Density functionals for the strong-interaction limit

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The strong-interaction limit of density-functional (DF) theory is simple and provides information required for an accurate resummation of DF perturbation theory. Here we derive the point-charge-plus-continuum (PC) model for that limit, and its gradient expansion. The exchange-correlation (xc) energy $E_{xc}[\rho] = \int \! d^3 r \, W_{xc}[\rho]$ follows from the xc potential energies $W_{\alpha}$ at different interaction strengths $\alpha \equiv 0$ [but at fixed density $\rho(\mathbf{r})$]. For small $\alpha \approx 0$, the integrand $W_{\alpha}$ is obtained accurately from perturbation theory, but the perturbation expansion requires resummation for moderate and large $\alpha$. For that purpose, we present density functionals for the coefficients in the asymptotic expansion $W_{\alpha} \rightarrow W_{\alpha} + W_{\alpha}^{PC} \alpha^{-1/2}$ for $\alpha \rightarrow \infty$ in the PC model. $W_{\alpha}^{PC}$ arises from strict correlation, and $W_{\alpha}^{PC}$ from zero-point vibration of the electrons around their strictly correlated distributions. The PC values for $W_{\alpha}$ and $W_{\alpha}^{PC}$ agree with those from a self-correlation-free meta-generalized gradient approximation, both for atoms and for atomization energies of molecules. We also (i) explain the difference between the PC cell and the exchange-correlation hole, (ii) present a density-functional measure of correlation strength, (iii) describe the electron localization and spin polarization energy in a highly stretched $\text{H}_2$ molecule, and (iv) discuss the soft-plasmon instability of the low-density uniform electron gas.

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I. INTRODUCTION

In density-functional theory (DFT) [1], the ground-state energy of a system of interacting electrons is presented as a functional of the ground-state density distribution $\rho(\mathbf{r})$ of the electrons,

$$E[\rho] = T_{s}[\rho] + \int d^3 r \, \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + U[\rho] + E_{xc}[\rho].$$

$T_{s}[\rho]$ is the kinetic energy of a system of noninteracting electrons with ground-state density $\rho$. The second contribution is the interaction with the external potential $v_{ext}(\mathbf{r})$, and $U[\rho] = \frac{1}{2} \int d^3 r d^3 r' \rho(\mathbf{r}) \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|$ is the classical Hartree-Coulomb energy. The exchange-correlation energy $E_{xc}[\rho]$ accounts for all the complexity of the quantum many-body problem ignored by the continuum functional $U[\rho]$. It also includes the interaction contribution $T_{c} = \langle \hat{T} \rangle - T_{s}$ to the kinetic energy.

This important functional is exactly represented by the coupling-constant integral [2,3],

$$E_{xc}[\rho] = \int_0^1 \! d \alpha W_{\alpha}[\rho],$$

$$W_{\alpha}[\rho] = \langle \Psi_{\alpha}[\rho] | \hat{V}_{xc} | \Psi_{\alpha}[\rho] \rangle - U[\rho].$$

The integrand $W_{\alpha}[\rho]$ (which is plotted approximately in Fig. 1) has only potential-energy contributions, including the expectation value of the Coulomb two-particle repulsion operator $\hat{V}_{xc} = \sum_{i<j} |\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|^{-1}$ in the ground state $\Psi_{\alpha}[\rho]$ of a hypothetical system where the repulsion between the electrons is scaled by a factor ("coupling constant") $\alpha \approx 0$, but which has the same ground-state density $\rho(\mathbf{r})$ as the real system with $\alpha = 1$. In general, $\Psi_{\alpha}[\rho]$ is the antisymmetrized $N$-electron wave function which minimizes the expectation value $\langle \hat{T} + \alpha \hat{V}_{xc} \rangle$ and, at the same time, yields the density $\rho$. If $\Psi_{1}[\rho]$ is the true ground state of a Hamiltonian with interaction $\alpha \hat{V}_{xc}$,

$$\hat{H}_\alpha = \hat{T} + \alpha \hat{V}_{xc} + \hat{V}_{ext}^{\alpha},$$

then the $\alpha$-dependent external potential $V_{ext}^{\alpha}(\mathbf{r})$, represented by the operator $\hat{V}_{xc}^{\alpha}$ in Eq. (3), is completely determined by the density $\rho$ [1]. Note that $W_{\alpha=1}[\rho] = E_{xc}[\rho] - T_{c}[\rho]$.

![FIG. 1. The ISI model (29) for the coupling-constant integrand of Eq. (2) in the case of the beryllium atom (solid curve; in hartree units). The coefficients $W_0$, $W_0'$, $W_\infty$, and $W_\infty^{PC}$ are taken from Table III, using $D=D_2$ for the latter one. The size of the shaded area, which indicates a contribution to the integral (2), is the predicted correlation energy $E_c^{int}[\rho] = -0.100$ hartree of the Be atom (exact value: $-0.096$ hartree). The expansions of $W_0^{PC}$ both for $\alpha \rightarrow 0$ and for $\alpha \rightarrow \infty$ are displayed in short dashes. The horizontal dashed line marks the asymptotic limit $W_\infty^{PC}$.](image)
The limit $\alpha \to 0$ of weak interaction in the integrand $W_a[\rho]$ of Eq. (2) is well understood. $\Psi_{\alpha=0}[\rho]$ is the Slater determinant of the occupied Kohn-Sham (KS) single-particle orbitals $\{\varphi_i(r, \sigma)\}_{i=1, \ldots, N}$. Correspondingly, $W_{\alpha=0}[\rho]$ is the DFT exchange energy,

$$W_0[\rho] = E_c[\rho] = -\frac{1}{2} \sum_{i,j=1}^{N} \sum_{\sigma} \int d^3r \, d^3r' \, \varphi_i^*(r, \sigma) \varphi_j^*(r', \sigma) \varphi_i(r', \sigma) \varphi_j(r, \sigma) \frac{\rho(r')}{|r-r'|}. \tag{4}$$

The first derivative at $\alpha = 0$,

$$W'_0[\rho] = (dW_0[\rho]/d\alpha)_{\alpha=0} = 2E_c^{GL}[\rho], \tag{5}$$

is, like $E_c$, also known [4] in terms of the KS orbitals as we shall see in the next paragraph.

In Görling-Levy (GL) perturbation theory [4], the correlation energy $E_c[\rho_a] = E_c[\rho_a] - E_c[\rho]$, for the density $\rho_a = \rho_1 + \alpha \rho_2$, is expanded around the high-density limit $\alpha \to 0$ (with $\alpha = 1/\lambda$),

$$E_c[\rho_{1\lambda}] = \sum_{n=2}^{\infty} E_{c,n}^{GL} [\rho] \alpha^{n-2} \quad (\alpha \to 0). \tag{6}$$

A hypothetic system where the electronic repulsion $\hat{V}_{ee}$ is scaled by the factor $\alpha$ is the correlation energy [5]

$$E_c^{\alpha}[\rho] = \alpha^2 E_c[\rho_{1\lambda}]. \tag{7}$$

Thus, $E_c^{\alpha}[\rho] = \sum_{n=2}^{\infty} E_{c,n}^{GL} [\rho] \alpha^n$. Since $E_c^{\alpha} = \int_0^\alpha d\alpha' (W_{\alpha'} - W_0)$, we have $W_{\alpha'}[\rho] = W_0 + \sum_{n=2}^{\infty} E_{c,n}^{GL} [\rho] \alpha^{n-1}$. Therefore, GL perturbation theory is equivalent to the Taylor expansion of $W_a[\rho]$ around the weak-interaction limit $\alpha = 0$, which implies Eqs. (4) and (5). For an explicit expression of $E_c^{GL}[\rho]$, see Ref. [4].

It has been shown recently [6,7] that the weak-interaction limit,

$$W_a[\rho] \to W_0[\rho] + W'_0[\rho] \alpha \quad (\alpha \to 0), \tag{8}$$

along with some additional information on the opposite limit $\alpha \to \infty$, where $W_a[\rho]$ approaches asymptotically a finite value $W_\infty[\rho]$ (see Fig. 1),

$$W_a[\rho] \to W_\infty[\rho] + W'_\infty[\rho] \alpha^{-1/2} \quad (\alpha \to \infty), \tag{9}$$

can be sufficient for an accurate evaluation of the integral (2).

As $\alpha \to \infty$, the external potential $v_{ee}^\alpha(r)$ that holds the density fixed becomes strongly attractive. In fact

$$\lim_{\alpha \to \infty} v_{ee}^\alpha(r) = -\int d^3r' \frac{\rho(r')}{|r-r'|} = \frac{\delta}{\delta \rho(r)} W_\infty[\rho], \tag{10}$$

since the Kohn-Sham potential which yields the density $\rho(r)$ for noninteracting electrons is

$$v_{ee}^0(r) = v_{ee}^\alpha(r) + \alpha \int d^3r' \frac{\rho(r')}{|r-r'|} + \frac{\delta}{\delta \rho(r)} E_{xc}^\alpha[\rho]; \tag{11}$$

here, $E_{xc}^\alpha[\rho] = \int d^3r \rho(r) W_{\alpha'}[\rho] \to \alpha W_\infty$ for $\alpha \to \infty$, which follows from the asymptotic behavior (9).

