PHYSICAL REVIEW VOLUME 165, NUMBER 1 5 JANUARY 1968

Correlation Energy of an Electron Gas with a Slowly Varying High Density*

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(Received 15 June 1967)

The correlation energy (the exact energy minus the Hartree-Fock energy) of an electron gas with a high and slowly varying density is examined. The term proportional to the square of the density gradient is evaluated by the application of perturbation theory to the external field and of the random-phase (or high-density) approximation to the Coulomb interaction. This term has the form $\Delta E_c[\rho]=\int d^3x\, B(\rho(x))\,|\nabla\rho(x)|^2$, where $\rho(x)$ is the electron density. $B(\rho)$ is found, by summing the leading divergent diagrams, to be $[8.470\times10^{-3}+O(\rho^{-1/3}\ln\rho)+O(\rho^{-1/3})]\rho^{-4/3}$ Ry, with the length measured in units of the Bohr radius. The role of the density gradient in the correlation energy problem of atoms is discussed.

I. INTRODUCTION

THE correlation energy problem of a many-electron system has not been extensively investigated except for a uniform electron gas at high density, where the random-phase approximation is applicable and the translational symmetry greatly simplifies the problem. The calculation of the correlation energy for a nonuniform electron gas or for systems with a finite number of electrons has not been carried out except for the lightest atoms,[1] although the Hartree-Fock energy for the most important nonuniform electron gas, namely, the many-electron atoms, can be calculated with high accuracy.[2] Because of its complexity, the calculation of the correlation energy of a general nonuniform electron gas seems to be beyond the technique available at present. However, the problem becomes tractable under the idealized condition that the density is high and slowly varying. When the density is slowly varying, the correlation energy may be expanded in powers of the density gradient. Such an expansion can be defined unambiguously with the aid of the density-functional formalism recently developed by Kohn and his coworkers.[3–5] When the density is high, the coefficients of the density gradient expansion may be calculated by the standard diagrammatic perturbation theory.

The objective of this paper is to examine the correlation energy in the limit of high and slowly varying density. The correction term to the correlation energy of a uniform electron gas which is proportional to the square of the density gradient is evaluated by analyzing the second-order contribution of the perturbation expansion in powers of the external field. Qualitative features of the correlation energy problem of atoms are also examined. In Sec. II, we describe the basic physical features of the problem and give a qualitative estimate of the effect of the density gradient on the correlation energy. Since the small density nonuniformity must be caused by an external field, the problem reduces to a study of the response of a uniform electron gas to an external field. Section III is devoted to a derivation of the expression of the correlation energy in terms of the long wavelength values of the density response function of a uniform electron gas. To separate the correlation energy from the total energy in a transparent and unambiguous way, we make moderate use of the basic language of the density-functional formalism[3]. The response function is studied in terms of diagrams, and the subset of diagrams contributing to the correlation energy are identified. The mathematical procedures for evaluating these diagrams are carried out in Sec. IV, and the explicit formula for the correlation energy is determined. In Sec. V, the role of the density gradient in atoms is considered. Because of the large density gradient in atoms, the density gradient expansion is shown to be a divergent series. It is also shown that the collective motion of electrons plays a much less important role in atoms than in the uniform or nearly uniform gas and the notion of the dielectric constant is not very useful in describing electrons in atoms.

The appendices are devoted to the mathematical details involving the derivatives of the Green's function and a few singular integrals needed in the text. Some useful formulas are listed. These appendices should serve as a convenient reference for other calculations involving the high-density electron gas.

II. QUALITATIVE FEATURES

Let us first review some of the basic characteristics of a uniform electron gas at high density. The average Coulomb repulsion among the electrons is canceled by the field of a uniform positive external charge background and thus, a uniform average density is maintained. By high density, we mean that the average interparticle distance r_0 is small compared to the Bohr radius, i.e.,

$$r_0\ll(e^2m)^{-1},$$

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* This research was supported by the Advanced Research Projects Agency (Project DEFENDER) and was monitored by the U. S. Army Research Office (Durham) under Contract No. DA-31-124-ARO-D-257.

[1] H. P. Kelly, Phys. Rev. **144**, 39 (1966).

[2] E. Clementi, J. Chem. Phys. **41**, 303 (1964).

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

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

[5] B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).

or

$$\frac{e^2}{r_0} \ll \frac{p_0^2}{2m}, \tag{2.1}$$

where $p_0 \sim r_0^{-1}$ is the Fermi momentum. The energy of the system is the sum of the kinetic energy and the interaction energy due to the correlation of density fluctuations. The correlation over a distance comparable to r_0 can be approximately described in terms of the motion of free electrons since, by (2.1), the Coulomb potential becomes much less than the kinetic energy of the electron states which contribute to the correlation. The correlation over a distance large compared to r_0 is mainly due to the long-range Coulomb force. On the other hand, the motion of the electrons tends to screen the Coulomb force produced by the density fluctuations. The screening may be characterized by the screening length L_s. The density fluctuations separated by a distance much larger than L_s become uncorrelated. The leading terms of the perturbation expansion in powers of e^2 and $\ln e^2$ based on the above physical picture has been extensively studied.[6,7,8] The screening length is given by

$$L_s \sim (e^2 m p_0)^{-1/2}. \tag{2.2}$$

Now suppose that the external charge distribution becomes nonuniform. Then, the average electron density will be nonuniform. There will be a change in the electrostatic energy of the charge distribution as a whole, a change in the kinetic energy E_{kin}, and a change in the interaction energy E_{int} due to the modification of the correlation of density fluctuations. Explicitly, the total energy is

$$E = \int d^3x\, \varphi(\mathbf{x})\rho(\mathbf{x}) + \tfrac{1}{2}\int d^3x d^3r\, \rho(\mathbf{x})\rho(\mathbf{x}+\mathbf{r})\frac{e^2}{r} + E_{\mathrm{kin}} + E_{\mathrm{int}}, \tag{2.3}$$

where $\varphi(\mathbf{x})$ is the potential due to the external charge and $\rho(\mathbf{x})$ is the average density. From the above discussion of a uniform electron gas, we see that E_{int} involves only the correlation of density fluctuations, which is small beyond a distance L_s. More explicitly,

$$E_{\mathrm{int}} \approx \tfrac{1}{2}\int d^3x d^3r\, \langle \rho'(\mathbf{x})\rho'(\mathbf{x}+\mathbf{r})\rangle \frac{e^2}{r},$$

$$\langle \rho'(\mathbf{x})\rho'(\mathbf{x}+\mathbf{r})\rangle \to 0, \quad \text{for } r \gg L_s,$$

where $\rho'(\mathbf{x})$ is the density fluctuation. Therefore, if $\rho(\mathbf{x})$ varies very little over a distance of a screening length, i.e., if

$$L_s^2 |\nabla\rho/\rho|^2 \equiv g \ll 1, \tag{2.4}$$

we expect that

$$E_{\mathrm{int}} \approx \int d^3x\, E_{\mathrm{int}}^0(\rho(x)), \tag{2.5}$$

where $E_{\mathrm{int}}^0(\rho)$ is the interaction energy per unit volume of a uniform gas with density ρ. To obtain better approximations for E_{int}, one naturally expects an expansion in powers of g to be helpful. Such an expansion is the "gradient expansion."[3]

We are only interested in the correlation energy of a nonuniform electron gas. The Hartree-Fock energy includes the first three terms of (2.3) and a part of E_{int} because of the correlation arising from the Pauli principle. If the condition (2.4) is satisfied, we expect that the correlation energy E_c may be written as

$$\begin{aligned} E_c &= \int d^3x\, E_c^0(\rho(x)) + \Delta E_c, \\ \Delta E_c &\equiv \int d^3x\, B(\rho(x))|\nabla\rho(x)|^2 + O(g^2), \end{aligned} \tag{2.6}$$

where $E_c^0(\rho)$ is the correlation energy per unit volume of a uniform electron gas of density ρ and $B(\rho)$ is a function to be determined in the next two sections. Let us give a crude estimate of B here.

In calculating the HF energy of a uniform gas, no screening is taken into account. The correlation energy is roughly the correction due to the effect of screening

$$E_c \approx \tfrac{1}{2}\int d^3x d^3r\, \{\langle \rho'(\mathbf{x})\rho'(\mathbf{x}+\mathbf{r})\rangle_{\mathrm{screened}} - \langle \rho'(\mathbf{x})\rho'(\mathbf{x}+\mathbf{r})\rangle_{\mathrm{unscreened}}\}\frac{e^2}{r}. \tag{2.7}$$

The unscreened density-fluctuation correlation function is well known to be[9]

$$-\tfrac{9}{2}\rho^2[(\sin p_0 r - p_0 r \cos p_0 r)/p_0^3 r^3]^2.$$

Thus, the screened correlation function is, for $r \gg p_0^{-1}$,

$$\langle \rho'(\mathbf{x})\rho'(\mathbf{x}+\mathbf{r})\rangle_{\mathrm{screened}} \approx -9/4(3\pi)^{-4/3}[\rho^{2/3}/r^4]e^{-r/L_s}, \tag{2.8}$$

where we have substituted $(3\pi^2\rho)^{1/3}$ for p_0 and $\tfrac{1}{2}$ for $\cos^2 p_0 r$. We need not consider the small r behavior of the correlation function because the effect of the density gradient is appreciable only for large r. The constants ρ and L_s in (2.8) are no longer defined for a nonuniform gas. However, if the density is nearly uniform, one may use the density at $\mathbf{x}$ to evaluate these constants. This approximation is good for r much less than L_s. As r becomes larger, one may use the density at $\mathbf{x}+\tfrac{1}{2}\mathbf{r}$ to evaluate these constants. As a function of $\mathbf{r}$, (2.8) be-

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[6] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

[7] K. Sawada, Phys. Rev. **106**, 372 (1957).

[8] K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, Phys. Rev. **108**, 507 (1957).

