

Tight bound and convexity constraint on the exchange-correlation-energy functional in the low-density limit, and other formal tests of generalized-gradient approximations

Mel Levy

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

John P. Perdew

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

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For the purpose of approximating the exact density-functional exchange-correlation energy $E_{xc}[n]$, we previously established the coordinate scaling identity $E_{xc}^\alpha[n] = \alpha^2 E_{xc}[n_\lambda]$ for $\alpha = \lambda^{-1}$, or $E_{xc}^\lambda[n_\lambda] = \lambda^2 E_{xc}[n]$, where $E_{xc}^\alpha[n]$ is the exchange-correlation energy functional for electronic charge $\sqrt{\alpha}e$ and where $n_\lambda(x, y, z) = \lambda^3 n(\lambda x, \lambda y, \lambda z)$. This identity is utilized here to derive the low-density limit $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle - (e^2/2) \int \int [n(\mathbf{r}_1)n(\mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|] d^3r_1 d^3r_2$, which allows us to express the Lieb-Oxford bound in the tightest-possible manner, namely, $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] \geq -C e^2 \int n^{4/3}(\mathbf{r}) d^3r$, where $1.43 \leq C \leq 1.68$. Meaningful adherences to and violations of the bound are presented to demonstrate that it is surprisingly tight and thus quite useful. Other key properties of $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda]$ are found, including the observation that $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] + (e^2/2) \int \int [n(\mathbf{r}_1)n(\mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|] d^3r_1 d^2r_2$ is *convex*, which is a severe constraint. We discuss these and other exact relationships as formal tests of generalized-gradient approximations (GGA's) for exchange and correlation. We find that the Perdew-Wang 1991 (PW91) GGA respects many of the known exact relationships, including those respected by the local-density approximation plus many others that are violated by the local-density approximation. We present a minor variant of the PW91 correlation-energy functional which additionally satisfies a strong $\lambda \rightarrow \infty$ (high-density) constraint. Finally, we show that atomic densities are much closer to the high-density than to the low-density limit.

I. INTRODUCTION

According to density-functional theory, the ground-state electronic energy $E_{g.s.}$ is given by

$$E_{g.s.} = \min_n \left\{ \int v(\mathbf{r})n(\mathbf{r})d^3r + T_s[n] + U[n] + E_{xc}[n] \right\}, \tag{1}$$

where $v(\mathbf{r})$ is the external potential (electron-nuclear attraction operator in Coulomb systems), $T_s[n]$ is the noninteracting kinetic energy, $U[n]$ is the classical electron-electron repulsion energy, and $E_{xc}[n]$ is the exchange-correlation energy. In other words

$$U[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_1 d^3r_2, \tag{2}$$

$$T_s[n] = \langle \Psi_n^0 | \hat{T} | \Psi_n^0 \rangle, \tag{3}$$

$$E_{xc}^\alpha[n] = \langle \Psi_n^\alpha | \hat{T} + \alpha \hat{V}_{ee} | \Psi_n^\alpha \rangle - \alpha U[n] - T_s[n], \tag{4}$$

so that

$$E_{xc}[n] = E_{xc}^1[n], \tag{5}$$

where, in atomic units,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad \hat{V}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N |\mathbf{r}_i - \mathbf{r}_j|^{-1},$$

and where α is a *coupling constant*. Consistent with the constrained-search orientation (see, for instance, Refs. 1-3 for reviews), Ψ_n^α is that antisymmetric wave function which yields n and minimizes $\langle \hat{T} + \alpha \hat{V}_{ee} \rangle$, or minimizes $\langle \alpha^{-1} \hat{T} + \hat{V}_{ee} \rangle$. Consequently, Ψ_n^1 is the original Hohenberg-Kohn⁴ wave function when Ψ_n^1 is the nondegenerate ground state of some interacting Hamiltonian, and Ψ_n^0 is the original Kohn-Sham⁵ single determinant when Ψ_n^0 is the nondegenerate ground state of some noninteracting Hamiltonian.

It is $E_{xc}[n]$ that must be approximated when one performs Kohn-Sham calculations, because $T_s[n]$ may often be evaluated explicitly in terms of the Kohn-Sham orbitals. In order to approximate E_{xc} , one usually invokes various equalities and inequalities which are satisfied by the exact E_{xc} . With this in mind, it is a main purpose of this paper to express the Lieb-Oxford⁶ bound in terms of E_{xc} in the tightest-possible manner by utilizing the following scaling identity of Levy and Perdew⁷ and Yang:⁸

$$E_{xc}^\alpha[n] = \alpha^2 E_{xc}[n_\lambda]; \quad \alpha = \lambda^{-1} \tag{6a}$$

or

$$E_{xc}^\lambda[n_\lambda] = \lambda^2 E_{xc}[n], \tag{6b}$$

where

$$n_\lambda(x, y, z) = \lambda^3 n(\lambda x, \lambda y, \lambda z). \tag{7}$$

Lieb and Oxford⁶ proved that there exists a universal

positive constant C , $C \leq 1.68$, such that

$$\inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle - U[n] \geq -C \int n^{4/3}(\mathbf{r}) d^3r, \quad (8)$$

where ‘‘inf’’ is the infimum or greatest lower bound. The optimum bounding constant C is unaffected by restrictions on the spin or statistics of the wave function Ψ , but can be reduced by restricting the particle number. In any case, the Ψ 's shall be made antisymmetric for the remainder of the paper to allow us to connect Eq. (8) with E_{xc} as defined in Eqs. (4) and (5). Recently, by employing results for a uniform electron gas in its low-density limit, Perdew⁹ has shown that $C \geq 1.43$, which means that Eq. (8) is capable of providing tight bounds for density functionals. Accordingly, in the next section we shall prove that the low-density limit for a nonuniform $n(\mathbf{r})$ is

$$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle - U[n], \quad (9)$$

so that

$$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] \geq -C \int n^{4/3}(\mathbf{r}) d^3r. \quad (10)$$