Unlike the realistic situation at $\alpha = 1$, this strong-interaction limit $\alpha \to \infty$ is also simple, but in a different way than the familiar limit $\alpha \to 0$ of weak interaction. As $\alpha \to \infty$, the electrons become strongly correlated. This situation is modeled by the concept of ‘strictly correlated electrons’ (SCE) [6,8,9] which is solved exactly for one-dimensional (1D) and, in particular, for any 3D two-electron system with a spherical density distribution $\rho(r)$. In the latter case [6,8], the two electrons always stay on opposite sides of the spherical center. The radial distance $r_1$ of the first electron strictly dictates that of the second electron, $r_2 = f(r_1)$, by virtue of an exact ‘correlation’ function $f(r)$. As a solution of the differential equation $f''(r) = -r^2 \rho(r)/f(r)^2 \rho(f(r))$, $f$ is unambiguously determined by the density $\rho$ [6,8]. (Apart from the minus sign and the appearance of only one function $\rho$ instead of two, this differential equation coincidentally resembles that of a local scaling transformation [54]). In terms of this function $f(r)$, SCE provides the functional [6,8]

$$W_\infty^{SCE}[\rho] = 2\pi \int_0^\infty dr' \frac{r'^2 \rho(r')}{r+f(r')} - U[\rho], \tag{12}$$

which is probably identical with the unknown exact $W_\infty[\rho]$ for spherical two-electron systems.

In the present paper we give the complete derivation of the point-charge-plus-continuum (PC) model [6,10] which is an approximation to the SCE concept but, in contrast to the latter, is straightforwardly applicable to any three-dimensional (3D) $N$-electron density $\rho(r)$. The PC model provides the simple explicit density functionals $W_\infty^{PC}[\rho]$ and $W'_\infty^{PC}[\rho]$, see Eqs. (23) and (24) below, for the coefficients in Eq. (9). It generalizes the standard spherical-cell model [11,12] of the Wigner crystal, and has a simple density-gradient expansion. (A constrained search for the strong-interaction limit has been discussed by Valone [13]. Some formal properties of this limit have been discussed by Levy and Perdew [14]).

In Sec. II we derive the functional $W_\infty^{PC}[\rho]$, while in Appendix A we explain the difference between the PC cell and the strong-interaction limit of the exchange-correlation (xc) hole. In Sec. III we consider the situation of large but finite $\alpha \gg 1$, and we derive in Appendix C the functional $W'_\infty^{PC}[\rho]$ for the next coefficient in the asymptotic expansion (9). We also discuss approximate self-interaction corrections (SIC’s) to the gradient expansion $W_\infty^{PC}[\rho]$. Using these functionals, we apply in Sec. IV the interaction-strength interpolation (ISI) $W_{\alpha'}^{ISI}[\rho]$ of Ref. [7] between the weak-interaction limit (8) and the strong-interaction limit (9). We obtain accurate correlation energies for those atoms where the coefficient $W'_0$ is known with reliable accuracy. The same method predicts in Ref. [7] remarkably accurate atomization energies for a set.
of 18 small molecules; a statistical summary is given in Sec. V, where we also discuss the strong-interaction limit for the atomization energy. We summarize our conclusions in Sec. VI.

The \( \alpha \) dependence of \( W_a[\rho] \) for specific finite or extended systems has been the subject of several recent investigations within density-functional [15–18] or wave-function [19–22] theories. Exact information about \( W_a[\rho] \), e.g., \( W_0 \) or \( W_0 \) and \( W_0 \), has been used to boost the accuracy of density-functional calculations [16–18] along the general direction suggested by Becke [23]. Unlike those approaches, which make use of density functionals for \( \alpha \approx 1 \), we make use of them for \( \alpha \rightarrow \infty \).

A density-functional measure of the correlation strength of the physical (\( \alpha = 1 \)) wave function is

\[
W_0 - W_1 \over W_0 - W_\infty
\]  

(13)

This measure varies between 0 for independent electrons and 1 for strictly correlated ones. For other measures, see Ref. [9].

II. POINT-CHARGE-PLUS-CONTINUUM (PC) MODEL FOR \( W_\ast[\rho] \)

The integrand \( W_a[\rho] \) in Eq. (2) is identical to the total electrostatic potential energy (expectation value) \( E^{\text{ex}}_a[\rho] \) of a fictitious system where discrete point electrons with the antisymmetrized and correlated wave function \( \Psi_a[\rho] \) are embedded in a rigid continuous background of positive charge with density \( \rho_+ (r) = \rho (r) \), since

\[
E^{\text{ex}}_a[\rho] = \langle \Psi_a[\rho] | \hat{V}_{\text{ex}} | \Psi_a[\rho] \rangle - 2U[\rho] + U[\rho] = W_a[\rho].
\]  

(14)

The three terms of Eq. (14) are, respectively, the electron-electron, electron-background, and background-background interactions. (It does not matter here whether \( \Psi_a[\rho] \) — which is defined in Eq. (2) above — is the ground state of this fictitious system or not. The positive background is merely an artifice invoked for the evaluation of \( W_a[\rho] \), and should not otherwise be taken seriously. The mock electrostatic energy of Eq. (14) provides a more convincing way to derive the PC model.)

Repeated simultaneous measurements of the \( N \) electronic positions in the state \( \Psi_a[\rho] \) would yield distribution sets \( \{ r_i \}_{i=1, \ldots, N} \) of \( N \) points which, in the ensemble average, represent the continuous density cloud \( \rho (r) \). The classical electrostatic energy of the neutral system composed of the \( N \) negative point charges of each set and the continuous positive background yields in the ensemble average the quantity \( E^{\text{ex}}_a[\rho] \). In the limit \( \alpha \rightarrow \infty \), where the electrons repel each other strongly, the points \( r_i \) in each set of the ensemble are distributed as uniformly as possible over the density \( \rho (r) \) without any accidental clustering. (Fluctuations of particle number in any finite volume fragment are strongly suppressed [9] as \( \alpha \rightarrow \infty \).) In other words, at large \( \alpha \), the continuous positive background is locally neutralized as well as this can be achieved by discrete negative point charges. Therefore, in a typical distribution set the hypothetical system can be divided up into \( N \) neutral cells, one around each electron at \( r \), and with zero or weak lower electric multipole moments, so that the interaction between different cells may be neglected. Consequently, the total electrostatic energy of the system, \( E^{\text{ex}}_a[\rho] \), is approximately the sum of the energies of these \( N \) individual cells.

In the following we present a model for the cell around an electron at position \( r \) in the density \( \rho \). This model cell has the energy \( E_{\text{cell}}[\rho](r) \). The sum \( \sum_{i=1}^{N} E_{\text{cell}}[\rho](r) \) for a set \( \{ r_i \} \) of electron positions becomes in the ensemble average an integral which is an approximation to the electrostatic energy (14) in the limit \( \alpha \rightarrow \infty \),

\[
W_\ast[\rho] \approx E^{\text{ex}}_\ast[\rho] = \int d^3r \rho (r) E_{\text{cell}}([\rho];r).
\]  

(15)

We call this the PC model because Eq. (15) treats one electron as a point charge at position \( r \) and the remaining \( N - 1 \) electrons as a continuous fluid of negative charge which perfectly neutralizes the positive background everywhere except for the region inside the cell around the point electron whose position is averaged over the system. Despite some similarities, the PC cell is not a model for the strong-interaction limit of the exchange-correlation hole; see Appendix A. By coincidence, the label PC is sometimes used to mean ‘‘perfect correlation’’ [24], the very situation for which our PC model is an approximation.

The key idea is that the electron at \( r \) plus its PC cell should have zero monopole and dipole electrostatic moments. In the local-density approximation (LDA), where the density \( \rho \) is assumed to be constant in the vicinity of each electron, the model cell around an electron at \( r \) is a concentric sphere with local radius \( r_r (r) = (3/4\pi)^{1/3} \rho (r)^{-1/3} \). The electrostatic energy of this cell,

\[
E_{\text{cell}}[\rho](r) = - 9 \over 10 \frac{1}{r_r (r)} \frac{1}{3},
\]  

(16)

is the self-energy \( \frac{1}{2} r_r^{-1} \) of the spherical piece of uniform positive background inside the cell plus its interaction \( - \frac{1}{2} r_r^{-1} \) with the central point electron.

Beyond the LDA is the gradient expansion approximation (GEA), in which the energy is expanded to second order in the density gradient. We assume the density \( \rho (r + s) \) in the vicinity of an electron at \( r \) to have a constant gradient \( \Gamma = \nabla \rho (r) \),

\[
\rho (r + s) = \rho_0 + \Gamma \cdot s,
\]  

(17)

where \( \rho_0 = \rho (r) \) is the density at the position of the point electron. If the gradient \( \Gamma \) is not too strong, \( \gamma = \Gamma r_s / \rho_0 \ll 1 \) where \( r_s = (4\pi^3/3) \rho_0^{-1/3} \), the cell is still approximately spherical. To have zero electric dipole moment, however, a positive spherical cell with a density gradient has its center shifted away from the negative point electron by a small displacement \( d \) (with magnitude \( d ) into the direction of \( - \Gamma \) (see Fig. 2). Still normalized to unity, the cell has now a
radius \( R > r_s \), fixed by \((4 \pi/3)R^3 \rho_c = 1\), where \( \rho_c = \rho_0 - \Gamma d = \rho_0(1 - \gamma d/r_s)\) is the density at the center of the cell.

In a coordinate system which has its origin \( u=0 \) at the center of the cell and its \( u_3 \) axis in the direction of \( \Gamma \), the electron is at \( u = -d = (0, 0, +d) \); see Fig. 2. The condition of zero dipole moment is \( \int_R \rho du_3 \pi(R^2 - u_3^2)(\rho_c + \Gamma u_3) = \delta(u_3 - d)|u_3 = 0\). This and the normalization condition \((4 \pi/3)R^3 \rho_c = 1\) can be written as

\[
R^2 = 5 \sqrt{R^2 - \gamma \frac{d}{r_s}} \quad \text{and} \quad R^2 = r_s^2 \left( 1 - \gamma \frac{d}{r_s} \right)^{-2/3},
\]

respectively. Expanding \( d = d_1 \gamma + d_2 \gamma^2 + \cdots \) in each of these equations and comparing coefficients, we find

\[
d(r) = r_s \left( \frac{1}{2} \gamma + \frac{1}{15} \gamma^2 \right) + O(\gamma^3),
\]

\[
R(r) = r_s \left( 1 + \frac{1}{15} \gamma^2 \right) + O(\gamma^4),
\]

where \( r_s = (3/4 \pi)^{1/3} \rho(r)^{-1/3} \) and \( \gamma = r_s(r) \left| \nabla \rho(r) \right| / \rho(r) \) depend on the position \( r \) of the point electron. The two quantities (19) determine both position and size of the spherical PC cell, depending on the position \( r \) of the point electron.

