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Correlation Energy of a Free Electron Gas

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The limits of validity of the correlation-energy calculations in the regions of high density, low density, and actual metallic electron densities are discussed. Simple physical arguments are given which show that the high-density calculation of Gell-Mann and Brueckner is valid for $r_s \lesssim 1$ while the low-density calculation of Wigner is valid for $r_s \gtrsim 20$. For actual metallic densities it is shown that the contribution to the correlation energy from long-wavelength momentum transfers ($k<\beta k_0<0.47 r_s^{\frac{1}{2}} k_0$) may be accurately calculated in the random phase approximation. This contribution is calculated using the Bohm-Pines extended Hamiltonian, and is shown to be

$$E(\beta)=\left(-0.458\frac{\beta^2}{r_s}+0.866\frac{\beta^3}{r_s^{\frac{3}{2}}}-0.98\frac{\beta^4}{r_s^2}+0.019\frac{\beta^4}{r_s}+0.706\frac{\beta^5}{r_s^{5/2}}+\cdots\right)\text{ ry.}$$

An identical result is obtained by a suitable expansion of the result of Gell-Mann and Brueckner; the validity of the Bohm-Pines neglect of subsidiary conditions in the calculation of the ground-state energy is thereby explicitly established. The contribution to the correlation energy from sufficiently high momentum transfers ($k \gtrsim k_0$) will arise only from the interaction between electrons of antiparallel spin, and may be estimated using second-order perturbation theory. The contribution arising from intermediate momentum transfers ($0.47 r_s^{\frac{1}{2}} k_0 \lesssim k \lesssim k_0$) cannot be calculated analytically; the interpolation procedures for this domain proposed by Pines and Hubbard are shown to be nearly identical, and their accuracy is estimated as ~15%. The result for the over-all correlation energy using the interpolation procedure of Pines is

$$E_c \cong (-0.115+0.031 \ln r_s)\text{ ry.}$$

I. INTRODUCTION

The ground-state energy of a free electron gas has now been calculated accurately in both the high- and the low-density limit. It depends only on the inter-electron spacing r_s, which is defined by $(4\pi r_s^3 a_0^3/3) = n^{-1}$, where n is the electron density.[1] The results of such calculations may be conveniently expressed in terms of the extent to which they represent an improvement over the Hartree-Fock calculation of the system energy. Thus we may write

$$E_0=\left(\frac{2.21}{r_s^2}-\frac{0.916}{r_s}+E_c\right)\text{ ry,}$$

where E_0 is the ground-state energy per electron, $2.21/r_s^2 + 0.916/r_s$ is that quantity calculated in the Hartree-Fock approximation, and E_c is the correlation energy.

The behavior of the electron gas is simple in the limit of high densities ($r_s \ll 1$) because here the Coulomb interaction is a relatively small perturbation on the motion of the electrons. Gell-Mann and Brueckner[2] have shown that in this case the correlation energy may be expressed as a series of the following type:

$$E_c=(A \ln r_s+C+D r_s \ln r_s+E r_s+\cdots)\text{ ry,} \tag{1}$$

and have calculated the coefficients A and C. Results which are equivalent to those of GB in the high-density limit have recently been obtained by a number of investigators.[3-5]

The behavior of the electron gas in the low-density limit is again simple because here the Coulomb interaction exerts a dominating influence on the electrons. As Wigner[6] first remarked, at sufficiently low densities the electrons may be expected to form a stable lattice in the sea of uniform positive charge. The potential energy keeps the electrons apart, and the kinetic energy for large r_s ($r_s \gg 10$) is insufficent to prevent the electrons becoming localized at fixed sites. The correlation energy may then be expanded as a power series in $(1/r_s)^{\frac{1}{2}}$,

$$E_c=\left(\frac{U}{r_s}+\frac{V}{r_s^{\frac{3}{2}}}+\frac{W}{r_s^2}+\cdots\right)\text{ ry.} \tag{2}$$

The coefficients U and V have been estimated by Wigner.[6]

The region of actual metallic densities ($1.8 \lesssim r_s \lesssim 5.6$) is essentially an intermediate density regime. The kinetic energy and the potential energy play roughly comparable roles in determining the electron behavior. *There exists no simple rigorous series expression for the correlation energy.* In some ways the behavior of the system resembles that of the high-density regime, in some ways that of the low-density regime. A detailed physical discussion of the electron behavior at metallic densities may be found in the work of Bohm and Pines.[7] Pines[8,9] has given a calculation of the correlation energy in this regime, together with calculations of the influence of electron interaction on the various one-electron

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[1] We adopt the notation of reference 7, unless we explicitly indicate otherwise.

[2] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957), hereafter referred to as GB.

[3] K. Sawada, Phys. Rev. **106**, 372 (1957); Sawada, Brueckner, Fukuda, and Brout, Phys. Rev. **108**, 507 (1957), hereafter referred to as SB; R. Brout, Phys. Rev. **108**, 515 (1957).

[4] J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957); Proc. Roy. Soc. (London) **A243**, 336 (1958).

[5] P. Nozières and D. Pines, Phys. Rev. **109**, 1009 (1958).

[6] E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[7] D. Bohm and D. Pines, Phys. Rev. **85**, 332 (1952), hereafter referred to as BP II; D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953), hereafter referred to as BP III. Where no specific reference is required, we refer to the approach developed in these papers, and in reference 8, as the BP approach.

[8] D. Pines, Phys. Rev. **92**, 625 (1953).

[9] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 373, hereafter referred to as SSP.

properties (specific heat, spin susceptibility, transport properties, etc.). The correlation-energy calculation is based on an approximate interpolation between the contribution to the system energy arising from the long wavelength part and that arising from the short wavelength part of the Coulomb interaction, both limits being accurately calculated.

The BP calculation of the correlation energy gives results which are in good agreement with the interpolation formula proposed by Wigner[6,10]:

$$E_c = -0.88/(r_s+7.8) \text{ ry}. \tag{3}$$

Recently Hubbard has proposed a somewhat different interpolation procedure which yields results in close agreement with those of Pines. The results of Pines, Hubbard, or the Wigner interpolation formula, when combined with the calculation of the remaining contributions to the cohesive energy of the alkali metals, are in satisfactory agreement with experiment for these simple metals.[9,11]

In a sense, then, the question of the correlation energy at actual metallic densities might be regarded as satisfactorily solved. However, because the procedures adopted by Pines and Hubbard are interpolation procedures, which do not yield exact results in either the high-density or the low-density regimes, it seems desirable to explore further the relationship between the various approaches. In particular, one would like to answer the following questions:

(1) What is the region of validity of the high-density result of Gell-Mann and Brueckner? Of the low-density result of Wigner?

(2) May one hope to obtain an accurate result for the correlation energy at metallic densities by calculating the next terms in either the high-density or low-density series expressions?

(3) What is the relationship between the interpolation procedures of Pines and Hubbard? How accurate are they for metallic densities?

