PHYSICAL REVIEW B VOLUME 54, NUMBER 24 15 DECEMBER 1996-II

# Gradient expansion of the exchange energy from second-order density response theory

P. S. Svendsen and U. von Barth
*Department of Theoretical Physics, University of Lund, Sweden*

(Received 17 June 1996; revised manuscript received 28 August 1996)

The basic idea behind the present work is that an atom is not a linear perturbation of the electron gas. We have thus analyzed the exchange energy of the inhomogeneous electron gas to third order in the deviation from a constant density. We give the symmetry properties obeyed by the corresponding second-order response function $L_x$, and demonstrate how $L_x$ gives rise to gradient corrections to the exchange energy. The expansion, which is taken up to sixth order in the density gradient, also includes the Laplacian of the density. In the case of a statically screened Coulomb interaction, we have calculated the coefficients of second- and fourth-order gradient terms both analytically and numerically. In analogy with the corresponding results from linear-response theory, the fourth-order coefficient is shown to diverge as the screening is made to vanish. For the bare Coulomb interaction we have not succeeded in obtaining analytical results, and, due to numerical problems at small-$q$ vectors, our numerically obtained coefficients have an estimated uncertainty of 20%. [S0163-1829(96)10148-X]

## I. INTRODUCTION

The utility and success of density-functional theory[1,2] with regard to the ground-state properties of solids is by now an established fact. Already, within the simple local-density approximation (LDA),[2] one obtains remarkably accurate vibrational frequencies and equilibrium distances.[3] Also, the trends in binding energies are usually correctly predicted, but absolute numbers are, unfortunately, not accurate enough for a proper description of, e.g., chemical reactions at surfaces. In order to approach chemical accuracy, ~0.1 eV, in calculated binding energies, much effort has been devoted to finding improvements on the LDA. Since the LDA becomes exact when the electron density is slowly varying, corrections involving the gradient of the density seem to be a natural extension of the LDA.[1] In the literature, one finds, however, numerous arguments against a straightforward gradient expansion of the exchange-correlation energy ($E_{\mathrm{xc}}$). Instead, different cutoff procedures are used to account for the fact that distances over which electrons are correlated in realistic inhomogeneous systems are determined more by actual variations in the density profile than by the screening length of an electron gas at the local value of the density.[4,5]

Nevertheless, the slowly varying limit (the long-wavelength limit in reciprocal space) of most existing extensions of the LDA are tailored according to linear-response theory. Exceptions to this rule are, e.g., real-space procedures like the weighted-density approximation of Gunnarsson, Jonson, and Lundqvist,[6] and the phenomenological approach followed by Becke for smaller molecules.[7,8] Even so, nearly all tested so-called *generalized gradient approximations* (GGA's) have only the first gradient of the density as an additional ingredient above the local density for constructing the full functional $E_{\mathrm{xc}}[n]$. It appears as if linear-response theory has formed a basis for most reciprocal-space attempts to go beyond the LDA, something that we find peculiar in view of the fact that an atom is *not* a linear perturbation of the electron gas. As a matter of fact, much effort has gone into finding successively more accurate approximations of the coefficient of the lowest-order gradient correction to the LDA using sophisticated treatments of correlation effects in the homogeneous gas.[9–12] These efforts, although interesting per se, seem to have overlooked the fact that energy contributions from higher-order gradients are usually larger than differences between lowest-order gradient corrections resulting from electron-gas theories of different degrees of sophistication. Consequently, we would like to encourage attempts also to include higher-order gradient corrections. Such attempts inevitably lead to second- and higher-order response treatments of the electron gas, the complications of which probably explain why little has been done in this regard.

Our conjecture concerning the importance of higher-order gradient corrections is further supported by the knowledge of the inadequacy of linear-response theory as far as the total energy of simple metals is concerned. Linear-response theory cannot distinguish between the total energies of different crystal structures having the same volume per atom. The directional dependencies of the energy are introduced only in second-order response theory with a nonisotropic response function depending on the angle between two momenta. Second-order response theory also gives rise to gradient corrections involving the Laplacian (second derivatives) of the density, a quantity clearly more susceptible to finer details in the density profile as compared to the gradient. The lowest-order gradient correction as well as nearly all GGA's involve only the square of the density gradient, and it is well known that all these extensions of the LDA essentially do nothing to correct the errors in the LDA as far as the so-called $s$-$p$ or $s$-$d$ transfer energies are concerned.[13]

Since this work represents an attempt at obtaining gradient corrections from second-order response theory, we here start by considering exchange only. We write *exchange only* as opposed to *Hartree-Fock* (HF) since we have in mind the Talman-Shadwick scheme,[14,15] sometimes referred to as the *optimized potential method* (OPM). Here we will not dwell upon the details of this method, but refer to the original papers,[14,15] or to discussions of the method in other papers.[4,16] Here we just state that, within the OPM, the expression for the exchange energy is the same as in the HF approximation, while the orbitals are all solutions to a one-electron Schrödinger equation with a local potential. This potential then acts as the variational parameter to minimize the expectation value of the Hamiltonian with respect to a Slater determinant consisting of those orbitals.

In Sec. II we set down some basic formulas, and show how one obtains gradient corrections from that second-order response function which gives the exchange energy to third order in the density deviations. The defining equations for the response function is deferred to Appendix A. Appendix B contains important symmetry relations obeyed by the response function. These symmetry relations, of which some have been mentioned earlier,[17] are very useful in the derivation of possible gradient terms. Section III contains details concerning the calculation of the actual gradient coefficient, both numerically and analytically. In Sec. IV we give our conclusions.

## II. BASIC FORMULAS

For a system without spin polarization, the exchange energy is given by

$$E_x[n]=-\tfrac{1}{4}\int |n(\mathbf{r},\mathbf{r}')|^2 v(\mathbf{r},\mathbf{r}')d^3r\, d^3r', \tag{1}$$

where $n(\mathbf{r},\mathbf{r}')$ is the one-electron density matrix

$$n(\mathbf{r},\mathbf{r}')=2\sum_{\mathbf{k}} n_{\mathbf{k}}\varphi_{\mathbf{k}}(\mathbf{r})\varphi^{*}_{\mathbf{k}}(\mathbf{r}'), \tag{2}$$

in terms of the one-electron orbitals $\varphi_k(\mathbf{r})$ which satisfy the Kohn-Sham equation

$$\left\{-\tfrac{1}{2}\nabla^2+w+\int vn\, d^3r'+v_x\right\}\varphi_{\mathbf{k}}=e_{\mathbf{k}}\varphi_{\mathbf{k}}. \tag{3}$$

Here, $w$ is the external potential, $v$ is the Coulomb interaction, $v(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$, $n(\mathbf{r})=n(\mathbf{r},\mathbf{r})$ is the particle density, $e_{\mathbf{k}}$ is the Kohn-Sham eigenvalue, and $v_x$ is the exchange potential of the exchange-only theory given by

$$v_x(\mathbf{r})=\frac{\delta E_x[n]}{\delta n(\mathbf{r})}. \tag{4}$$

The $n_{\mathbf{k}}$'s in Eq. (2) are occupation numbers, being 1 for occupied states and 0 for unoccupied states. (We use atomic units throughout the paper.)

The functional $E_x[n]$, being a differentiable functional of the density $n$, can be expanded in the deviation $\delta n$ from a constant density $(n_0)$ appropriate to the homogeneous electron gas:

$$\begin{aligned}E_x[n]=&E_x[n_0]+\int v_x(\mathbf{r}_1;n_0)\,\delta n(\mathbf{r}_1)d^3r_1\\&+\tfrac{1}{2}\int K_x(\mathbf{r}_1,\mathbf{r}_2;n_0)\,\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)d^3r_1d^3r_2\\&+\tfrac{1}{6}\int L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;n_0)\,\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)\\&\times\delta n(\mathbf{r}_3)d^3r_1d^3r_2d^3r_3+\cdots\,,\end{aligned} \tag{5}$$

where

$$K_x(\mathbf{r}_1,\mathbf{r}_2)=\frac{\delta v_x(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)}=\frac{\delta^2E_x[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)} \tag{6}$$

and

$$L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\frac{\delta K_x(\mathbf{r}_1,\mathbf{r}_2)}{\delta n(\mathbf{r}_3)}=\frac{\delta^3E_x[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)\,\delta n(\mathbf{r}_3)}. \tag{7}$$

Since our main interest is in obtaining gradient corrections to the local-density approximation, we remind the reader of the expression for the latter:

$$E_x^{\mathrm{LDX}}[n]=\int \epsilon_x(n(\mathbf{r}))n(\mathbf{r})d^3r. \tag{8}$$

We have here used the exchange-only version of the LDA (designated by LDX) and consequently $\epsilon_x(n)$ is the exchange energy per particle of a homogeneous electron gas of density $n$. Thus $\epsilon_x(n)=-3k_F/(4\pi)$, where $k_F$ is the local Fermi wave vector of the gas, $k_F^3=3\pi^2n$. Also the energy $E_x^{\mathrm{LDX}}$ of the LDA can be expanded to third order in the density deviations from a constant density of the electron gas:

$$\begin{aligned}E_x^{\mathrm{LDX}}[n]=&E_x[n_0]+\frac{\partial(n\epsilon_x(n))_0}{\partial n}\int \delta n(\mathbf{r})d^3r\\&+\frac{1}{2}\frac{\partial^2(n\epsilon_x(n))_0}{\partial n^2}\int[\delta n(\mathbf{r})]^2d^3r\\&+\frac{1}{6}\frac{\partial^3(n\epsilon_x(n))_0}{\partial n^3}\int[\delta n(\mathbf{r})]^3d^3r.\end{aligned} \tag{9}$$