Again, as in the LDA (16), the energy of the PC cell with constant gradient is the self-energy \( U_{cell} \) of the piece of positive background inside the cell plus its interaction with the point electron,

\[
E^{\text{GEA}}_{cell}([\rho];r) = U_{cell} - \Phi^{(c)}_{cell}(u = -d(r)).
\]

The electrostatic potential at \( u \) of the positive background, with \( u = 0 \) at the center of the cell. Using for \( U_{cell} \) and \( \Phi^{(c)}_{cell}(u) \) the expressions (B6) and (B4) from Appendix B, with \((4 \pi/3)R^3 \rho_c = 1\), we obtain

\[
E^{\text{GEA}}_{cell}([\rho];r) = \left[ \frac{3}{5} + \frac{1}{35} \frac{\Gamma R^3}{\rho_c} \right] R^{-1} - \left[ \frac{1}{2} \left( 3 - \frac{d^2}{R^2} \right) + \frac{1}{10} \frac{\Gamma d}{R^3} \left( 5 - \frac{3d^2}{R^2} \right) \right] R^{-1}.
\]

Using \( \Gamma d/R^3 = \frac{1}{2} \gamma^2 + O(\gamma^4) \) and the expansions (19), we find, in generalization of Eq. (16),

\[
E^{\text{GEA}}_{cell}([\rho];r) = \left( \frac{9}{10} + \frac{3}{350} \gamma^2 \right) r_s(r)^{-1} + O(\gamma^4).
\]

As for the unknown functional \( W_{\infty}^{\text{MGGA}}[\rho] \), the coefficients are \( A = -(9/10)(4 \pi/3)^{1/3} = -1.451 \) and \( B = (3/50)(3/4 \pi)^{1/3} = 5.317 \times 10^{-3} \). The functional (23) has the correct scaling behavior, \( W^{\text{PC}}_{\infty}[\rho_A] = \lambda W^{\text{PC}}_{\infty}[\rho] \), as predicted in Eq. (31).

The standard local-density approximation for \( E_{xc} \) is not accurate in the limit \( \alpha \rightarrow \infty \), because of a serious self-correlation error which develops in that limit. As a result, this approximation [as well as the generalized gradient approximation (GGA)] cannot properly describe the Wigner crystallization of the low-density uniform electron gas [25]. The strongly interacting limit of the PBE GGA is essentially local and spin independent, as shown by the flatness of the \( r_s \) enhancement factors in Fig. 1 of Ref. [26]: \( W^{\text{GGA}}_{\infty}[\rho_1, \rho_2] \approx W^{\text{LSD}}_{\infty}[\rho_1, \rho_2] \approx 2 E^{\text{LDA}}_{\infty}[\rho] \). (Although LDA and GGA exchange energies suffer a self-interaction error, this error is typically small and does not change as \( \rho_{\infty} [\rho] \) approaches the strong-interaction limit. The LDA and GGA correlation energies suffer a self-interaction error which grows alarmingly towards this limit.)

However, we can test the accuracy of the functional (23) against the meta-generalized gradient approximation (MGGA) for the correlation energy [27], which is constructed from first principles without adjusting any parameters to experimentally known data. MGGA yields accurate energies for very different kinds of electronic systems such as atoms, molecules, solids, and surfaces. Due to its exact self-correlation correction (SIC), MGGA should work particularly well in the strong-interaction limit, where LDA and GGA do not. MGGA has an extra ingredient: not only the local density and its gradient, but also the orbital kinetic energy density.

For a set of 12 atoms, Table I gives a comparison of \( W^{\text{PC}}_{\infty}[\rho] \) with the functional \( W^{\text{MGGA}}_{\infty}[\rho] \) which is the model for \( W_{\infty}^{\text{MGGA}}[\rho] \) as extracted (Appendix D) from the MGGA functional. The good agreement of the results from the PC model with the ones from the MGGA functional in Table I is particularly encouraging, since two completely independent approaches to the strong-interaction limit are compared here.
TABLE I. Values for $W_\alpha[\rho]$ (in units of 1 hartree = 27.21 eV) for atoms, obtained for exchange-only Krieger, Li, and Iafrate (KLI) [50] densities from the LSD, GGA, and MGGA functionals (Appendix D) and from the PC model.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$W_\alpha^{LSD}$</th>
<th>$W_\alpha^{GGA}$</th>
<th>$W_\alpha^{MGGA}$</th>
<th>$W_\alpha^{PC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>−0.421</td>
<td>−0.417</td>
<td>−0.308</td>
<td>−0.313</td>
</tr>
<tr>
<td>He</td>
<td>−1.720</td>
<td>−1.689</td>
<td>−1.502</td>
<td>−1.463</td>
</tr>
<tr>
<td>Li</td>
<td>−2.958</td>
<td>−2.904</td>
<td>−2.575</td>
<td>−2.557</td>
</tr>
<tr>
<td>Be</td>
<td>−4.504</td>
<td>−4.424</td>
<td>−3.955</td>
<td>−3.947</td>
</tr>
<tr>
<td>N</td>
<td>−11.176</td>
<td>−11.048</td>
<td>−10.043</td>
<td>−10.187</td>
</tr>
<tr>
<td>Ne</td>
<td>−21.469</td>
<td>−21.294</td>
<td>−19.752</td>
<td>−20.018</td>
</tr>
<tr>
<td>Na</td>
<td>−24.848</td>
<td>−24.652</td>
<td>−22.916</td>
<td>−23.261</td>
</tr>
<tr>
<td>P</td>
<td>−40.298</td>
<td>−40.055</td>
<td>−37.524</td>
<td>−38.101</td>
</tr>
<tr>
<td>Ar</td>
<td>−54.240</td>
<td>−53.946</td>
<td>−50.831</td>
<td>−51.562</td>
</tr>
<tr>
<td>Kr</td>
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<td>−172.002</td>
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<td>−167.334</td>
</tr>
<tr>
<td>Xe</td>
<td>−331.981</td>
<td>−331.355</td>
<td>−321.204</td>
<td>−324.524</td>
</tr>
</tbody>
</table>

The true functional $W_\alpha[\rho]$ is known exactly in two particular cases: For one-electron systems (like the H atom in Table I), $W_\alpha[\rho]=-U[\rho]$, for all $\alpha\gg0$. For the H atom, $\rho(r)=e^{-2r}/\pi$ and $-U[\rho]=-\frac{1}{2}\rho=-0.3125$ which is reproduced almost perfectly by the PC model and, as a result of the self-correlation correction, accurately by the MGGA approach. For spherical two-electron systems (like the He atom in Table I), the strong-interaction limit is probably exactly solved by the concept of strictly correlated electrons (SCE) [6,8] which by Eq. (12) predicts $W_\alpha[\rho\text{He}]=-1.500$ for the He density used in Table I.

In density-functional theory, gradient expansions like Eq. (23) are usually constructed to be exact to order $|\nabla \rho|^2$ for slowly varying densities, and often fail (unless suitably generalized [28]) for realistic densities. However, because our Eq. (23) is derived differently, it need not share any of these features with traditional gradient expansions. In particular, the PC cell to order $|\nabla \rho|^2$ is properly normalized, Eq. (A2) of Appendix A, while the exchange-correlation hole to order $|\nabla \rho|^2$ is not [28]. Thus, we do not necessarily interpret the coefficient $B$ of Eq. (23) as the low-density limit of the second-order gradient coefficient of $E_\alpha[\rho]$ for a slowly varying density $\rho$.

The high-density limit of this coefficient is believed to be $1.854\times10^{-3}=-2.381\times10^{-3}+4.235\times10^{-3}$, where the first term is from exchange [29] and the second from correlation [30–32]. In Appendix E we use Eq. (23) to investigate the soft-plasmon instability of the low-density uniform electron gas against the formation of static charge-density waves.

III. MODELS FOR THE COEFFICIENT $W_\alpha^D[\rho]$

Strongly interacting electrons at large but finite $\alpha\gg1$ are expected to exhibit a zero-point vibration around their strictly correlated distribution at $\alpha=\infty$ [8]. While strictly correlated electrons at $\alpha=\infty$ are moving on a constant potential-energy surface, the zero-point vibration at finite $\alpha \gg 1$ is driven by a strong oscillator-type effective potential of the order $\alpha$ [8]. We therefore expect that the strongly correlated motion of the electrons at large $\alpha\gg1$ can be understood in terms of a slowly correlated motion, superimposed by fast small-amplitude collective oscillations. Correspondingly, as in the Born-Oppenheimer treatment of the nuclear motion in molecules, we take the strictly correlated motion as infinitely slow and consider oscillations in an otherwise static array of electrons.

If all the electrons are strictly correlated, then the net force on one electron at $\mathbf{r}$ [due to the other $N-1$ electrons and the external potential $\nu_{\text{ext}}^\alpha(\mathbf{r})$] vanishes to order $\alpha$, and this remains true when the electron moves to $\mathbf{r}+\mathbf{s}$. But suppose that the other $N-1$ electrons do not follow. Then there is a restoring force which drives the electron back to $\mathbf{r}$.