As an indication of the power of this bound, we note that it is violated by the random-phase approximation for the uniform electron gas.¹⁰ Previously, Perdew and Wang^{9,11} (PW91) were the first to actually utilize the Lieb-Oxford bound, Eq. (8), to help approximate E_{xc} . The PW91 approximation to E_{xc} has been constructed to satisfy

$$E_{xc}[n] \geq -C \int n^{4/3} d^3r. \quad (11)$$

Perdew⁹ arrived at Eq. (11) by implicitly utilizing

$$\langle \Psi_n^1 | \hat{V}_{ee} | \Psi_n^1 \rangle \geq \inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle \quad (12)$$

and

$$E_{xc}[n] \geq \langle \Psi_n^1 | \hat{V}_{ee} | \Psi_n^1 \rangle - U[n]. \quad (13)$$

The latter inequality arises from Eq. (4) plus the fact that

$$\langle \Psi_n^1 | \hat{T} | \Psi_n^1 \rangle \geq \langle \Psi_n^0 | \hat{T} | \Psi_n^0 \rangle. \quad (14)$$

For a given n , Eq. (10) is even tighter than Eq. (11) because Eqs. (9) and (13) dictate that

$$E_{xc}[n] \geq \lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda], \quad (15)$$

which also follows from Eq. (115) in Ref. 12:

$$E_{xc}[n] \geq \lambda^{-1} E_{xc}[n_\lambda]; \quad \lambda \leq 1. \quad (16)$$

In fact, for a given n , Eq. (9) dictates that $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda]$ is the *most negative* meaningful number that may be used for the left-hand side of the Lieb-Oxford bound for the case of fermion pure states. (Generalization to ensembles shall be discussed later.) However, it is important to note that if an approximate E_{xc} satisfies Eq. (11) for *all* n , then this approximate E_{xc} automatically satisfies Eq. (10).

II. THEORY

We start with Eq. (6) which implies

$$\lim_{\lambda \rightarrow 0} \lambda E_{xc}^\alpha[n] = \lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda]. \quad (17)$$

Next, note that Eq. (4) gives

$$\lim_{\lambda \rightarrow 0} \lambda E_{xc}^\alpha[n] = \lim_{\alpha \rightarrow \infty} \langle \Psi_n^\alpha | \hat{V}_{ee} | \Psi_n^\alpha \rangle - U[n], \quad (18)$$

and observe that

$$\lim_{\alpha \rightarrow \infty} \langle \Psi_n^\alpha | \hat{V}_{ee} | \Psi_n^\alpha \rangle = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle, \quad (19)$$

because, by definition, Ψ_n^∞ yields n and minimizes $\lim_{\alpha \rightarrow \infty} \langle \alpha^{-1} \hat{T} + \hat{V}_{ee} \rangle$. Finally, Eq. (9) follows from a combination of Eqs. (17)–(19). Note that we have employed the fact that

$$\lim_{\alpha \rightarrow \infty} \alpha^{-1} [\langle \Psi_n^\alpha | \hat{T} | \Psi_n^\alpha \rangle - \langle \Psi_n^0 | \hat{T} | \Psi_n^0 \rangle] = 0$$

which, in turn, follows from^{12,13}

$$\alpha^{-1} [\langle \Psi_n^\alpha | \hat{T} | \Psi_n^\alpha \rangle - \langle \Psi_n^0 | \hat{T} | \Psi_n^0 \rangle] = \frac{\partial E_{xc}[n_\lambda]}{\partial \lambda} - \lambda^{-1} E_{xc}[n_\lambda]$$

and from the fact that $E_{xc}[n_\lambda]$ goes¹³ linearly in λ as $\lambda \rightarrow 0$.

Earlier, we deduced⁷ Eq. (6) from $U[n_\lambda] = \lambda U[n]$, $T_s[n_\lambda] = \lambda^2 T_s[n]$, and from the observation¹² that $\beta^{3N/2} \Psi_n^\gamma(\beta \mathbf{r}_1 \cdots \beta \mathbf{r}_N)$ yields $n_\beta(x, y, z) = \beta^3 n(\beta x, \beta y, \beta z)$ and minimizes $\langle \hat{T} + \gamma \beta \hat{V}_{ee} \rangle$. In this connection, see also the related work in Ref. 14.

We now present additional key properties of $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda]$. First, notice that the definition of the functionals in this paper may be directly generalized to include ensemble constrained searches,^{1–3,15} as first reported by Valone.¹⁵ In fact, Lieb² has noted that the ensemble search version of $\inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$ is convex. This means that with

$$A[n] = \lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] + U[n], \quad (20)$$

we have

$$A[d_1 n_1 + d_2 n_2] \leq d_1 A[n_1] + d_2 A[n_2], \quad (21a)$$

where $\sum_{i=1}^2 d_i = 1$ and $d_i \geq 0$, or

$$\left. \frac{\partial^2 A[n + \varepsilon \Delta n]}{\partial \varepsilon^2} \right|_{\varepsilon=0} \geq 0, \quad (21b)$$

or

$$\iint \left[\frac{\delta^2 A[n]}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} \right] \Delta n(\mathbf{r}_1) \Delta n(\mathbf{r}_2) d^3r_1 d^3r_2 \geq 0, \quad (21c)$$

for arbitrarily Δn such that $\int \Delta n(\mathbf{r}) d^3r = 0$.