[9] See, for example, C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), Chap. V.

comes distorted from the density correlation function for a uniform gas as a result of the slight variation of the constants. An estimate of the effect of the density gradient on the correlation energy may be deduced from such a distortion, which is given by the difference

$$\Delta(\mathbf{x},\mathbf{r})\equiv\rho^{2/3}(\mathbf{x}+\mathbf{r}/2)\{\exp[-r/L_s(\rho(\mathbf{x}+\mathbf{r}/2))]-1\} -\rho^{2/3}(\mathbf{x})\{\exp[-r/L_s(\rho(\mathbf{x}))]-1\}. \quad (2.9)$$

Expanding (2.9) in powers of $\nabla\rho(x)$ assuming

$$\rho\left(\mathbf{x}+\frac{\mathbf{r}}{2}\right)=\rho(\mathbf{x})+\frac{\mathbf{r}}{2}\cdot\nabla\rho(\mathbf{x}),$$

we find, keeping only the second order in $\nabla\rho(\mathbf{x})$

$$\Delta(\mathbf{x},\mathbf{r})=\left\{-\frac{r^3}{12}\nabla\rho^{2/3}\cdot\nabla L_s^{-1}+\frac{r^4}{24}\rho^{2/3}(\nabla L_s^{-1})^2\right\}e^{-r/L_s}. \quad (2.10)$$

A crude estimate of the effect of the density gradient on the correlation energy is given by

$$\Delta E_c\sim\tfrac{1}{2}\int d^3xd^3r[-9(3\pi^2)^{-4/3}/4r^4]\Delta(\mathbf{x},\mathbf{r})\frac{e^2}{r}. \quad (2.11)$$

The r integrals are easily performed. One finds

$$\Delta E_c\sim 8^{-1}3^{-1/3}\pi^{-5/3}e^2\int d^3x\{L_s\nabla\rho^{2/3}\cdot\nabla L_s^{-1} -\tfrac{1}{2}\rho^{2/3}(L_s\nabla L_s^{-1})^2\}. \quad (2.12)$$

Using the fact that $L_s\sim(e^2mp_0)^{-1/2}$ is proportional to $\rho^{-1/6}$, (2.12) reduces to

$$\Delta E_c\sim 2.7\times10^{-3}e^2\int d^3x\,\rho^{-4/3}(\mathbf{x})|\nabla\rho(\mathbf{x})|^2. \quad (2.13)$$

Although (2.13) is a very crude estimate, it does show that $B(\rho)$ [see (2.6)] is of the order $O(e^2)$. Since E_c^0, the correlation energy of a uniform gas, is of $O(e^4)+O(e^4\ln e^2)$ [see (3.16)] and $L_s^2=O(e^{-2})$, one might expect, by (2.4), that $\Delta E_c=O(gE_c^0)=O(e^2)+O(e^2\ln e^2)$. Equation (2.13) and the calculation in the next sections show that the $O(e^2\ln e^2)$ term is absent.

The above estimate is based on the picture of a distorted density correlation function and a distorted screening length. The distortion is described by the average density $\rho(x)$, which is regarded as a parameter slowly varying in space. However, nothing has been said about the physical processes which give rise to the distortions. Since the nonuniform density is due to an external field, we have to study the response of the many-electron system to an external field. When the density variation is small, the analysis reduces to the analysis of the density response of a uniform electron gas. The next two sections are devoted to the determination of $B(\rho)$ based on such an analysis.

III. FORMULATION

In this section, we search for a formula of the form of (2.6) for the correlation energy of a nearly uniform electron gas. It is clear, from the qualitative discussion in the previous section, that the problem should reduce to an analysis of the response of a uniform gas to a weak external field, which causes the small density nonuniformity. From such an analysis, one can determine the energy and the density in terms of the external field. One then looks for a way to eliminate the explicit dependence of the correlation energy on the external field and obtain an expression in terms of the density only. We find it convenient to start our analysis with the density-functional formulation.[3]

The energy E and the average density $\rho(\mathbf{x})$ may be obtained by minimizing the energy functional $E[\rho]$ keeping the total number of electrons fixed. We break up $E[\rho]$ into two parts:

$$E[\rho]\equiv E_{\mathrm{HF}}[\rho]+E_c[\rho]. \quad (3.1)$$

$E_{\mathrm{HF}}[\rho]$ is defined such that, by minimizing it, one would obtain the energy and the density in the Hartree-Fock approximation. $E_c[\rho]$ is the "correlation energy functional." When the density variation is small, we expect that $E_c[\rho]$ may be expanded in powers of the density gradient $\nabla\rho(\mathbf{x})$. If only the two lowest-order terms are kept, one has

$$E_c[\rho]=\int d^3x\,\{A(\rho(\mathbf{x}))+B(\rho(\mathbf{x}))|\nabla\rho(\mathbf{x})|^2\}, \quad (3.2)$$

where $A(\rho)$, $B(\rho)$ can be determined by applying (3.1) and (3.2) to a weakly perturbed uniform gas in the following way.

Consider an electron gas in a unit volume perturbed by a weak static field:

$$\varphi(\mathbf{x})=\sum_{k\neq0}\varphi_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{x}}.$$

The perturbing Hamiltonian is then

$$\mathcal{H}=\sum_{k\neq0}\varphi_{\mathbf{k}}\hat{\rho}_{-\mathbf{k}},$$

where $\hat{\rho}_{\mathbf{k}}$ is the density operator. The energy to the second order in φ is

$$E=E^0(n)+\sum_{k\neq0}\varphi_{\mathbf{k}}\varphi_{-\mathbf{k}}\sum_m\frac{\langle0|\hat{\rho}_{\mathbf{k}}|m\rangle\langle m|\hat{\rho}_{-\mathbf{k}}|0\rangle}{E^0-E^m}$$
$$=E^0(n)+\tfrac{1}{2}\sum_{k\neq0}\varphi_{\mathbf{k}}\varphi_{-\mathbf{k}}\mathfrak{F}(\mathbf{k},0), \quad (3.3)$$

where n, $|0\rangle$, E^0, $|m\rangle$, E^m are, respectively, the density, the exact ground and excited states and their energies of a uniform electron gas, and $\mathfrak{F}(k,\omega)$ is the density response function of a uniform electron gas given by

$$\mathfrak{F}(\mathbf{k},\omega)\equiv -i\int d^4x\, e^{-i\mathbf{k}\cdot\mathbf{x}+i\omega t}\langle T(\hat{\rho}(\mathbf{x},t)\hat{\rho}(0))\rangle$$

$$=\mathfrak{F}(-\mathbf{k},\omega)=\mathfrak{F}(\mathbf{k},-\omega). \qquad (3.4)$$

The average $\langle\cdots\rangle$ is taken over the ground state of a uniform electron gas. The density, to the first order in φ, is given by

$$\rho_{\mathbf{k}}=\varphi_{\mathbf{k}}\mathfrak{F}(\mathbf{k},0),$$

$$\rho_0=n. \qquad (3.5)$$

Equations (3.3) and (3.5) summarize the effect of the external field. $\mathfrak{F}(\mathbf{k},0)$ contains the full information of the response of the uniform electron gas to the external field. Now we have to separate the correlation energy and Hartree-Fock energy from the total energy. This is accomplished in the following manner.

The results (3.3) and (3.5) may be obtained by minimizing the functional

$$E[\rho]=E^0(n)+\sum_{k\neq0}\varphi_{-\mathbf{k}}\rho_{\mathbf{k}}-\tfrac{1}{2}\sum_{k\neq0}\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\mathfrak{F}^{-1}(\mathbf{k},0). \qquad (3.6)$$

Similarly, minimizing the functional

$$E_{\mathrm{HF}}[\rho]=E^0{}_{\mathrm{HF}}(n)+\sum_{k\neq0}\varphi_{-\mathbf{k}}\rho_{\mathbf{k}}-\tfrac{1}{2}\sum_{k\neq0}\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\mathfrak{F}_{\mathrm{HF}}{}^{-1}(\mathbf{k},0) \qquad (3.7)$$

will give the density and energy in the Hartree-Fock approximation. Here $\mathfrak{F}_{\mathrm{HF}}$ is the density-response function in the Hartree-Fock approximation. It is the sum of all the Hartree-Fock energy diagrams perturbed twice by an external field. (See Fig. 1.) Thus, the correlation energy functional for a weakly perturbed uniform gas is, by (3.1), (3.6), (3.7),

$$E_c[\rho]=E[\rho]-E_{\mathrm{HF}}[\rho]$$

$$=E_c{}^0(n)-\tfrac{1}{2}\sum_{k\neq0}\rho_{\mathbf{k}}\rho_{-\mathbf{k}}(\mathfrak{F}^{-1}(\mathbf{k},0)-\mathfrak{F}^{-1}{}_{\mathrm{HF}}(\mathbf{k},0)), \qquad (3.8)$$

where

$$E_c{}^0(n)\equiv E^0(n)-E_{\mathrm{HF}}{}^0(n),$$

is the correlation energy of a uniform electron gas. The density-response function $\mathfrak{F}$ may be expressed as a geometric sum (see Fig. 2)

$$\mathfrak{F}=F+FVF+FVFVF+\cdots$$

$$=F/(1-VF),$$

and hence,

$$\mathfrak{F}^{-1}=F^{-1}-V,$$

where

$$V\equiv 4\pi e^2/k^2,$$

and F contains no isolated interaction line. Equation (3.8) now becomes

$$E_c[\rho]=E_c{}^0(n)-\tfrac{1}{2}\sum_{k\neq0}\rho_{\mathbf{k}}\rho_{-\mathbf{k}}(F^{-1}(\mathbf{k},0)-F_{\mathrm{HF}}{}^{-1}(\mathbf{k},0)). \qquad (3.9)$$

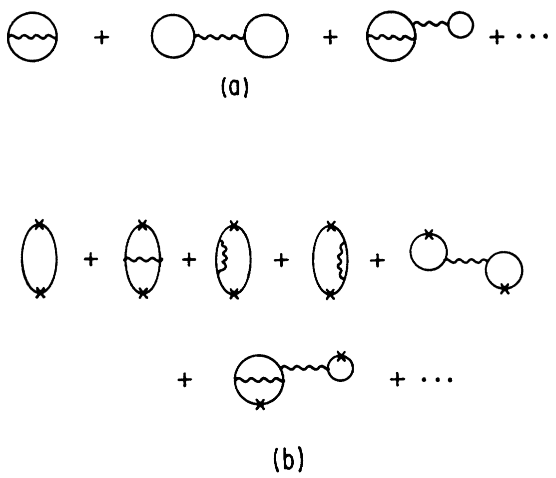

FIG. 1. (a) The Hartree-Fock energy diagrams. Because of the translational symmetry and the uniform charge background, only the first diagram is nonzero for a uniform electron gas. (b) The first diagram gives the second-order perturbation on the kinetic energy. Each cross represents a density vertex with the momentum of the external field.