We demonstrate in Appendix C how the PC approximation (15) for the limit $\alpha\rightarrow\infty$ can be generalized to the present situation with oscillations at large but finite $\alpha\gg1$. $W_\alpha[\rho]$ can still be evaluated exactly as the electrostatic energy (14) with a positive background. The restoring force mentioned in the preceding paragraph, however, is not affected by this positive background which is entirely fictitious. This force is due only to the repulsion by the other $N-1$ electrons plus the unknown external potential $\nu_{\text{ext}}^\alpha(\mathbf{r})$. In Appendix C we present the PC model for $-\nabla \nu_{\text{ext}}^\alpha(\mathbf{r})$ and the restoring force on the electron. Then, with the modified charge distribution of an oscillating electron, Eq. (15) yields $W_\alpha[\rho]=W_\alpha^{PC}[\rho]+W_\alpha^{SIC}[\rho] \alpha^{-1/2}$ (for $\alpha\gg1$), where the coefficient $W_\alpha^{PC}[\rho]$, like $W_\alpha^{PC}[\rho]$ in Eq. (23), is obtained as a gradient expansion,

$$W_\alpha^{PC}[\rho]=\int d^3r \left( C \rho(\mathbf{r})^{3/2}+D \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{7/6}} \right).$$

This is the PC GEA for the coefficient $W_\alpha^D[\rho]$ in Eq. (9).

The LDA coefficient in Eq. (24) is $C=\frac{1}{2}(3\pi)^{1/2}=1.535$, in agreement with the spherical-cell treatment of the zero-point vibration in a Wigner crystal in Ref. [12]. To provide an approximate self-interaction correction (SIC) for one-electron densities for which the true functional $W_\alpha^D[\rho]$ is exactly zero, the gradient correction in Eq. (24) should have a sign opposite to that of the LDA term. Our derivation in Appendix C, however, yields the small but positive number $D_0=\frac{1}{2}(3\pi)^{1/2}=0.0197$ for the coefficient $D$. Unless there is a mistake in Appendix C, the effective PC gradient coefficient $D$ for small density gradients is positive, while that for typical gradients is negative (as estimated in the next paragraph).

Formally, however, the functional (24) has the correct [8] scaling behavior of the true functional $W_\alpha^D[\rho]$. $W_\alpha^{PC}[\rho]=\lambda^{3/2}W_\alpha^{PC}[\rho]$. Therefore, we can keep Eq. (24) and determine a more realistic value for the coefficient $D$ from a physically motivated condition. If we put, e.g., $D=D_1=-0.030676$, expression (24) is identically zero for any exponential (i.e., hydrogenic) one-electron spherical density $\rho(r)=\lambda^3 e^{-2\lambda r}/\pi (\lambda>0)$. In Table II we compare the values $W_\alpha^{PC}[\rho]$ with the corresponding values of the functional $W_\alpha^{MGGA}[\rho]$ which is extracted (Appendix D) from the MGGA exchange-correlation-functional of Ref. [27]. In all
that $W_\infty^{\text{PC}} \approx W_\infty^{\text{MGGA}}$ agree for the two-electron density of the He atom.

Functions of the form (23) and (24) are at least potentially exact for the electron gas of uniform density. While we have no exact solution for the strong-interaction or low-density limit, the SCE energy should be close to that of a bcc Wigner crystal [33–35],

$$E_\infty^{\text{W}} = -\frac{0.89593}{r_s} + 1.325 + \cdots.$$  

(25)

This is not far from the prediction of Eqs. (2), (9), (23), and (24) for the uniform gas as $r_s \to \infty$,

$$E_\infty^{\text{W}} = -\frac{0.90000}{r_s} + 1.500 + \cdots.$$  

(26)

The closeness of the energies for the Wigner crystal and for the uniform gas as $r_s \to \infty$ has been observed elsewhere [36,37].

The accuracy of gradient-corrected functionals can sometimes be improved by using the separate up- and down-spin densities instead of the total density, but this is not the case for our Eqs. (24) and (23), which assume that two electrons cannot be found together at the same point in space. The functionals $W_\infty^{\text{s}}[\rho]$ and $W_\infty^{\text{a}}[\rho]$ are in fact the same for bosons as for fermions.

### IV. Correlation Energies of Atoms

We can use the results from Tables I and II to evaluate the “interaction strength interpolation” (ISI) functional for the correlation energy of Ref. [7], $E_\infty^{\text{ISI}}[\rho] = E_\infty^{\text{ISI}}[\rho] - E_\infty^{\text{PC}}[\rho]$, using information only on the relatively simple extreme limits $\alpha \to 0$ and $\alpha \to \infty$,

$$E_\infty^{\text{ISI}}[\rho] = W_\infty + \frac{2X}{Y} \left( 1 + \frac{1}{1 + \frac{1}{1 + Z[a + Z]} \ln \left( 1 + \frac{1}{Y[a + Z]} \right) \right),$$  

(27)

where the coefficients require information only on the weak- and strong-interaction limits,

$$X[\rho] = \frac{xy^2}{e^2}, \quad Y[\rho] = \frac{x^2y^2}{e^4}, \quad Z[\rho] = \frac{xy^2}{e^3} - 1.$$  

(28)

with $x = -2W_\alpha^0[\rho]$, $y = W_\alpha^0[\rho]$, and $z = W_\alpha^0[\rho] - W_\infty[\rho]$. Table III summarizes the results for some cases in which the coefficient $W_\alpha^0[\rho]$ is known with reliable accuracy [51]. (For the atoms not shown in Table III, the core-core contribution to $W_\alpha^0[\rho]$ is not accurately known.)

Equation (27) is obtained in Ref. [7] by analytical integration, according to Eq. (2), of the ISI model for the integrand $W_\alpha[\rho]$.

$$E_\infty^{\text{ISI}}[\rho] = W_\infty[\rho] + \frac{X[\rho]}{\sqrt{1 + Y[\rho] / \alpha + Z[\rho]}}.$$  

(29)

### TABLE II. Values for $W_\infty^{\text{s}}[\rho]$ (in units of 1 hartree = 27.21 eV) for atoms, obtained from the LSD, GGA, and MGGA functionals (Appendix D) and from the PC model. The local term in the LSD, GGA, and MGGA has been slightly modified here to agree with the local term in the PC model. See the caption of Table I.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$W_\infty^{\text{LSD}}$</th>
<th>$W_\infty^{\text{GGA}}$</th>
<th>$W_\infty^{\text{MGGA}}$</th>
<th>$W_\infty^{\text{PC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.257</td>
<td>0.243</td>
<td>0.000</td>
<td>0.043</td>
</tr>
<tr>
<td>He</td>
<td>1.535</td>
<td>1.516</td>
<td>0.728</td>
<td>0.729</td>
</tr>
<tr>
<td>Li</td>
<td>3.252</td>
<td>3.176</td>
<td>1.532</td>
<td>1.623</td>
</tr>
<tr>
<td>Be</td>
<td>5.561</td>
<td>5.448</td>
<td>2.723</td>
<td>2.919</td>
</tr>
<tr>
<td>N</td>
<td>35.483</td>
<td>35.283</td>
<td>23.886</td>
<td>24.425</td>
</tr>
<tr>
<td>Na</td>
<td>42.966</td>
<td>42.745</td>
<td>29.586</td>
<td>30.115</td>
</tr>
<tr>
<td>Mg</td>
<td>51.115</td>
<td>50.886</td>
<td>35.867</td>
<td>36.352</td>
</tr>
<tr>
<td>P</td>
<td>79.473</td>
<td>79.202</td>
<td>58.244</td>
<td>58.378</td>
</tr>
<tr>
<td>Ar</td>
<td>114.391</td>
<td>114.082</td>
<td>86.761</td>
<td>86.179</td>
</tr>
<tr>
<td>Kr</td>
<td>463.955</td>
<td>463.481</td>
<td>390.997</td>
<td>381.015</td>
</tr>
<tr>
<td>Xe</td>
<td>1042.900</td>
<td>1042.223</td>
<td>914.250</td>
<td>886.290</td>
</tr>
</tbody>
</table>

### TABLE III. Increasingly accurate approximations to the correlation energy (in units of 1 hartree = 27.21 eV) of atoms with KLI [50] densities and the two-electron system with exponential density $\rho(r) = 2 \exp(-2r)/\pi$ (labeled as Exp.), using information only on the extreme limits $\alpha \to 0$ and $\alpha \to \infty$.

<table>
<thead>
<tr>
<th>System</th>
<th>$W_0$</th>
<th>$W_0^*$</th>
<th>$E_{c}^{\text{GL2}} = \frac{1}{2} W_0$</th>
<th>$W_{\infty}^{\text{PC}}$</th>
<th>$E_{c}^{\text{ISI}}$</th>
<th>$\bar{W}_{\infty}^{\text{[6]}}$</th>
<th>$W_{\infty}^{\text{PC}}$</th>
<th>$E_{c}^{\text{ISI}}$</th>
<th>$E_{c}^{\text{exact}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>−1.025</td>
<td>−0.101</td>
<td>−0.505</td>
<td>−1.463</td>
<td>−0.041</td>
<td>0.647</td>
<td>0.729</td>
<td>−0.041</td>
<td>−0.042</td>
</tr>
<tr>
<td>Exp.</td>
<td>−0.625</td>
<td>−0.093</td>
<td>−0.047</td>
<td>−0.886</td>
<td>−0.035</td>
<td>0.309</td>
<td>0.345</td>
<td>−0.034</td>
<td>−0.037</td>
</tr>
<tr>
<td>Be</td>
<td>−2.674</td>
<td>−0.250</td>
<td>−0.125</td>
<td>−3.943</td>
<td>−0.105</td>
<td>2.022</td>
<td>2.919</td>
<td>−0.100</td>
<td>−0.096</td>
</tr>
<tr>
<td>Ne</td>
<td>−12.084</td>
<td>−0.938</td>
<td>−0.469</td>
<td>−20.018</td>
<td>−0.420</td>
<td>16.323</td>
<td>24.425</td>
<td>−0.405</td>
<td>−0.394</td>
</tr>
</tbody>
</table>
This analytic function is plotted in Fig. 1. The choice (28) of the coefficients guarantees that the model (29) has the exact asymptotic properties (8) and (9).