Observe that expression (21b) follows directly from the *minimization* in Eq. (1) when n_λ is the ground-state density of some external potential $v_\lambda(\mathbf{r})$, as $\lambda \rightarrow 0$. The minimizing property of n_λ then implies that

$$\frac{\partial^2}{\partial \varepsilon^2} \lim_{\lambda \rightarrow 0} \lambda^{-1} \left\{ \int v_\lambda(\mathbf{r}) g_\lambda^\varepsilon(\mathbf{r}) d^3r + T_s[g_\lambda^\varepsilon] + U[g_\lambda^\varepsilon] + E_{xc}[g_\lambda^\varepsilon] \right\} \geq 0$$

about $\varepsilon=0$, where $g_\lambda^\varepsilon = n_\lambda + \varepsilon \Delta n_\lambda$. Expression (21b) results because the integral involving v_λ vanishes due to the fact that the integral is linear in ε , because $\lim_{\lambda \rightarrow 0} \lambda^{-1} T_s[g_\lambda^\varepsilon] = 0$, and because

$$A[n + \varepsilon \Delta n] = \lim_{\lambda \rightarrow 0} \lambda^{-1} \{ U[g_\lambda^\varepsilon] + E_{xc}[g_\lambda^\varepsilon] \} .$$

Valone¹⁶ has very recently investigated approximations to the right-hand side of Eq. (9) by using constrained searches involving second-order density matrices (or pair-correlation functions). With this in mind, observe that Eq. (9) implies

$$A[n] = \inf_{\Gamma \rightarrow n} \int \Gamma(\mathbf{r}_1 \mathbf{r}_2 | \mathbf{r}_1 \mathbf{r}_2) r_{12}^{-1} d^3 r_1 d^3 r_2 , \quad (22)$$

so that $A[n]$ is bounded from above through

$$A[n] \leq \int \Gamma(\mathbf{r}_1 \mathbf{r}_2 | \mathbf{r}_1 \mathbf{r}_2) r_{12}^{-1} d^3 r_1 d^3 r_2 , \quad (23)$$

where $\Gamma(\mathbf{r}_1 \mathbf{r}_2 | \mathbf{r}_1 \mathbf{r}_2)$ is the diagonal part of any N -representable second-order reduced density matrix which is defined by

$$\begin{aligned} \Gamma(\mathbf{r}_1 \mathbf{r}_2 | \mathbf{r}_1 \mathbf{r}_2) &= \frac{N(N-1)}{2} \int \Psi(x_1 \cdots x_N)^* \Psi(x_1 \cdots x_N) \\ &\quad \times d^3 r_3 \cdots d^3 r_N ds_1 \cdots ds_N , \end{aligned} \quad (24)$$

and where Ψ is any antisymmetric wave function such that

$$n(\mathbf{r}) = \frac{2}{(N-1)} \int \Gamma(\mathbf{r} \mathbf{r}_2 | \mathbf{r} \mathbf{r}_2) d^3 r_2 . \quad (25)$$

Incidentally, we already know the identity

$$\langle \Psi_n^1 | \hat{V}_{ee} | \Psi_n^1 \rangle = U[n] + 2E_{xc}[n] - \left[\frac{\partial E_{xc}[n_\lambda]}{\partial \lambda} \right]_{\lambda=1} \quad (26)$$

from equations in previous works.¹²

The following are unusual properties of $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda]$ because multiple asymptotic scalings are involved. Let us first define $B[n]$ by

$$B[n] = \lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] . \quad (27)$$

Then, by Eq. (9) it follows that

$$B[n] \geq -\frac{1}{2} \int n(\mathbf{r}_1) n(\mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} d^3 r_1 d^3 r_2 \quad (28)$$

which means

$$\lim_{\lambda \rightarrow 0} B[n_\lambda^x] \geq -\frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2) d^3 r_1 d^3 r_2}{[(y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}} > -\infty \quad (29)$$

and

$$\begin{aligned} \lim_{\lambda \rightarrow 0} \lambda^{-1} B[n_\lambda^{xy}] &\geq -\frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2) d^3 r_1 d^3 r_2}{[(x_1 - x_2)^2 + (y_1 - y_2)^2]^{1/2}} \\ &> -\infty , \end{aligned} \quad (30)$$

where $n_\lambda^x(x, y, z) = \lambda n(\lambda x, y, z)$ and $n_\lambda^{xy}(x, y, z) = \lambda^2 n(\lambda x, \lambda y, z)$ are nonuniformly scaled densities. (See Refs. 9, 11, 13, and 17–21 for presentations of and utilizations of the properties of n_λ^x and n_λ^{xy} .)

III. DISCUSSION

The relationships presented in this paper are meant to serve as vehicles to help in the continuing evolution of ever more accurate approximate exchange-correlation functionals. With this in mind, Sec. IV is devoted to a discussion of generalized-gradient approximations (GGA's). It has already been noted^{9,11} that Eq. (11) is satisfied by the 1991 GGA of Perdew and Wang (PW91),¹¹ but violated^{9,11} by their 1986 GGA functional^{22,23} as well as by the exchange functional of Becke.²⁴ Equation (11) is always satisfied by the local-density approximation for E_{xc} , but is not always satisfied by the local-density approximation for correlation plus the exact exchange.

Equation (10) offers the quickest mechanism for the testing of Eq. (11) with approximations to E_{xc} because many terms of E_{xc} are eliminated by simple inspection when $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda]$ is taken.

Conditions (29) and (30) are violated by many present approximations to E_{xc} (e.g., the local-density approximation and most GGA's), because the approximations tend to become $-\infty$ in the two limiting situations. However, the right-most inequalities are respected by PW91.