Here, the small index 0 on the derivatives indicate that they are to be evaluated at the constant density $n_0$. Since the LDA is exact for constant densities, the first term of this expression is the same as the first term on the right-hand side of Eq. (5). We will find this useful when subtracting Eq. (9) from Eq. (5) in order to obtain the corrections beyond the LDX. We will also find it convenient to go to reciprocal space. Because of the translational invariance of the gas, we can write

$$K_x(\mathbf{r}_1,\mathbf{r}_2;n_0)=\sum_{\mathbf{q}} K_x(\mathbf{q};n_0)e^{i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \tag{10}$$

and

$$L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;n_0)=\sum_{\mathbf{q},\mathbf{q}'} L_x(\mathbf{q},\mathbf{q}';n_0)e^{i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_3)}e^{-i\mathbf{q}'\cdot(\mathbf{r}_2-\mathbf{r}_3)}, \tag{11}$$

where $\Sigma_{\mathbf{q}}$ is short for $\int d^3\mathbf{q}(2\pi)^{-3}$ and the dependencies on the constant density $n_0$ have been clearly indicated. With these definitions we now obtain, to third order in $\delta n$,

$$\begin{aligned}E_x[n]=&E_x^{\mathrm{LDX}}[n]+\tfrac{1}{2}\sum_{\mathbf{q}}\{K_x(\mathbf{q};n_0)-K_x(\mathbf{0};n_0)\}|\delta n_{\mathbf{q}}|^2\\&+\tfrac{1}{6}\sum_{\mathbf{q},\mathbf{q}'}\{L_x(\mathbf{q},\mathbf{q}';n_0)\\&-L_x(\mathbf{0},\mathbf{0};n_0)\}\,\delta n_{\mathbf{q}}\,\delta n_{-\mathbf{q}'}\,\delta n_{\mathbf{q}'-\mathbf{q}}.\end{aligned} \tag{12}$$

Here the quantity $\delta n_{\mathbf{q}}$ is defined through the relation $n(\mathbf{r}) = n_0 + \Sigma_{\mathbf{q}} \delta n_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$.

At this point we take the opportunity to derive two, as it turns out, important derivative theorems relating the functional derivatives $v_x$, $K_x$, and $L_x$. From Eq. (6) we have

$$v_x[\mathbf{r}_1, n_0 + \delta n] = v_x[n_0] + \int \frac{\delta v_x[\mathbf{r}_1, n_0]}{\delta n(\mathbf{r}_2)} \delta n(\mathbf{r}_2) d^3 r_2$$

$$= v_x(n_0) + \int K_x(\mathbf{r}_1, \mathbf{r}_2; n_0) \delta n(\mathbf{r}_2) d^3 r_2 .$$

Specializing to a constant density change $\delta n$ and going to reciprocal space, we then obtain

$$\frac{\partial v_x}{\partial n_0} = K_x(\mathbf{q}=\mathbf{0}; n_0). \tag{13}$$

Notice that $v_x(n_0) = -k_F/\pi$ and thus $K_x(\mathbf{q}=\mathbf{0}; n_0) = -\pi/k_F^2$.

Similarly, from Eq. (7),

$$K_x(\mathbf{r}_1, \mathbf{r}_2; n_0 + \delta n) = K_x(\mathbf{r}_1, \mathbf{r}_2; n_0) + \int L_x(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; n_0) \delta n(\mathbf{r}_3) d^3 r_3 ,$$

giving

$$\frac{\partial K_x(\mathbf{q}; n_0)}{\partial n_0} = L_x(\mathbf{q}, \mathbf{q}; n_0), \tag{14}$$

a relation that puts severe restrictions on the actual form of $L_x(\mathbf{q},\mathbf{q}'; n_0)$, and without which the gradient expansion becomes ill-defined (see below). Notice also that the $\mathbf{q}=\mathbf{0}$ limit of Eq. (14) gives $L_x(\mathbf{0},\mathbf{0}; n_0) = 2\pi^3/k_F^5$.

In order to transform the equation above to actual gradient corrections, a constraint beyond the assumption of small amplitudes $\delta n$ has to be imposed. In addition, we will now consider density changes $\delta n$ which are slowly varying in space, i.e., densities with appreciable Fourier components $\delta n_{\mathbf{q}}$ only for $q < 2k_F$. Both response functions $K_x$ and $L_x$ turn out to be singular at $q = q' = |\mathbf{q} - \mathbf{q}'| = 2k_F$. At $q = (q' = |\mathbf{q} - \mathbf{q}'|) = 0$ we will assume that they are analytic, and they are, in fact, reasonably well described by polynomial expansions around $q = 0$. As we will now see, it is this small-$q$ limit of the kernels which is of interest here. Equations (B3) and (B16) in Appendix B and the $\mathbf{q}=\mathbf{0}$ results above then give the following expressions:

$$K_x(\mathbf{q}; n) = K_x^{(0)}(n) + K_x^{(2)}(n) q^2 + K_x^{(4)}(n) q^4 + \cdots$$

$$= -\frac{\pi}{k_F^2} \{1 + K_2 Q^2 + K_4 Q^4 + \cdots\},$$

$$L_x(\mathbf{q}, \mathbf{q}'; n) = L_x^{(0)}(n) + L_x^{(2)}(n)(q^2 + q'^2 - \mathbf{q}\cdot\mathbf{q}') + L_x^{(4)}(n)(q^2 + q'^2 - \mathbf{q}\cdot\mathbf{q}')^2 + L_x'^{(4)}(n)(q^2 q'^2 - (\mathbf{q}\cdot\mathbf{q}')^2) + \cdots$$

$$= \frac{2\pi^3}{k_F^5} \{1 + L_2(Q^2 + Q'^2 - \mathbf{Q}\cdot\mathbf{Q}') + L_4(Q^2 + Q'^2 - \mathbf{Q}\cdot\mathbf{Q}')^2 + L_4'(Q^2 Q'^2 - (\mathbf{Q}\cdot\mathbf{Q}')^2) + \cdots\}, \tag{15}$$

where $\mathbf{Q} = \mathbf{q}/k_F$.

Gradient corrections can now be constructed by first inserting the right-side expressions of Eq. (15) into Eq. (12), and subsequently Fourier transforming back to real space. We will only illustrate this rather straightforward procedure for a few important cases:

$$\sum_{\mathbf{q}} K_x^{(2)}(n_0) q^2 |\delta n_{\mathbf{q}}|^2 = \sum_{\mathbf{q}} K_x^{(2)}(n_0) \int \delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2) \mathbf{q}\cdot\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}_1} e^{-i\mathbf{q}\cdot\mathbf{r}_2} d^3 r_1 d^3 r_2$$

$$= \int K_x^{(2)}(n_0) \nabla_{\mathbf{r}_1}(\delta n(\mathbf{r}_1)) \nabla_{\mathbf{r}_2}(\delta n(\mathbf{r}_2)) \delta(\mathbf{r}_1 - \mathbf{r}_2) d^3 r_1 d^3 r_2 = \int K_x^{(2)}(n_0) |\nabla \delta n(\mathbf{r})|^2 d^3 r$$

and

$$\sum_{\mathbf{q},\mathbf{q}'} L_x^{(2)}(n_0) q^2 \delta n_{\mathbf{q}} \delta n_{-\mathbf{q}'} \delta n_{\mathbf{q}'-\mathbf{q}} = -\sum_{\mathbf{q}\cdot\mathbf{q}'} \int L_x^{(2)}(n_0) \delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2) \delta n(\mathbf{r}_3) (\nabla_{\vec{r}_1}^2 e^{i\mathbf{q}\cdot\mathbf{r}_1}) e^{-i\mathbf{q}'\cdot\mathbf{r}_2} e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}_3} d^3 r_1 d^3 r_2 d^3 r_3$$

$$= -\int L_x^{(2)}(n_0) (\nabla^2 \delta n(\mathbf{r}_1)) \delta n(\mathbf{r}_1) \delta n(\mathbf{r}_3) \delta(\mathbf{r}_1 - \mathbf{r}_3) \delta(\mathbf{r}_3 - \mathbf{r}_2) d^3 r_1 d^3 r_2 d^3 r_3$$

$$= -\int L_x^{(2)}(n_0) (\delta n(\mathbf{r}))^2 \nabla^2 \delta n(\mathbf{r}) d^3 r = 2 \int L_x^{(2)}(n_0) \delta n(\mathbf{r}) |\nabla \delta n(\mathbf{r})|^2 d^3 r.$$

The contributions from $L_x^{(2)}(n)(q'^2-\mathbf{q}\cdot\mathbf{q}')$ can be similarly computed, and in total we obtain

$$\sum_{\mathbf{q},\mathbf{q}'} \tfrac{1}{6}L_x^{(2)}(n_0)(q^2+q'^2-\mathbf{q}\cdot\mathbf{q}')\,\delta n_{\mathbf{q}}\delta n_{-\mathbf{q}'}\delta n_{\mathbf{q}'-\mathbf{q}} = \tfrac{1}{2}\int L_x^{(2)}(n_0)\,\delta n(\mathbf{r})|\nabla\,\delta n(\mathbf{r})|^2 d^3r. \quad (16)$$

It should be noted that in going from reciprocal to real space, ''surface terms'' have been neglected, i.e., we assume that the system at hand can be contained within a large surface with zero electronic density.