The contribution of the $-V$ term of $\mathfrak{F}^{-1}$

$$\tfrac{1}{2}\sum_{k\neq0}\rho_{\mathbf{k}}\rho_{-\mathbf{k}}(4\pi e^2/k^2)$$

cancels that in $\mathfrak{F}_{\mathrm{HF}}{}^{-1}$. This cancellation means that the electrostatic energy of the electron charge distribution as a whole is included in the Hartree-Fock energy and plays no part in the correlation energy.

Equation (3.9) is an expression with no explicit dependence on the external field. Furthermore, it is applicable even if the density varies rapidly in space as long as the amplitude of the variation is small compared to n. To obtain A and B of (3.2), we only need the long-wavelength part of (3.9). On the other hand, (3.2) makes sense even if the density varies appreciably as long as it is slowly varying, i.e., as long as it varies very little over a screening length, according to the qualitative discussion of the previous section. Therefore, to compare (3.9) and (3.2), we expand the integrand of (3.2) in powers of $(\rho(\mathbf{x})-n)$ and the $(F^{-1}-F_{\mathrm{HF}}{}^{-1})$ of

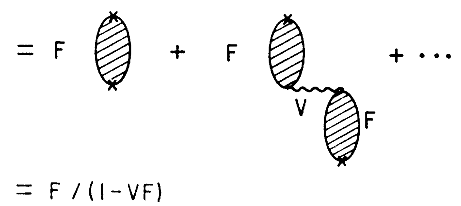

FIG. 2. The full density-response function as a geometric sum of F.

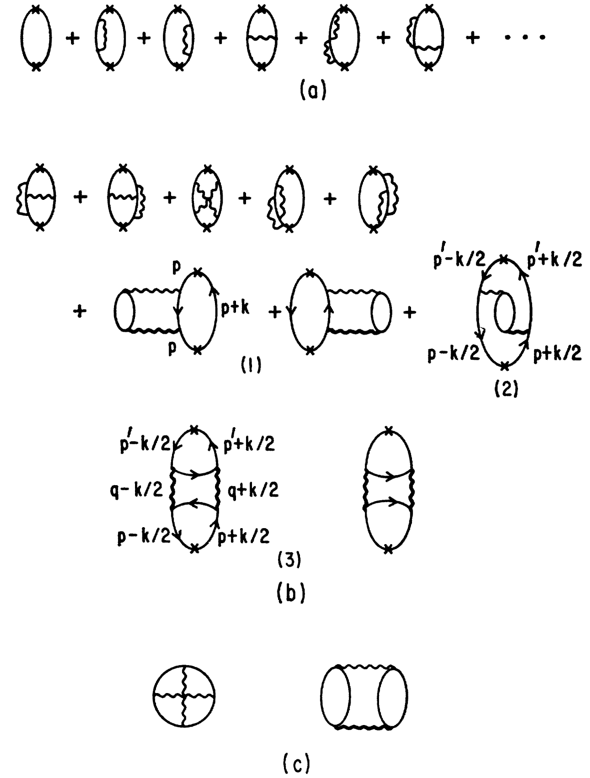

FIG. 3. (a) Diagrams for $F_{\mathrm{HF}}(\mathbf{k},0)$. (b) Additional terms for $F(\mathbf{k},0)$. (c) The correlation energy diagrams calculated by Gell-Mann and Brueckner. The thick wavy line represents an interaction line modified by the dielectric constant in the random-phase approximation.

(3.9) in powers of k^2. Let

$$F(\mathbf{k},0)=a^{-1}+bk^2+\cdots, \tag{3.10}$$

then

$$F^{-1}(\mathbf{k},0)=a-a^2bk^2+\cdots. \tag{3.11}$$

a^{-1} is given by the "compressibility sum rule"[10]

$$a^{-1}=\lim_{k\to 0} F(\mathbf{k},0)=-dn/d\mu.$$

Therefore,

$$a=-(d^2/dn^2)E^0(n). \tag{3.12}$$

Expanding (3.2) gives

$$E_c[\rho]=A(n)+\frac{d^2}{dn^2}A(n)\tfrac{1}{2}\sum_{k\neq 0}\rho_{\mathbf{k}}\rho_{-\mathbf{k}} +B(n)\sum_{k\neq 0}k^2\rho_{\mathbf{k}}\rho_{-\mathbf{k}}. \tag{3.13}$$

Substituting (3.11), (3.12) in (3.9) and comparing the result with (3.13), we conclude that

$$\begin{aligned} A(n)&=E_c^0(n),\\ B(n)&=\tfrac{1}{2}(a^2b-a_{\mathrm{HF}}^2b_{\mathrm{HF}}). \end{aligned} \tag{3.14}$$

The correlation energy can be calculated once A and B are substituted in (3.2). If we regard $E_c[\rho]$ as a small correction to $E_{\mathrm{HF}}[\rho]$, the correlation energy E_c is approximately given by

$$E_c=E_c[\rho_{\mathrm{HF}}], \tag{3.15}$$

where $\rho_{\mathrm{HF}}(\mathbf{x})$ is the density in the Hartree-Fock approximation, and minimizes $E_{\mathrm{HF}}[\rho]$:

$$\left\{\frac{\delta}{\delta\rho(\mathbf{x})}E_{\mathrm{HF}}[\rho]\right\}_{\rho=\rho_{\mathrm{HF}}}=0.$$

The remaining task is to evaluate (3.14), i.e., to find the ground-state energy and the long-wavelength behavior of the density-response function for the uniform electron gas. For such an analysis, we proceed to apply the perturbation theory, which seems to be the only technique available. The perturbation expansion is an expansion in powers of e^2m/p_0, which is valid only in the high-density limit. In this limit, the ground-state energy is well known.

$$\begin{aligned} E^0&\equiv E_{\mathrm{HF}}^0+E_c^0,\\ E_{\mathrm{HF}}^0&=n\{\tfrac{3}{5}p_0^2/2m-(3/4\pi)e^2p_0\},\\ E_c^0&=\tfrac{1}{2}e^4mn(0.0622\ln r_s-0.096)+o(e^4), \end{aligned} \tag{3.16}$$

where

$$r_s\equiv\frac{e^2m}{p_0}\left(\frac{9\pi}{4}\right)^{1/3},$$

and p_0 is the Fermi momentum. a, a_{HF} can be obtained by differentiating E^0 and E_{HF}^0, respectively [see (3.12)]. The function $F(\mathbf{k},0)$, and hence b, can be calculated using the perturbation expansion given in Fig. 3. The sum of the diagrams in Fig. 3(a) gives F_{HF}. The sum of all the diagrams in Fig. 3(a) and Fig. 3(b) gives F. Let

$$b\equiv b_{\mathrm{HF}}+b_c. \tag{3.17}$$

b_c is then the contribution of Fig. 3(b). The diagrams may seem to indicate that $b_c=O(e^4)$, but the last five diagrams of Fig. 3(b) diverge unless the interaction lines are properly modified by the dielectric constant. As one would expect, after introducing the dielectric constant (in the random-phase approximation), Fig. 3(b) becomes the correlation energy diagrams of Gell-Mann and Brueckner perturbed twice by an external field. [See Fig. 3(c).]

The qualitative argument in the previous section has shown that

$$b_c=O(e^2). \tag{3.18}$$

By (3.14) and (3.17),

$$2B(n)=(a^2-a_{\mathrm{HF}}^2)b_{\mathrm{HF}}+a^2b_c. \tag{3.19}$$

Since $a-a_{\mathrm{HF}}=O(e^4)$, we have

$$B(n)=\left(\frac{\pi^2}{p_0m}\right)^2\tfrac{1}{2}b_c+o(e^2), \tag{3.20}$$

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[10] See, for example, D. Pines, in *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1964), Vol. II.

using the fact that

$$a=-\frac{d^2E^0}{dn^2}$$

$$=\frac{-\pi^2}{p_0m}+O(e^2).$$

The formula (3.20) may be understood qualitatively in the following way. b is the long-range part of $F(\mathbf{k},0)$, which may be viewed as the second derivative of the energy with respect to the external potential as is clearly demonstrated by the diagrams. π^2/p_0m is the derivative of the chemical potential, or roughly of the external field, with respect to the density. Thus, $B(n)$ is qualitatively the second derivative of the correlation energy with respect to the long-range variation of the density.

The fact that b_c diverges without the modification of the dielectric constant shows that one must have the screening of the Coulomb force for the local density and the expansion in the density gradient to be meaningful. This is obvious in view of the qualitative discussion in Sec. II. By using the dielectric constant, one effectively sums the leading divergent diagrams of all orders and defines a lower cutoff for the divergent integral over the momentum transfer of the Coulomb interaction.

IV. EVALUATION OF b_c

To calculate b_c to $O(e^2)$, we only need to consider the last five diagrams [labeled by (1), (2), and (3)] in Fig. 3(b). It is not practical to evaluate the diagrams for an arbitrary k and then identify b_c with the coefficient of k^2 in the k expansion, because multidimensional integrals are involved in the evaluation. We shall instead obtain an expression for b_c by expanding the integrand and extract the coefficient of k^2. Then, the integral to be performed, involving no k, becomes much simpler. Consider the diagrams (1) first.