It is the aim of the present paper to discuss the foregoing questions with a minimum of mathematical detail. We use simple physical arguments to estimate the region of validity of the present calculations of the correlation energy in the high- and low-density limits. We conclude that for $r_s \lesssim 1$, the GB result should be accurate, while for $r_s \gtrsim 20$, the Wigner result should apply. We establish the close relationship of the interpolation procedures of Pines and Hubbard and estimate the accuracy of either method as no worse than 15% for actual metallic densities. We do not give a definitive answer to question (2), but we give plausibility arguments which lead us to conclude that such a systematic extension does not appear profitable.

In Sec. II, we review the different methods for the high-density limit calculation, all of which are based on the random phase approximation (RPA) introduced by Bohm and Pines. We identify the region of electron density for which the breakdown of the RPA may be expected to alter appreciably the calculation of the correlation energy, and discuss the role played by the exchange diagrams which lie outside the RPA. The RPA works best for the contribution to the correlation energy coming from the long-range part of the Coulomb interaction. Therefore, in order to make a quantitative study of the breakdown of the RPA it is necessary to study this long-range part of the correlation energy in some detail. We carry out such an investigation in Sec. IV, and summarize there the detailed results of our studies, which are based on the BP collective description.

We find that the contribution to the correlation energy from a given momentum transfer k of the Coulomb interaction may be expressed as a power series in k in the form obtained by BP. We first calculate the coefficients of the leading terms of this expansion within the RPA. In an appendix we show that, contrary to the recent opinion expressed by Sawada *et al.*, the GB result may likewise be expressed as a power series in k. The resulting expression is identical with that obtained using the BP method. This result establishes the validity of the BP scheme as a method for calculating the individual particle contribution to the correlation energy, and represents an explicit justification of their use of an extended Hamiltonian for this problem. We then proceed to estimate the alteration of this power series expansion arising from the breakdown of the RPA by calculating two leading correction terms which arise outside the RPA. We find these terms are small, so that it is not unlikely that the RPA calculation of the long-range part of the correlation energy is valid even in the region of metallic densities.

In Sec. III we discuss the region of validity of the low-density correlation energy calculation of Wigner. In Sec. V we consider the relationship between the interpolation schemes of Pines and Hubbard, and the accuracy these possess for metallic densities.

We do not here consider the applicability of any of the above approaches to the problem of electron interaction in actual solids. We refer the interested reader to a series of recent papers which deal with the generalization of the BP collective approach to electrons in solids.[12] A similar generalization may be carried out in the high-density regime, as indicated in reference 5.

II. HIGH-DENSITY ELECTRON GAS

The Hamiltonian for the free electron gas may be written as

$$H = \sum_i \frac{p_i^2}{2m} + \sum_k{}' \frac{2\pi e^2}{k^2}(\rho_k{}^*\rho_k - n), \tag{4}$$

where ρ_k is the density fluctuation of momentum k

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[10] E. P. Wigner, Phys. Rev. **46**, 1002 (1934).

[11] H. Brooks, Phys. Rev. **91**, 1027 (1953).

[12] P. Nozières and D. Pines, Phys. Rev. **109**, 741 (1958); **109**, 762 (1958); **109**, 1062 (1958), hereafter referred to as NP I, NP II, NP III.

defined by

$$\rho_k=\int d\mathbf{x}\,\rho(\mathbf{x})e^{-i\mathbf{k}\cdot\mathbf{x}}=\sum_i e^{-i\mathbf{k}\cdot\mathbf{x}_i}. \tag{5}$$

The prime in the summation in (4) indicates that we leave out the Fourier component with momentum zero; this part of the electron interaction is cancelled by the uniform background of positive charge. The prime will be understood in all similar sums over k which follow.

The total system interaction energy in the ground state is defined by

$$E_{\text{int}}(e^2)=\sum_k \frac{2\pi e^2}{k^2}\{\langle\Psi_0^*(e)|\rho_k^*\rho_k|\Psi_0(e)\rangle-n\}, \tag{6}$$

where $\Psi_0(e)$ is the ground-state wave function for the interacting electron system. One may obtain the ground-state energy, E_G, from (6) by regarding the charge as a variable parameter and making use of the relation, valid for any normalized $\Psi_0(e)$,[13]

$$E_G=\tfrac{3}{5}nE_F+\int_0^{(e')^2}\frac{d(e')^2}{(e')^2}E_{\text{int}}[(e')^2], \tag{7}$$

where E_F is the energy of an electron at the top of the Fermi distribution. The correlation energy is then given by

$$E_C=\left(\frac{E_G}{n}-\frac{2.21}{r_s{}^2}+\frac{0.916}{r_s}\right)\text{ry}, \tag{8}$$

provided E_G is expressed in rydbergs. The form of Eqs. (6) and (7) shows that, in principle, one can compute the contribution to the system energy from each interaction momentum, k, separately.

The correlation energy in the high-density limit may now be obtained by a number of different methods. We review these briefly here. The first accurate calculation was that of Gell-Mann and Brueckner (GB)[2] who used a method deriving from an earlier calculation of Macke.[14] From an examination of the perturbation theory expansion they show that the energy may be expanded as a power series of the form (1) in the high-density limit. The basic GB procedure involves the summation, under the integral sign, of the most divergent terms of the perturbation theory expansion of the energy. The summation was carried out with the aid of techniques similar to those used by Feynman in quantum electrodynamics. In lowest order, this procedure is equivalent to making the random phase approximation (RPA) of Bohm and Pines for all interaction momenta. In the RPA the contribution to the system energy from each interaction momentum k depends only on the effect of the kth component of the interaction on $\Psi_0(e)$, and may be computed independently of all the other interaction momenta.

The result obtained by GB, on neglecting contributions to the coefficients, D, E, etc. in (1) which arise within the RPA, is

$$A=0.0622,\quad C=-0.142 \tag{9}$$

for the leading coefficients of the correlation-energy expansion, (1). The result for A is exact. There is a further contribution to C from the exchange part of the second-order interaction energy for electrons of parallel spin

$$E_b{}^{(2)}=+\frac{3}{16\pi^5}\frac{\int d\mathbf{k}\int d\mathbf{p}\int d\mathbf{q}}{k^2(\mathbf{k}+\mathbf{p}+\mathbf{q})^2\mathbf{k}\cdot(\mathbf{p}+\mathbf{q}+\mathbf{k})}\text{ ry}. \tag{10}$$

In (10), all momenta are measured in units of k_0, the wave-vector of an electron at the top of the Fermi distribution. The limits of integration are $p<k_0$, $q<k_0$, and $|\mathbf{p}+\mathbf{k}|>k_0$, $|\mathbf{q}+\mathbf{k}|>k_0$, GB report a numerical integration of $E_b{}^{(2)}$ by the Monte-Carlo technique, which yields the result

$$E_b{}^{(2)}=(0.046\pm0.02)\text{ ry}. \tag{11}$$

Their final result for C is then

$$C=-0.096\text{ ry}. \tag{12}$$

The actual procedure which Gell-Mann and Brueckner followed was somewhat open to question, in that the series which they sum is convergent only for large momentum transfers [actually $(k/k_0)\gtrsim0.814r_s{}^{\frac{1}{2}}$]. They assumed that the result thereby obtained could be analytically continued into the region of low momentum transfer. This procedure is difficult to justify directly. However, Sawada *et al.*[3] (SB) have obtained the result (9) by a different method. They make use of the fact that the RPA, as emphasized by BP, is equivalent to linearizing the equations of motion of the density fluctuations. They then find the normal modes of the electron gas (the q_k of BP II and BP III) and use field-theoretic techniques to calculate the system energy. Their calculation, like that of BP, includes an explicit plasmon contribution to the energy. The SB form of the correlation energy [from which (9) may be calculated] differs from that of GB; the equivalence of the two expressions is established by SB.