In many important applications, like say, total-energy calculations on atomic clusters or molecules, it is difficult to define a background or average density $n_0$ unambiguously. Here one usually makes the substitution $n_0 \rightarrow n(\mathbf{r})$, $n$ being the local density $n(\mathbf{r})$. The gradient functional arising from $K_x^{(2)}(n(\mathbf{r}))q^2$ can then be viewed as an infinite summation, the first two terms of which are

$$\begin{aligned}\tfrac{1}{2}\int K_x^{(2)}(n(\mathbf{r}))|\nabla n(\mathbf{r})|^2 d^3r &= \tfrac{1}{2}\int K_x^{(2)}(n_0)|\nabla n(\mathbf{r})|^2 d^3r \\ &\quad + \tfrac{1}{2}\int \left(\frac{\partial K_x^{(2)}(n)}{\partial n}\right)_{n=n_0} \delta n(\mathbf{r})|\nabla n(\mathbf{r})|^2 d^3r + \cdots \\ &= \tfrac{1}{2}\int K_x^{(2)}(n_0)|\nabla n(\mathbf{r})|^2 d^3r \\ &\quad + \tfrac{1}{2}\int L_x^{(2)}(n_0)\,\delta n(\mathbf{r})|\nabla n(\mathbf{r})|^2 d^3r + \cdots . \end{aligned} \quad (17)$$

The last line in Eq. (17) above is a consequence of the following relation between the coefficients $K_x^{(j)}$ and $L_x^{(j)}$,

$$L_x^{(j)}(n) = \frac{\partial K_x^{(j)}(n)}{\partial n}, \quad j=0,2,\ldots . \quad (18)$$

Notice that Eq. (18) is a simple consequence of Eq. (14). A comparison of Eqs. (16)–(18) demonstrates an often overlooked but very important point regarding gradient corrections. Equation (18) in short ensures that real-space terms from the $q^2$ part of $L_x$ are *already accounted for* in the expansion of $K_x^{(2)}(n)$ above. A violation of Eq. (18), on the other hand, would lead to the appearance of terms of the form $\int\delta n(\mathbf{r})|\nabla\,\delta n(\mathbf{r})|^2 d^3r$. Such terms would be difficult to calculate without a completely unambiguous separation of the density in a constant $n_0$ and variable part $\delta n(\mathbf{r})$. As a matter of fact, the very existence of gradient expansions, as applied to real systems, relies on the validity of Eq. (14).

The contribution from $K_x^{(4)}(n)q^4$ can be similarly expanded to show that terms of the form $\int\delta n(\mathbf{r})(\nabla^2\delta n)^2 d^3r$ do not occur in the final gradient-expansion given below,

$$\begin{aligned} E_x[n] &= E_x^{\mathrm{LDX}}[n] + \tfrac{1}{2}\int K_x^{(2)}(n)|\nabla n(\mathbf{r})|^2 d^3r \\ &\quad + \tfrac{1}{2}\int K_x^{(4)}(n)|\nabla^2 n(\mathbf{r})|^2 d^3r \\ &\quad + \tfrac{1}{4}\int (L_x^{(4)}(n) - L_x'^{(4)}(n))|\nabla n(\mathbf{r})|^2\nabla^2 n(\mathbf{r}) d^3r \\ &= A_x\int n(\mathbf{r})^{4/3} d^3r + B_x^{(2)}\int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}} d^3r \\ &\quad + B_x^{(4)}\int \frac{|\nabla^2 n(\mathbf{r})|^2}{n(\mathbf{r})^2} d^3r \\ &\quad + C_x^{(4)}\int \frac{|\nabla n(\mathbf{r})|^2\nabla^2 n(\mathbf{r})}{n(\mathbf{r})^3} d^3r. \end{aligned} \quad (19)$$

The coefficients in Eq. (19) are related to the small-$q$ expansion coefficients as follows:

$$A_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3},$$

$$B_x^{(2)} = -\frac{1}{6\pi(3\pi^2)^{1/3}}K_2 = -\frac{5}{216\pi(3\pi^2)^{1/3}},$$

$$B_x^{(4)} = -\frac{1}{18\pi^3}K_4 = -\frac{73}{64800\pi^3},$$

$$C_x^{(4)} = \frac{1}{54\pi^3}(L_4 - L_4'). \quad (20)$$

The $K_2$ and $K_4$ coefficients were first calculated analytically by Engel and Vosko.[18] Their values were later confirmed by analytical calculations using two completely different techniques.[16,19] These coefficients have also been available from numerical work by Kleinman[20] ($K_2$) and, much earlier, by Geldart and Taylor.[21]

The unprimed $L_x$ coefficients can then easily be calculated from Eq. (18) as

$$L_j = \tfrac{1}{2}(j+2)K_j, \quad (21)$$

which yields $L_2 = 2K_2 = \frac{5}{18}$, and $L_4 = 3K_4 = \frac{73}{1200}$.

As pointed out in Appendix B, $L_4'$ (and, consequently, $C_x^{(4)}$) *can only be found by evaluating* $L_x(\mathbf{q},\mathbf{q}')$ *for values of* $\mathbf{q}$ *not parallel to* $\mathbf{q}'$. Possible schemes for obtaining this coefficient will be the subject of Sec. III.

When applied to real systems with regions of small or vanishing electronic densities, both the third and fourth terms in the gradient expansion will give large and spurious contributions. This is not, however, an inherent deficiency of the gradient scheme, since the condition $q \ll 2k_F$ for a given $q$ will be violated as $n, k_F \rightarrow 0$. Some quantitative criterion for when gradient corrections should *not* be applied is therefore clearly necessary. In actual calculations such a criterion must be introduced into the gradient part of the exchange-energy functional as a cutoff or soft regularization. The following often used condition (with first-order gradient corrections) has the merit of reducing to $q \ll 2k_F$ when the density is dominated by one $\mathbf{q}$ value:

$$\frac{|\nabla^2 n|}{2k_F|\nabla n|} \ll 1. \tag{22}$$

In this context, with $K_x$ and $L_x$ expanded up to and including the $q^4$ term, the condition above is, however, somewhat too strict. It can be shown that $K_x(\mathbf{q})$ differs from the truncated form in Eq. (15) by less than 1% up to $Q \simeq 1.2$. It would thus seem reasonable to replace $\ll$ with $<$ in Eq. (22) above.

Finally, we again want to stress that each contribution in Eq. (19) represents a summation to infinite order (in $\delta n$) while still originating in the response functions of no higher than second order. The expression is therefore somewhat ill suited to ascertain the order-by-order convergence of the $q$ space expansion of $E_x[n]$. This question will be addressed in a forthcoming paper.[22]

## III. CALCULATING THE SECOND-ORDER COEFFICIENT

We will now turn our attention to the actual calculation of the unknown coefficient $L_4'$. The requirement of $\mathbf{q}$ not being parallel to $\mathbf{q}'$ will be satisfied by choosing, for example $\mathbf{q}' = \mathbf{q}_\perp$, where $q = q_\perp$ and $\mathbf{q}\cdot\mathbf{q}_\perp = 0$. The determining equation (A6) for $L_x$ then takes the form

$$\begin{aligned}(\chi_0(\mathbf{q}))^2 \chi_0(\sqrt{2}\mathbf{q}) L_x(\mathbf{q},\mathbf{q}_\perp) \\ = I_\Sigma(\mathbf{q},\mathbf{q}_\perp) + I_V(\mathbf{q},\mathbf{q}_\perp) - \chi_0(\mathbf{q},\mathbf{q}_\perp) \\ \times[2K_x(\mathbf{q})\chi_0(\mathbf{q}) + K_x(\sqrt{2}\mathbf{q})\chi_0(\sqrt{2}\mathbf{q})],\end{aligned} \tag{23}$$

since $K_x(\mathbf{q}) = K_x(q)$ and $\chi_0(\mathbf{q}) = \chi_0(q)$.

We now proceed to expand the equation above in its entirety to fourth order in $Q$, thus enabling us to find $L_4'$. So far, we have only managed to achieve this analytically with a statically screened Coulomb interaction,

$$v(\mathbf{q}) = \frac{4\pi}{q^2 + \lambda^2}, \tag{24}$$

where $\lambda$ is an inverse screening length.

All expansion coefficients of $K_x$ and $L_x$ will in this case consequently be $\lambda$ dependent:

$$\begin{aligned}K_x(\mathbf{q};n,\Lambda) &= -\frac{\pi}{k_F^2}\{K_0(\Lambda) + K_2(\Lambda)Q^2 + K_4(\Lambda)Q^4 + \cdots\},\\ L_x(\mathbf{q},\mathbf{q}_\perp;n,\Lambda) &= \frac{2\pi^3}{k_F^5}\{L_0(\Lambda) + 2L_2(\Lambda)Q^2 \\ &\quad + (4L_4(\Lambda) + L_4'(\Lambda))Q^4 + \cdots\}, \qquad (25)\\ \chi_0(\mathbf{q};n) &= -\frac{k_F}{\pi^2}\{1 - \tfrac{1}{12}Q^2 - \tfrac{1}{240}Q^4 + \cdots\},\\ \chi_0(\mathbf{q},\mathbf{q}_\perp;n) &= \frac{1}{\pi^2 k_F}\{1 + \tfrac{1}{6}Q^2 + \tfrac{11}{240}Q^4 + \cdots\},\end{aligned}$$

where $\Lambda = \lambda/k_F$.

The last equation above is a special case of the general small-$q$ expansion of Eq. (A15):

$$\begin{aligned}\chi_0(\mathbf{q},\mathbf{q}';n) = \frac{1}{\pi^2 k_F}\{1 + \tfrac{1}{12}(Q^2 + Q'^2 - \mathbf{Q}\cdot\mathbf{Q}') \\ + \tfrac{1}{80}(Q^2 + Q'^2 - \mathbf{Q}\cdot\mathbf{Q}')^2 \\ - \tfrac{1}{240}(Q^2Q'^2 - (\mathbf{Q}\cdot\mathbf{Q}')^2)\}.\end{aligned} \tag{26}$$

Finally, we may assume that (all other parts being expandable) $I = I_\Sigma + I_V$ can be expanded as well:

$$I(\mathbf{q},\mathbf{q}_\perp;n,\Lambda) = \frac{1}{\pi^3 k_F^2}\{I_0(\Lambda) + I_2(\Lambda)Q^2 + I_4(\Lambda)Q^4 + \cdots\}. \tag{27}$$

$L_4'(\Lambda)$ can now formally be expressed as

$$\begin{aligned}L_4'(\Lambda) = \tfrac{41}{1440}K_0(\Lambda) + \tfrac{1}{12}K_2(\Lambda) + 3K_4(\Lambda) - \tfrac{7}{720}L_0(\Lambda) \\ + \tfrac{2}{3}L_2(\Lambda) - 4L_4(\Lambda) - \tfrac{1}{2}I_4(\Lambda).\end{aligned} \tag{28}$$