A. Diagrams (1)

These two diagrams have the same value. Their contribution to $F(\mathbf{k},0)$ is

$$F^{(1)}(\mathbf{k},0)=2\times2\int dp\,G(p)^2\Sigma(p)G(p+\mathbf{k}),\quad(4.1)$$

where the symbol $\int dp$ always denotes the four-dimensional integral

$$\int\frac{d^4p}{(2\pi)^4i}.$$

The Green's function is given by

$$G(p)\equiv[\epsilon-\epsilon_p+\mu+i\eta\,\operatorname{sgn}(\epsilon_p-\mu)]^{-1},\quad(4.2)$$

$$\epsilon_p\equiv p^2/2m,$$

$$\mu=p_0^2/2m,$$

and

$$\Sigma(p)\equiv-\int dqV^-(q)G(p+q),\quad(4.3)$$

with

$$V^-(q)\equiv\frac{4\pi e^2}{q^2}\left(\frac{1}{\epsilon(q)}-1\right).\quad(4.4)$$

$\epsilon(\mathbf{q},\omega)$ is the dielectric constant in the random-phase approximation. The extra factor of 2 in (4.1) is due to the spin multiplicity. The precise meaning of $G^2(p)$ in (4.1) is

$$G^2(p)\equiv-\frac{\partial G(p)}{\partial\epsilon},\quad(4.5)$$

which has a double pole (forced by momentum conservation) at $\epsilon=\epsilon_p-\mu-i\eta\,\operatorname{sgn}(\epsilon_p-\mu)$. The derivatives of $G(p)$ are discussed in more detail in Appendix A. As will be seen shortly, we need to make the substitution

$$-\frac{\partial}{\partial\epsilon}G(p)=-\frac{\partial}{\partial\mu}G(p)+2\pi i\delta(\epsilon)\delta(\mu-\epsilon_p),\quad(4.6)$$

for $G^2(p)$ in (4.1), which becomes, after integrating the $\delta(\epsilon)\delta(\mu-\epsilon_p)$ term

$$F^{(1)}(\mathbf{k},0)=-4\int dp\,\Sigma(p)G(p+\mathbf{k})\frac{\partial}{\partial\mu}G(p)$$

$$+\Sigma(p_0,0)\frac{\partial}{\partial\mu}F^0(\mathbf{k},0),\quad(4.7)$$

where

$$F^0(\mathbf{k},\omega)\equiv-2\int\frac{d^3p}{(2\pi)^3}\frac{n_{\mathbf{p}+\mathbf{k}}-n_{\mathbf{p}}}{\omega-\epsilon_{\mathbf{p}+\mathbf{k}}+\epsilon_p+i\eta\,\operatorname{sgn}\omega},\quad(4.8)$$

$$n_p\equiv\theta(\mu-\epsilon_p).$$

To find the k^2 term of $F^{(1)}(\mathbf{k},0)$, we expand $(\partial/\partial\mu)F^0(\mathbf{k},0)$ and $G(p+\mathbf{k})$:

$$\frac{\partial}{\partial\mu}F^0(\mathbf{k},0)=-\frac{m}{\pi^2v_0}+\frac{k^2}{p_0^2}\frac{m}{12\pi^2v_0}+\cdots,\quad(4.9)$$

$$v_0\equiv p_0/m,$$

$$G(p+\mathbf{k})=G(p)+\mathbf{k}\cdot\nabla_pG(p)+\tfrac{1}{2}(\mathbf{k}\cdot\nabla_p)^2G(p)+\cdots$$

$$=G(p)-(\mathbf{k}\cdot\mathbf{p}/m+k^2/2m)\frac{\partial}{\partial\mu}G(p)$$

$$+\frac{(\mathbf{k}\cdot\mathbf{p})^2}{2m^2}\frac{\partial^2}{\partial\mu^2}G(p)+\cdots.\quad(4.10)$$

By symmetry, $(\mathbf{k}\cdot\mathbf{p})^2$ may be replaced by $k^2p^2/3$.

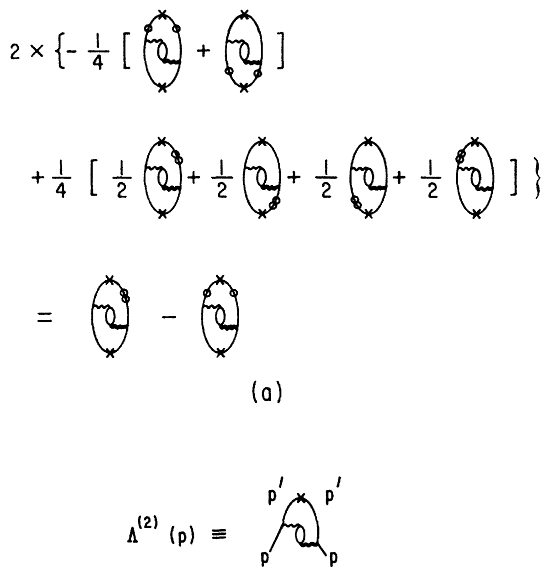

FIG. 4. (a) The k^2 term of the diagram (2) in Fig. 3(b). Each circle represents a factor $\mathbf{k}\cdot\nabla$ operating on the line on which the circle is drawn. (b) The zero-momentum-transfer vertex function which constitutes the lower parts of the last two diagrams in (a).

Therefore, the k^2 term of $-G(p+\mathbf{k})\partial G(p)/\partial\mu$ is

$$\lim_{\delta\to 0}\left\{-\frac{k^2}{2m}\frac{\partial}{\partial\mu}G(p+\boldsymbol{\delta})+\frac{k^2p^2}{6m^2}\frac{\partial^2}{\partial\mu^2}G(p+\boldsymbol{\delta})\right\}\left\{-\frac{\partial}{\partial\mu}G(p)\right\}$$
$$=-\frac{k^2}{2m}\times\tfrac{1}{6}\frac{\partial^3}{\partial\mu^3}G(p)+\frac{2k^2}{3m}\epsilon_p\times\tfrac{1}{24}\frac{\partial^4}{\partial\mu^4}G(p).\quad(4.11)$$

We have used the identity (see Appendix A)

$$\lim_{\delta\to 0}\frac{1}{(m-1)!}\left(-\frac{\partial}{\partial\mu}\right)^{m-1}G(p+\boldsymbol{\delta})\frac{1}{(n-1)!}\left(-\frac{\partial}{\partial\mu}\right)^{n-1}G(p)$$
$$=\frac{1}{(m+n-1)!}\left(-\frac{\partial}{\partial\mu}\right)^{m+n-1}G(p),\quad(4.12)$$

where m, n are integers greater than zero. Therefore, by (4.9) and (4.11), the k^2 term of $F^{(1)}(\mathbf{k},0)$ is

$$\frac{k^2}{m}\int dp\,\Sigma(p)\left\{-\tfrac{1}{3}\frac{\partial^3}{\partial\mu^3}G(p)+\tfrac{1}{9}\epsilon_p\frac{\partial^4}{\partial\mu^4}G(p)\right\}$$
$$-k^2\Sigma(p_0,0)/24\pi^2v_0\mu\equiv b^{(1)}k^2.\quad(4.13)$$

B. Diagrams (2) and (3)

The k^2 term of diagram (2) in Fig. 3(b) is given in Fig. 4(a). A circle represents a factor $\mathbf{k}\cdot\nabla$. The ∇ operator operates on the momentum variable of the Green's-function line on which the circle is drawn. The over-all factor of 2 is due to the spin multiplicity.

Figure 4(b) defines the vertex function $\Lambda^{(2)}(p)$, i.e.,

$$\Lambda^{(2)}(p)=-\int dp'\,V^{-}(p-p')\left(-\frac{\partial G(p')}{\partial\mu}\right).\quad(4.14)$$

With the aid of the identity (4.12), the analytic expression for the diagrams in Fig. 4(a) can be obtained:

$$\frac{k^2}{m}\int dp\,\Lambda^{(2)}(p)\left(\frac{1}{2}\frac{\partial^2}{\partial\mu^2}G(p)-\tfrac{1}{9}\epsilon_p\frac{\partial^3}{\partial\mu^3}G(p)\right)$$
$$\equiv b^{(2)}k^2.\quad(4.15)$$

Diagrams (3), the last two in Fig. 3(b), contribute equally to the k^2 term. Similar to Fig. 4(a), 5(a) gives the k^2 term of diagrams (3). The over-all factor of 4 is due to the fact that each vertex has a spin multiplicity 2. The last two terms of Fig. 5(a) give

$$-\tfrac{1}{8}\int dq\left(\frac{\partial}{\partial\mu}F^0(q)\right)^2\{V(q)(\mathbf{k}\cdot\nabla_q)^2V(q)-[\mathbf{k}\cdot\nabla_qV(q)]^2\}$$
$$\equiv b_1{}^{(3)}k^2,\quad(4.16)$$

where

$$F^0(\mathbf{q},\omega)\equiv 2\int dp\,G(p+q)G(p)$$

is also given by (4.8). Each triangular loop gives a factor $-\tfrac{1}{4}\partial F^0/\partial\mu$. $V(q)$ is defined by

$$V(q)\equiv 4\pi e^2/q^2\epsilon(q).$$

Let the vertex function $\Lambda^{(3)}(p)$ be defined by Fig. 5(b). Then the first two terms in Fig. 5(a) are the same as those in Fig. 4(a) except that $\Lambda^{(2)}$ is replaced by $\Lambda^{(3)}$. Thus, their contribution $b_2{}^{(3)}\,k^2$ is obtained by substituting $\Lambda^{(3)}$ for $\Lambda^{(2)}$ in (4.15). Now b_c can be obtained from

$$b_c=b^{(1)}+b^{(2)}+b_1{}^{(3)}+b_2{}^{(3)}.$$

The sum is, by (4.13), (4.15), and (4.16),

$$b_c=b'+b''+b'''-\Sigma(p_0,0)/24\pi^2v_0\mu,\quad(4.17)$$

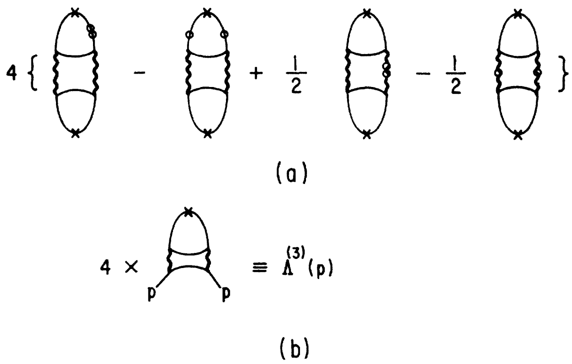

FIG. 5. (a) The k^2 term of diagrams (3) in Fig. 3(b). (b) The vertex function constituting the lower parts of the first two diagrams in (a).

