in terms of the mass or the charge of the electron. Incidentally, it is quite easy to construct ${}^{0}E_{c}^{1,1}[n_{\lambda}]$ from ${}^{0}E_{c}^{1,1}[n]$; it literally takes no more than a few minutes. With this in mind, new nonuniform as well as uniform coordinate scaling properties of ${}^{0}E_{c}^{1,1}$ have recently been elucidated.[12,14,15]

In the high-density limit[12] [$\lambda\to\infty$ in Eq. (16)], it has been shown[14–16] that $E_c\sim\lambda^{0}$, where $E_c[n]\equiv{}^{0}E_{c}^{1,1}[n]$. (The correlation energy per electron tends to a constant for a finite system and becomes proportional to $\ln\lambda$ for an infinite metal.) Then, by Eq. (15a),

TABLE I. T_c, the correlation contribution to the total interacting kinetic energy: The GGA is that of Ref. 18. The GGA′ is as modified in Ref. 12. The exact results are from Ref. 21 (1 hartree=27.21 eV).

	T_c (eV)				
Atom	LSD	GEA	GGA	GGA′	Exact
H	0.3	0.6	0.1	0.1	0.0
He	1.9	2.4	1.0	1.0	1.0
Li^+	2.4	2.9	1.2	1.1	1.1
Be^{2+}	2.7	3.3	1.3	1.2	1.1
Li	2.6	3.1	1.3	1.3	1.7
Be	3.8	4.4	2.0	2.0	2.0

$$\lim_{\lambda\to\infty} T_c[n_\lambda]/(-E_c[n_\lambda])=1 , \tag{27}$$

where $T_c[n]\equiv T_{xc}[n]$. (Note that there is no kinetic contribution to $E_x[n]$.) In the low-density limit[12] [$\lambda\to 0$ in Eq. (16)], it has been shown[12,14] that $E_c\sim\lambda$. So, by Eq. (15a),

$$\lim_{\lambda\to 0} T_c[n_\lambda]/(-E_c[n_\lambda])=0 . \tag{28}$$

Equations (27) and (28) have been derived by Perdew.[17]

The constrained-search derivation of Eqs. (11)–(14) is easily generalized to spin-density functional theory: Just replace $n(\mathbf{r})$ by $n_\uparrow(\mathbf{r})$, $n_\downarrow(\mathbf{r})$, with the result

$$T_c[n_\uparrow,n_\downarrow]=a_0\frac{\partial}{\partial a_0}E_c[n_\uparrow,n_\downarrow] . \tag{29}$$

The generalized gradient approximation (GGA) for $E_c[n_\uparrow,n_\downarrow]$ is

$$E_c[n_\uparrow,n_\downarrow]=\int d\mathbf{r}\, n\varepsilon_x(n,0)F_c(r_s,\zeta,s) , \tag{30}$$

where $\varepsilon_x(n,0)=-(3e^2/4\pi)(3\pi^2 n)^{1/3}$ is the uniform-gas exchange energy (with $n=n_\uparrow+n_\downarrow$),

$$r_s=(4\pi n a_0^3/3)^{-1/3} \tag{31}$$

is the local-density parameter,

$$\zeta=(n_\uparrow-n_\downarrow)/(n_\uparrow+n_\downarrow) \tag{32}$$

is the local-spin polarization, and

$$s=|\nabla n|/2k_F n \tag{33}$$

is the reduced-density gradient [with $k_F=(3\pi^2 n)^{1/3}$]. By Eq. (29) the GGA for $T_c[n_\uparrow,n_\downarrow]$ is

$$T_c[n_\uparrow,n_\downarrow]=-\int d\mathbf{r}\, n\varepsilon_x(n,0)r_s\frac{\partial}{\partial r_s}F_c(r_s,\zeta,s) , \tag{34}$$

which generalizes the expression of Perdew[17] to nonzero ζ.

Replacing $F_c(r_s,\zeta,s)$ by its expansion to zeroth or second order in s yields the local-spin density (LSD) and gradient-expansion (GEA) approximations, respectively. Tables I–III display atomic values for E_c and T_c from the LSD and GEA, as well as results from the generalized gradient approximation (GGA) of Perdew and Wang.[18]

TABLE II. $-E_c$, or -1 times the correlation energy, and T_c, the correlation contribution to the total interacting kinetic energy. See caption of Table I. The GGA values of $-E_c$ are nearly exact for the neutral atoms from H to Ar. Note that the LSD overestimates $-E_c$ by about a factor of 2, while the GEA predicts the wrong sign.