Note that $x,y,z \geq 0$, and that $dW_{\tilde{\alpha}}^S/d\alpha < 0$ and $d^2W_{\tilde{\alpha}}^S/d\alpha^2 > 0$ for $\alpha \geq 0$. Note also that $W_{\tilde{\alpha}}^S[\rho]$ remains finite even when $W_0 \to -\infty$,

$$\lim_{W_0 \to -\infty} W_{\tilde{\alpha}}^S = W_\infty + \frac{W_0 - W_\infty}{1 + \frac{W_\infty}{\alpha}};$$

the interpolation (29) does not break down completely even for metals, although it is more appropriate to finite systems or to insulators where $W_0$ is finite. Equations (29) and (28) generalize Eqs. (7) and (8) of Ref. [6], in which $Z[\rho] = 0$ so that $W_\infty[\rho]$ cannot be chosen independently but is fixed by $W_\infty[\rho] = \{W_0 - W_\infty\}^2(-2W_0')^{1/2}$, see Fig. 4 of Ref. [8].

Our functionals (23) and (24) have the scaling behavior

$$W_{\tilde{\alpha}}^{PC}[\rho_\lambda] = \lambda W_{\tilde{\alpha}}^{PC}[\rho], \quad W_{\tilde{\alpha}}^{rPC}[\rho_\lambda] = \lambda^{3/2} W_{\tilde{\alpha}}^{rPC}[\rho],$$

where the scaled density $\rho_\lambda(\mathbf{r}) = \lambda^2 \rho(\lambda \mathbf{r})$ is generated from a given density $\rho(\mathbf{r})$ by a scaling factor $\lambda > 0$. Since $W_{\tilde{\alpha}}[\rho_\lambda] = \lambda W_{\tilde{\alpha}}[\rho]$ and $W_{\tilde{\alpha}}'[\rho_\lambda] = W_{\tilde{\alpha}}'[\rho]$, the relations (31) guarantee that our model integrand (29) fulfills

$$W_{\tilde{\alpha}}^{SIS}[\rho] = \alpha W_{\tilde{\alpha}}^{SIS}[\rho_{\lambda = 1/\alpha}],$$

which is a key property [5] of the unknown exact integrand $W_{\alpha}[\rho]$. Equation (32) shows in particular how the strong-interaction limit ($\alpha \to \infty$) is related to the low-density limit ($\lambda \to 0$). A graphical illustration of $W_{\tilde{\alpha}}[\rho]$ with its integral is displayed in Fig. 1, for which the four functionals $W_{\tilde{\alpha}}[\rho]$, $W_{\tilde{\alpha}}'[\rho]$, $W_{\tilde{\alpha}}^{PC}[\rho]$, and $W_{\tilde{\alpha}}^{rPC}[\rho]$ have been evaluated with an accurate ground-state density $\rho_{Be}$ of the beryllium atom.

An important property of the exact $E_{xc}[\rho]$ is its size consistency: $E_{xc}[\rho_1 + \rho_2] = E_{xc}[\rho_1] + E_{xc}[\rho_2]$ for two well-separated densities $\rho_1$ and $\rho_2$. Because our inputs $W_{\tilde{\alpha}}[\rho]$, $W_{\tilde{\alpha}}'[\rho]$, $W_{\tilde{\alpha}}^{PC}[\rho]$, and $W_{\tilde{\alpha}}^{rPC}[\rho]$ are size consistent, so is our $W_{\tilde{\alpha}}[\rho]$ in the weak- and strong-interaction limits. But, because Eqs. (29) and (27) are nonlinear, our $E_{xc}^{SIS}[\rho]$ is not generally size consistent (although it behaves properly for $\rho_1 = \rho_2$). This failure could be mild, since it arises from the uncertainty in our interpolation formula of Eq. (29). To achieve full size consistency, we could make our interpolation not globally but at each point $\mathbf{r}$ of space.

V. ATOMIZATION ENERGIES
IN THE INTERACTION STRENGTH INTERPOLATION
AND IN THE STRONG-INTERACTION LIMIT

We have calculated atomization energies for 18 small molecules within the ISI model of Eq. (27) in Ref. [7]. The model accurately reproduces the experimental atomization energies with a mean absolute error of only about 4 kcal/mole = 0.006 hartree or 2.8% of the mean experimental atomization energy. This accuracy is even more remarkable for the fact that it was achieved without the typical cancellation of errors between the exchange and the correlation energies exhibited by density functionals like LSD or GGA, because the ISI model makes use of the exact exchange energy. In Ref. [42] we found a similar interpolation error for the ISI model when all the input quantities were calculated within the meta-GGA.

For the 18 molecules studied in Ref. [7], Table IV compares the (signed) mean and mean absolute errors of the atomization energies in LSD, GGA, meta-GGA, HF (unrestricted Hartree-Fock), second-order Görling-Levy (GL2), and ISI. While HF underbinds severely and GL2 overbinds severely, ISI is rather realistic.

For this work we have studied the change upon atomization of $W_{\tilde{\alpha}}$ and $W_{\tilde{\alpha}}'$ within the different density-functional approximations. The results are shown in Tables V and VI, respectively. Similar to the results for atoms, the meta-GGA typically gives a much closer agreement for $\Delta W_{\tilde{\alpha}}$ with the PC model than both LSD and GGA (which yield results very similar to one another). This is probably due to the fact that the meta-GGA is self-correlation-free while LSD and GGA are not. It should be kept in mind, however, that the meta-GGA exchange is not exactly self-interaction free.

As is evident from Fig. 1, the total exchange-correlation energy $E_{xc}$ of an atom is close to its weak-interaction limit $E_{xc}$ and far from its strong-interaction limit $W_{\tilde{\alpha}}$. But the atomization energy of a molecule is close to neither limit. For the 18 molecules in Tables V and VI, the weak-interaction limit (exact $E_{xc}$ and no correlation) underbinds by an average 66 kcal/mole = 0.11 hartree or 44%, while the strong-interaction limit ($W_{\tilde{\alpha}}^{PC}$) overbinds by an average 336 kcal/mole = 0.54 hartree or 222% of the mean experimental atomization energy.

For most electronic systems, strong interaction is of interest only as a limit. The heavier and more classical ions in a low-temperature plasma or liquid metal come much closer to
TABLE V. Changes upon atomization, $\Delta W_n$ = $W_n$(separated atoms) − $W_n$(molecule) (in units of 1 hartree = 27.21 eV), of the exchange-correlation functional in the strongly interacting limit in LSD, GGA, and meta-GGA (Appendix D) and within the PC model. The functionals were evaluated with self-consistent GGA densities at experimental geometries. The calculations were performed using a modified version of the CACPA program [53].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta W_n^{\text{LSD}}$</th>
<th>$\Delta W_n^{\text{GGA}}$</th>
<th>$\Delta W_n^{\text{MGGA}}$</th>
<th>$\Delta W_n^{\text{PC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.273</td>
<td>0.260</td>
<td>0.352</td>
<td>0.313</td>
</tr>
<tr>
<td>LiH</td>
<td>0.224</td>
<td>0.219</td>
<td>0.264</td>
<td>0.258</td>
</tr>
<tr>
<td>Li$_2$</td>
<td>0.078</td>
<td>0.078</td>
<td>0.097</td>
<td>0.111</td>
</tr>
<tr>
<td>LiF</td>
<td>0.533</td>
<td>0.536</td>
<td>0.570</td>
<td>0.616</td>
</tr>
<tr>
<td>Be$_2$</td>
<td>0.078</td>
<td>0.083</td>
<td>0.095</td>
<td>0.122</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.252</td>
<td>1.247</td>
<td>1.556</td>
<td>1.536</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1.065</td>
<td>1.062</td>
<td>1.329</td>
<td>1.293</td>
</tr>
<tr>
<td>OH</td>
<td>0.391</td>
<td>0.389</td>
<td>0.521</td>
<td>0.473</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.801</td>
<td>0.795</td>
<td>1.042</td>
<td>0.973</td>
</tr>
<tr>
<td>HF</td>
<td>0.454</td>
<td>0.450</td>
<td>0.570</td>
<td>0.551</td>
</tr>
<tr>
<td>B$_2$</td>
<td>0.266</td>
<td>0.277</td>
<td>0.360</td>
<td>0.375</td>
</tr>
<tr>
<td>CN</td>
<td>0.664</td>
<td>0.679</td>
<td>0.773</td>
<td>0.806</td>
</tr>
<tr>
<td>CO</td>
<td>0.743</td>
<td>0.748</td>
<td>0.895</td>
<td>0.891</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.808</td>
<td>0.818</td>
<td>0.918</td>
<td>0.942</td>
</tr>
<tr>
<td>NO</td>
<td>0.659</td>
<td>0.666</td>
<td>0.798</td>
<td>0.801</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.536</td>
<td>0.540</td>
<td>0.722</td>
<td>0.689</td>
</tr>
<tr>
<td>O$_3$</td>
<td>0.857</td>
<td>0.860</td>
<td>1.163</td>
<td>1.142</td>
</tr>
<tr>
<td>F$_2$</td>
<td>0.272</td>
<td>0.269</td>
<td>0.340</td>
<td>0.384</td>
</tr>
</tbody>
</table>

VI. CONCLUSIONS

Standard density functionals for the exchange-correlation energy (the local density approximation and the generalized gradient approximation) fail in the strong-interaction or low-density limit as a result of self-interaction error [25]. Thus, to describe real strongly correlated systems like transition-metal oxides, one needs a self-interaction correction [39] or Hubbard $U$ [40].