where

$$b' \equiv -\frac{1}{m}\frac{\partial}{\partial\mu}\int dp\,\Sigma(p)\left(\tfrac{1}{2}\frac{\partial^2}{\partial\mu^2}G(p)-\tfrac{1}{9}\frac{\partial^3}{\partial\mu^3}G(p)\epsilon_p\right),$$

$$b'' \equiv \frac{1}{m}\int dp\,\Sigma(p)\tfrac{1}{6}\frac{\partial^3}{\partial\mu^3}G(p), \qquad (4.18)$$

$$b''' \equiv -\tfrac{1}{24}\int dq\left(\frac{\partial}{\partial\mu}F^0(q)\right)^2 \times\left[V(q)\nabla_q{}^2V(q)-\left(\frac{d}{dq}V(q)\right)^2\right].$$

In deriving (4.18), we have used the identity

$$\Lambda^{(2)}(p)+\Lambda^{(3)}(p)=-\frac{\partial\Sigma(p)}{\partial\mu}, \qquad (4.19)$$

which is easily seen by putting a density vertex of zero momentum on the diagrams for $\Sigma(p)$ in all possible ways.

C. Evaluation of the Integrals

The next step is to evaluate the integrals in (4.18) and $\Sigma(p_0,0)$ to the order $O(e^2)$. Since $\Sigma(p_0,0)$ is known to be $O(e^4 \ln e^2)$,[11] we need only to consider b', b'', and b'''.

Recall that [see (4.3), (4.4)]

$$\Sigma(p)=-\int dq\,V^-(q)G(p+q). \qquad (4.3)$$

Since the $O(e^2)$ term of b_c is due to the small q part of the Coulomb interaction, and since the Green's function and its derivatives are highly singular, it is more desirable to substitute (4.3) in (4.18) and perform the p integration first. Then the remaining q integral is nonsingular and the $O(e^2)$ term can be extracted easily. Of course, no p integral is needed for b'''.

Substituting (4.3) in (4.18), we have

$$b'=-\frac{1}{m}\frac{\partial}{\partial\mu}\int dq\,V^-(q)[\tfrac{1}{2}I_1(q)-\tfrac{1}{9}I_3(q)],$$

$$b''=-\frac{1}{m}\int dq\,V^-(q)\tfrac{1}{6}I_2(q), \qquad (4.20)$$

where

$$I_1(q)\equiv\int dp\,G(p+q)\frac{\partial^2}{\partial\mu^2}G(p),$$

$$I_2(q)\equiv\int dp\,G(p+q)\frac{\partial^3}{\partial\mu^3}G(p), \qquad (4.21)$$

$$I_3(q)\equiv\int dp\,G(p+q)\frac{\partial^3}{\partial\mu^3}G(p)\epsilon_p.$$

For the sake of continuity and clarity, we leave the detailed algebra of these p integrals in Appendix B, and quote the results when they are needed.

The q integral is a four-dimensional integral

$$\int dq \equiv \int\frac{d^3q}{(2\pi)^3}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}.$$

It is convenient to turn the ω-integral contour to the imaginary axis and let the dimensionless variable y be defined by

$$\omega=iqv_0y. \qquad (4.22)$$

Then, by spherical symmetry and (4.22),

$$\int dq=\frac{4\pi v_0}{(2\pi)^3}\int_0^{\infty}q^3dq\int_{-\infty}^{\infty}\frac{dy}{2\pi}. \qquad (4.23)$$

We consider the q integrals for b', b'', and b''' separately.

Since b_c has the dimension of an inverse velocity, and $\partial/\partial\mu=v_0^{-1}\partial/\partial p_0$, b' must be of the form [see Eq. (4.20)]

$$b'=\frac{e^2m}{v_0}\int_0^{\infty}\frac{dq}{q}\frac{\partial}{\partial p_0}\int_{-\infty}^{\infty}\frac{dy}{2\pi}\left(\frac{1}{\epsilon}-1\right)f\left(\frac{q}{p_0},y\right), \qquad (4.24)$$

where $f(x,y)$ is a dimensionless function. Notice that e^2m, the inverse Bohr radius, has the dimension of a momentum. Equations (B26) and (B28) show that $I_1(q,y)$ and $I_3(q,y)$ are of $O(q^{-2})$ as $q\to0$. Therefore, $f(x,y)=O(1)$ as $x\to0$. The dielectric constant has the form

$$\epsilon=1-\frac{4\pi e^2}{q^2}F^0(q,iqv_0y) =1+\frac{e^2mp_0}{q^2}\frac{4}{\pi}R\left(\frac{q}{p_0},y\right), \qquad (4.25)$$

where $R(x,y)$ is a dimensionless function, and [see (B16) and (B17)]

$$R(0,y)\equiv R(y)=1-y\tan^{-1}y^{-1}. \qquad (4.26)$$

The $O(e^2)$ term of (4.24) can be easily extracted. It comes from the lower limit of the q integral. Let us introduce an arbitrary upper cutoff at $q=p_0$. Above any finite cutoff, the integral is of $O(e^4)$. Explicitly, the q integral is now

$$e^2\int_0^{p0}\frac{dq}{q}\frac{d}{dp_0}\left[\left(\frac{1}{\epsilon}-1\right)f\left(\frac{q}{p_0},y\right)\right]+o(e^2)$$
$$=e^2\frac{d}{dp_0}\int_0^1\frac{dx}{x}\left[1+\frac{e^2m}{p_0x^2}\frac{4}{\pi}R(y)\right]^{-1}f(0,y) -e^2f(0,y)/p_0+o(e^2)$$
$$=-e^2f(0,y)/2p_0+o(e^2). \qquad (4.27)$$

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[11] J. Quinn and R. Ferrell, Phys. Rev. **112**, 812 (1958).

Substituting (4.27) in (4.24) and using the expressions for I_1, I_3 given by (B26) and (B28), we have

$$b' = \frac{4\pi}{(2\pi)^3} 4\pi e^2 \frac{m}{(2\pi)^2 v_0} \int_{-\infty}^{\infty} \frac{dy}{2\pi} \left(-\frac{1}{2p_0} \right) \times \left\{ \frac{-2y^2}{(1+y^2)^2} + \frac{y^2(5+9y^2)}{9(1+y^2)^3} \right\} + o(e^2)$$

$$= \tfrac{5}{9} \frac{e^2 m}{(2\pi)^3 v_0 p_0} + o(e^2). \quad (4.28)$$

Again, by dimensional argument, b'' [see (4.20)] must have the form

$$b'' = \frac{e^2 m}{p_0 v_0} \int_0^{\infty} \frac{dq}{q} \int_{-\infty}^{\infty} \frac{dy}{2\pi} \left(\frac{1}{\epsilon} - 1 \right) g\left(\frac{q}{p_0}, y \right), \quad (4.29)$$

where $g(x,y)$ is a dimensionless function. From (B27), we see that

$$g(0,y) = -\frac{4}{(2\pi)^3} \frac{y^2(3-y^2)}{(1+y^2)^3}. \quad (4.30)$$

Since

$$\int_{-\infty}^{\infty} dy\, g(0,y) = 0,$$

(4.29) becomes, after the q integral is performed,

$$b'' = \frac{e^2 m}{p_0 v_0} \int_{-\infty}^{\infty} \frac{dy}{2\pi} [-\tfrac{1}{2} \ln R(y)] g(0,y) + o(e^2)$$

$$= \frac{e^2 m}{p_0 v_0} \frac{1}{(2\pi)^3} 0.82872 + o(e^2). \quad (4.31)$$

The y integral was performed numerically.

b''' [see (4.18)] may be obtained in the same manner although the algebra is more tedious. With the aid of the formulas given in Appendix B, b''' reduces to, after some algebra,

$$b''' = \frac{e^2 m}{p_0 v_0 (2\pi)^3} \times \tfrac{2}{9} \int_{-\infty}^{\infty} \frac{dy}{2\pi} \left(2 + \frac{1}{1+y^2} \right) \frac{1}{(1+y^2)^2 R(y)}$$

$$= \frac{e^2 m}{p_0 v_0 (2\pi)^3} \times 0.59136. \quad (4.32)$$

Combining (4.28), (4.31), and (4.32), we have

$$b_c = b' + b'' + b''' + o(e^2)$$

$$= \frac{e^2 m}{p_0 v_0 (2\pi)^3} \times 1.97563 + o(e^2). \quad (4.33)$$

The evaluation of b_c to $O(e^2)$ is thus completed. One easily verifies that the small term $o(e^2)$ in (4.33) is of the order $O(e^4) + O(e^4 \ln e^2)$.