Just as $T_s[n]$ is the constrained minimization of just $\langle \hat{T} \rangle$, we have here identified $\lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}[n_\lambda] + U[n]$ as the constrained minimization of just $\langle \hat{V}_{ee} \rangle$. In fact, Eq. (23), which utilizes any antisymmetric wave function, is the first bound to our knowledge connecting $\langle \hat{V}_{ee} \rangle$ for any arbitrary antisymmetric wave function (or pair-correlation function) and a component of $E_{xc}[n]$. In contrast, the equality in Eq. (26), although also useful, requires knowledge of the exact ground-state wave function for the given n .

The requirement that $A[n]$ is convex, Eq. (21), appears to be a reasonably severe constraint upon approximations to E_{xc} . For instance, the local-density approximation (LDA) for $A[n]$, $A^{\text{LDA}}[n]$, does not satisfy the constraint because of the negative sign in

$$\begin{aligned} \frac{\partial^2 A^{\text{LDA}}[n + \varepsilon \Delta n]}{\partial \varepsilon^2} \Big|_{\varepsilon=0} &= -\frac{4|c|}{9} \int d^3 r n^{-2/3}(\mathbf{r}) \Delta n(\mathbf{r})^2 \\ &\quad + \int \int \frac{\Delta n(\mathbf{r}_1) \Delta n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \times d^3 r_1 d^3 r_2 , \end{aligned} \quad (31)$$

where c is a constant. [In fact, the first term actually diverges to $-\infty$ with all $\Delta n(\mathbf{r})^2$ which vanish more slowly than $n^{2/3}(\mathbf{r})$ as $|\mathbf{r}| \rightarrow \infty$.] The above expression is obtained by inserting

$$A^{\text{LDA}}[n] = -|c| \int d^3 r n^{4/3}(\mathbf{r}) + U[n] \quad (32)$$

into Eq. (21b). [Note, by the way, that $-\int n^{4/3}(\mathbf{r}) d^3 r$ is all that remains in the $\lambda \rightarrow 0$ limit of the local-density ap-

proximation for correlation as well as for exchange.] Similarly, any approximate exchange-correlation functional which contains a $-\int d^3r n^{4/3}(\mathbf{r})$ component, including the PW91 GGA, is not likely to satisfy condition (21). [For example, the spin-density functional versions of LDA and PW91 GGA do not satisfy condition (21a) for the one-electron densities $n_1(r)=e^{-2r}/\pi$ and $n_2(r)=(1+2r)e^{-2r}/4\pi$.]

Equation (6) itself provides an important constraint upon approximations to E_{xc} . With this in mind, it was previously asserted by Levy and Perdew⁷ that both the exchange and correlation components of E_{xc} satisfy an equation analogous to Eq. (6). Namely,

$$E_x^\alpha[n]=\alpha^2 E_x[n_\lambda] \quad (33)$$

and

$$E_c^\alpha[n]=\alpha^2 E_c[n_\lambda] \quad (34)$$

where again $\alpha=\lambda^{-1}$, and where

$$E_x^\alpha[n]=\langle \Psi_n^0 | \alpha \hat{V}_{ee} | \Psi_n^\alpha \rangle \quad (35)$$

and

$$E_c^\alpha[n]=\langle \Psi_n^\alpha | \hat{T} + \alpha \hat{V}_{ee} | \Psi_n^\alpha \rangle - \langle \Psi_n^0 | \hat{T} + \alpha \hat{V}_{ee} | \Psi_n^0 \rangle. \quad (36)$$

(Note that $E_x[n]$ and $E_c[n]$ may be projected¹³ from E_{xc} by $E_x[n]=\lim_{\lambda \rightarrow \infty} \lambda^{-1} E_{xc}[n_\lambda]$ and $E_c[n]=E_{xc}[n] - \lim_{\lambda \rightarrow \infty} \lambda^{-1} E_{xc}[n_\lambda]$.) Both LDA and PW91 obey Eq. (34).

Key conditions result from expression (36) in combination with the fact that Ψ_n^α is defined to minimize $\langle \hat{T} + \alpha \hat{V}_{ee} \rangle$. Namely, for $\alpha \geq 0$,

$$\frac{\partial E_c^\alpha[n]}{\partial \alpha} = \langle \Psi_n^\alpha | \hat{V}_{ee} | \Psi_n^\alpha \rangle - \langle \Psi_n^0 | \hat{V}_{ee} | \Psi_n^0 \rangle \leq 0, \quad (37)$$

$$\frac{\partial^2 E_c^\alpha[n]}{\partial \alpha^2} = \frac{\partial}{\partial \alpha} \langle \Psi_n^\alpha | \hat{V}_{ee} | \Psi_n^\alpha \rangle \leq 0, \quad (38)$$

where the right-hand inequalities in both expressions were previously noted.¹² We utilize here expression (34) for $E_c^\alpha[n]$ to now transform Eqs. (37) and (38) into forms which are usable as conditions for testing approximate functionals. Namely,

$$2E_c[n_\lambda] - \lambda \frac{\partial E_c[n_\lambda]}{\partial \lambda} \leq 0 \quad (39)$$

and

$$2E_c[n_\lambda] - 2\lambda \frac{\partial E_c[n_\lambda]}{\partial \lambda} + \lambda^2 \frac{\partial^2 E_c[n_\lambda]}{\partial \lambda^2} \leq 0. \quad (40)$$

Equations (39) and (40) also follow from combination of expressions (74), (75), and (80) in Ref. 13.