However, we have found good agreement in this limit between the meta-generalized gradient expansion of Ref. [27], which is exactly self-correlation free, and our PC gradient expansions of Eqs. (23) and (24), which are approximately self-correlation-free. Thus, we suspect that the low-density limit is under control, and that it should be possible to use the meta-GGA to study, for example, the Wigner crystallization of the uniform electron gas.

The agreement between the PC gradient expansion and the meta-GGA in the strong-interaction limit is remarkable, as these are very different approximations derived in different ways and from different ingredients. The agreement found here for atoms and molecules cannot persist for very rapidly varying densities, such as those of narrow quantum wells [41], where large reduced density gradients can make $W_n^{\text{PC}}$ improperly positive and $W_n^{\text{PC}}$ improperly negative.

Our Eqs. (23) and (24) can be used along with GL2 perturbation theory in the “interaction strength interpolation” of Eqs. (27) and (29). Accurate correlation energies are found both for atoms (this work) and molecules (Ref. [7]). As explained in Ref. [7], the ISI correlation energy functional is compatible with exact exchange, in a way that standard density functionals are not. The ISI of Eq. (27) also provides an estimate [7] for the radius of convergence of density-functional perturbation theory. The ISI interpolation error has been estimated [42] to be 0.1% for the exchange-correlation energy of an atom and 4 kcal/mole = 0.17 eV for the atomization energy of a molecule, via tests made within the meta-generalized gradient approximation. For the uni-
form electron gas, ISI predicts a correlation energy which is finite but (except at low densities) inaccurate [42]. For a uniform gas with an artificially imposed energy gap [43], it becomes increasingly accurate as the gap increases.

We have further explained the point-charge-plus-continuum (PC) model which is the basis for Eqs. (23) and (24). The mock electrostatic energy of Eq. (14) is evaluated in the strongly interacting limit by dividing the system up into nonoverlapping, neutral, weakly interacting cells. Despite some similarities, the PC cell is not the strongly interacting limit of the exchange-correlation hole (Appendix A), because the exchange-correlation holes overlap even in this limit. The relatively short range of the PC cell helps to explain the accuracy of a second-order gradient expansion in the strongly interacting limit.

ACKNOWLEDGMENTS

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APPENDIX A: EXCHANGE-CORRELATION HOLE VERSUS PC CELL

The density \( n_{xc}(\mathbf{r}, \mathbf{r}') \) at \( \mathbf{r}' \) of the exchange-correlation hole [3] around an electron at \( \mathbf{r} \) is defined such that \( \tilde{\rho}(\mathbf{r}') = \rho(\mathbf{r}') + n_{xc}(\mathbf{r}, \mathbf{r}') \) is the effective charge density, seen by the electron due to the \( N-1 \) other electrons. ‘Effective charge density’ means that the two contributions to the energy functional (1) that describe the electron-electron interaction can be written in the Hartree form

\[
U[\rho] + E_{xc}[\rho] = \frac{1}{2} \int d^3 r \rho(\mathbf{r}) \int d^3 r' \frac{\rho(\mathbf{r}') + n_{xc}(\mathbf{r}, \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|}.
\]

(A1)

Note, however, that \( \tilde{\rho}(\mathbf{r}') \) also accounts for the kinetic-energy contribution \( T_s[\rho] = \left( \hat{T} - T_s[\rho] \right) \) in \( E_{xc}[\rho] \).

Here we discuss the relationship between the exchange-correlation hole \( n_{xc}(\mathbf{r}, \mathbf{r}') \) and the density shift \( n_{PC}(\mathbf{r}, \mathbf{r}') \) that arises at \( \mathbf{r}' \) due to the creation of a PC cell around an electron at \( \mathbf{r} \). Both are normalized to \(-1\),

\[
\int d^3 r' n_{xc}(\mathbf{r}, \mathbf{r}') = \int d^3 r' n_{PC}(\mathbf{r}, \mathbf{r}') = -1,
\]

(A2)

and for strong interaction both tend to \(-\rho(\mathbf{r})\) as \( \mathbf{r}' \rightarrow \mathbf{r} \). Both give \( E_{xc} \) in the strongly interacting limit (where \( E_{xc}[\rho] = W_o[\rho] \)), but not in the same way,

\[
E_{xc} = \frac{1}{2} \int d^3 r \rho(\mathbf{r}) \int d^3 r' \frac{n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \int d^3 r \rho(\mathbf{r}) \int d^3 r' \frac{n_{PC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \int d^3 r \rho(\mathbf{r}) \int d^3 r_1 \int d^3 r_2 \frac{n_{PC}(\mathbf{r}, \mathbf{r}_1) n_{PC}(\mathbf{r}, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}.
\]

(A3)

Thus the PC cell is not a model for the strong-interaction limit of the exchange-correlation hole; it arises from a different way of dividing up the charge around an electron.

For the uniform electron gas in the strong-interaction limit, the exchange-correlation energy per electron is

\[
\frac{1}{2} \int d^3 r' \frac{n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = - \frac{9}{10r_s},
\]

(A4)

while

\[
\frac{1}{2} \int d^3 r' \frac{n_{PC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = - \frac{3}{4r_s}.
\]

(A5)

These are significantly different, although both approaches give the same energy.

For any one-electron system, the exact \( n_{xc}(\mathbf{r}, \mathbf{r}') \) and the exact \( n_{PC}(\mathbf{r}, \mathbf{r}') \) (but not their gradient expansions) are equal to one another and to \(-\rho(\mathbf{r}')\), so in this limit the two forms of Eq. (A3) are manifestly identical.

APPENDIX B: ELECTROSTATIC POTENTIAL AND ENERGY OF A CHARGED SPHERE WITH A CONSTANT DENSITY GRADIENT

The sphere of radius \( R \) has the charge density

\[
\rho_{cell}(\mathbf{u}) = (\rho_c + \Gamma \cdot \mathbf{u}) \Theta (R-u),
\]

(B1)

where \( u = |\mathbf{u}| \) and \( \Theta (\mathbf{r}) \) is the step function. \( \rho_c \) is the density at the center \( \mathbf{u} = 0 \) of the sphere.

To calculate the electrostatic potential \( \Phi_{cell}(\mathbf{u}) = \int d^3 r \rho_{cell}(\mathbf{r}) \frac{1}{|\mathbf{u} - \mathbf{r}|} \) of this charge distribution at some position \( \mathbf{u} \) inside the sphere, we choose the \( z \) axis in the direction of \( \mathbf{u} \). Then, the \( x \) and \( y \) terms of \( \Gamma \cdot \mathbf{r} = \Gamma_1 x + \Gamma_2 y + \Gamma_3 z \) in \( \rho_{cell}(\mathbf{r}) \) do not contribute to the integral \( \Phi_{cell}(\mathbf{u}) \).

Consequently, in spherical coordinates \( \{r, \phi, \theta\} \) for \( \mathbf{r} \) (with \( z = r \cos \theta \)),

\[
\Phi_{cell}(\mathbf{u}) = 2\pi \int_0^R dr \int_0^\pi \int_0^{2\pi} d\phi \sin \theta \left[ \rho_c + \Gamma_3 r \cos \theta \right] r^2 dr \sin \theta \frac{r^2}{r^2 - u^2} P_l(\cos \theta),
\]

(B2)

We have here used the multipole expansion of \( |\mathbf{u} - \mathbf{r}|^{-1} \) in the usual notation of Ref. [44], where \( r_{\infty} = \min \{|r,u|\} \) is the long-range \( r_{\infty} = \max \{|r,u|\} \). Substituting \( \xi = \cos \theta \), the term in square brackets can be written as \( \left[ \rho_c P_0(\xi) + \Gamma_3 r P_1(\xi) \right] \), since the Legendre
polynomials are \( P_q(t) = 1 \), \( P_t(t) = t \), etc. Due to the orthogonality relation \( \int_{-1}^{1} dt \, P_n(t) \, P_m(t) = 2 \delta_{m,n}/(2m + 1) \), only the \( l = 0 \) and \( l = 1 \) terms contribute to the \( \theta \) integral of Eq. (B2),

\[
\Phi_{cell}(u) = 4 \pi \rho_c \int_0^R \frac{r^2}{dr} \, \frac{4 \pi}{3} \Gamma_3 \int_0^R \frac{r^3}{r^2}. \tag{B3}
\]

\( \Gamma_3 \) is the component of \( \Gamma \) in the direction of \( u \). We choose the \( u_3 \) axis in the direction of \( \Gamma \) so that \( \Gamma_3 = \Gamma u_3 / u \). The \( r \) integrations in (B3) yield

\[
\Phi_{cell}(u) = \frac{2 \pi}{3} \rho_c (3 R^2 - u^2) + \frac{2 \pi}{15} \Gamma u_3 (5 R^2 - 3 u^2)
\]

\((u \equiv R) \). (B4)

In the same way, the potential outside the cell is obtained,

\[
\Phi_{ext}(u) = \frac{4 \pi}{3} R^3 \left( \rho_c \frac{\Gamma R^2 u_3}{u} \right) \tag{B5}
\]

\( \Phi_{cell}(u) \) is that solution of the Poisson equation \( \nabla^2 \Phi_{cell} = -4 \pi \rho_{cell} \) that approaches zero as \( u \rightarrow \infty \).