Substituting (4.33) in (3.20), one obtains $B(\rho)$. Then (3.2) reads

$$E_c[\rho] = \int d^3x\, E_c{}^0(\rho(x)) + \Delta E_c[\rho],$$

$$\Delta E_c[\rho] = 4.235 \times 10^{-3} e^2 \int d^3x\, \rho^{-4/3} |\nabla\rho(x)|^2 \times [1 + O(e^2 \ln e^2) + O(e^2)]. \quad (4.34)$$

If we measure lengths in units of the Bohr radius $(e^2 m)^{-1}$, we have

$$\Delta E_c[\rho] = (8.470 \times 10^{-3}\ \mathrm{Ry}) \int d^3x\, \rho^{-4/3} |\nabla\rho(x)|^2 \times [1 + O(\rho^{-1/3} \ln\rho) + O(\rho^{-1/3})]. \quad (4.35)$$

We see that the results here agree in order of magnitude with the estimate given in Sec. II. [See (2.13).]

The correlation energy is given by (3.15), i.e., by substituting the electron density in the Hartree-Fock approximation in (4.34) or (4.35).

In the above evaluation of b_c, there was no approximation made until we performed the q integration, where only the contribution of the small q is extracted. The dielectric constant, which describes the collective motion of the electrons, behaved like a lower cutoff of the otherwise linearly divergent q integral. The lower q cutoff by the dielectric constant near $(e^2 m p_0)^{1/2}$ is equivalent to the cutoff of the density correlation outside a sphere of radius $L_s \sim (e^2 m p_0)^{-1/2}$. The number of electrons inside this sphere is of the order $(p_0/e^2 m)^{3/2}$, which is large in the high-density limit. Thus, the long range correlation and the collective motion of many electrons contribute substantially to the correlation energy.

The above mathematical procedure is very straightforward and involves no numerical work except for two one-dimensional integrals. The calculation of the next-order term, i.e., $O(e^4) + O(e^4 \ln e^2)$, would involve more complicated numerical work for the evaluation of the exchange diagrams [the first five of Fig. 3(b)]. We have demonstrated the power of the many-body diagram technique combined with the density-functional formalism. Such a technique may be generalized to study other many-body systems with slowly varying densities.

V. DENSITY GRADIENT IN ATOMS

For a many-electron atom, a large fraction of the electrons is concentrated within one Bohr radius around the nucleus and the density there becomes very high. In spite of the qualitative difference between the high-density uniform electron gas and the atoms, which we shall discuss in detail later, it is instructive to apply to the atoms the correlation energy formula for a high-

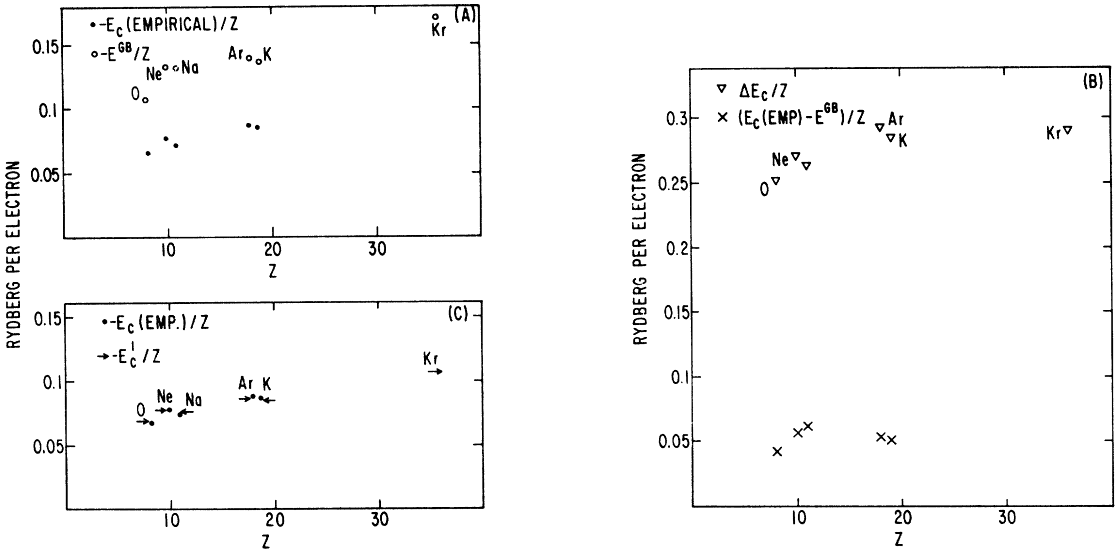

FIG. 6. $-E_c$ (empirical) is taken from the last column of Table III of Ref. 5. E^{GB} is given by (5.1) and (3.16), ΔE_c from (4.36) and E_c' from (5.2).

density uniform electron gas. The integral

$$E^{\mathrm{GB}}=\int d^3x\, E_c{}^0(\rho(\mathbf{x}))\,, \qquad (5.1)$$

using the Hartree-Fock electron density[12] for $\rho(\mathbf{x})$ and $E_c{}^0$ given by (3.16), can be easily evaluated numerically. Figure 6(a) shows E^{GB} and the empirical correlation energy[13] for a few atoms. We see that E^{GB} over-estimates the correlation energy by about a factor of 2 in every case. The obvious reason for the discrepancy is the fact that the density is not uniform. To estimate the effect of the nonuniformity, the formula (4.35) can be used to compute the correction to (5.1). The results are shown in Fig. 6(b). We see that (4.35) overestimates in every case by about a factor of 5 the correction needed to reproduce the empirical correlation energy. These overestimates can be easily understood as follows.

If one uses the Thomas-Fermi density instead of the Hartree-Fock density [although, strictly, the latter should be used according to (3.15)], (4.35) would be a logarithmically divergent integral due to the $r^{-3/2}$ behavior of the density near the nucleus, i.e.,

$$4\pi\int r^2dr\,[\rho(r)^{-4/3}|\nabla\rho(r)|^2]_{\mathrm{TF}}$$

$$\sim\int r^2dr\,[(r^{-3/2})^{-4/3}|r^{-5/2}|^2]\sim\int\frac{dr}{r}\,.$$

This divergence is weak, however, and can be cutoff at a very small r to match the result given by the Hartree-Fock density, which is very high (although finite) at $r=0$. This suggests that the density gradient is too high for the gradient expansion to be useful. Recall that the physical picture behind the correlation energy formula for a uniform electron gas is the long-range correlation due to the Coulomb force. This long range is made finite by the effect of screening owing to the collective motion of electrons. Thus, qualitatively, the correlation energy involves an integral over a sphere of radius L_s, the screening length. The same physical picture is behind the formula for the density-gradient square correction term with more emphasis on the outer region of the sphere since b_c is essentially the second moment of the density fluctuation correlation function. One encounters the same situation, when evaluating higher-order terms in the gradient expansion, with the outer region of the sphere contributing even more substantially to the integrals. In an atom, however, the electrons are concentrated around the nucleus (see Fig. 7, for example), so concentrated that a sphere of radius L_s becomes larger than the high-density core, i.e., the outer region of the sphere is essentially empty.[14] In view of the above discussion, it is clear that the gradient expansion tends to overestimate and that the higher the order, the worse the overestimate. In short, the density gradient in atoms is so large that the gradient expansion becomes a divergent series.

The divergent series must be summed formally before it is used for computation. The formal sum is unknown, but a crude estimate can be made as follows. We look for a function $f(\rho,|\nabla\rho|^2)$ which is well behaved for

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[12] T. G. Strand and R. A. Bonham, J. Chem. Phys. **40**, 1686 (1964). We are grateful to Dr. Jerry Peacher for pointing out this and related references to us.

[13] The empirical correlation energy has been obtained for many atoms by Clementi (see Ref. 2) by subtracting the HF energy from the experimental total energy.

[14] This point was made by C. Herring during discussion at the Slater Symposium held on Sanibal Island, January, 1967.

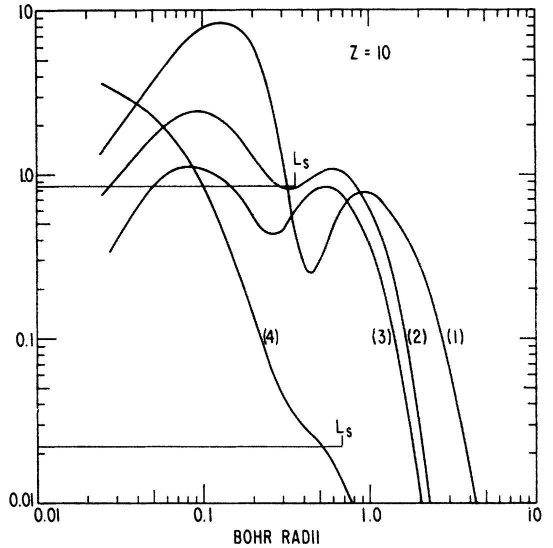

FIG. 7. (1) $4\pi r^2 B(\rho(r))|\nabla\rho(r)|^2$, see (4.36). (2) $4\pi r^2 E_c{}^0(\rho(r))$, see (3.16). (3) $4\pi r^2 f(\rho(r),\nabla\rho(r))$, see (5.3). (4) $\rho(r)/100$, the Hartree-Fock density in units of hundred electrons per cubic Bohr radius (Ref. 12). The screening length $L_s \sim r_s{}^{1/2}$ is shown for $r=0.1$ ($L_s \sim 0.37$) and for $r=0.5$ ($L_s \sim 0.68$).

infinite $|\nabla\rho|^2$ and which reduces to the integrand of (4.34) for small $|\nabla\rho|^2$. Then the difficulty arising from the very high density gradient may be avoided, and we expect

$$E_c' \equiv \int_0^\infty 4\pi r^2 dr\, f(\rho(r), |\nabla\rho(r)|^2) \qquad (5.2)$$

to be a reasonable estimate of the correlation energy. Since, if the density gradient is high, a higher density gradient would imply a smaller region in space for the distribution of the same number of electrons, and since the correlation energy is mainly a long range effect, we expect the correlation energy per electron to decrease as the density gradient increases in the region of high density gradient. Since $E_c{}^0(\rho)$ is roughly proportional to the density, the function

$$f(\rho, |\nabla\rho|^2) = E_c{}^0(\rho)/[1 - B(\rho)|\nabla\rho|^2/(yE_c{}^0(\rho))]^y \qquad (5.3)$$

where y is an adjustable constant greater than zero, satisfies the above requirements. We found, if $y=0.32$, then E_c' given by (5.2), agrees well with the empirical value. [See Fig. 6(c).] The integrand of (5.2) is shown in Fig. 7 together with the integrands of (4.34) and the density for $Z=10$. We see that the integral is mainly contributed by the electrons in the middle and outer shells where the density is high.