Hubbard has developed a method for the electron gas which involves the regrouping of the perturbation series expansion into a summation over certain polarization diagrams. With the aid of a procedure analogous to that used by Dyson for summing the vacuum polarization terms in quantum electrodynamics, Hubbard obtains a set of coupled integral equations from which the energy of the system may be calculated. Hubbard's first approximation, that of keeping only the simplest set of polarization diagrams, is equivalent to making the RPA, and yields the correct high-density result.[5] This same high-density result may also be obtained by a slight modification of the basic BP technique, in which the stopping power is calculated using the minority carrier technique of NP II, and use is made of a simple

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[13] See, for instance, K. Sawada, Phys. Rev. **106**, 372 (1957).

[14] W. Mäcke, Z. Naturforsch. **5a**, 192 (1950).

relationship between the stopping power and the ground-state energy of the system.[5]

A derivation of the high-density result which does not involve the use of field-theoretic techniques may be given along the following lines. We have recently shown (details will be given elsewhere)[15] that the *exact* interaction energy in the ground state is given by

$$E_{\text{int}}=\frac{\hbar}{2\pi}\,\text{Im}\int_0^\infty d\Omega\frac{1}{\epsilon(k,\Omega)},\tag{13}$$

where $\epsilon(k,\Omega)$ is the *exact* dielectric constant at wave-vector k and frequency Ω for the free electron gas. The exact ground-state energy may then be obtained from (7). The correct high-density result for the correlation energy then follows if we substitute for $\epsilon(k,\Omega)$ in (13) its value calculated in the random phase approximation,

$$\epsilon(k,\Omega)=1+\frac{8\pi e^2}{\hbar k^2}\sum_{\substack{p<k_0\\|\mathbf{k}+\mathbf{p}|>k_0}}\left\{\frac{[(\mathbf{k}\cdot\mathbf{p}/m)+(k^2\hbar/m)]}{[(\mathbf{k}\cdot\mathbf{p}/m)+(\hbar k^2/2m)]^2-\Omega^2}+\frac{i\pi}{2}\delta\left[\Omega-\left(\frac{\mathbf{k}\cdot\mathbf{p}}{m}+\frac{\hbar k^2}{2m}\right)\right]\right\}.\tag{14}$$

The use of the RPA in obtaining the dielectric constant is discussed in some detail in NP II, where it is shown that it corresponds to neglecting local field corrections. With the substitution (14), the result (13) is in the form given by Hubbard.

How far may the high-density result (9) and (12) be extrapolated toward the region of actual metallic densities? The validity of the result depends on the applicability of the RPA. Physically, as is discussed in some detail in BP, it is clear that the RPA can succeed only when the wavelengths of interest are long compared to the inter-particle spacing. In the high-density limit, the dominant contributions to the energy come from wave-vectors less than or of the order of magnitude of

$$k_c=(0.814r_s^{\frac{1}{2}})k_0,\tag{15}$$

where k_0 is the wave-vector of an electron at the top of the Fermi distribution. This result follows by inspection of either the expression (14) or the direct perturbation series expansion. It corresponds to the fact that the correlations induced by the Coulomb interaction act over a characteristic screening length, λ_c, here k_c^{-1}. Each electron may thus be regarded as surrounded by a correlation hole, which corresponds to the effective range over which electron interaction takes place, that is, the screening length. The gain in energy from this screening process is the correlation energy. The screening length corresponding to (15) is simply the Fermi-Thomas screening length, a not unsurprising result in view of the fact that we here deal with long wavelengths and high kinetic energies.

The breakdown of the RPA arises from the exchange diagrams in the perturbation series expansion of the system energies. In order for this approximation to be satisfactory, these exchange diagrams should not be important for $k\sim k_c$. Now exchange effects occur only for electrons of parallel spin, over a range λ_{exch}, equal to the diameter of the exchange hole. Practically, λ_{exch} is of the order of the interparticle spacing[16]

$$\lambda_{\text{exch}}\simeq(0.5k_0)^{-1}\sim r_s.\tag{16}$$

In the high-density limit, with the estimates (15) and (16), we find that $(\lambda_{\text{exch}}/\lambda_c)\propto r_s^{\frac{1}{2}}$, so that this limit is characterized by an exchange length which is small compared to the screening length. Physically this result means that the most effective interaction present is that brought about by the Pauli principle between electrons of parallel spin, a result which is equivalent to saying that the exchange energy is large compared to the correlation energy in the high-density limit. It is this smallness of the exchange length which also makes possible the neglect of exchange diagrams, since the dominant contribution to the higher order terms in the perturbation series expansion of the energy come from momentum transfers for which k is small compared to $\lambda_{\text{exch}}^{-1}$.

We are led to the following picture of the high-density correlation energy results. For $r_s\ll 1$, the RPA is certainly valid; the dominant contribution to the correlation energy is the $A\ \ln r_s$ term which is calculated exactly within the RPA. As r_s increases, exchange diagrams become of importance, being certainly important for values of r_s for which there are contributions to the energy from momentum transfers comparable to λ_{exch}. This will be the case for $r_s\lesssim 1$. In this region, however, there is still the possibility of carrying out a tolerably accurate calculation of the correlation energy by including the simplest set of exchange terms, those which arise in second-order perturbation series, and yield the $E_b^{(2)}$ of Eq. (10). These exchange terms act to reduce the random phase value of C to some $\frac{2}{3}$ of its value, and therefore represent a not inappreciable correction to the correlation energy.

As we further increase r_s, the higher order exchange terms become important. One might try to calculate the exact contribution made by processes involving one more exchange, which GB have shown gives rise to the r_s and $r_s\ln r_s$ terms in (1), two more exchange terms, etc. In fact such a procedure appears hopeless for actual metallic densities, for the GB series shows little sign of convergence there. It may easily be seen that for momentum transfers which are large compared to $\lambda_{\text{exch}}^{-1}$, that is $k>0.5k_0$, exchange terms of all orders in a perturbation series expansion will play an important role. Fortunately, in this limit that role tends to be simple: the exchange diagrams roughly cancel one-half the contribution to the energy from the direct diagrams.

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[15] P. Nozières and D. Pines (to be published). Equation (13) has been independently derived by J. Hubbard (private communication).