The coefficients $K_j(\Lambda)$ up to $j=4$ can be found by first expanding the *integrands* in Eq. (29) of Svendsen and von Barth[16] up to order $Q^4$. The ensuing integrals are sufficiently simple to be carried out analytically, and we find

$$\begin{aligned}K_0(\Lambda) &= 1 - \tfrac{1}{4}\Lambda^2 \ln\left(\frac{4+\Lambda^2}{\Lambda^2}\right),\\ K_2(\Lambda) &= \frac{1}{(4+\Lambda^2)^2}\{\tfrac{14}{9} + \tfrac{3}{2}\Lambda^2 + \tfrac{1}{4}\Lambda^4\} \\ &\quad - \tfrac{1}{16}\Lambda^2 \ln\left(\frac{4+\Lambda^2}{\Lambda^2}\right), \qquad (29)\\ K_4(\Lambda) &= \frac{1}{\Lambda^2(4+\Lambda^2)^4}\{\tfrac{32}{45} + \tfrac{608}{225}\Lambda^2 + \tfrac{974}{135}\Lambda^4 + \tfrac{103}{27}\Lambda^6 \\ &\quad + \tfrac{7}{9}\Lambda^8 + \tfrac{1}{18}\Lambda^{10}\} - \tfrac{1}{72}\Lambda^2 \ln\left(\frac{4+\Lambda^2}{\Lambda^2}\right).\end{aligned}$$

A method due to Geldart and Taylor[21] for calculating $K_x(\mathbf{q};n,\Lambda=0)$ numerically can be used to calculate $K_x(\mathbf{q};n,\Lambda)$ for the less subtle case of, say, $\Lambda \sim \frac{1}{2}$ with very high accuracy. We may then extract the coefficients $K_j(\Lambda)$ for given values of $\Lambda$ by a least-squares polynomial fit. Resulting figures from this ''integration first and expansion afterwards'' approach can then be compared to results from the opposite procedure above by defining [see Eq. (25)]

$$J(Q,\Lambda) = \frac{-\pi^{-1}k_F^2 K_x(\mathbf{q};n,\Lambda) - K_0(\Lambda) - K_2(\Lambda)Q^2}{K_4(\Lambda)Q^4}, \tag{30}$$

where the values of $K_j(\Lambda)$ are taken from the analytic calculations, whereas $K_x(\mathbf{q};n,\Lambda)$ is calculated numerically. If analytic and numerical work are equivalent, we would expect $J(Q,\Lambda)$ to approach 1 smoothly as $Q \to 0$. From Fig. 1 we see that $J(Q,\Lambda)$ indeed has this feature for a number of $\Lambda$ values. We may therefore safely conclude that *the order in*

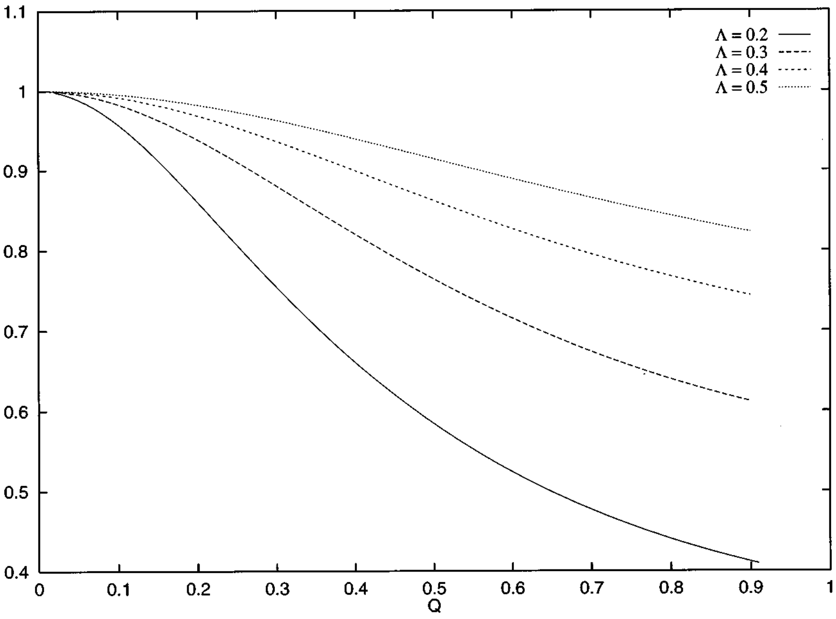

FIG. 1. $J(Q,\Lambda)$ for a number of values of $\Lambda$.

*which we perform, respectively, integrations and expansions in q is immaterial as long as* $\Lambda>0$.

From Eq. (18) we can generalize Eq. (21) to

$$L_j(\Lambda)=\tfrac{1}{2}\left\{(j+2)K_j(\Lambda)+\Lambda\,\frac{\partial K_j(\Lambda)}{\partial\Lambda}\right\}. \tag{31}$$

This gives $L_0(\Lambda)$, $L_2(\Lambda)$, and $L_4(\Lambda)$:

$$L_0(\Lambda)=1+\frac{\Lambda^2}{4+\Lambda^2}-\tfrac{1}{2}\,\Lambda^2\,\ln\!\left(\frac{4+\Lambda^2}{\Lambda^2}\right),$$

$$\begin{aligned}L_2(\Lambda)=&\frac{1}{(4+\Lambda^2)^3}\left\{\tfrac{112}{9}+22\Lambda^2+\tfrac{15}{2}\,\Lambda^4+\frac{3}{4}\,\Lambda^6\right\}\\&-\frac{3}{16}\,\Lambda^2\,\ln\!\left(\frac{4+\Lambda^2}{\Lambda^2}\right),\end{aligned} \tag{32}$$

$$\begin{aligned}L_4(\Lambda)=&\frac{1}{\Lambda^2(4+\Lambda^2)^5}\{\tfrac{256}{45}+\tfrac{6976}{225}\,\Lambda^2+\tfrac{85696}{675}\,\Lambda^4+\tfrac{2444}{27}\,\Lambda^6\\&+\tfrac{751}{27}\,\Lambda^8+4\Lambda^{10}+\tfrac{2}{9}\,\Lambda^{12}\}-\tfrac{1}{18}\,\Lambda^2\,\ln\!\left(\frac{4+\Lambda^2}{\Lambda^2}\right).\end{aligned}$$

The only remaining unknown in Eq. (28), $I_4(\Lambda)$, requires an expansion of $I(\mathbf{q},\mathbf{q}_\perp;n,\Lambda)$ to $Q^4$. This turned out to be a rather formidable (albeit straightforward) task involving, for example, derivatives like $(\partial^n\Sigma^{\mathrm{HF}}(\mathbf{k};\Lambda)/\partial k^n)_{k=k_F}$ up to $n=6$. In spite of the sheer complexity of such calculations we have great confidence in the final results since the bulk of the actual work was checked with the help of a symbol manipulating program (MATHEMATICA). The analytical results are also in very good agreement with numerical calculations of $I$ with $\Lambda\sim0.5$. These numerical results will be discussed in more detail shortly in the context of the $\Lambda=0$ limit.

Without any further details we now finally give the resulting $I_4(\Lambda)$ coefficient below as

$$\begin{aligned}I_4(\Lambda)=&-\frac{1}{\Lambda^2(4+\Lambda^2)^5}\{\tfrac{896}{45}-\tfrac{38176}{225}\,\Lambda^2+\tfrac{4408}{75}\,\Lambda^4\\&+\tfrac{1166}{15}\,\Lambda^6+\tfrac{1201}{45}\,\Lambda^8+\tfrac{361}{90}\,\Lambda^{10}+\tfrac{11}{48}\,\Lambda^{12}\}\\&+\tfrac{11}{192}\,\Lambda^2\,\ln\!\left(\frac{4+\Lambda^2}{\Lambda^2}\right).\end{aligned} \tag{33}$$

Inserting into Eq. (28), for $L_4'$ we then obtain

$$\begin{aligned}L_4'(\Lambda)=&-\frac{1}{\Lambda^2(4+\Lambda^2)^5}\{\tfrac{64}{15}+\tfrac{9488}{675}\,\Lambda^2+\tfrac{3524}{75}\,\Lambda^4\\&+\tfrac{1429}{45}\,\Lambda^6+\tfrac{2639}{270}\,\Lambda^8+\tfrac{7}{5}\,\Lambda^{10}+\tfrac{7}{90}\,\Lambda^{12}\}\\&+\tfrac{7}{360}\,\Lambda^2\,\ln\!\left(\frac{4+\Lambda^2}{\Lambda^2}\right).\end{aligned} \tag{34}$$

To zeroth order in $\Lambda$ ($\Lambda\rightarrow0$ being the unscreened limit), this gives

$$\begin{aligned}L_4'(\Lambda)&=-\frac{1}{240\Lambda^2}-\frac{23}{2700},\\L_4(\Lambda)&=\frac{1}{180\Lambda^2}+\frac{7}{300}.\end{aligned} \tag{35}$$

($L_4$ expansion added for comparison).

$L_4-L_4'$ and, by Eq. (20), therefore also the gradient coefficient $C_x^{(4)}$, are in other words singular as $\Lambda\rightarrow0$. It can be shown that the coefficient $B_x^{(4)}$ has this feature as well,[16] which is rather disturbing considering the significance still attached to the screened $B_x^{(j)}$ values. We would like to point out, however, that the unscreened $\Lambda\rightarrow0$ limit of the above coefficients does *not*, in any sense, imply infinite exchange corrections. While the unscreened expansion can be viewed as a limit of $\lambda < q < 2k_F$ as $\lambda \rightarrow 0$, in the screened case it can be shown (numerically) that $L_x$ (and $K_x$) can only be expanded in a polynomial for values of $q < \lambda (\lambda < 2k_F)$. As the above contributions to $L_x$ will be of order $q^4/\lambda^2$, $E_x$ in Eq. (12) will remain finite for an arbitrarily small $\lambda$. Unfortunately, this also means that the range of validity of the screened coefficients shrink as $\lambda \rightarrow 0$, effectively rendering them meaningless per se for calculations on anything but model systems. One could, of course, surmise that the singularities are canceled by singularities of opposite sign from similarly (screened) correlation gradient coefficients. If this turns out to be the case, it would still be necessary to show that the coefficients are insensitive to whether $q < \lambda$ or $\lambda < q$ as both approach 0.