From the above discussion, we arrive at the following qualitative conclusions on the calculation of the atomic correlation energy. First, the gradient expansion cannot be used unless it is formally summed to infinite orders. Second, the screening due to the collective motion of electrons is not as important as it is in a uniform electron gas because the small size of the atom effectively cuts off the long-range correlation between electrons.

ACKNOWLEDGMENT

This investigation was initiated as a result of the remarks on the problem of correlation energy in atoms made by Professor J. C. Slater at the Slater Symposium, January, 1967.

APPENDIX A

In this Appendix, we review a few of the basic mathematical properties of the Green's function:

$$G(p) = [\epsilon - \epsilon_p + \mu + i\eta \operatorname{sgn}(\epsilon_p - \mu)]^{-1}$$

$$= P\frac{1}{\epsilon - \epsilon_p + \mu} - \pi i \delta(\epsilon - \epsilon_p + \mu) \operatorname{sgn}(\epsilon_p - \mu). \qquad (A1)$$

Since

$$\delta(\epsilon - \epsilon_p + \mu) \operatorname{sgn}(\epsilon_p - \mu) = \delta(\epsilon - \epsilon_p + \mu) \operatorname{sgn}\epsilon,$$

we have

$$G(p) = [\epsilon - \epsilon_p + \mu + i\eta \operatorname{sgn}\epsilon]^{-1}. \qquad (A2)$$

Equation (A2) is a convenient form if G is regarded as a function of μ or ϵ_p. Because the infinitesimal imaginary number $i\eta$ has a variable coefficient, extra care is needed in manipulating the Green's function. For example, differentiating (A1) with respect to ϵ and (A2) with respect to μ, we have

$$-\frac{\partial}{\partial\epsilon}G(p) = [\epsilon - \epsilon_p + \mu + i\eta \operatorname{sgn}(\epsilon_p - \mu)]^{-2}, \qquad (A3)$$

$$-\frac{\partial}{\partial\mu}G(p) = [\epsilon - \epsilon_p + \mu + i\eta \operatorname{sgn}\epsilon]^{-2}. \qquad (A4)$$

Although the right-hand sides of (A3) and (A4) both appear as the square of G, they are not the same. The Green's function is a *distribution*. The square of a distribution is in general not defined without additional specifications. Equation (A3) represents a double pole, or the square of the simple pole $G(p)$, only if we regard it as a function of ϵ. Similarly, (A4) is the square of $G(p)$ only if it is regarded as a function of μ or ϵ_p. Equations (A3) and (A4) are simply related. Differentiating the last line of (A1) shows that

$$-\frac{\partial}{\partial\mu}G(p) = -\frac{\partial}{\partial\epsilon}G(p) - 2\pi i \delta(\epsilon)\delta(\mu - \epsilon_p). \qquad (A5)$$

Similarly, higher powers of $G(p)$ in the variable ϵ are different from those in the variable ϵ_p or μ. Their relationship can be found by direct differentiation. For example,

$$\frac{\partial^2}{\partial\mu^2}G(p)=\frac{\partial}{\partial\epsilon}\frac{\partial}{\partial\mu}G(p)+2\pi i\delta(\epsilon)\delta'(\mu-\epsilon_p),$$

$$=\frac{\partial^2}{\partial\epsilon^2}G(p)+2\pi i\delta'(\epsilon)\delta(\mu-\epsilon_p)$$

$$+2\pi i\delta(\epsilon)\delta'(\mu-\epsilon_p), \quad \text{(A6)}$$

and

$$-\frac{\partial^3}{\partial\mu^3}G(p)=-\frac{\partial^3}{\partial\epsilon^3}G(p)-2\pi i\delta''(\epsilon)\delta(\mu-\epsilon_p)$$

$$-2\pi i\delta'(\epsilon)\delta'(\mu-\epsilon_p)-2\pi i\delta(\epsilon)\delta''(\mu-\epsilon_p). \quad \text{(A7)}$$

At a static density vertex of the infinitesimal momentum **δ**, one encounters the limit

$$\lim_{\delta\to 0}G(p+\boldsymbol{\delta})G(p)$$

$$\equiv\lim_{\delta\to 0}G(\epsilon,\mathbf{p}+\boldsymbol{\delta})G(\epsilon,\mathbf{p}). \quad \text{(A8)}$$

Regarding the G's as simple poles in the μ plane, we see that (A8) reduces to a double pole in the μ plane, i.e.,

$$\lim_{\delta\to 0}G(p+\boldsymbol{\delta})G(p)$$

$$=\lim_{\delta\to 0}(\epsilon-\epsilon_{\mathbf{p}+\boldsymbol{\delta}}+\mu+i\eta\operatorname{sgn}\epsilon)^{-1}(\epsilon-\epsilon_{\mathbf{p}}+\mu+i\eta'\operatorname{sgn}\epsilon)^{-1}$$

$$=(\epsilon-\epsilon_p+\mu+i\eta\operatorname{sgn}\epsilon)^{-2}$$

$$=-\frac{\partial}{\partial\mu}G(p). \quad \text{(A9)}$$

More generally, when an mth-order pole approaches an nth-order pole, the result is an $(m+n)$th-order pole. Thus, we have the identity

$$\lim_{\delta\to 0}\frac{1}{(m-1)!}\left(-\frac{\partial}{\partial\mu}\right)^{m-1}G(p+\boldsymbol{\delta})\frac{1}{(n-1)!}\left(-\frac{\partial}{\partial\mu}\right)^{n-1}G(p)$$

$$=\frac{1}{(m+n-1)!}\left(-\frac{\partial}{\partial\mu}\right)^{m+n-1}G(p),$$

$$m,n=1,2,3,\cdots. \quad \text{(A10)}$$

APPENDIX B

We perform the integrals

$$I_1(q)=\int dp\,G(p+q)\frac{\partial^2}{\partial\mu^2}G(p),$$

$$I_2(q)=\int dp\,G(p+q)\frac{\partial^3}{\partial\mu^3}G(p), \quad \text{(4.19)}$$

$$I_3(q)=\int dp\,G(p+q)\frac{\partial^3}{\partial\mu^3}G(p)\epsilon_p,$$

and give explicit expressions of the functions needed in the text.

Consider $I_1(q)$. By (A6),

$$I_1(q)=\int\frac{d^3p}{(2\pi)^3}\left\{\int\frac{d\epsilon}{2\pi i}G(p+q)\frac{\partial^2}{\partial\epsilon^2}G(p)\right.$$

$$+\delta(\mu-\epsilon_p)\left[-\frac{\partial}{\partial\epsilon}G(p+q)\right]_{\epsilon=0}$$

$$\left.+\delta'(\mu-\epsilon_p)G(\omega,\mathbf{p}+\mathbf{q})\right\}. \quad \text{(B1)}$$

The first term on the right-hand side of (B1) is

$$\int\frac{d^3p}{(2\pi)^3}\left[n_{\mathbf{p}+\mathbf{q}}(1-n_{\mathbf{p}})\frac{\partial^2}{\partial\epsilon^2}G(p)\right.$$

$$\left.-n_{\mathbf{p}}(1-n_{\mathbf{p}+\mathbf{q}})\frac{\partial^2}{\partial\epsilon^2}G(p)\right]_{\epsilon=\epsilon_{\mathbf{p}+\mathbf{q}}}$$

$$=-\frac{\partial^2}{\partial\omega^2}\int\frac{d^3p}{(2\pi)^3}\frac{n_{\mathbf{p}+\mathbf{q}}-n_{\mathbf{p}}}{D}$$

$$=\frac{\partial^2}{\partial\omega^2}\tfrac{1}{2}F^0(\mathbf{q},\omega), \quad \text{(B2)}$$

where

$$D\equiv[G^{-1}(\omega,\mathbf{p}+\mathbf{q})]_{\mu=\epsilon_p}$$
$$=\omega-\epsilon_{\mathbf{p}+\mathbf{q}}+\epsilon_{\mathbf{p}}+i\eta\operatorname{sgn}(\epsilon_{\mathbf{p}+\mathbf{q}}-\epsilon_{\mathbf{p}}), \quad \text{(B3)}$$

and F^0 has been defined by (4.8). The second term on the right-hand side of (B1) is

$$\int\frac{d^3p}{(2\pi)^3}\delta(\mu-\epsilon_p)\left(-\frac{\partial}{\partial\omega}D^{-1}\right). \quad \text{(B4)}$$

Since we are interested eventually only in evaluating the q, ω integral, to which only the part which is even in ω will contribute, we symmetrize (B4) with respect to ω and obtain

$$-\tfrac{1}{4}\frac{\partial^2}{\partial\omega\partial\mu}J(\mathbf{q},\omega)\,, \tag{B5}$$

where

$$J(\mathbf{q},\omega)\equiv 2\int\frac{d^3p}{(2\pi)^3}\frac{n_{\mathbf{p}+\mathbf{q}}+n_{\mathbf{p}}}{D}\,. \tag{B6}$$

Henceforth in our formulas we only keep the even ω part. The third term on the right-hand side of (B1) is

$$\int\frac{d^3p}{(2\pi)^3}\delta'(\mu-\epsilon_p)G(\omega,\,\mathbf{p}+\mathbf{q})$$

$$=\int\frac{d^3p}{(2\pi)^3}\Big\{\delta'(\mu-\epsilon_p)[G(\omega,\,\mathbf{p}+\mathbf{q})]_{\mu=\epsilon_p}$$

$$+\delta(\mu-\epsilon_p)\Big[-\frac{\partial}{\partial\mu}G(\omega,\,\mathbf{p}+\mathbf{q})\Big]_{\mu=\epsilon_p}\Big\}$$

$$=\tfrac{1}{4}\frac{\partial^2}{\partial\mu^2}F^0-\tfrac{1}{4}\frac{\partial^2}{\partial\omega\partial\mu}J-2\pi i\delta(\omega)S(q)\,, \tag{B7}$$

where

$$S(q)\equiv\int\frac{d^3p}{(2\pi)^3}\delta(\mu-\epsilon_p)\delta(\mu-\epsilon_{p+q})$$

$$=\frac{m^2}{(2\pi)^2q}\theta(2p_0-q)\,. \tag{B8}$$

Combining (B2), (B5), and (B7), we have

$$I_1(q)=\tfrac{1}{2}F_{\omega\omega}{}^0-\tfrac{1}{2}J_{\mu\omega}+\tfrac{1}{4}F_{\mu\mu}{}^0-2\pi i\delta(\omega)S(q)\,. \tag{B9}$$

We have used subscripts to denote partial differentiations.