[16] See F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 241–242.

Hence, in a given order, there remains approximately only half the direct interaction, which corresponds then to an interaction between electrons of antiparallel spin only.

Physically this result is a consequence of the fact that the Pauli principle renders it unlikely that electrons of parallel spin approach closely to one another; therefore they cannot further interact through a short-range interaction which gives rise to high momentum transfers. The electrons of antiparallel spin are under no such inhibition of course, and thus the major influence of the high momentum transfer part of the interaction is on electrons of antiparallel spin. We return to this question in a later section.

III. LOW-DENSITY ELECTRON SOLID

The electron gas in the low-density limit represents an extreme example of the breakdown of the RPA. The electrons will be found in a periodic array in the sea of positive charge. Hence a typical term which in the high-density limit may be assumed small compared to n because of the RPA,

$$\rho_k=\sum_i e^{-i\mathbf{k}\cdot\mathbf{x}_i}, \quad (k\neq 0)$$

will assume the value n whenever $\mathbf{k}$ is equal to the reciprocal lattice vector $\mathbf{K}$. As another indication of the quite different physical behavior in the low-density limit, the series expansion for the correlation energy assumes the form, (2),

$$E_c=\left(\frac{U}{r_s}+\frac{V}{r_s^{\frac{3}{2}}}+\frac{W}{r_s^2}+\cdots\right)\text{ ry}.$$

The first term represents the difference between the potential energy of the electrons on fixed lattice sites and the exchange energy. The second arises from the zero-point oscillations of the electrons about their equilibrium positions. The third comes from higher order terms in the expansion of the electronic vibrations about their equilibrium positions.

The constant U may be calculated by carrying out an Ewald sum for the assumed lattice structure. If one is not concerned with the actual lattice structure, one may calculate U by making the Wigner-Seitz approximation of replacing the actual unit cell by a sphere. A simple electrostatic calculation then yields[9]

$$U=-0.088\text{ ry}. \tag{17}$$

A precise determination of the constant V requires consideration of the spectrum of the oscillations of the electrons, a spectrum which depends upon the particular form of the lattice one assumes.[17] We may, however, place upper and lower bounds on V in the following way. The sum of the squares of the phonon frequencies satisfies the relation[17,18]:

$$\sum_\mu \Omega_k^2(\mu)=\omega_p^2, \tag{18}$$

where ω_p is the plasma frequency,

$$\omega_p=(4\pi ne^2/m)^{\frac{1}{2}}. \tag{19}$$

If one takes an Einstein model for the oscillations, as did Wigner, one finds one longitudinal and two transverse oscillations at $\omega_p/\sqrt{3}$ for each value of k. The constant V would then be 3. The alternative extreme, also consistent with the sum rule (18), would be to assume only longitudinal phonons (plasmons) with a constant frequency ω_p. In the latter case one finds $V=1.73$. We therefore have

$$1.73\text{ ry}\lesssim V\lesssim 3\text{ ry}. \tag{20}$$

The constant W has not yet been evaluated.

For what values of r_s may we expect the energy to be well represented by a power series expansion of the form (2)? As we start from the low-density side, and reduce r_s, we may expect to reach a value of r_s for which the electronic solid will "melt," in that the electrons will no longer be bound in their equilibrium positions. This melting as a result of increasing pressure could take place at absolute zero; it is therefore not clear whether the phase transition would in fact be a sharp one. We may estimate the density at which it occurs in the following way.

In ordinary solids melting may be regarded as arising from the increase with temperature of the vibrational amplitudes of the atoms oscillating about their equilibrium positions. This is the underlying physical basis of the notably successful Lindemann melting-point formula.[19] The Lindemann formula may be interpreted to state that any solid will melt when the mean vibrational amplitude $\langle\delta R^2\rangle_{\text{Av}}^{\frac{1}{2}}$ reaches a certain critical fraction of the interatomic spacing R_0,[20]

$$(\langle\delta R^2\rangle_{\text{Av}}^{\frac{1}{2}}/R_0)=\delta. \tag{21}$$

The constant δ varies somewhat from one solid to another but is of the order of $\frac{1}{4}$ for most simple lattice types. For our electronic solid at $T=0$, $\langle\delta R^2\rangle_{\text{Av}}$ is determined solely by the zero-point vibrations of the electrons. We underestimate their efficacy if we assume only longitudinal phonons at a frequency ω_p. We then have

$$\frac{\langle\delta R^2\rangle_{\text{Av}}^{\frac{1}{2}}}{R_0}=\left(\frac{\hbar}{2m\omega_p}\right)^{\frac{1}{2}}\frac{1}{r_s}=\left(\frac{1}{12r_s}\right)^{\frac{1}{4}},$$

and we expect that below $r_s\sim 20$ the electronic solid will not be stable.

Of course, even after the electronic solid has been transformed to an electronic liquid, there may still be a

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[17] An investigation of the phonon modes for simple lattice structures has been carried out by W. Kohn and T. Kjeldaas (private communication).

[18] D. Pines, lecture notes in Solid State Physics, Princeton University, 1957 (unpublished).

[19] N. F. Mott and H. Jones, *The Theory of Metals and Alloys* (Clarendon Press, Oxford, 1936).

[20] See reference 18 for a further discussion of this interpretation, together with a derivation of (21).

considerable range of r_s for which the expansion (2) is approximately valid for the correlation energy. Some indication that this may be the case may be found in an approximate calculation by one of us,[9] in which the BP approach was applied to the low-density electron gas. In general, however, we tend to believe that the low-density limit is not a particularly illuminating guide to the behavior of electrons at metallic densities.

IV. CONTRIBUTIONS TO THE CORRELATION ENERGY FROM DIFFERENT REGIONS OF MOMENTUM TRANSFER

Thus far we have concentrated on the r_s behavior of the correlation energy in various limiting cases. We have seen on the basis of our qualitative discussion in Sec. II that the concept of the contribution to the correlation energy arising from a given set of momentum transfers is particularly useful in assessing the accuracy of a given method for computing the correlation energy. We now study this aspect of the problem in some detail. As we have remarked, it is in principle possible to evaluate separately the contribution, $E_c(k)$, to the correlation energy from each interaction momentum k of the Coulomb interaction energy. We shall find it convenient to express our results in terms of the long-range correlation energy

$$E_c^{\mathrm{lr}}(\beta)=\textstyle\sum_{k<\beta k_0}E(k), \tag{22a}$$

and the short-range correlation energy

$$E_c^{\mathrm{sr}}(\beta)=\textstyle\sum_{k>\beta k_0}E(k). \tag{22b}$$

We begin our study with a consideration of the long-range correlation energy. Since the RPA breaks down as one goes to larger values of k, it should be possible to study the onset of the breakdown by considering the way in which exchange diagrams affect the long-range correlation energy. Within the RPA, as one of us has shown,[9] the long-range correlation energy may be expressed as a simple series expansion in β. The following terms were explicitly calculated:

$$E_c^{\mathrm{lr}}(\beta)=a\frac{\beta^2}{r_s}+c\frac{\beta^3}{r_s^{\frac{3}{2}}}+d\frac{\beta^4}{r_s^2}+d'\frac{\beta^4}{r_s}+e\frac{\beta^5}{r_s^{\frac{5}{2}}}+f'\frac{\beta^6}{r_s^2}+g'\frac{\beta^7}{r_s^{\frac{5}{2}}}\ \mathrm{ry}. \tag{23}$$