The desired unscreened value of $L_4'$ could possibly be inferred from our screened analytic calculation by assuming, say, the ratio between the screened $\lim_{\lambda \rightarrow 0}(L_4'/L_4)$, and unscreened coefficients $(L_4'/L_4)_{\lambda=0}$ to be the same. This would imply a value of $L_4' = -\frac{3}{4}L_4$.

Aside from such (in the absence of higher-order gradient expansion coefficients of the correlation energy) rather speculative considerations, there is, obviously, also the option of obtaining $L_4'$ from a numerical calculation of $I(\mathbf{q},\mathbf{q}';n,\Lambda=0)$ for selected values of $\mathbf{q}$ and $\mathbf{q}'$. Unfortunately, no way of adding all the vertex- ($I_V$) and self-energy ($I_\Sigma$) contributions in the style of Geldart and Taylors[21] similar calculation suggests itself. Instead one is faced with ''brute force'' and rather lengthy calculations of the separate contributions, where great care must be exercised when integrating over the bare (or almost bare) Coulomb interaction. Of the technical aspects of the integration, we will just mention that both $I_\Sigma$ and $I_V$ can be reduced to a number of three-dimensional integrals to be performed numerically. Both the Green's functions and the (bare) Coulomb interaction give singularities in the integrand, which are, however, all integrable. We have performed such calculations for a number of $\mathbf{q}'$, $\mathbf{q}$, and $\lambda$ values including $\lambda=0$. The agreement between the numerical calculations and the analytic results given above for $q < \lambda$ is very good. To illustrate this, we define the function $N$,

$$N(Q,\Lambda) = \frac{\pi^3 k_F^2 I(\mathbf{q},\mathbf{q}_\perp;n,\Lambda) - I_0(\Lambda) - I_2(\Lambda)Q^2}{I_4(\Lambda)Q^4}, \tag{36}$$

where $I(\mathbf{q},\mathbf{q}_\perp;n,\Lambda)$ is calculated numerically. A polynomial least-squares fit to $N(Q,0.5)$ then gives

$$N(Q,0.5) = 1.00206 + 2.78383Q^2 - 19.5296Q^4 + 117.474Q^6. \tag{37}$$

As we see from the fit, $N(Q,0.5)$ here does indeed approach 1 as $Q \rightarrow 0$.

When turning to the numerical calculations of $I(\mathbf{q},\mathbf{q}_\perp;n,\Lambda)$ with $\Lambda \simeq 0$ it should thus be kept in mind that the basic correctness of the computer code for these calculations has been verified for any $\Lambda$. In practice, it will, of course, be slightly more difficult to converge calculations properly with a ''bare'' Coulomb-interaction. Judging from rates of convergence, our final results appear to be fully converged to at least five digits of accuracy. However, since no direct analytic comparison exists in this case, subtle numerical difficulties cannot be entirely ruled out.

It is still rather surprising that the resulting values, while reproducing the constant term $(I_0 = 3K_0 - 2L_0 = 1)$ quite well (better than 0.1%), do *not* reproduce the $Q^2$ coefficient prescribed by the derivative theorem [Eq. (14), $I_2 = \frac{1}{6}K_0 + 4K_2 + \frac{2}{3}L_0 - 4L_2 = \frac{5}{18}$] with even closely the same accuracy ($I_n$, with the $\Lambda$ argument dropped implies, as for $K_n$ and $L_n$, $\Lambda=0$). We should add that the calculated values of $I_n$ follow from a least-squares fit for values of $Q$ in the range $Q=0.1$–$0.6$. As noted previously, the fulfillment of the derivative theorem is a necessary requirement for the construction of gradient corrections. Therefore, a slightly erroneous value of $I_2$ can only be accepted if the value of $K_2$ is adjusted accordingly. We do not consider this a viable option. There is, by

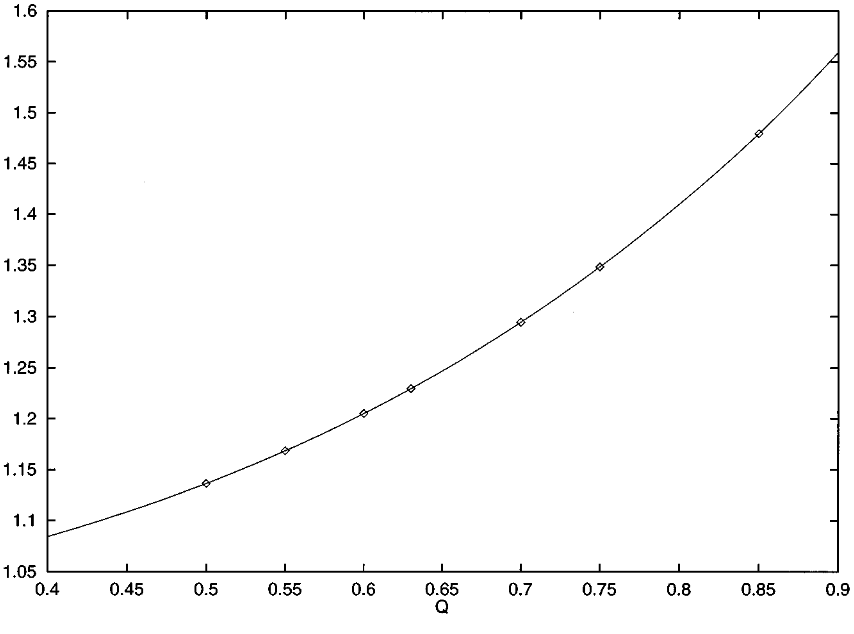

FIG. 2. $k_F^5/(2\pi^3)L_x(\mathbf{q},\mathbf{q}_\perp;n)$ from numerical calculation vs the polynomial fit from Eq. (38).

now, quite ample evidence (from a variety of techniques[21,23,18,16,19]) for a value of $K_2 = \frac{5}{36}$.

Whatever the reason for the present inaccuracy in the ''reproduced'' values $I_2$ and $K_2$—numerical error or a more fundamental breakdown of the exchange-energy expansion in terms of response kernels—we suggest the following scheme to extract a value of $L_4'$ as accurately as possible. We solve the determining equation (23) with respect to $L_x(\mathbf{q},\mathbf{q}_\perp)$ for a range of $Q$ values sufficiently large so as to ensure that contributions from (and therefore relative errors in) terms of order $Q^4$ are (almost) of the same magnitude as terms of order $Q^2$. For the noninteracting response function $\chi_0(\mathbf{q},\mathbf{q}')$ we have here used a closed expression given by Lloyd and Sholl[24]. Since $|\mathbf{Q}-\mathbf{Q}_\perp| = \sqrt{2}Q$, we are restricted by $Q < \sqrt{2}$. We have performed calculations in this way for seven values between $Q = 0.5$ and $Q = 1.0$. A least-squares fit to order $Q^6$ of these values gives the following result:

$$\frac{k_F^5}{2\pi^3} L_x(\mathbf{q},\mathbf{q}_\perp;n) = 0.999\,221 + 0.504\,478Q^2 + 0.152\,542Q^4 + 0.096\,659\,4Q^6 \tag{38}$$

(see Fig. 2). The $Q^2$ coefficient which should properly be $2L_2 \simeq 0.556$ is off by some 10%. Consequently, the $Q^4$ coefficient $(=4L_4 + L_4')$ can be expected to be in error by 20% at most. This yields an estimate of $L_4' = -0.091 \pm 0.03$ and $L_4 - L_4' = 0.15 \pm 0.03$.

We have also performed calculations of $L_x(\mathbf{q},\mathbf{q}';n)$ with $\mathbf{q}' = 2\mathbf{q}_\perp$ within a somewhat narrower range of $Q$ values. In this case the calculated property can be expressed as

$$\frac{k_F^5}{2\pi^3} L_x(\mathbf{q},2\mathbf{q}_\perp;n) = 1 + 5L_2Q^2 + (25L_4 + 4L_4')Q^4 + \cdots . \tag{39}$$

A least-squares-fit to order $Q^6$ of ten calculated values between $Q = 0.18$ and 0.39 gives

$$\frac{k_F^5}{2\pi^3} L_x(\mathbf{q},2\mathbf{q}_\perp;n) = 0.999\,85 + 1.269\,34Q^2 + 1.1244Q^4 + 1.534\,48Q^6 \tag{40}$$

(see Fig. 3). The expression above reproduces the *calculated* values typically to within $10^{-6}$. Since $5L_2 = 1.389$ we see again that $L_2$ is in error by some 10%. The value for $L_4'$ from this fit, $L_4' = -0.099$ is rather more unreliable, since the $Q^2$ term will dominate in this range. It is nevertheless worth noting that it is consistent with the value for $L_4'$ above (within the stated error limits).

## IV. CONCLUDING REMARKS

The basic idea underlying the present work is that an atom is *not* a linear perturbation on the electron gas. From the notion that a molecule or a solid is a collection of atoms, it then follows that the construction of gradient approximations for such systems should be based on higher-order response functions of the homogeneous system. In this work we took the first step beyond linear response, and tried to obtain gradient corrections from second-order response theory. This leads to corrections to the LDA which involve the Laplacian of the particle density—an ingredient absent from nearly all approximations presently in use. Some preliminary results on model solids[22] indicate that the Laplacian is indeed a useful additional ingredient.