IV. FORMAL TESTS OF GENERALIZED-GRADIENT APPROXIMATIONS

Generalized-gradient approximations^{9,11,22-26} (GGA's) are perhaps the most accurate of the current density functionals for exchange and correlation, although GGA energies are typically more satisfactory than GGA potentials.²⁷ GGA improvement over the local-density ap-

proximation is striking in chemical applications,^{28,29} but somewhat mixed in solid-state applications.^{30,31} Well-constructed GGA's reduce in the slowly varying limit to the familiar gradient expansion, whose leading term is the local-density approximation. Here, we investigate the implications of our formal results for GGA's. We display the GGA dependence on the fundamental constants e^2 , \hbar , and m , which did not appear in previous sections because of the use of atomic units. More generally, we present a compendium of relationships satisfied by the exact exchange-correlation energy $E_{xc}[n]$, and test various approximations (local spin density, gradient expansion, GGA) against those relationships.

The GGA for exchange is^{23,24}

$$E_x^{\text{GGA}}[n] = -De^2 \int d^3r n^{4/3} F_x(s), \quad (41)$$

where

$$s = |\nabla n| / 2k_F n, \quad (42)$$

$$k_F = (3\pi^2 n)^{1/3}, \quad (43)$$

$$D = \frac{3}{4\pi} (3\pi^2)^{1/3} = 0.7386, \quad (44)$$

and e is the electronic charge. The characteristic inverse length for exchange is the local Fermi wave vector k_F . Under uniform scaling which transforms $n(\mathbf{r})$ into $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda\mathbf{r})$, the reduced density gradient $s(\mathbf{r})$ is transformed into $s(\lambda\mathbf{r})$. Thus, the exact scaling property¹²

$$E_x[n_\lambda] = \lambda E_x[n] \quad (45)$$

is obeyed, as is Eq. (31). [A spin-density-functional extension^{9,11,32} is achieved by allowing F_x to depend upon the local polarization $\zeta = (n_\uparrow - n_\downarrow)/n$, where $n = n_\uparrow + n_\downarrow$. Since $\zeta(\mathbf{r})$ scales uniformly to $\zeta(\lambda\mathbf{r})$, this extension poses no formal problem and will not be discussed further here.]

$F_x(s)$ is an enhancement factor with respect to local exchange. The condition $E_x \leq 0$ will be satisfied if

$$F_x \geq 0. \quad (46)$$

In the slowly varying limit ($s \rightarrow 0$), F_x has the gradient expansion³³

$$F_x(s) = 1 + 0.1234s^2 + O(s^4). \quad (47)$$

The dimensionally correct GGA for correlation is

$$E_c^{\text{GGA}}[n] = \frac{e^2}{a_0} \int d^3r n h(na_0^3, s), \quad (48)$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius. Equation (48) may be recast as

$$E_c^{\text{GGA}}[n] = -De^2 \int d^3r n^{4/3} F_c(na_0^3, s), \quad (49)$$

where $F_c = -D^{-1}(na_0^3)^{-1/3}h$. Equation (49) obviously obeys Eq. (34). Equation (16) will be obeyed if

$$F_c(\lambda^3 na_0^3, s) \geq F_c(na_0^3, s) \quad (\lambda \leq 1). \quad (50)$$

The exact condition $E_c \leq 0$ will be satisfied if

$$F_c \geq 0 . \quad (51)$$

The exact relationship¹³

$$\lim_{\lambda \rightarrow \infty} \lambda^{-1} E_{xc}[n_\lambda] = E_x[n] \quad (52)$$

implies that

$$\lim_{\lambda \rightarrow \infty} F_c(\lambda^3 n a_0^3, s) = 0 . \quad (53)$$

The stronger condition¹³

$$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda] = \text{constant} \quad (54)$$

implies that

$$\lim_{\lambda \rightarrow \infty} h(\lambda^3 n a_0^3, s) > -\infty (s \neq 0) . \quad (55)$$

Equation (55) ensures that the correlation energy is of order e^4 when $e^2 \rightarrow 0$, as the nondegenerate perturbation theory requires for many densities. (In this connection, see the recent work of Görling and Levy²¹ which evaluates the coefficient. See also Perdew's private communication in Ref. 34.)

In the slowly varying limit ($s \rightarrow 0$), F_c has the gradient expansion³⁵

$$F_c(n a_0^3, s) = F_c(n a_0^3, 0) - 51.83 [\tilde{C}(n a_0^3) + 0.000714] s^2 + O(s^4) , \quad (56)$$

where

$$F_c(n a_0^3, 0) = \frac{\epsilon_c}{\epsilon_x} = \frac{e^2}{a_0} \frac{h(n a_0^3, 0)}{-e^2 D n^{1/3}} \quad (57)$$

is the ratio of correlation to exchange energy per particle in a uniform electron gas. This ratio varies from 0 in the high-density limit ($n a_0^3 \rightarrow \infty$) to 0.93 in the low-density limit ($n a_0^3 \rightarrow 0$).³⁶ The $n a_0^3$ dependence of \tilde{C} has been given by Rasolt and Geldart;³⁷ it makes the coefficient of the s^2 term in Eq. (56) vary from -0.2565 in the high-density limit to -0.1234 in the low-density limit.

Now consider exchange and correlation together,

$$E_{xc}^{\text{GGA}}[n] = -D e^2 \int d^3 r n^{4/3} F_{xc}(n a_0^3, s) , \quad (58)$$

where

$$F_{xc}(n a_0^3, s) = F_x(s) + F_c(n a_0^3, s) . \quad (59)$$

We find that the low-density limit of E_{xc}^{GGA} is

$$B^{\text{GGA}}[n] = \lim_{\lambda \rightarrow 0} \lambda^{-1} E_{xc}^{\text{GGA}}[n_\lambda] = -D e^2 \int d^3 r n^{4/3} F_{xc}(0, s) . \quad (60)$$

The bound of Eq. (10) will be satisfied if

$$F_{xc}(0, s) \leq C/D . \quad (61)$$

The optimum bounding constant C is less than 1.68, so the optimum C/D is less than 2.27. From the uniform electron gas in the low-density limit,³⁶ we learn that the

optimum C/D is greater than or equal to 1.93; we conjecture that this is, in fact, the optimum value.