In the same manner, we can express $I_2(q)$ and $I_3(q)$ in terms of F^0, J, and S. By (A7),

$$I_2(q)=\int\frac{d^3p}{(2\pi)^3}\Big\{\int\frac{d\epsilon}{2\pi i}G(p+q)\frac{\partial^3}{\partial\epsilon^3}G(p)$$

$$+\delta(\mu-\epsilon_p)\Big[\frac{\partial^2}{\partial\epsilon^2}G(p+q)\Big]_{\epsilon=0}$$

$$+\delta'(\mu-\epsilon_p)\Big[-\frac{\partial}{\partial\epsilon}G(p+q)\Big]_{\epsilon=0}$$

$$+\delta''(\mu-\epsilon_p)G(\omega,\,\mathbf{p}+\mathbf{q})\Big\} \tag{B10}$$

$$=\tfrac{1}{2}F_{\omega\omega\omega}{}^0+\tfrac{1}{4}F_{\omega\omega}{}^0{}_\mu$$

$$+\int\frac{d^3p}{(2\pi)^3}\Big\{\Big[-\frac{\partial}{\partial\omega}G(\omega,\,\mathbf{p}+\mathbf{q})\Big]_{\mu=\epsilon_p}\delta'(\mu-\epsilon_p)$$

$$+\Big[\frac{\partial^2}{\partial\omega\partial\mu}G(\omega,\,\mathbf{p}+\mathbf{q})\Big]_{\mu=\epsilon_p}\delta(\mu-\epsilon_p)$$

$$+[G(\omega,\,\mathbf{p}+\mathbf{q})]_{\mu=\epsilon_p}\delta''(\mu-\epsilon_p)$$

$$+2\Big[-\frac{\partial}{\partial\mu}G(\omega,\mathbf{p}+\mathbf{q})\Big]_{\mu=\epsilon_p}\delta'(\mu-\epsilon_p)$$

$$+\Big[\frac{\partial^2}{\partial\mu^2}G(\omega,\,\mathbf{p}+\mathbf{q})\Big]_{\mu=\epsilon_p}\delta(\mu-\epsilon_p)\Big\}$$

$$=\frac{\partial}{\partial\mu}[\tfrac{3}{4}F_{\omega\omega}{}^0-\tfrac{3}{4}J_{\mu\omega}+\tfrac{1}{4}F_{\mu\mu}{}^0-3\pi i\delta(\omega)S(q)]\,. \tag{B11}$$

Remember that only even parts in ω are kept.

The factor ϵ_p in $I_3(q)$ slightly complicates the integration. Again, by (A7),

$$I_3(q)=\int\frac{d^3p}{(2\pi)^3}\Big\{\int\frac{d\epsilon}{2\pi i}G(p+q)\frac{\partial^3}{\partial\epsilon^3}G(p)\epsilon_p$$

$$+\Big[\frac{\partial^2}{\partial\epsilon^2}G(p+q)\Big]_{\epsilon=0}\delta(\mu-\epsilon_p)\mu$$

$$+\Big[-\frac{\partial}{\partial\epsilon}G(p+q)\Big]_{\epsilon=0}(\delta'(\mu-\epsilon_p)\mu+\delta(\mu-\epsilon_p))$$

$$+G(\omega,\,\mathbf{p}+\mathbf{q})[\delta''(\mu-\epsilon_p)\mu+2\delta'(\mu-\epsilon_p)\Big\}\,. \tag{B12}$$

The (even part of) first term is

$$\int\frac{d^3p}{(2\pi)^3}(n_{\mathbf{p}+\mathbf{q}}-n_{\mathbf{p}})\frac{\partial^3}{\partial\omega^3}\frac{1}{D}\times\tfrac{1}{2}(\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}+\mathbf{q}})$$

$$=\tfrac{1}{2}\int\frac{d^3p}{(2\pi)^3}(n_{\mathbf{p}}-n_{\mathbf{p}+\mathbf{q}})\frac{\partial^3}{\partial\omega^3}\Big(-1+\frac{\omega}{D}\Big)$$

$$=\tfrac{3}{4}F_{\omega\omega}{}^0+\tfrac{1}{4}\omega F_{\omega\omega\omega}{}^0\,.$$

All the other terms in (B12) have been evaluated before. Thus,

$$I_3(q)=\tfrac{1}{4}\omega F_{\omega\omega\omega}{}^0+\tfrac{3}{4}(F_{\omega\omega}{}^0-J_{\mu\omega})$$

$$+\tfrac{1}{2}F_{\mu\mu}{}^0-4\pi i\delta(\omega)S(q)$$

$$+\mu\frac{\partial}{\partial\mu}[\tfrac{3}{4}F_{\omega\omega}{}^0-\tfrac{3}{4}J_{\mu\omega}+\tfrac{1}{4}F_{\mu\mu}{}^0-3\pi i\delta(\omega)S(q)]\,. \tag{B13}$$

F^0 and J can be obtained from the definitions (4.8) and (B6). Explicitly,

$$F^0(q,\omega)=\frac{2mp_0}{(2\pi)^2}\left\{-1+\frac{m}{2qv_0}\left[(\alpha_-^2-v_0^2)\ln\left(\frac{\alpha_--v_0}{\alpha_-+v_0}\right)+(\alpha_+^2-v_0^2)\ln\left(\frac{\alpha_++v_0}{\alpha_+-v_0}\right)\right]\right\},\quad\text{(B14)}$$

$$\frac{\partial}{\partial\mu}J(q,\omega)=\frac{m^2}{(2\pi)^2q}\left[\ln\left(\frac{\alpha_-+v_0}{\alpha_--v_0}\right)-\ln\left(\frac{\alpha_+-v_0}{\alpha_++v_0}\right)\right],$$

where

$$\alpha_\pm\equiv\frac{\omega}{q}\pm\frac{q}{2m}.$$

ω is regarded as a complex number. Explicit expressions for I_1, I_2, and I_3 can then be obtained by differentiating (B14). The ω integration contour is below the real axis for $\omega<0$ and above for $\omega>0$. Thus, when differentiating with respect to ω, one must take into account the discontinuities of the functions at $\omega=0$ across the real axis. Let

$$\omega\equiv iqv_0y,$$
$$R(y)\equiv1-y\tan^{-1}y^{-1}.\quad\text{(B15)}$$

The following formulas are useful. For $q\rightarrow0$, and y fixed,

$$F^0(q,iqv_0y)=\frac{-4mp_0}{(2\pi)^2}R(y)+O(q^2),\quad\text{(B16)}$$

$$\frac{\partial}{\partial\mu}F^0=-\frac{4m}{(2\pi)^2v_0}(1+y^2)^{-1}+O(q^2),\quad\text{(B17)}$$

$$\frac{\partial^2}{\partial\mu^2}F^0=\frac{4}{(2\pi)^2v_0^3}(1-y^2)(1+y^2)^{-2}+O(q^2),\quad\text{(B18)}$$

$$\frac{\partial^2}{\partial\omega^2}F^0=-4\pi i\delta(\omega)S(q)+\frac{8m^2}{(2\pi)^2v_0q^2}(1+y^2)^{-2}+O(1),\quad\text{(B19)}$$

$$\frac{\partial^2}{\partial\mu\partial\omega}J=-8\pi i\delta(\omega)S(q)+\frac{8m^2}{(2\pi)^2v_0q^2}(1+y^2)^{-1}+O(1),\quad\text{(B20)}$$

$$\omega\frac{\partial^3}{\partial\omega^3}F^0=4\pi i\delta(\omega)S(q)-\frac{32m^2}{(2\pi)^2v_0q^2}y^2(1+y^2)^{-3}+O(1),\quad\text{(B21)}$$

$$\frac{\partial}{\partial\mu}(F_{\omega\omega}{}^0-J_{\mu\omega})=\frac{8m}{(2\pi)^2q^2v_0^3}y^2(3-y^2)(1+y^2)^{-3}+O(1),\quad\text{(B22)}$$

$$\frac{\partial}{\partial q}F^0=\frac{4m^2v_0}{(2\pi)^2q}[-(1+y^2)^{-1}+R(y)]+O(q),\quad\text{(B23)}$$

$$\frac{\partial^2}{\partial q^2}F^0=\frac{8m^2v_0}{(2\pi)^2q^2}[(1+y^2)^{-2}-R(y)]+O(1),\quad\text{(B24)}$$

$$I_1(q)=\frac{-4m^2}{(2\pi)^2v_0q^2}y^2(1+y^2)^{-2}+O(1),\quad\text{(B25)}$$

$$I_2(q)=\frac{6m}{(2\pi)^2v_0^3q^2}y^2(3-y^2)(1+y^2)^{-3}+O(1),\quad\text{(B26)}$$

$$I_3(q)=\frac{-m^2}{(2\pi)^2v_0q^2}y^2(5+9y^2)(1+y^2)^{-3}+O(1).\quad\text{(B27)}$$