The effective limiting value of β is proportional to $r_s^{\frac{1}{2}}$, so that the unprimed terms contribute to the constant C in the GB expansion, (1), while the primed terms contribute to E. In going beyond the RPA we shall consider two of the lowest order (in β) contributions of the exchange diagrams: the alteration of d' and a new term

$$e'\beta^5/r_s^{\frac{3}{2}} \tag{24}$$

so introduced into $E_c^{\mathrm{lr}}(\beta)$. A comparison of d and d', e and e', then enables us to estimate the values of r_s for which $E_c^{\mathrm{lr}}(\beta)$ may be reliably calculated within the RPA.

We shall make use of the collective description of Bohm and Pines, which is well-suited to the present investigation. Bohm and Pines did not work directly with the Hamiltonian, (4). Instead they developed a method designed to take advantage of the fact that at long wavelengths the electron interactions give rise to organized oscillations of the electron system as a whole, the plasma oscillations. The plasmons (the quantized modes of plasma oscillation) are the dominant low momentum elementary excitations of the electron gas; they possess a minimum frequency which is the classical frequency of plasma oscillation, ω_p. BP describe the plasmons explicitly in terms of a suitable set of field coordinates. This is done by introducing a Hamiltonian which is equivalent to (4) and which corresponds to a collection of plasmons of wave-vector less than some βk_0 interacting with the electron system. In this Hamiltonian the density fluctuations with $k<\beta k_0$ no longer appear; their effect resides entirely in the plasmon coordinates. The contribution to the system energy coming from the plasmons and their interaction with the electrons is then evaluated within certain well-defined approximations described below.

The equivalent Hamiltonian is given by

$$H=\sum_i\frac{p_i^2}{2m}+\sum_{k<\beta k_0}\left\{\frac{\pi_k^*\pi_k+\omega_p^2Q_k^*Q_k}{2}-\frac{2\pi ne^2}{k^2}\right\}+H_{\mathrm{int}}+U+H_{\mathrm{sr}}, \tag{25}$$

where π_k and Q_k are the momentum and coordinate of a plasmon of wave-vector $\mathbf{k}$.[21] In (25)

$$H_{\mathrm{int}}=-i\sum_{i,\,k<\beta k_0}\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}}\left(\frac{\mathbf{k}\cdot\mathbf{p}_i}{m}+\frac{\hbar k^2}{2m}\right)Q_ke^{-i\mathbf{k}\cdot\mathbf{x}_i}, \tag{26a}$$

and describes a linear coupling between the plasmons and the electrons;

$$U=\sum_{\substack{i,\,k<\beta k_0\\ l<\beta k_0\\ k\neq l}}\frac{2\pi e^2(\mathbf{k}\cdot\mathbf{l})^2}{k^2l^2m}Q_kQ_l\exp[i(\mathbf{k}-\mathbf{l})\cdot\mathbf{x}_i], \tag{26b}$$

and describes a nonlinear coupling between plasmons and electrons;

$$H_{\mathrm{sr}}=\sum_{\substack{k>\beta k_0\\ i\neq j}}\frac{2\pi e^2}{k^2}\exp[i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)], \tag{26c}$$

and describes the short-range part of the Coulomb interaction.

Within the RPA, the long-range correlation energy is obtained by solving the reduced Hamiltonian given by the first three terms of (25). The effect of U and H_{sr} on the low momentum transfer part of the Hamiltonian

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[21] For a detailed discussion of this equivalence, and of the role played by the BP subsidiary conditions (which we here omit) we refer the interested reader to Bohm, Huang, and Pines, Phys. Rev. **107**, 71 (1957).

gives rise to corrections to the RPA. There exists a simple series expansion (23) for $E_c^{\mathrm{lr}}(\beta)$ because the reduced Hamiltonian has a simple structure for long wavelengths. The coupling between free electrons and free plasmons induced by H_{int} is weak, and may be treated by means of a systematic perturbation series expansion. The coupling constant which measures the strength of the interaction between a plasmon of momentum $\hbar\mathbf{k}$ and an electron of momentum $\mathbf{p}$ is[22]

$$g_k^2(p)=\frac{(\mathbf{k}\cdot\mathbf{p}+\frac{1}{2}k^2\hbar)^2}{m^2\omega_p^2}=\frac{3\pi}{4\alpha r_s k_0^4}[(\mathbf{k}\cdot\mathbf{p})^2+\tfrac{1}{4}\hbar k^4],\quad (27)$$

where

$$\alpha=(4/9\pi)^{\frac{1}{3}}.$$

The expansion (23) is a simple expansion in powers of $g_k^2(p)$, suitably averaged over electron momentum $\mathbf{p}$.

The leading terms, which are of zeroth order in g_k^2, are obtained by neglecting H_{int} entirely. The ground-state energy is then given by the difference between the zero-point vibrational energy of the plasmons and the self-energy of the charge distribution they have replaced,

$$\sum_{k<\beta k_0}\left(\frac{\hbar\omega_p}{2}-\frac{2\pi Ne^2}{k^2}\right).\quad (28)$$

To get the correlation energy, subtract from (28) the exchange energy associated with the interaction momenta $k<\beta k_0$; (28) then becomes

$$\sum_{k<k_c}\left(\frac{\hbar\omega_p}{2}-\frac{2\pi e^2}{k^2}\langle\rho_k{}^*\rho_k\rangle_{\mathrm{Av}}\right),\quad (29)$$

where the second term is now the sum of the exchange and self-energies of the charge distribution which has been described by the plasmons. From (29), we find

$$E_c^{\mathrm{lr}}=\left[-\frac{3\beta^2}{2\pi\alpha r_s}+\frac{\sqrt{3}}{2}\frac{\beta^3}{r_s^{\frac{3}{2}}}+\left(\frac{3}{96\pi\alpha}\right)\frac{\beta^4}{r_s^2}\right]\mathrm{ry},$$

or

$$E_c^{\mathrm{lr}}\cong\left(-0.458\frac{\beta^2}{r_s}+0.866\frac{\beta^3}{r_s^{\frac{3}{2}}}+0.019\frac{\beta^4}{r_s}\right)\mathrm{ry}.\quad (30)$$

The next terms in (23) are of order g_k^2. They may be obtained directly by transforming from (25) to a Hamiltonian in which there is no longer any coupling between the electrons and the plasmons to this order. The canonical transformation required is given in BP III; the new Hamiltonian is

$$H=\sum_i\frac{p_i^2}{2m}+\sum_{k<\beta k_0}\left\{\frac{P_k{}^*P_k+\omega^2Q_k{}^*Q_k}{2}-\frac{2\pi ne^2}{k^2}\right\}+H_{\mathrm{rp}}+H_{\mathrm{sr}}.\quad (31)$$