It is easy to construct a density for which s is arbitrarily large almost everywhere. An example is the ground-state density for one electron bound by a potential which is fixed and periodic inside a large volume Ω , and vanishes outside. For this density, $s \sim \Omega^{1/3}$ diverges as $\Omega \rightarrow \infty$. Thus, the $s \rightarrow \infty$ of Eq. (61) is a *necessary* condition for a GGA to satisfy Eq. (11) for all densities, as well as a sufficient one.

Now consider the nonuniform scalings of Eqs. (29) and (30). Under one-dimensional scaling ($n \rightarrow n_\lambda^x$ and $\lambda \rightarrow \infty$), $s \propto \lambda^{2/3}$. Under two-dimensional scaling ($n \rightarrow n_\lambda^y$ and $\lambda \rightarrow 0$), $s \propto \lambda^{-2/3}$. Thus, Eqs. (29) and (30) will be satisfied if

$$\lim_{s \rightarrow \infty} s^{1/2} F_{xc}(n a_0^3, s) < \infty . \quad (62)$$

Perdew and Wang 1991 (Ref. 11) have developed a GGA based upon real-space cutoff of the spurious long-range components of the gradient expansion for the exchange-correlation hole. PW91 (after modifying the small Gaussian term as in Appendix A) satisfies all the exact conditions set forth in this section, with the exception of Eq. (54). [Also, as stated in the previous section, PW91 does not satisfy Eq. (21).] In Appendix A, we show that the original PW91 functional almost satisfies Eq. (54), and may be made to satisfy this limit exactly by a minor modification. This is an important indicator that the real-space cutoff method used to construct PW91 is correct.

Figure 1 displays the PW91 enhancement factor

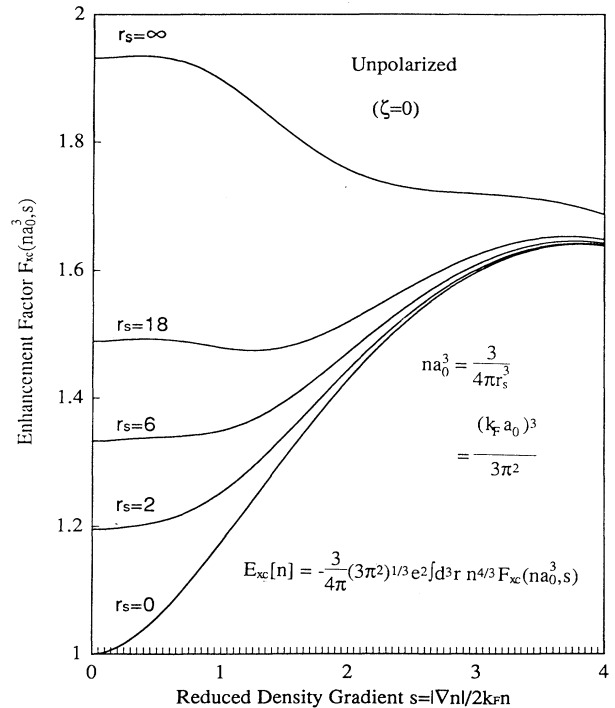


FIG. 1. The enhancement factor of Eq. (58) for the PW91 generalized-gradient approximation, for several values of r_s , Eq. (63). The nonlocality of the functional is borne by the s dependence of each curve.

$F_{xc}(na_0^3, s)$ for several values of

$$r_s = \left[\frac{3}{4\pi na_0^3} \right]^{1/3}. \quad (63)$$

The high- and low-density limits correspond to $r_s \rightarrow 0$ ($n \rightarrow \infty, \lambda \rightarrow \infty$, or $e^2 \rightarrow 0$) and $r_s \rightarrow \infty$ ($n \rightarrow 0, \lambda \rightarrow 0$, or $e^2 \rightarrow \infty$), respectively. Typical valence-electron densities fall in the range $1 < r_s < 6$. On the scale of Fig. 1, the difference between the original PW91 functional and the variant of Appendix A cannot be distinguished. The condition of Eq. (61) is clearly respected. The condition of Eq. (50) is also satisfied, since the curves of Fig. 1 do not cross. Early tests of PW91 for atoms, molecules, solids, and surfaces³² indicate close agreement with experiment. In Appendix B, we apply PW91 to study the instabilities of the low-density uniform electron gas.

The local-density approximation $F_{xc}(na_0^3, s) \rightarrow F_{xc}(na_0^3, 0)$ replaces the curves of Fig. 1 by horizontal straight lines. It satisfies all the conditions of this section except Eqs. (47), (55), (56), and (62). The second-order gradient expansion $F_{xc}(na_0^3, s) \rightarrow F_{xc}(na_0^3, 0) + \frac{1}{2}F''_{xc}(na_0^3, 0)s^2$ replaces the curves of Fig. 1 by downward-turning parabolas. It violates several exact conditions, most importantly Eqs. (51) and (53).

Earlier GGA's were constructed by Langreth and Mehl²⁶ (LM), Perdew and Wang 1986 (PW86),^{22,23} and Becke.²⁴ These GGA's violate a number of exact conditions. In particular, we note that LM and PW86 violate Eqs. (50) and (51), while all three of these earlier GGA's violate Eqs. (55), (61), and (62). The GGA of Lee, Yang, and Parr²⁵ satisfies Eq. (55).