The electrostatic self-energy \( U_{cell} = \frac{1}{2} \int d^3 u \, \Phi_{cell}(u) \rho_{cell}(u) \) of the sphere with charge density \( (B1) \) is easily evaluated in spherical coordinates where \( u_3 = u \cos \theta \).

\[
U_{cell} = \frac{3}{5} \left( \frac{4 \pi}{3} R^3 \rho_c \right)^2 R^{-1} + \frac{4 \pi}{35} \left( \frac{4 \pi}{3} R^3 \rho_c \right)^2 \left( \frac{\Gamma R}{\rho_c} \right)^2 R^{-1}. \tag{B6}
\]

**APPENDIX C:**

**THE PC MODEL FOR THE COEFFICIENT \( W_{\alpha}^{\beta} \) [\( \rho \)]

We consider oscillations of electrons around a static SCE set of positions \( \{ r_i \}_{i=1, \ldots, N} \) in a given density \( \rho(r) \), as explained in the opening paragraph of Sec. III. If we ignore the collective character of the oscillations as in the Einstein model for phonons, each electron is oscillating independently around an equilibrium position. Since the amplitude of these oscillations asymptotically approaches zero as \( \alpha \rightarrow \infty \), the PC model still applies. Now, in evaluating the electrostatic energy of the PC cell in Eq. (15) we must merely replace the strictly localized point electron by the smooth charge distribution of an oscillating one. The restoring force on this oscillating electron is the repulsion (scaled by the factor \( \alpha \)) by the other \( N-1 \) electrons, distributed continuously outside a static PC cell, plus the force due to the unknown external potential \( v_{ext}^\alpha(r) \). Although the positive background, introduced with Eq. (14), can be used to evaluate the electrostatic energy (15), it is entirely fictitious and, of course, has no effect on the restoring force on the oscillating electron. To obtain this restoring force, we need a model for the true external potential \( v_{ext}^\alpha(r) \).

At large \( \alpha \gg 1 \), \( v_{ext}^\alpha(r) \) must become strongly attractive to maintain a given density distribution \( \rho(r) \) of the strongly repulsive electrons. In the limit \( \alpha \rightarrow \infty \) when the kinetic energy becomes negligible, we expect that the strictly correlated electrons are moving on a constant potential-energy surface. For spherical two-electron systems, this can be achieved [8] by

\[
v_{ext}^\alpha(r) \rightarrow \alpha w(r) \quad (\alpha \rightarrow \infty), \tag{C1}
\]

where \( w(r) \) is a smooth finite function which is entirely determined by the density \( \rho(r) \).

In the PC model for the strictly correlated limit \( \alpha \rightarrow \infty \), the repulsive force, exerted on the point electron at position \( r \) by the other \( N-1 \) other electrons, is due to a distribution of continuous negative charge with density \( \rho(r') \) outside the PC cell. This force can obviously be canceled exactly by an external force \( F_{ext}^{PC}(r) \) which is chosen as though it was due to an equivalent distribution of continuous positive charge with the same density outside the cell. The force \( F_{ext}^{PC}(r) \) is a model for the gradient \(-\nabla w(r)\). If it is a conservative force, we can write \( F_{ext}^{PC}(r) = -\nabla w_{PC}(r) \) where \( w_{PC}(r) \) is the PC model for \( w(r) \). At least for densities that vary only in the radial or \( z \) directions, the construction of \( w_{PC}(r) \) is always possible.

To simplify our language, we denote in the following paragraphs by ‘‘\( C(x) \)’’ the spherical region inside the PC cell of a point electron at \( r = x \) in the strictly correlated limit \( \alpha \rightarrow \infty \).

In the PC model for strictly correlated motion in the limit \( \alpha \rightarrow \infty \), the electron carries its PC cell along as it is moving from \( r \) to a close-by position \( r+s \). Correspondingly, the external force \( F_{ext}^{PC}(r+s) \) at the new position \( r+s \) must be calculated from a different distribution of positive charge which is now outside the new PC cell \( C(r+s) \). As in the work of Harbola and Sahni [45], we have a position-dependent ‘‘hole’’ from which we calculate the electrostatic force at each electron position.

At finite \( \alpha \), in contrast, when the strictly correlated motion is taken to be infinitely slow, there is a static PC cell \( C(r) \) around an oscillating electron. Therefore, as this oscillating electron has moved from its equilibrium position \( r \) to the close-by position \( r+s \), the external force \( F_{ext}^{PC}(r+s) \) at \( r+s \) due to positive charge outside \( C(r+s) \), does not cancel the repulsive force due to the other \( N-1 \) electrons which are still outside the static PC cell \( C(r) \); see Fig. 3. Consequently, there is a restoring net force \( F_{net}^\alpha(s) \). This force can be derived electrostatically from a net charge density \( \rho^\alpha(s) \) which is zero everywhere outside the finite region \( C(r) \cup C(r+s) \), covered by these two cells. It is the same as a positive charge distribution with density \( \rho(r') \) inside \( C(r) \), plus a negative charge distribution with density \( \rho(r') \) inside \( C(r+s) \).

In the constant-gradient model (17), \( \rho^\alpha(s) \) is the charge distribution of two oppositely charged overlapping spheres \( C(r) \) and \( C(r+s) \) with a constant charge-density gradient \( \Gamma \) (Fig. 3). The net force exerted by this charge distribution on the oscillating electron at \( r+s \) is

\[
F_{net}^\alpha(s) = \left[ \nabla_u \Phi_{cell}^\alpha(u) \right]_{u=s-d} - \left[ \nabla_u \Phi_{cell}^{r+s}(u) \right]_{u=-d} = d(r+s). \tag{C2}
\]
The probability distribution or charge density of an electron performing zero-point oscillations in the potential (C3) is

$$\rho_{osc}^{(r)}(s) = \frac{k_1^{1/2} k_3^{1/4}}{\pi^{3/2}} \exp\left[ - \left| k_1 (s_1^2 + s_2^2 + k_3^{1/2} s_3^2) \right| \right].$$  \hfill (C5)

Using this charge distribution in evaluating the electrostatic energy, we now have instead of Eq. (20)

$$E_{cell, a}^{GEA}([\rho] ; r) = U_{cell} - \int d^3 s \Phi_{cell}^{(r)}(s - d(r)) \rho_{osc}^{(r)}(s).$$  \hfill (C6)

To evaluate the s integral here, we put the s_3 axis in the direction of \Gamma so that \( d = \{0,0,-d\} \). Setting \( u = s - d(r) \) = \( s_1, s_2, s_3 + d \) in Eq. (B4) yields

$$\Phi_{cell}^{(r)}(s - d(r)) = (\frac{1}{2} + \frac{2}{50} \gamma) R^{-1} + \Phi_{odd}(s)$$

$$- \left[ (\frac{1}{2} + \frac{2}{50} \gamma)^2 s_1^2 + s_2^2 \right] \frac{R}{2^2}$$

$$+ (\frac{1}{2} + \frac{2}{50} \gamma) s_3^3 \frac{R}{2^2} + O(\gamma^4).$$  \hfill (C7)

Here, \( \Phi_{odd}(s) \) summarizes the terms containing odd powers of s_1, s_2, or s_3 which do not contribute to the integral in Eq. (C6), since \( \rho_{osc}^{(r)}(s) \) is an even function of the s_i. Since \( \int d^3 s \rho_{osc}^{(r)}(s) = 1 \), the first (constant) term of Eq. (C7) reproduces in Eq. (C6) exactly the expression (21) for \( E_{cell}^{GEA}([\rho] ; r) \). For the contribution \( \partial E_{cell, a}^{GEA}([\rho] ; r) \) of the quadratic term to the integral in Eq. (C6) we note that

$$\int d^3 s s_i^2 \rho_{osc}^{(r)}(s) = \frac{k_1^{1/2}}{\pi^{3/2}} \int_{-\infty}^{\infty} ds_i s_i^2 e^{-k_1 s_i^2} = \frac{1}{2 k_1^{1/2}}.$$

Therefore,

$$\partial E_{cell, a}^{GEA}([\rho] ; r) = (\frac{1}{2} + \frac{2}{50} \gamma) \frac{2}{2R^3 k_1^{1/2}} + (\frac{1}{2} + \frac{2}{50} \gamma)^2$$

$$\times \frac{1}{2 R^3 k_1^{1/2}} + O(\gamma^4).$$  \hfill (C9)

Since \( k_1 \) and \( k_3 \) from Eq. (C4) are proportional to \( \alpha \), this contribution is of the order \( \alpha^{-1/2} \), as expected. Using the expansions (19), we obtain from Eq. (C4)

$$\frac{1}{R^3 k_1^{1/2}} = (1 - \frac{4}{50} \gamma^2) r_s(r)^{-3/2} \alpha^{-1/2} + O(\gamma^4),$$

$$\frac{1}{R^3 k_3^{1/2}} = (1 - \frac{9}{50} \gamma^2) r_s(r)^{-3/2} \alpha^{-1/2} + O(\gamma^4).$$  \hfill (C10)

Then, expansion of Eq. (C9) yields
Using this expression for the PC model, where the coefficients are given by the GEA equations (23) and (24).

While we have not proved that the density $\rho(r)$ is unaffected by the oscillations, we suspect that it is. Clearly

$$\int d^3r \rho(r) \rho_{\text{osc}}(r'|r) = \rho(r')$$

(C12)

when $\rho(r) = \rho(r') + \nabla \rho(r') \cdot (r' - r)$.

**APPENDIX D: EXPRESSIONS FOR $W_x[\rho]$ AND $W_s[\rho]$ IN LSD, GGA, AND META-GGA**

For a given approximate exchange-correlation energy functional $E_{xc}^{\text{approx}}[\rho] = E_{xc}^{\text{approx}}[\rho] + E_c^{\text{approx}}[\rho]$, the corresponding coupling-constant integrand $W_{xc}^{\text{approx}}[\rho]$ can be found by the following formula [4]:

$$W_{xc}^{\text{approx}}[\rho_1, \rho_2] = E_{xc}^{\text{approx}}[\rho_1, \rho_2] + \frac{d}{d\alpha}(\alpha^2 E_{xc}^{\text{approx}}[\rho_1, \rho_2, 1/\alpha]),$$

(D1)

where $\rho_{\alpha, 1/\alpha}(r) = \alpha^{-3} \rho(r/\alpha)$ is the spin density scaled uniformly with a parameter $\lambda = 1/\alpha$.