To start with the simplest possible realistic case, we have here limited ourselves to the study of exchange energies for which accurate answers are easily provided by full calculations. We chose the particular version of exchange known as the Talman-Shadwick scheme, or sometimes the optimized-potential model, and here referred to as the exchange-only approximation (EXOA). In this scheme exchange energies are strictly linear in $e^2$, i.e., the strength of the Coulomb interaction. We worked out an analytical formula giving the

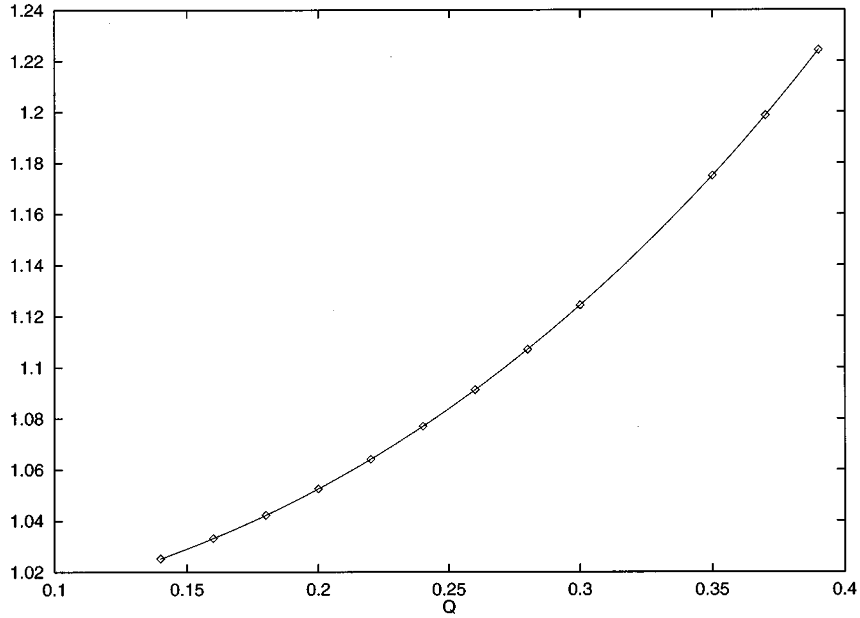

FIG. 3. $k_F^5/(2\pi^3)L_x(\mathbf{q},2\mathbf{q}_\perp;n)$ from numerical calculation vs the polynomial fit from Eq. (40).

second-order response kernel $L_x$ defined to be the third functional derivative with respect to the density of the exchange energy $E_x$ within the EXOA. In its most general form, $L_x$ is a three-point function or a function of three momenta in reciprocal space. Due to the translational and rotational invariance of the homogeneous electron gas, $L_x$ is a function of only three numbers and we have given the explicit polynomial form that $L_x$ must have at small momentum transfers (small $\mathbf{q}$'s). We have considered polynomials up to sixth order, and demonstrated how these polynomial representations in reciprocal space give rise to gradient corrections in real space. We stress that the possibility of constructing gradient corrections is crucially dependent on the validity of a derivative theorem which relates the limit of $L_x$ when one momentum vanishes to density derivatives of the linear-response kernel $K_x$. The latter is the second functional derivative with respect to density of $E_x$.

The expression for $L_x$ has been evaluated numerically at different momentum transfers $\mathbf{q}$'s for different values of the screening length $1/\lambda$ in a screened Coulomb interaction. At small but finite $\lambda$, the calculations are numerically stable for all $\mathbf{q}$'s and confirm the correctness of our analytical small-$q$ expansion of $L_x$. As was the case for $K_x$,[16] the coefficients of the terms that are fourth order in $\mathbf{q}$ are shown to be singular (blow up) as $\lambda$ tends to zero.

Approaching the true Coulomb potential, i.e., the limit $\lambda \rightarrow 0$, the numerical calculations become unstable for certain combinations of the independent momentum variables $\mathbf{q}$ and $\mathbf{q}'$ when these are very small. This difficulty could be the result of our inability to find a sufficiently stable form (in the numerical sense) of the constituent integrals. It could also have a more fundamental reason. In the case of a bare Coulomb interaction, it could be that $L_x$ is not analytic at zero momenta and, therefore, that the gradient expansion does not exist in the orthodox sense. Such a situation would be surprising in view of the fact that $K_x$ is analytic at zero momentum ($q \rightarrow 0$). We remind the reader, however, that $K_x$ is not analytic in the HF approximation (not to be confused with the EXOA), (Ref. 25) and that work by Langreth and Vosko[26] on density response in the high density electron gas indicates that analyticity is not restored by taking correlation into account. $K_{\mathrm{xc}}$ ($=K_x$ including correlation) has a $q^2$ term but the next-higher-order terms contain $q^3$ and $q^3 \ln q$.

Nevertheless, we have found it quite possible to obtain an accurate polynomial fit to our calculated values for $L_x(\mathbf{q},\mathbf{q}')$ in the region of momenta from $\sim 0.5 k_F$ to $\sim k_F$. The coefficients of the fourth-order terms in a sixth-order polynomial fit to the numerical data are combined to form our result for the fourth-order gradient correction. The corresponding second-order coefficient is in slight violation (10%) of the derivative theorem [Eq. (14)]. Therefore, we believe our total gradient coefficient to be accurate to within 20%.

Response functions might or might not have a Taylor expansion at small momenta. If they have, calculation of the corresponding coefficients could prove to be intractable. It seems appropriate to recall the purpose of the entire procedure, namely, to approximate the response kernels over some region of momenta between zero and $\sim k_F$. It could well be that the Taylor expansion is not the best way of achieving this end. To illustrate the point, we might think of a world with a Yukawa interaction between electrons and only exchange effects. If the Yukawa screening length $1/\lambda$ is much larger than an atom, the HF treatment of that atom would be virtually the same in the real world and the Yukawa world. A gradient approximation based on a Taylor series at small momenta would have the coefficients given by Eqs. (29), (32), and (34), which would give very bad results (see the discussion at the end of Sec. III). On the other hand, a gradient approximation with suitably chosen coefficients could still produce reasonable results. It is in this spirit that we have obtained the gradient corrections of the present work. We suggest that gradient coefficients be determined by fitting appropriate gradient expressions to accurately calculated exchange energies for weakly perturbed electron gases. Such work is presently in progress.[22]

## ACKNOWLEDGMENTS

The authors wish to thank C.-O. Almbladh for many useful discussions during the course of this work.

## APPENDIX A

The first-order change in $E_x$ with respect to variations in the effective potential $V=w+\int nv+v_x$ [Eq. (3)] is easily worked out directly from Eq. (1) and the definition of $v_x$ [Eq. (4)]:[14,15]

$$\int \chi_0(\mathbf{r},\mathbf{r}_1)v_x(\mathbf{r}_1)d^3r_1 = -\tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r})v(\mathbf{r}_1,\mathbf{r}_2)n(\mathbf{r}_2,\mathbf{r}_1)d^3r_1 d^3r_2 . \qquad \text{(A1)}$$

In this and the following equations, a generalized $n$th-order response function of noninteracting electrons is defined by

$$\chi_0(\mathbf{r},\mathbf{r}';\mathbf{r}_1\ldots,\mathbf{r}_n)=\frac{\delta\chi_0(\mathbf{r},\mathbf{r}';\mathbf{r}_1\ldots,\mathbf{r}_{n-1})}{\delta V(\mathbf{r}_n)} = \frac{\delta n(\mathbf{r},\mathbf{r}')}{\delta V(\mathbf{r}_1)\cdots\delta V(\mathbf{r}_n)} . \qquad \text{(A2)}$$

A further variation of $E_x$ with respect to $V$ gives a determining equation for $K_x$,

$$\int \chi_0(\mathbf{r},\mathbf{r};\mathbf{r}',\mathbf{r}_1)v_x(\mathbf{r}_1)d^3r_1 + \int \chi_0(\mathbf{r},\mathbf{r}_1)K_x(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}')d^3r_1 d^3r_2 = -\tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r},\mathbf{r}')v(\mathbf{r}_1,\mathbf{r}_2)n(\mathbf{r}_2,\mathbf{r}_1)d^3r_1 d^3r_2 - \tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r})v(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}_1;\mathbf{r}')d^3r_1 d^3r_2 . \qquad \text{(A3)}$$

Still one further variation with respect to $V$ produces the determining equation for $L_x$:

$$\begin{aligned}\int &\chi_0(\mathbf{r},\mathbf{r};\mathbf{r}',\mathbf{r}'',\mathbf{r}_1)v_x(\mathbf{r}_1)d^3r_1+\int \chi_0(\mathbf{r},\mathbf{r};\mathbf{r}',\mathbf{r}_1)K_x(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}'')d^3r_1d^3r_2\\ &+\int \chi_0(\mathbf{r}'',\mathbf{r}'';\mathbf{r},\mathbf{r}_1)K_x(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}')d^3r_1d^3r_2+\int \chi_0(\mathbf{r}',\mathbf{r}';\mathbf{r}'',\mathbf{r}_1)K_x(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r})d^3r_1d^3r_2\\ &+\int \chi_0(\mathbf{r},\mathbf{r}_1)\chi_0(\mathbf{r}',\mathbf{r}_2)\chi_0(\mathbf{r}'',\mathbf{r}_3)L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d^3r_1d^3r_2d^3r_3=-\tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r},\mathbf{r}',\mathbf{r}'')v(\mathbf{r}_1,\mathbf{r}_2)n(\mathbf{r}_2,\mathbf{r}_1)d^3r_1d^3r_2\\ &-\tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r},\mathbf{r}')v(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}_1;\mathbf{r}'')d^3r_1d^3r_2-\tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'',\mathbf{r})v(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}_1;\mathbf{r}')d^3r_1d^3r_2\\ &-\tfrac{1}{2}\int \chi_0(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}',\mathbf{r}'')v(\mathbf{r}_1,\mathbf{r}_2)\chi_0(\mathbf{r}_2,\mathbf{r}_1;\mathbf{r})d^3r_1d^3r_2. \end{aligned} \tag{A4}$$

Now assuming translational invariance (electron-gas limit) the Green's function of the system can be written in the usual form

$$G(q)=G(\mathbf{k},\omega)=\frac{1}{\omega-\epsilon_{\mathbf{k}}+i\delta\ \mathrm{sgn}(\omega-\epsilon_F)},\quad \delta=0^+. \tag{A5}$$