Conditions (39) and (40) will be satisfied by a GGA [Eq. (49)] if the appropriate integrands are everywhere negative, i.e., if, respectively,

$$[1 + r_s \partial / \partial r_s] F_c(3/4\pi r_s^3, s) \geq 0, \quad (39')$$

$$[2r_s \partial / \partial r_s + r_s^2 \partial^2 / \partial r_s^2] F_c(3/4\pi r_s^3, s) \geq 0, \quad (40')$$

for all $r_s \geq 0$ and $s \geq 0$. Conditions (39') and (40') are satisfied by the local-density approximation and by both versions of PW91, but not by the second-order gradient expansion. In fact, condition (39') will be satisfied by any GGA obeying Eqs. (50) and (51).

Other exact conditions²⁰ that the PW91 GGA respects naturally (from the real-space cutoff, without additional

constraint) are

$$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[n_{\lambda}^x] = 0, \quad (64)$$

$$\lim_{\lambda \rightarrow \infty} E_c[n_{\lambda\lambda}^{xy}] = 0, \quad (65)$$

$$\lim_{\lambda \rightarrow \infty} E_c[n_{\lambda}^x] = 0, \quad (66)$$

$$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[n_{\lambda\lambda}^{xy}] = 0. \quad (67)$$

The first two exact limits are derived²⁰ with the help of a Taylor expansion of E_c in powers of e^2 . The last two limits are derived without this assumption. Note that the local-density approximation yields $-\infty$ for the limits (64)–(67) and that of the GGA's mentioned in this paper, only PW91 and its variant in Appendix A satisfy conditions (64)–(67).

Geldart and Rasolt³⁸ assert that the second-order gradient expansion for exchange and correlation should be valid for extended systems with $s = |\nabla n|/2k_F n \ll 1$ and $|\nabla^2 n|/2k_F |\nabla n| \ll 1$. But, we shall show that another necessary condition is $t \ll 1$, where t is defined after Eq. (A5). Consider the density

$$n(x, y, z) = \bar{n} [1 + A \cos(Qx)], \quad (68)$$

where $Q = B(2\bar{k}_F)$. Here, $\bar{n} = \bar{k}_F^3/3\pi^2$, and A and B are constants, with $|A| < 1$ and $|B| \ll 1$. When this density is scaled uniformly to the high-density limit [$n(\mathbf{r}) \rightarrow \lambda^3 n(\lambda \mathbf{r})$ and $\lambda \rightarrow \infty$], the correlation energy per electron tends to $-\infty$ as $-\ln \lambda$ in the local-density approximation. But in the gradient expansion, it tends to $+\infty$ as λ ; this unphysical result is found because $t \rightarrow \infty$ as $\lambda^{1/2}$. In the modified PW91 GGA of Appendix A, the correlation energy per electron more correctly tends to a negative constant when $\lambda \rightarrow \infty$.

V. ATOMIC DENSITIES SCALED TO THE HIGH- AND LOW-DENSITY LIMITS

For an atom, the reduced gradient s takes all values greater than about 0.2 and diverges into the surrounding vacuum. However, the interior of the atom, which dominates its total energy, has $s \lesssim 1$. Since the PW91 curves of Fig. 1 “go flat” for $s \lesssim 1$ in the low-density limit $r_s \rightarrow \infty$, the PW91 functional becomes rather “local” in this limit. In Table I, we show PW91 values for $E_x[n]$, $E_{xc}[n]$, and $B[n]$ [Eq. (27)], evaluated for the densities³⁹ of the rare-gas atoms. We also show the ratio

TABLE I. GGA values for the exchange-correlation energy $E_{xc}[n]$, its high-density limit $E_x[n]$ of Eq. (52), and its low-density limit $B[n]$ of Eq. (27), for Hartree-Fock densities of the rare-gas atoms. Also shown is the ratio $B[n]/E_x^{\text{LDA}}[n]$, where $E_x^{\text{LDA}}[n]$ is the local-density approximation for exchange. Estimated percent errors are shown in parentheses. The GGA is the modified PW91 functional of Appendix A; the original PW91 GGA gives the same $E_x[n]$ and $B[n]$, but slightly different $E_{xc}[n]$ for these atoms (given in hartrees).

Atom	$E_x[n]$		$E_{xc}[n]$		$B[n]$	B/E_x^{LDA}
He	-1.017	(-0.9%)	-1.059	(-0.8%)	-1.680	1.900
Ne	-12.115	(0.1%)	-12.466	(-0.3%)	-21.188	1.920
Ar	-30.123	(-0.2%)	-30.830	(-0.5%)	-53.657	1.926
Kr	-93.831	(-0.1%)	-95.598		-171.137	1.931
Xe	-178.986	(-0.1%)	-181.904		-329.599	1.932

$B[n]/E_x^{\text{LDA}}[n]$, where E_x^{LDA} is the local-density approximation for the exchange energy. This ratio in PW91 is always very close to its LDA value, 1.93, which in turn is our conjectured upper bound.

We think it is fair to conclude that $B[n]/E_x^{\text{LDA}}[n]$ is considerably greater than 1 for atomic densities, although neither LDA nor PW91 is necessarily trustworthy in the low-density limit. For an exponential or Gaussian one-electron density, where the exact $E_{xc}[n]$ cancels the spurious self-interaction $U[n]$, we find the exact result

$$B[n]/E_x^{\text{LDA}}[n] = 1.47 \quad (N=1), \quad (69)$$

which is smaller than our PW91 value (1.88) but still somewhat greater than 1. [Note that PW91 thus violates Eq. (28), and an appeal to spin-density-functional theory

cannot help since E_{xc} becomes nearly independent of polarization ξ in the low-density limit.] Because $E_{xc}[n]$ for atomic densities is always closer to $E_x[n]$ of Eq. (52) than to $B[n]$ of Eq. (27) (Table I), atoms are closer to the high- than to the low-density limit, as expected intuitively.⁴⁰

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APPENDIX A: PW91 GENERALIZED-GRADIENT APPROXIMATION

The exchange energy functional has the form of Eq. (41), with

$$F_x(s) = \frac{1 + 0.19645s \sinh^{-1}(7.7956s) + (0.2743 - 0.1508e^{-100s^2})s^2}{1 + 0.19645s \sinh^{-1}(7.7956s) + 0.004s^4}. \quad (A1)$$

Equation (A1) is a modification of Becke's²⁴ analytic form for $F_x(s)$.