In LSD the correlation energy is given by

$$E_{c}^{\text{LSD}}[\rho, \rho] = \int d^3r \rho(r) e_{\text{unif}}^{\text{LSD}}(r, \zeta(r)).$$

(D2)

where $e_{\text{unif}}^{\text{LSD}}(r, \zeta)$ is the correlation energy per electron of the uniform electron gas with parameters $r_s = (3/4\pi \rho)^{1/3}$, $\rho = \rho_1 + \rho_2$, and $\zeta = (\rho_1 - \rho_2)/(\rho_1 + \rho_2)$. We are interested in the strictly correlated ($\alpha \to \infty$) limit of LSD. Since $\rho_{1/\alpha}$ is a low density in this limit, we can use the low-density ($r_s \to \infty$) expansion of $e_{\text{unif}}^{\text{LSD}}$:

$$e_{\text{unif}}^{\text{LSD}}(r_s, \zeta) \to -\frac{d_0(\zeta)}{r_s^3} + \frac{d_1(\zeta)}{r_s^3} + O(r_s^{-2}).$$

(D3)

Using this expression for the (local) scaled density parameter $r_s^{1/3}(r) = \alpha r_s(r/\alpha)$ and inserting into Eq. (D1), one obtains the functionals for the strong-interaction limit [see Eq. (9)] in LSD

$$W_{xc}^{\text{LSD}}[\rho_1, \rho_2] = E_{xc}^{\text{LSD}}[\rho_1, \rho_2] - \int d^3r r_s(\zeta(r)) r_s(r)$$

$$= -\left(\frac{4\pi}{3}\right)^{1/3} \int d^3r d_{xc}(\zeta(r)) \rho(r)^{3/3}$$

(D4)

For the coefficients $d_0$ and $d_{xc}$ in Eq. (D4) we use the low-density limit of the parametrization of $e_{\text{unif}}^{\text{LSD}}(r_s, \zeta)$ suggested by Perdew and Wang [37]. $d_{xc}(\zeta)$ is then given by Eq. (28) of Ref. [37] and $d_0$ by

$$d_0(\zeta) = d_{xc}(\zeta) - \frac{3}{8\pi} \left(\frac{9\pi}{4}\right)^{1/3} \left[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}\right].$$

(D6)

One finds that $d_{xc}(\zeta)$ is very close to 0.9, the value for the PC model, and almost independent of the spin polarization (see Table IV of Ref. [37]). On the other hand, the coefficient $d_1$ obtained from the Perdew-Wang parametrization varies as a function of $\zeta$ from $d_1(\zeta = 0) = 1.4408$ to $d_1(\zeta = 1) = 1.7697$. However, just as for $d_{xc}$, we expect the exact coefficient $d_1$ to be independent of $\zeta$, because in a low-density electron gas any two electrons will avoid one another, no matter how their spins are aligned relative to one another. In Eq. (D5) and the corresponding expressions for GGA and MGGA [Eqs. (D14) and (D16)], we will therefore use the spin-independent coefficient from the PC model, $d_1 = 1.5$, which we believe to be more correct. Thus, in Tables I–VI, all our functionals for $W_s$ and $W_r$ will agree closely for a uniform density.

In the GGA of Perdew, Burke, and Ernzerhof, the correlation energy functional is given by Eqs. (3), (7), and (8) of Ref. [26]. Under uniform scaling to the low-density limit, the function $A$ given by Eq. (8) of Ref. [26] scales to

$$A(\alpha r_s, \zeta) \to B_1(r_s, \zeta) \alpha + B_2(r_s, \zeta) \alpha^{1/2} + O(\alpha^0),$$

(D7)

with

$$B_1(r_s, \zeta) = \frac{\beta}{d_0(\zeta)} \phi(\zeta)^3 r_s$$

(D8)

and

$$B_2(r_s, \zeta) = \frac{\beta d_1(\zeta)}{d_0(\zeta)^2} \phi(\zeta)^3 r_s^{1/2}.$$  

(D9)

Here, $\beta = 0.066725$ is the coefficient of the second-order gradient expansion of the correlation energy of a slowly varying electron gas, $\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}] / 2$, and $d_0$ and $d_1$ are the coefficients of the low-density expansion of $e_{\text{unif}}^{\text{LSD}}(r_s, \zeta)$.

In the same low-density limit, the function $H$ given by Eq. (7) of Ref. [26] scales as

$$H(\alpha r_s, \zeta, \alpha^{1/2} t) \to H_1(r_s, \zeta, t) \alpha^{1/2} + H_2(r_s, \zeta, t) \alpha^{-3/2} + O(\alpha^{-2}),$$

(D10)
where \( t = \frac{1}{\sqrt{2\phi(\xi)k_F}} \) is a reduced density gradient with \( k_F = \sqrt{4k_F/\pi} \) and \( k_F = (3\pi^2\rho)^{1/3} \). The functions \( H_1 \) and \( H_2 \) are defined by

\[
H_1(r_s,\xi,t) = \frac{\beta \phi(\xi)^2 t^2}{1 + B_1 t^2} t^2
\]

and

\[
H_2(r_s,\xi,t) = -\frac{\beta \phi(\xi)^2 B_2 t^4}{1 + B_1 t^2} (1 + B_1 t^2 + B_1 t^4)^2. \tag{D12}
\]

Insertion into Eq. (D1) then yields

\[
W^{\text{MGGF}}_{\infty}[\rho,\rho] = E^{\text{MGGF}}_{\infty}[\rho,\rho] + \int d^3 r \left\{ \rho(r) \left( -\frac{d_0(\xi(r))}{r_s(r)} + H_1(r_s(r),\xi(r),t(r)) \right) + 1 + C \left( \frac{\sum \tau^W_{\sigma}}{\sum \tau_{\sigma}} \right)^{2/3} \right\}
\]

and

\[
W_{\infty}^{\text{MGGF}}[\rho,\rho] = \frac{1}{2} \int d^3 r \left\{ \rho(r) \left( \frac{d_{1}(\xi(r))}{r_s(r)} + H_2(r_s(r),\xi(r),t(r)) \right) + 1 + C \left( \frac{\sum \tau^W_{\sigma}}{\sum \tau_{\sigma}} \right)^{2/3} \right\}
\]

Here

\[
\tau^W_{\sigma} = \frac{1}{8} \frac{[\nabla \rho_{\sigma}]^2}{\rho_{\sigma}} \tag{D17}
\]

is the Weizsäcker kinetic energy density,

\[
\tau_{\sigma} = \frac{1}{2} \sum_{i} \frac{a_{\text{corr}}}{[\nabla \varphi_{i\sigma}]^2} \tag{D18}
\]

is the kinetic energy density of the Kohn-Sham orbitals \( \varphi_{i\sigma} \).

\( C = 0.53 \) is a constant parameter, and \( r_{s,\sigma} \) and \( t_{\sigma} \) are constructed like \( r_s \) and \( t \), but using \( \rho_{\sigma} \) instead of \( \rho \).

\[
\delta \rho(z) = \tilde{\rho} A \cos(Qz) \tag{E1}
\]
of small amplitude $A$ produces an energy change per electron
\[ \frac{\delta E}{N} = e(k_F, Q)A^2 + O(A^4), \] (E2)
where the coefficient $e$ is given by their Eq. (43), $e < 0$ indicates instability against the formation of a charge-density wave of infinitesimal amplitude.

In the limit $\tilde{p} \rightarrow 0$, in which the wave function $\Psi_\alpha(\tilde{p})$ for all $\alpha > 0$ is correlated as in the strong-interaction limit ($\alpha \rightarrow \infty$), Eq. (2) implies that $E_{xc} = W_{\infty}$. Using our PC expression (23) for $W_{\infty}$, Eq. (43) of Ref. [46] becomes
\[ e = \frac{k_F}{12\pi^2}[1 - 1.965x^2 + 1.241x^4], \] (E3)
where $x = Q/2k_F$. The first term of Eq. (E3) arises from the Hartree electrostatic energy, the second from the local part of $E_{xc}$, and the third from the second-order gradient contribution to $E_{xc} = W_{\infty}$. Equation (E3) is always positive but has a minimum very close to zero at $x \approx 1$ or $Q \approx 2k_F$. Thus our PC gradient expansion almost predicts the correct low-density instability of the uniform electron gas.

This instability can also be regarded as a “soft plasmon”: The plasmon frequency $\omega_p(Q)$ decreases from $\omega_p(0) = \sqrt{4\pi\rho}$ as $Q$ increases, and goes to zero around $Q = 2k_F$. Within the PC model, the low-density limit for the plasmon dispersion is $\omega_p(Q) = \omega_p(0)(1 - 1.965x^2 + 1.241x^4)^{1/2}$, consistent with Fig. 2 of Ref. [47]. Figure 5 of Ref. [48] suggests that the plasmon dispersion changes sign around $r_s = 10$, although the soft-plasmon instability appears around $r_s = 65$ [49].

If the electron-electron interaction were attractive, the Hartree term in Eq. (E3) would be negative. Then Eq. (43) of Ref. [46] shows that the uniform phase for any $\tilde{p}$ would be unstable against long-wavelength ($Q \rightarrow 0$ or $x \rightarrow 0$) charge-density waves.

[22] K. Burke (private communication).
[51] M. Ernzerhof (private communication) (method of Ref. [17]).