The determining equation of $L_x$ above can then be Fourier transformed to

$$\begin{aligned}\chi_0(\mathbf{q})\chi_0(\mathbf{q}')\chi_0(\mathbf{q}'-\mathbf{q})L_x(\mathbf{q},\mathbf{q}')&=I_\Sigma(\mathbf{q},\mathbf{q}')+I_V(\mathbf{q},\mathbf{q}')\\ &+I_x(\mathbf{q},\mathbf{q}')-\chi_0(\mathbf{q},\mathbf{q}')[K_x(\mathbf{q})\chi_0(\mathbf{q})+K_x(\mathbf{q}')\chi_0(\mathbf{q}')\\ &+K_x(\mathbf{q}'-\mathbf{q})\chi_0(\mathbf{q}'-\mathbf{q})],\end{aligned} \tag{A6}$$

where

$$\begin{aligned}I_V(\mathbf{q},\mathbf{q}')=-4\sum_{q_1q_2}&G(q_1)G(q_1+q')G(q_1+q)v(\mathbf{q}_1-\mathbf{q}_2)\\ &\times\{G(q_2)G(q_2+q')+G(q_2)G(q_2+q)\\ &+G(q_2+q)G(q_2+q')\},\end{aligned} \tag{A7}$$

$$\begin{aligned}I_\Sigma(\mathbf{q},\mathbf{q}')=-4\sum_{q_1}&G(q_1)G(q_1+q')G(q_1+q)\\ &\times\{G(q_1)\Sigma^{\mathrm{HF}}(\mathbf{q}_1)+G(q_1+q')\Sigma^{\mathrm{HF}}(\mathbf{q}_1+\mathbf{q}')\\ &+G(q_1+q)\Sigma^{\mathrm{HF}}(q_1+q)\},\end{aligned} \tag{A8}$$

$$\begin{aligned}I_x(\mathbf{q},\mathbf{q}')=-4v_x\sum_{q_1}&G(q_1)G(q_1+q')G(q_1+q)\\ &\times\{G(q_1)+G(q_1+q)+G(q_1+q')\},\end{aligned} \tag{A9}$$

and $\Sigma^{\mathrm{HF}}$ is the HF-self-energy,

$$\Sigma^{\mathrm{HF}}(\mathbf{k})=-\sum_{\mathbf{q}}v(\mathbf{k}-\mathbf{q})n(\mathbf{q}). \tag{A10}$$

Furthermore

$$\chi_0(\mathbf{q})=2\sum_{q_1}G(q_1)G(q_1+q), \tag{A11}$$

$$\chi_0(\mathbf{q},\mathbf{q}')=4\sum_{q_1}G(q_1)G(q_1+q)G(q_1+q') \tag{A12}$$

represents the Fourier-transforms of $\chi_0(\mathbf{r},\mathbf{r};\mathbf{r}_1)$ and $\chi_0(\mathbf{r},\mathbf{r};\mathbf{r}_1,\mathbf{r}_2)$, respectively. Here $\Sigma_q$ above should be interpreted as $\int d^3\mathbf{q}\,d\omega(2\pi)^{-4}/i$. The frequency integrations in Eqs. (A7)–(A12) are trivially carried out to yield

$$\begin{aligned}I_\Sigma(\mathbf{q},\mathbf{q}')=4\sum_{\mathbf{q}_1}\Bigg[&\frac{1}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}\left(\frac{n_{\mathbf{q}_1+\mathbf{q}'}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1}}-\frac{n_{\mathbf{q}_1+\mathbf{q}}-n_{\mathbf{q}_1+\mathbf{q}'}}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1+\mathbf{q}'}}\right)\frac{\Sigma^{\mathrm{HF}}(\mathbf{q}_1+\mathbf{q}')-\Sigma^{\mathrm{HF}}(\mathbf{q}_1)}{\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1}}\\ &+\frac{1}{\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1}}\left(\frac{n_{\mathbf{q}_1+\mathbf{q}}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}-\frac{n_{\mathbf{q}_1+\mathbf{q}}-n_{\mathbf{q}_1+\mathbf{q}'}}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1+\mathbf{q}'}}\right)\frac{\Sigma^{\mathrm{HF}}(\mathbf{q}_1+\mathbf{q})-\Sigma^{\mathrm{HF}}(\mathbf{q}_1)}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}\\ &+\frac{n_{\mathbf{q}_1+\mathbf{q}'}-n_{\mathbf{q}_1+\mathbf{q}}}{(\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1+\mathbf{q}})^2}\left(\frac{\Sigma^{\mathrm{HF}}(\mathbf{q}_1+\mathbf{q})-\Sigma^{\mathrm{HF}}(\mathbf{q}_1)}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}-\frac{\Sigma^{\mathrm{HF}}(\mathbf{q}_1+\mathbf{q}')-\Sigma^{\mathrm{HF}}(\mathbf{q}_1)}{\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1}}\right)\Bigg],\end{aligned} \tag{A13}$$

$$I_V(\mathbf{q},\mathbf{q}')=-4\sum_{\mathbf{q}_1\mathbf{q}_2}\frac{1}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1+\mathbf{q}'}}\left(\frac{n_{\mathbf{q}_1+\mathbf{q}}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}-\frac{n_{\mathbf{q}_1+\mathbf{q}'}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1}}\right)\left(\frac{n_{\mathbf{q}_2+\mathbf{q}}-n_{\mathbf{q}_2}}{\epsilon_{\mathbf{q}_2+\mathbf{q}}-\epsilon_{\mathbf{q}_2}}+\frac{n_{\mathbf{q}_2+\mathbf{q}'}-n_{\mathbf{q}_2}}{\epsilon_{\mathbf{q}_2+\mathbf{q}'}-\epsilon_{\mathbf{q}_2}}+\frac{n_{\mathbf{q}_2+\mathbf{q}}-n_{\mathbf{q}_2+\mathbf{q}'}}{\epsilon_{\mathbf{q}_2+\mathbf{q}}-\epsilon_{\mathbf{q}_2+\mathbf{q}'}}\right)v(\mathbf{q}_1-\mathbf{q}_2),$$

$$I_x=0$$

and

$$\chi_0(\mathbf{q})=2\sum_{\mathbf{q}_1}\frac{n_{\mathbf{q}_1+\mathbf{q}}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}, \tag{A14}$$

$$\chi_0(\mathbf{q},\mathbf{q}')=4\sum_{\mathbf{q}_1}\frac{1}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1+\mathbf{q}'}}\times\left(\frac{n_{\mathbf{q}_1+\mathbf{q}}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}}-\epsilon_{\mathbf{q}_1}}-\frac{n_{\mathbf{q}_1+\mathbf{q}'}-n_{\mathbf{q}_1}}{\epsilon_{\mathbf{q}_1+\mathbf{q}'}-\epsilon_{\mathbf{q}_1}}\right). \tag{A15}$$

Here $n_{\mathbf{q}}=\theta(k_F-q)$ and $\epsilon_{\mathbf{q}}=q^2/2$. With $I_x=0$ and $\mathbf{q}'=\mathbf{q}_\perp$ we finally arrive at Eq. (23). (Note that $I_\Sigma$ has been somewhat rearranged to facilitate numerical evaluation.)

## APPENDIX B

Here we will present some relations of importance for the kernels in Eqs. (6) and (7). Assuming full rotational, translational and inversion symmetry, we may write:

$$K_x(\mathbf{r},\mathbf{r}')=K_x(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R}),$$

$$K_x(\mathbf{r},\mathbf{r}')=K_x(R\mathbf{r},R\mathbf{r}'), \tag{B1}$$

$$K_x(\mathbf{r},\mathbf{r}')=K_x(-\mathbf{r},-\mathbf{r}'),$$

where $\mathbf{R}$ and $R$ represent, respectively, arbitrary translations and rotations. Since $K_x$ is then (spatially) only a function of the relative coordinate $\mathbf{r}-\mathbf{r}'$ we obtain Eq. (10).

Inverting Eq. (10), we find

$$K_x(\mathbf{q})=\int K_x(\mathbf{r},0)e^{-i\mathbf{q}\cdot\mathbf{r}}d^3r, \tag{B2}$$

which, together with Eq. (B1), gives $K_x(R\mathbf{q})=K_x(\mathbf{q})$ and $K_x(-\mathbf{q})=K_x(\mathbf{q})$. (The density, $n$, dependence of the response functions is suppressed, where it is not of importance to the reasoning). The following ‘‘small-$q$’’ expansion must therefore be valid:

$$K_x(\mathbf{q};n)=K_x(0)\{1+K_2Q^2+K_4Q^4+K_6Q^6+\ldots\}. \tag{B3}$$

Similarly, for $L_x$ we have full translational,

$$L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=L_x(\mathbf{r}_1+\mathbf{R},\mathbf{r}_2+\mathbf{R},\mathbf{r}_3+\mathbf{R}), \tag{B4}$$

and rotational

$$L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=L_x(R\mathbf{r}_1,R\mathbf{r}_2,R\mathbf{r}_3), \tag{B5}$$

symmetry.