The correlation-energy functional has the form of Eq. (48), with

$$h(na_0^3, s) = \varepsilon_c(r_s) + h_{nl}(r_s, s). \quad (A2)$$

$\varepsilon_c(r_s)$ is the correlation energy per electron of a uniform electron gas,^{11,41} expressed in units where $e^2 = a_0 = 1$. It has the high- and low-density limits^{36,41}

$$\varepsilon_c(r_s) \approx 0.03109 \ln r_s \quad (r_s \ll 1) \quad (A3)$$

$$\varepsilon_c(r_s) \approx -\frac{0.4269}{r_s} \quad (r_s \gg 1). \quad (A4)$$

The nonlocal contribution to h is

$$h_{nl}(r_s, s) = \frac{\beta^2}{2\alpha} \ln \left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2t^4} \right] + \nu [C_c(r_s) - 0.003521] t^2 e^{-100s^2/\beta(r_s)}. \quad (A5)$$

Here $t = |\nabla n|/2k_s n$, $k_s = (4k_F/\pi a_0)^{1/2}$, $\nu = (16/\pi) \times (3\pi^2)^{1/3}$, $\beta = \nu C_c(0)$, $C_c(0) = 0.004235$, $C_c(r_s) = \tilde{C}(na_0^3)$, and

$$A = \frac{2\alpha}{\beta} \frac{1}{e^{-2\alpha\varepsilon_c(r_s)/\beta^2} - 1}. \quad (A6)$$

In the original PW91 functional, $\alpha = 0.09$ and $p(r_s) = 1$. Without changing the low-density limit, we can slightly modify the high-density limit to satisfy Eq. (54). First, we take $p(r_s) = -r_s \varepsilon_c(r_s)/0.4269$. Then, the $r_s \rightarrow 0$ leading behavior is

$$E_c[n] \rightarrow \frac{e^2}{a_0} \int d^3r n \left[0.03109 - \frac{\beta^2}{2\alpha} \right] \ln r_s, \quad (A7)$$

which is proportional to $e^4 \ln e$. So, we take $\alpha = \beta^2/2(0.03109) = 0.0716$. With these modifications, the limit of Eq. (54) is rapidly achieved as $\lambda \rightarrow \infty$. As an example, Table II displays the correlation energy for the two-electron exponential density

$$n(r) = \lambda^3 \frac{2}{\pi} e^{-2\lambda r}. \quad (A8)$$

Extension to a spin-density functional is straightforward.^{9,11,32} The only subtlety is that one should use the unpolarized $\varepsilon_c(r_s)$ in $p(r_s)$, as defined above.

For most practical purposes, this variant will give essentially the same valence-electron correlation energies

TABLE II. Correlation energy for the scaled two-electron exponential density of Eq. (A8). The exact $\lambda \rightarrow \infty$ limit is estimated as -0.05 hartree from Ref. 44. LDA: local-density approximation. GEA: second-order gradient expansion. GGA: original PW91. GGA': PW91 as modified in Appendix A (given in hartrees).

λ	LDA	GEA	GGA	GGA'
0.5	-0.0661	-0.0045	-0.0360	-0.0351
1	-0.0919	0.0453	-0.0437	-0.0415
2	-0.1218	0.1713	-0.0501	-0.0456
6	-0.1764	0.7468	-0.0586	-0.0483
12	-0.2143	1.6525	-0.0640	-0.0485
24	-0.2541	3.4934	-0.0697	-0.0485

as the original PW91 form,^{9,11,32} which we continue to recommend. The significant point is that only a relatively minor modification is needed in the original PW91 form to make it satisfy Eq. (54). This fact is an important indicator that the real-space cutoff method used to construct PW91 is correct.

APPENDIX B: STUDY OF THE INSTABILITIES OF THE LOW-DENSITY UNIFORM ELECTRON GAS

Low electron densities are realized experimentally in metal-ammonia solutions, and theoretically in jellium (a rigid uniform positive background neutralized by electrons). The uniform-fluid phase of jellium becomes unstable against charge-density waves of infinitesimal amplitude and wave vector Q when the density is low enough.^{42,43} In LDA, this instability occurs at $r_s = 30$

and $Q/2k_F = 1.11$. In PW91, it occurs at $r_s = 33$ and the same $Q/2k_F$. The critical wave vector Q is almost exactly the first reciprocal-lattice vector G for a face-centered-cubic ($G/2k_F = 1.11$) or body-centered-cubic ($G/2k_F = 1.14$) crystal with one electron per site. Thus, the charge-density wave might be regarded as^{42,43} an itinerant-electron or metallic precursor of Wigner crystallization, which localizes each electron on its own lattice site at a still lower density ($r_s \approx 100$).³⁶ (In the exchange-only approximation, which neglects correlations, the instability of a uniform, spin-unpolarized jellium against a charge-density wave of infinitesimal amplitude appears at $r_s = 64$ and $Q/2k_F = 1.36$ in LDA, but at $r_s = 19$ and $Q/2k_F = 1.24$ in PW91.) Note that for density variations of infinitesimal amplitude, the reduced density gradient s is arbitrarily small and PW91 reduces to the second-order gradient expansion.

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