	$-E_c$ (hartree)				T_c (hartree)			
Atom	LSD	GEA	GGA	GGA′	LSD	GEA	GGA	GGA′
H	0.022	−0.044	0.007	0.006	0.012	0.022	0.005	0.005
He^+	0.030	−0.114	0.007	0.006	0.018	0.031	0.006	0.006
He	0.113	−0.125	0.046	0.042	0.068	0.087	0.038	0.038
Li^+	0.135	−0.260	0.051	0.045	0.087	0.108	0.043	0.042
Be^{2+}	0.150	−0.401	0.054	0.046	0.100	0.122	0.046	0.044
Li	0.151	−0.222	0.058	0.051	0.095	0.113	0.048	0.047
Be^+	0.173	−0.344	0.062	0.054	0.112	0.132	0.053	0.051
Be	0.224	−0.314	0.094	0.086	0.138	0.162	0.073	0.072
Ne^{6+}	0.334	−1.186	0.123	0.104	0.231	0.259	0.104	0.096
N	0.427	−0.567	0.199	0.181	0.276	0.305	0.159	0.155
Ne	0.743	−0.780	0.382	0.351	0.496	0.530	0.313	0.307
Ar	1.424	−1.534	0.771	0.707	0.973	1.013	0.631	0.614
Zn^{12+}	1.800	−3.576	0.924	0.824	1.307	1.346	0.792	0.755
Zn^{2+}	2.578	−2.624	1.485	1.368	1.832	1.870	1.250	1.218
Zn	2.655	−2.467	1.525	1.406	1.873	1.906	1.282	1.250
Kr	3.269	−3.024	1.914	1.767	2.324	2.361	1.613	1.573
Xe	5.177	−4.685	3.149	2.918	3.738	3.772	2.666	2.599

TABLE III. T_c, the correlation contribution to the total interacting kinetic energy, evaluated for the scaled two-electron exponential density $n_\uparrow = n_\downarrow = (\lambda^3/\pi)\exp(-2\lambda r)$. See caption of Table I.

	T_c (hartree)				$T_c/(-E_c)$
λ	LSD	GEA	GGA	GGA′	GGA′
0.5	0.0323	0.0438	0.0241	0.0245	0.70
1	0.0516	0.0684	0.0335	0.0339	0.82
2	0.0758	0.0966	0.0416	0.0413	0.91
6	0.1234	0.1454	0.0511	0.0473	0.98
12	0.1581	0.1758	0.0561	0.0485	1.00
24	0.1957	0.2033	0.0611	0.0488	1.00

This GGA was constructed nonempirically via a real-space cutoff of the spurious long-range part of the gradient expansion for the correlation hole. A minor modification[12] (GGA′) of this functional, which displays the proper high-density scaling, is also considered. Atomic Hartree-Fock densities[19] $n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})$ have been employed in Eqs. (30) and (34) to construct Tables I and II.

Table I shows that the LSD and GEA overestimate T_c for the light atoms, where T_c is known exactly.[20] In nonlocal-density functional calculations of T_c, we find GGA and GGA′ to be more realistic. Table II shows that, for many atoms, $T_c \leq -E_c$. Table III displays the correct high-density scaling of T_c in the GGA′; the analogous table for E_c was presented by Levy and Perdew.[12] The more accurate results for T_c in neutral atoms are probably those of the GGA, which seems to predict the more accurate values for E_c.[12,18]

The correlation energy is often written as

$$E_c[n_\uparrow,n_\downarrow] = \frac{e^2}{2}\int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}' \frac{\rho_c([n_\uparrow,n_\downarrow];\mathbf{r},\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} , \tag{35}$$

where $\rho_c([n_\uparrow,n_\downarrow];\mathbf{r},\mathbf{r}')$, the density at $\mathbf{r}'$ of the correlation hole about an electron at $\mathbf{r}$, is an average over the coupling constant (as in Appendix A) of the Coulomb hole $n_c([n_\uparrow,n_\downarrow];\mathbf{r},\mathbf{r}')$, which describes the physical correlations at full electron change. Moreover,

$$E_c[n_\uparrow,n_\downarrow] - T_c[n_\uparrow,n_\downarrow] = \frac{e^2}{2}\int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}' \frac{n_c([n_\uparrow,n_\downarrow];\mathbf{r},\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} . \tag{36}$$

Consistent with Eqs. (29) and (36), it can be shown[21] that

$$n_c([n_\uparrow,n_\downarrow];\mathbf{r},\mathbf{r}') = \left[1 - a_0 \frac{\partial}{\partial a_0}\right] \rho_c([n_\uparrow,n_\downarrow];\mathbf{r},\mathbf{r}') . \tag{37}$$

Equation (37), a generalization to *nonuniform* $n(\mathbf{r})$ of Eq. (90) of Wang and Perdew,[22] helps to explain why the GEA is not as bad for T_c as it is for E_c (Table II): The most spurious and most long-ranged ($|\mathbf{r}'-\mathbf{r}| \rightarrow \infty$) gradient contribution to ρ_c does not depend[23] upon a_0 and thus makes no contribution to the GEA for T_c.