Furthermore, for a response function of the homogeneous electron gas, we must require full symmetry in terms of all possible coordinate permutations:

$$L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=L_x(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_3)=L_x(\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_2)=L_x(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_1)$$
$$=L_x(\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_1)=L_x(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_2). \tag{B6}$$

For the purposes of calculating gradient-correction coefficients, we need to know the small-$q$ ($q<2k_F$) expansion of the kernel $\tilde{L}_x(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$, which is defined as

$$\tilde{L}_x(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)=\int L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)e^{-i\mathbf{q}_1\cdot\mathbf{r}_1}e^{-i\mathbf{q}_2\cdot\mathbf{r}_2}e^{-i\mathbf{q}_3\cdot\mathbf{r}_3}d^3r_1d^3r_2d^3r_3. \tag{B7}$$

The fact that [Eq. (B4)] $L_x(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ is only a function of the coordinate differences $\mathbf{r}_1-\mathbf{r}_3$ and $\mathbf{r}_2-\mathbf{r}_3$ was already explicitly taken into account in defining $L_x(\mathbf{q},\mathbf{q}')$. We may now insert Eq. (11) into Eq. (B7) to obtain the relation

$$\tilde{L}_x(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)=(2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)L_x(\mathbf{q}_1,-\mathbf{q}_2). \tag{B8}$$

From Eqs. (B5) and (B7) above, we see that $\tilde{L}_x(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$ is rotationally invariant as well. $\tilde{L}_x$, when expanded around $\mathbf{q}_1=\mathbf{q}_2=\mathbf{q}_3=\mathbf{0}$, must therefore be expressible as a constant plus terms being multiples of $\{Q_{11},Q_{22},Q_{33},Q_{12},Q_{23},Q_{31}\}$, where $Q_{ij}=\mathbf{q}_i\cdot\mathbf{q}_j$. Now, since $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3=\mathbf{0}$, $Q_{ij}$, $i\neq j$ are all expressible as linear combinations of the diagonal terms $Q_{ii}$. We may then use $\{Q_{11},Q_{22},Q_{33}\}$ as the ‘‘building blocks’’ to construct the general form of $L_x$ to any order in $Q$.

Finally, we utilize permutational invariance to establish the proper linear combination of the $Q_{ii}$. The group of operations for permuting the arguments $\mathbf{q}_1$, $\mathbf{q}_2$, and $\mathbf{q}_3$ as described in Eq. (B6) is isomorphic to $D_3$, that is, the rotation group of order 3.

We are now in a position to work out the proper form of $L_x$ to second order in $Q$. The three-dimensional representation $\Gamma^{(2)}$ for which the $\{Q_{ii}\}$, $i=1,2,3$ form a basis can be decomposed in the irreducible representations of $D_3$ by inspection. We obtain $\Gamma^{(2)}=A_1+E$. In order to obtain the completely symmetric function belonging to $A_1$ we may operate with the projection operator $P^{(A_1)}=\frac{1}{6}\Sigma_R P_R$ on, say, $Q_{11}$. We obtain

$$P^{(A_1)}Q_{11}=\tfrac{1}{6}\sum_R P_RQ_{11}\sim Q_{11}+Q_{22}+Q_{33}. \tag{B9}$$

To fourth order in $Q$

$$\{Q_{11}^2,Q_{22}^2,Q_{33}^2,Q_{11}Q_{22},Q_{22}Q_{33},Q_{33}Q_{11}\}$$

form a six-dimensional representation $\Gamma^{(4)}$. We decompose again to obtain $\Gamma^{(4)}=2A_1+2E$. In the same way as before, we project out the two functions belonging to the two representations $A_1$ in the $\Gamma^{(4)}$ decomposition:

$$P^{(A_1)}Q_{11}^2=\tfrac{1}{6}\sum_R P_RQ_{11}^2\sim Q_{11}^2+Q_{22}^2+Q_{33}^2, \tag{B10}$$

$$P^{(A_1)}Q_{11}Q_{22}=\tfrac{1}{6}\sum_R P_RQ_{11}Q_{22}\sim Q_{11}Q_{22}+Q_{22}Q_{33}+Q_{33}Q_{11}. \tag{B11}$$

[The results in the equations above are, of course, the same with the projection operator acting on any $Q_{ii}^2$ in Eq. (B10) and $Q_{ii}Q_{jj}$, $i\neq j$ in Eq. (B11)].

Continuing to sixth order, we have a ten-dimensional representation $\Gamma^{(6)}$ from the elements $\{Q_{ii}^3\}$, $\{Q_{ii}^2Q_{jj}\}$, and

$Q_{11}Q_{22}Q_{33}$; $i,j=1,2,3$. Decomposing, $\Gamma^{(6)}=3A_1+A_2+3E$. Projecting out the three completely symmetric functions, we obtain

$$P^{(A_1)}Q_{11}^3=\tfrac{1}{6}\sum_R P_R Q_{11}^3 \sim Q_{11}^3+Q_{22}^3+Q_{33}^3, \tag{B12}$$

$$\begin{aligned} P^{(A_1)}Q_{11}^2Q_{22} &= \tfrac{1}{6}\sum_R P_R Q_{11}^2Q_{22}, \\ &\sim Q_{11}^2Q_{22}+Q_{11}^2Q_{33}+Q_{22}^2Q_{11} \\ &\quad +Q_{22}^2Q_{33}+Q_{33}^2Q_{11}+Q_{33}^2Q_{22}, \end{aligned} \tag{B13}$$

$$P^{(A_1)}Q_{11}Q_{22}Q_{33}=\tfrac{1}{6}\sum_R P_R Q_{11}Q_{22}Q_{33} \sim Q_{11}Q_{22}Q_{33}. \tag{B14}$$

In short, we have now demonstrated that to order $Q^6$, $L_x$ can be written as

$$\begin{aligned} \tilde{\mathbf{L}}_x(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) &= L_x(\mathbf{0},\mathbf{0},\mathbf{0})+l_2(Q_{11}+Q_{22}+Q_{33}) \\ &\quad +l_4(Q_{11}^2+Q_{22}^2+Q_{33}^2) \\ &\quad +l_4'(Q_{11}Q_{22}+Q_{22}Q_{33}+Q_{33}Q_{11}) \\ &\quad +l_6(Q_{11}^3+Q_{22}^3+Q_{33}^3)+l_6'(Q_{11}^2Q_{22}+Q_{11}^2Q_{33} \\ &\quad +Q_{22}^2Q_{11}+Q_{22}^2Q_{33}+Q_{33}^2Q_{11}+Q_{33}^2Q_{22}) \\ &\quad +l_6''Q_{11}Q_{22}Q_{33}. \end{aligned} \tag{B15}$$

According to Eq. (B8) the ‘‘reduced’’ $L_x$ contains (in our case) the same information, and may as well be used as the full $L_x(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$. Now, setting $\mathbf{q}_1=\mathbf{q}$, $\mathbf{q}_2=-\mathbf{q}'$ (and consequently $\mathbf{q}_3=\mathbf{q}'-\mathbf{q}$), Eq. (B15) may be rearranged to yield an equation for the small-$Q$ expansion of $L_x$. Here we have chosen a different (but completely equivalent) combination of the invariant polynomials given in Eqs. (B9)–(B14). The reason for our particular choice will shortly be apparent:

$$\begin{aligned} L_x(\mathbf{q},\mathbf{q}') &= L_x(\mathbf{0},\mathbf{0})\{1+L_2(Q^2+Q'^2-\mathbf{Q}\cdot\mathbf{Q}') \\ &\quad +L_4(Q^2+Q'^2-\mathbf{Q}\cdot\mathbf{Q}')^2+L_4'(Q^2Q'^2 \\ &\quad -(\mathbf{Q}\cdot\mathbf{Q}')^2)+L_6(Q^2+Q'^2-\mathbf{Q}\cdot\mathbf{Q}')^3 \\ &\quad +L_6'(Q^2+Q'^2-\mathbf{Q}\cdot\mathbf{Q}')(Q^2Q'^2-(\mathbf{Q}\cdot\mathbf{Q}')^2) \\ &\quad +L_6''Q^2Q'^2(\mathbf{Q}-\mathbf{Q}')^2+\cdots\}. \end{aligned} \tag{B16}$$

Inserting $\mathbf{q}=\mathbf{q}'$ into Eq. (B16) and comparing with Eq. (14), we now see that a knowledge of the small-$q$ expansion of $K_x$ also determines the coefficients $L_i$, while the primed coefficients have to be determined by other means.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[3] U. von Barth, *Lectures on Methods of Electronic Structure Calculations*, edited by V. Kumar, O. K. Andersen, and A. Mookerjee (World Scientific, Singapore, 1994), p. 21.

[4] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983); **29**, 2310 (1984).

[5] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[6] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).

[7] A. D. Becke, J. Chem. Phys. **96**, 2155 (1992).

[8] A. D. Becke, J. Chem. Phys. **97**, 9173 (1992).

[9] S.-K. Ma and K. A. Bruckner, Phys. Rev. **165**, 18 (1968).

[10] C. D. Hu and D. C. Langreth, Phys. Scr. **32**, 391 (1985).

[11] D. J. W. Geldart and M. Rasolt, Phys. Rev. B **13**, 1477 (1976).

[12] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[13] O. Gunnarsson and R. O. Jones, Phys. Rev. B **31**, 7588 (1985).

[14] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[15] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[16] P. S. Svendsen and U. von Barth, Int. Quantum Chem. **56**, 351 (1995).

[17] E. Engel and S. H. Vosko, Phys. Rev. B **50**, 10 498 (1994).

[18] E. Engel and S. H. Vosko, Phys. Rev. B **42**, 4940 (1990); **44**, 1446 (1991).

[19] M. L. Glasser, Phys. Rev. B **51**, 7283 (1995).

[20] L. Kleinman and S. Lee, Phys. Rev. B **37**, 4634 (1988).

[21] D. J. W. Geldart and R. Taylor, Can. J. Phys. **48**, 155 (1970).

[22] M. Springer, P. S. Svendsen, and U. von Barth, Phys. Rev. B **54**, 17 392 (1996), this issue.

[23] J. A. Chevary and S. H. Vosko, Bull. Am. Phys. Soc. **33**, 238 (1988); Phys. Rev. B **42**, 5320 (1990).

[24] P. Lloyd and C. A. Sholl, J. Phys. C **1**, 1620 (1968).

[25] D. J. W. Geldart, M. Rasolt, and C.-O. Almbladh, Solid State Commun. **16**, 243 (1975).

[26] D. C. Langreth and S. H. Vosko, Phys. Rev. Lett. **59**, 497 (1987).

[27] D. J. W. Geldart, M. L. Glasser, E. Dunlap, and M. R. A. Shegelski, Solid State Commun. **88**, 81 (1993).