The plasmon frequency has been modified to ω, and is defined through the dispersion relation

$$1=\frac{4\pi e^2}{m}\sum_{p<k_0}\left\{\frac{1}{\left[\left(\omega-\frac{\mathbf{k}\cdot\mathbf{p}}{m}\right)^2-\frac{\hbar^2k^4}{4m^2}\right]}\right\},\quad (32)$$

which reads, to order g_k^2,

$$\omega^2=\omega_p^2+\sum_{p<k_0}\left[3\left(\frac{\mathbf{k}\cdot\mathbf{p}}{m\omega_p}\right)^2+\frac{\hbar^2k^4}{4m^2\omega_p^2}\right].\quad (33)$$

The electrons interact through a weak long-range interaction

$$H_{\mathrm{rp}}=\sum_{\substack{ij\\k<\beta k_0}}\frac{\mathbf{k}\cdot(\mathbf{p}_i-\frac{1}{2}\hbar\mathbf{k})\mathbf{k}\cdot(\mathbf{p}_j+\frac{1}{2}\hbar\mathbf{k})}{2k^2mn}\times\exp[i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)].\quad (34)$$

The results (33) and (34) confirm the identification of g_k^2 as the coupling constant. The relative shift in plasmon frequency is of order g_k^2; H_{rp} represents an interaction between electrons which is reduced in effectiveness by one order of g_k^2 from the original Coulomb interaction.

The terms d, e', f', and g' in the series expansion (23) arise from the interaction H_{rp} and from the correction to the plasmon zero-point energy, $\hbar(\omega-\omega_p)/2$. The latter yields

$$e=0.70\ \mathrm{ry};\quad g'=0.21\ \mathrm{ry}.\quad (35)$$

The contribution made by H_{rp} to the correlation energy was estimated in SSP by calculating the expectation value, $\langle H_{\mathrm{rp}}\rangle_{\mathrm{Av}}$, that is, the exchange energy associated with H_{rp}. One finds then

$$d=\frac{9}{64\alpha^2}\approx0.517\ \mathrm{ry};\quad f'=0.058\ \mathrm{ry}.\quad (36)$$

There are, however, contributions of order β^4/r_s^2 and β^6/r_s^2 arising from all higher-order terms in a perturbation series expansion of the energy associated with H_{rp}. The contribution these make to d is simply calculable by means of the GB summation technique. We consider only the correction to d; the calculation is given in Appendix I. The result, combined with (36), yields for d the value

$$d=0.98\ \mathrm{ry}.\quad (37)$$

We see that the series expansion (23) contains two kinds of terms. The first, corresponding to odd powers of β, and involving inverse powers of $r_s^{\frac{1}{2}}$, arise from the zero-point energy of the plasmons. The plasmon frequency ω may in general be expanded as

$$\omega=\omega_p+\frac{k^2}{m}E_1+k^4\left(\frac{E_2}{m}\right)^2+\cdots.\quad (38)$$

The β^3 term arises from ω_p; the β^5, β^7, etc. terms arise

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[22] The coupling constant introduced in BP III and SSP is simply the average of g_k^2 over plasmon and electron momenta, $g^2\cong\beta^2/2r_s$.

from the k dependence of ω. The second class of terms, those even in β and involving inverse powers of r_s, arise from the interaction between the individual particles. The β^2 term comes from the long-range part of the exchange energy, as does part of the β^4/r_s term; there are contributions of order $\beta^4/r_s^2+\beta^6/r_s^2$ from H_{rp}; there will be a β^6/r_s^3 term when one considers the screened particle interaction to one higher order in g_k^2, etc.

The power series expansion, (23), may also be obtained from the GB and Hubbard expressions for the correlation energy. The derivation of the coefficients through β^5 within the RPA (and of the β^6/r_s^3 term) using the GB method may be found in Appendix I, where the odd and even terms in β are also seen to possess a different origin. The coefficient d obtained by the GB method is shown there to be identical with that calculated using the BP collective description. There has been little doubt as to the validity of the BP approach for plasmons; this identity verifies the validity of that approach for the interaction between individual particles, and the contribution arising thereby to the correlation energy: we thus obtain an explicit justification within the RPA of the BP neglect of subsidiary conditions in the calculation of the ground-state energy.

What is the radius of convergence of the series expansion (23)? An upper limit may be obtained by setting the coupling constant for the most strongly coupled plasmon equal to unity. If we neglect the k^4 term in (27), a proper procedure at both high and metallic densities, we then find

$$\frac{3\pi}{4\alpha r_s}\beta_{\max}{}^2=1;\quad \beta_{\max}=0.47r_s^{\frac{1}{2}}. \tag{39}$$

The choice (39) represents the wave-vector beyond which it is certainly not proper to regard the plasmon as an elementary excitation of the system. It likewise indicates the maximum wave-vector for which it is useful to use the BP approach, since the latter has as its basis the simplicity introduced in the problem by working explicitly with the plasmons in the region of wavelengths for which they are a well-defined elementary excitation. This cutoff for the plasmons essentially agrees with that proposed by SB and by Ferrell,[23] that the cutoff occurs for that value of k for which the plasmon spectrum merges with the individual electron continuum.[24] If one seeks to represent the long-range correlation energy accurately by the first few terms of the series (23), it may well be advisable to choose a somewhat smaller value of β. In any event, it is clear from these considerations that at high densities the long-range part of the correlation energy will not approximate the total correlation energy well, since the latter contains important contributions arising from momentum transfers of the order of the Fermi-Thomas wave-vector, $0.814r_s^{\frac{1}{2}}$.

We now consider the corrections to (23) arising from exchange diagrams. In the collective approach these arise from two kinds of terms; those involving U, which correspond to the coupling between different long-wavelength density fluctuations, and those involving the coupling between H_{int} and H_{sr} which is a coupling between the low and high momentum transfer part of the Coulomb interaction. The latter appear at a lower order in β, and we calculate them first.