The equation

$$n_c([n];\mathbf{r},\mathbf{r}') = \left[1 + \frac{d}{d\lambda}\right] \lambda^3 \rho_c([n_{1/\lambda}];\lambda\mathbf{r},\lambda\mathbf{r}')\Big|_{\lambda=1} \tag{38}$$

is related to Eq. (37) in a similar way as Eqs. (15) and (14) are related for $T_{\mathrm{xc}}[n]$. Equations (37) and (38) are of interest because it is ρ_c which is most often approximated in the literature, whereas it is n_c which is related directly to the second-order density matrix of the real system (full electron charge). As in the case of $T_{\mathrm{xc}}[n]$ [Eqs. (15) and (14)], Eq. (38) has the advantage that it can be applied if ρ_c is given in atomic units and thus if the mass and the charge of the electron do not appear explicitly. In the special case of the uniform electron gas, Eq. (38) reduces to Eq. (7) of Ref. 21. For the derivation of Eq. (38), see Appendix B.

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APPENDIX A

We here demonstrate that our definition for the exchange-correlation energy in Eq. (5), ${}^{\gamma}E_{\mathrm{xc}}^{\alpha,\beta}[n]$, for $\alpha=\beta=1$, is the same as Bauer's, which is displayed in his paper through the coupling-constant integration formula. In the process we generalize a constrained-search proof[24] of the coupling-constant integration formula at constant n.[6,7] To begin, note that

$$\frac{\partial}{\partial\beta}\langle {}^{\gamma}\Psi_{[n]}^{1,\beta} | \hat{T} + \beta\hat{V}_{ee} + \gamma\hat{A} | {}^{\gamma}\Psi_{[n]}^{1,\beta} \rangle = \langle {}^{\gamma}\Psi_{[n]}^{1,\beta} | \hat{V}_{ee} | {}^{\gamma}\Psi_{[n]}^{1,\beta} \rangle , \tag{A1}$$

because, by definition [Eq. (2)], ${}^{\gamma}\Psi^{1,\beta'}$ minimizes $\langle \hat{T} + \beta\hat{V}_{ee} + \gamma\hat{A} \rangle$ when $\beta'=\beta$. Next, integrate both sides of Eq. (A1) from $\beta=0$ to 1, and then subtract $U[n]$ from both sides of the resultant expression to obtain

$$\langle {}^{\gamma}\Psi_{[n]}^{1,1} | \hat{T} + \hat{V}_{ee} + \gamma\hat{A} | {}^{\gamma}\Psi_{[n]}^{1,1} \rangle - \langle {}^{\gamma}\Psi_{[n]}^{1,0} | \hat{T} + \gamma\hat{A} | {}^{\gamma}\Psi_{[n]}^{1,0} \rangle - U[n] = \int_0^1 d\beta \langle {}^{\gamma}\Psi_{[n]}^{1,\beta} | \hat{V}_{ee} | {}^{\gamma}\Psi_{[n]}^{1,\beta} \rangle - U[n] . \tag{A2}$$

Equation (A2) shows the equivalence of both definitions of the exchange-correlation energy; the left-hand-side of Eq. (A2) is our ${}^{\gamma}E_{\rm xc}^{1,1}$, while the right-hand-side is the corresponding expression of Bauer.

APPENDIX B

To derive Eq. (38), first define

$$\Gamma_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')=\Gamma^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')-\Gamma^{1,0}([n];\mathbf{r},\mathbf{r}') \ . \quad \text{(B1)}$$

In Eq. (B1), $\Gamma^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')$ is the second-order density matrix of the wave function ${}^{0}\Psi_{[n]}^{\alpha,\beta}$ so that $\Gamma^{1,0}([n];\mathbf{r},\mathbf{r}')$ is the second-order density matrix of ${}^{0}\Psi_{[n]}^{1,0}$. The Coulomb hole $n_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')$ is given by

$$n_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')=\frac{2\Gamma_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')}{n(\mathbf{r})} \ . \quad \text{(B2)}$$