The lowest order in β influence of exchange diagrams on the individual particle contribution to the correlation energy is of order β^4/r_s. We may estimate this term by using the Hamiltonian (31); there will be a contribution arising from the second-order exchange diagram, involving H_{rp} once and H_{sr} once. This is

$$\frac{9}{64\pi^4}\frac{1}{\alpha r_s}\frac{\int d^3k\int d^3p\int d^3q(\mathbf{k}\cdot\mathbf{p})(\mathbf{k}\cdot\mathbf{q})}{[\mathbf{k}\cdot(\mathbf{k}+\mathbf{p}+\mathbf{q})](\mathbf{k}+\mathbf{p}+\mathbf{q})^2k^2}\ \mathrm{ry}, \tag{40}$$

where the regions of integration for $\mathbf{p}$ and $\mathbf{q}$ are subject to the usual limits imposed by the Pauli principle, as for Eq. (10), and that for $\mathbf{k}$ is given by $k<\beta$.[25] On dropping terms which contribute to higher order than β^4, we have

$$\Delta d'=\frac{9}{64\pi^2}\frac{1}{\alpha r_s}\frac{\int d^3k\int d^3p\int d^3q(\mathbf{k}\cdot\mathbf{p})(\mathbf{k}\cdot\mathbf{q})}{k^2\mathbf{k}\cdot(\mathbf{p}+\mathbf{q})(\mathbf{p}+\mathbf{q})^2}\ \mathrm{ry}, \tag{41}$$

which may be estimated rather well by[26]

$$\approx\frac{9}{64\pi^2}\frac{1}{\alpha r_s}\frac{\int d^3k\int d^3p\int d^3q(\mathbf{k}\cdot\mathbf{p})(\mathbf{k}\cdot\mathbf{q})}{2k^2\mathbf{k}\cdot(\mathbf{p}+\mathbf{q})}\ \mathrm{ry}.$$

We thus find

$$\Delta d'=\frac{9}{160\pi}\frac{\beta^4}{\alpha r_s}\{2\ln 2-1\}\approx 0.0136\frac{\beta^4}{r_s}\ \mathrm{ry}. \tag{42}$$

The exchange terms (40) and (42) represent a "screened" version of the long-range part of $E_b^{(2)}$. The latter is given by

$$E_b^{(2)}=\frac{3}{16\pi^5}\frac{\int d^3k\int d^3p\int d^3q}{k^2(\mathbf{k}+\mathbf{p}+\mathbf{q})^2\mathbf{k}\cdot(\mathbf{k}+\mathbf{p}+\mathbf{q})}\cong 0.015\beta^2\ \mathrm{ry}, \tag{43}$$

where the limits are the same as in (40) and the nu-

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[23] R. Ferrell, Phys. Rev. **107**, 450 (1957).

[24] In fact, we would get just their criterion if we had defined $g_k^2=\omega_{n0}^2(kp)/\omega^2$, $\omega_{n0}(kp)$ being the free-electron excitation frequency, instead of our choice, $g_k^2=\omega_{n0}^2(p,k)/\omega_p^2$. We believe the latter choice is better suited to the determination of the radius of convergence of the power series expansion of $E_c^{\mathrm{lr}}(\beta)$, and also represents a realistic choice for the maximum plasmon wave-vector.

[25] In the remainder of this section we measure momenta in units of k_0.

[26] A similar estimate for the low momentum part of $E_b^{(2)}$ may be shown to be accurate to $\sim 5\%$.

merical result has been obtained from the Monte-Carlo calculations carried out for Gell-Mann and Brueckner.[27] In (40) we have taken into account the screening of the long-range interactions between the electrons, which reduces the exchange contribution (43) by a factor of order g_k^2.

The lowest order exchange correction to the plasmon frequency is of order k^2, and hence contributes to the β^5 coefficient in the long-range correlation energy. It appears when we take into account the cross-terms between H_{int} and H_{sr} which arise, for instance, when we decouple the electrons from the plasmons to order g_k^2 by means of a canonical transformation. We estimate one such term, which involves only one power of H_{sr}, in Appendix II. We find that the e' of Eq. (24) is given approximately by

$$e'=0.039\ \mathrm{ry}. \tag{44}$$

The contribution to the correlation energy from U is simply estimated using second-order perturbation theory, and is approximately[28]

$$g''\frac{\beta^7}{r_s^{\frac{3}{2}}}=-\frac{\sqrt{3}}{96}\frac{\beta^7}{r_s^{\frac{3}{2}}}\sim-0.018\frac{\beta^7}{r_s^{\frac{3}{2}}}\ \mathrm{ry}. \tag{45}$$

U thus first gives rise to a correction to the plasmon frequency of order k^4; its importance may be assessed by comparing (39) with the contribution from the two k^4 terms which arise within the random phase approximation[23]

$$g\frac{\beta^7}{r_s^{7/2}}+g'\frac{\beta^7}{r_s^{\frac{5}{2}}}=\left(0.21\frac{\beta^7}{r_s^{\frac{5}{2}}}-0.084\frac{\beta^7}{r_s^{7/2}}\right)\ \mathrm{ry}. \tag{46}$$

We may make the following remarks on the basis of our investigation of the role of the exchange diagrams:

(1) There are no corrections to the β^2 and β^3 terms of the series expansion (23). Hence for sufficiently long wavelengths, the RPA is valid *for any density* in the calculation of the long-range correlation energy.

(2) The β^4 and β^5 terms in the expansion of the long-range correlation energy may be written, approximately, as

$$-\beta^4\left(+\frac{0.98}{r_s^2}-\frac{0.033}{r_s}+\cdots\right)\ \mathrm{ry}, \tag{47a}$$

$$\frac{\beta^5}{r_s^{\frac{1}{2}}}\left(\frac{0.70}{r_s^2}-\frac{0.039}{r_s}+\cdots\right)\ \mathrm{ry}. \tag{47b}$$

The terms in parentheses of order $1/r_s$ represent the contribution from exchange diagrams involving H_{sr} once as well as the β^4/r_s term from (30). They are negligible in the high-density limit, as they should be. The corrections are numerically small for actual metallic densities. We do not at present know whether the higher order terms in the series (in β) display a similar behavior.

It is clear that where E_{lr}^c is accurately calculated by keeping terms only through β^4 or β^5, say, the use of the RPA result for these terms should provide a quite adequate approximation.

(3) On the basis of the structure of the exchange terms involving one power of H_{sr} in (47), it is tempting to conjecture that the result of taking into account all RPA corrections would be to yield an expression β^4 which is

$$\beta^4\left(\frac{s}{r_s^2}+\frac{t}{r_s}+u\ln r_s+v+wr_s\ln r_s+\cdots\right).$$

Thus the coefficients of β^4, $\beta^5/r_s^{\frac{1}{2}}$, etc., themselves may possess a power series expansion in r_s analogous to that for the electron energy in the high-density limit. We have not verified this conjecture in detail. If it is true, it is clear already in (47) that the coefficients of that expansion will not be the same as in the system energy; hence it might be possible to use the β^4, β^5, etc., contributions to the correlation energy with some confidence, even though the series expansion (2) does not apply. However, the question is by no means settled, and merely points up the difficulty of drawing definitive conclusions from our calculation of the first set of exchange corrections.