Now, through a coupling-constant integration[6,7] (see also Appendix A), the corresponding averaged correlation hole

$$\rho_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')=\int_0^{\beta} d\beta'\, n_c^{\alpha,\beta'}([n];\mathbf{r},\mathbf{r}') \quad \text{(B3)}$$

gives the correlation energy ${}^{0}E_c^{\alpha,\beta}$ by

$${}^{0}E_c^{\alpha,\beta}/\beta=\frac{e^2}{2}\int d\mathbf{r}\, n(\mathbf{r})\int d\mathbf{r}' \frac{\rho_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ . \quad \text{(B4)}$$

If $\rho_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')$ in Eq. (B4) is replaced by $n_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')$, the electron-electron repulsion part of ${}^{0}E_c^{\alpha,\beta}/\beta$ is obtained [see Eqs. (35) and (36); there $n_c([n];\mathbf{r},\mathbf{r}')=n_c^{1,1}([n];\mathbf{r},\mathbf{r}')$ and $\rho_c([n];\mathbf{r},\mathbf{r}')=\rho_c^{1,1}([n];\mathbf{r},\mathbf{r}')$].

In Refs. 10–15, it is shown that

$$\begin{aligned}&{}^{0}\Psi_{[n]}^{\alpha,\beta}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\\ &\quad=\left[\frac{\beta}{\alpha}\right]^{3N/2} {}^{0}\Psi_{[n_{\alpha/\beta}]}^{1,1}\left[\frac{\beta}{\alpha}\mathbf{r}_1,\frac{\beta}{\alpha}\mathbf{r}_2,\ldots,\frac{\beta}{\alpha}\mathbf{r}_N\right] , \quad \text{(B5)}\end{aligned}$$

with N being the number of electrons [$n_{\alpha/\beta}$ is defined according to Eq. (16)]. This leads to

$$n_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')=\left[\frac{\beta}{\alpha}\right]^3 n_c^{1,1}\left[[n_{\alpha/\beta}];\frac{\beta}{\alpha}\mathbf{r},\frac{\beta}{\alpha}\mathbf{r}'\right] , \quad \text{(B6)}$$

which reduces to Eq. (40) in Ref. 14 for $\alpha=1$.

From Eq. (B3) it follows that

$$\rho_c^{1,1}([n_{\alpha/\beta}];\mathbf{r},\mathbf{r}')=\int_0^1 d\omega\, n_c^{1,\omega}([n_{\alpha/\beta}];\mathbf{r},\mathbf{r}') \ , \quad \text{(B7)}$$

and with Eq. (B6),

$$\begin{aligned}&\left[\frac{\beta}{\alpha}\right]^3 \rho_c^{1,1}\left[[n_{\alpha/\beta}];\frac{\beta}{\alpha}\mathbf{r},\frac{\beta}{\alpha}\mathbf{r}'\right]\\ &\quad=\int_0^1 d\omega \left[\frac{\beta}{\alpha}\right]^3 n_c^{1,\omega}\left[[n_{\alpha/\beta}];\frac{\beta}{\alpha}\mathbf{r},\frac{\beta}{\alpha}\mathbf{r}'\right]\\ &\quad=\int_0^1 d\omega\, n_c^{\alpha,\beta\omega}([n];\mathbf{r},\mathbf{r}') \quad \text{(B8)}\\ &\quad=\frac{1}{\beta}\int_0^{\beta} d\beta'\, n_c^{\alpha,\beta'}([n];\mathbf{r},\mathbf{r}') \quad \text{(B9a)}\\ &\quad=\frac{1}{\beta}\rho_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}') \ . \quad \text{(B9b)}\end{aligned}$$

Equation (B9b) is the equivalent of Eq. (B6) for $\rho_c^{\alpha,\beta}$ instead of $n_c^{\alpha,\beta}$. Differentiation of Eq. (B9a) results in

$$\begin{aligned}&n_c^{\alpha,\beta}([n];\mathbf{r},\mathbf{r}')\\ &\quad=\left[1+\beta\frac{d}{d\beta}\right]\left[\frac{\beta^3}{\alpha}\right]\rho_c^{1,1}\left[[n_{\alpha/\beta}];\frac{\beta}{\alpha}\mathbf{r},\frac{\beta}{\alpha}\mathbf{r}'\right] , \quad \text{(B10)}\end{aligned}$$

which is identical to Eq. (38) for $\alpha=\beta=1$. Note that, for an approximate $\rho_c^{1,1}$, Eqs. (37) and (38) or (B10) give the same $n_c^{1,1}$ provided Eq. (B9b) holds for the approximate $\rho_c^{1,1}$. Again, an approximate $\rho_c^{\alpha,\beta}$ is obtained from a given approximate $\rho_c^{1,1}$ by replacing the inverse of the electron mass $(1/m_e)$ by (α/m_e) and the square of the electron charge (e^2) by (βe^2).

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