We conclude this section by considering $E^{\mathrm{sr}}(\beta)$ briefly. We have given physical arguments in Sec. II that for a sufficiently large β this part of the correlation energy arises almost entirely from the interaction between electrons of antiparallel spin. We may obtain an idea of how well this hypothesis is born out by studying the contribution to $E_c^{\mathrm{sr}}(\beta)$ arising from electrons of parallel spin, as calculated in second-order perturbation theory. This is

$$E_{11}^{(2)}=-\frac{3}{16\pi^5}\frac{\int d\mathbf{k}\int d\mathbf{p}\int d\mathbf{q}}{\mathbf{k}\cdot(\mathbf{k}+\mathbf{p}+\mathbf{q})}\times\left\{\frac{1}{k^4}-\frac{1}{k^2(\mathbf{k}+\mathbf{p}+\mathbf{q})^2}\right\}\ \mathrm{ry}. \tag{48}$$

The momenta here are measured in units of k_0 and the limits of integration are as in (10); the first term in the parenthesis is the direct contribution, the second is the exchange contribution. For large momentum transfers, ($k>1$), the regions of $\mathbf{p}$ and $\mathbf{q}$ which contribute to $E_{11}^{(2)}$ become small compared to $\mathbf{k}$, and the exchange contribution tends to cancel the direct term. The integration (48) may be carried out explicitly for $k>\beta$; one finds, with the aid of (43) and Eq. (6.22) of SSP,

$$E_{11}^{(2)}\approx(+0.021+0.062\ln\beta-0.021\beta^2)\ \mathrm{ry}. \tag{49}$$

The result (49) is valid for $\beta\lesssim\frac{3}{4}$, the limitation being imposed by the accuracy of (43); for larger values of β

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[27] We should like to thank Professor M. Gell-Mann for making this result available to us.

[28] We have corrected the value given in BP III by a factor of 2, and estimated the reduction in the sum over states due to the Pauli principle by the approximate value β.

it is an underestimate. The values of $E_{11}^{(2)}(\beta)$ calculated from (49) tend to support our physical argument concerning the short-range correlation energy associated with electrons of parallel spin.

We have been discussing the breakdown of the RPA for $E_c^{\mathrm{sr}}(\beta)$ due to the coupling between different short wavelength momentum transfers. We have also considered the breakdown of the RPA for $E_c^{\mathrm{lr}}(\beta)$ due to the contributions arising from H_{sr}. We may mention that there will also be contributions to $E_c^{\mathrm{sr}}(\beta)$ arising from the long-wavelength momentum transfers. We do not consider these corrections here because $E_c^{\mathrm{sr}}(\beta)$ is itself so imperfectly known once one leaves the high-density limit.

V. INTERPOLATION PROCEDURES FOR ACTUAL METALLIC DENSITIES

On the basis of our qualitative and quantitative discussion of the preceding section we have reached the following conclusions.

(1) It does not appear feasible to extend systematically the GB scheme into the region of actual metallic densities. Therefore it is necessary to consider the possibility of developing suitable interpolation procedures to calculate the correlation energy at metallic densities.

(2) The behavior of the correlation energy at a given r_s as a function of interaction momentum, $E_c(k)$, provides a natural basis for the development of interpolation procedures. In the low momentum region, the RPA calculation of $E_c(k)$ is rigorous for the k and k^2 terms, and provides quite a good approximation for the k^3 and k^4 terms throughout the region of actual metallic densities. The maximum value of β for which $E_c(k)$ may be reliably calculated in the RPA is $\beta=0.47r_s^{\frac{1}{2}}$, for which $g_k^2\cong1$. For sufficiently large k, the exchange diagrams cancel one-half the direct diagrams, so that one need consider only interactions between electrons of antiparallel spin. This region begins at approximately $\beta=1$.

One possible interpolation scheme would involve plotting $E_c(k)$ for all k according to the following prescription: (1) for $k<\beta_1$, take the value given by the RPA; β_1 should then be $\lesssim0.47r_s^{\frac{1}{2}}$; (2) for $k>\beta_2$, take the value given by second-order perturbation theory, in which only interactions between electrons of antiparallel spin are considered; β_2 should be $\gtrsim1.5$; and (3) for $\beta_1\lesssim k\lesssim\beta_2$, draw a smooth curve between the portions defined by (1) and (2). To get the correlation energy for a given value of r_s, one would then carry out a numerical integration of $E_c(k)$ over all interaction momenta k.

A somewhat simpler scheme, which yields an explicit formula for the correlation energy as a function of r_s, and very nearly the same numerical values as the above procedure, is based on the following expressions for the long-range and short-range parts of the correlation energy:

$$E_c^{\mathrm{lr}}(\beta_1)\cong\left(-0.458\frac{\beta_1^2}{r_s}+0.866\frac{\beta_1^3}{r_s^{\frac{3}{2}}}-0.98\frac{\beta_1^4}{r_s^2}+0.706\frac{\beta_1^5}{r_s^{\frac{5}{2}}}\right)\text{ ry},\tag{50}$$

$$E_c^{\mathrm{sr}}(\beta_2)\cong(-0.025+0.062\ln\beta_2-0.006\beta_2^2)\text{ ry}.\tag{51}$$

The long-range part of the correlation energy, $E_c^{\mathrm{lr}}(\beta_1)$, is calculated in the RPA. Only terms through β_1^5 are kept, because for actual metallic densities the β_1^6 terms are comparable with the exchange corrections to the β_1^4 term, and (50) may be regarded as accurate only as long as both such terms are small. The short-range part of the correlation energy, $E_c^{\mathrm{sr}}(\beta_2)$, is calculated in second-order perturbation theory, and only interactions between electrons of antiparallel spin are kept. If we now choose $\beta_1=\beta_2=\beta$, it is clear that there will be a discontinuity in $E_c(k)$ at $k=\beta$, because both expressions (50) and (51) are approximations; however for a suitable choice of β this will not introduce any appreciable error. It is desirable to choose β as large as possible, in order that (51) represent a tolerably accurate approximation; on the other hand, if β is taken as too large, the long-range correlation energy will no longer be well represented by (50). We accordingly take for β that maximum value for which (50) is still a rapidly converging series,

$$\beta=0.47r_s^{\frac{1}{2}}.\tag{52}$$

With this choice, we find

$$E_c^{\mathrm{lr}}(\beta)\cong-0.043\text{ ry},\tag{53}$$

$$E_c^{\mathrm{sr}}(\beta)\cong(-0.072+0.031\ln r_s)\text{ ry}.\tag{54}$$

We have dropped the β^2 term in $E_c^{\mathrm{sr}}(\beta)$ since it is of the same order as the β^4/r_s exchange term. The total correlation energy is given by the sum of (53) and (54),

$$E_c\cong(-0.115+0.031\ln r_s)\text{ ry}.\tag{55}$$

The foregoing interpolation scheme is very nearly the same as that proposed earlier by one of us in SSP. The present proposal differs in that we have used the correct RPA coefficient of the β^4 term in $E_c^{\mathrm{lr}}(\beta)$, instead of the lowest order approximation to it utilized in SSP. This has enabled us to go to a larger value of β.

Hubbard has proposed an alternative interpolation procedure, which is equivalent to multiplying the RPA value of $E_c(k)$ by a phenomenological correction factor, which is 1 for small k and $\frac{1}{2}$ for large k. This procedure is obviously satisfactory for large k. Detailed investigation shows that his procedure does not yield the β^4/r_s exchange correction, so that for small k Hubbard's result cannot be regarded as any more accurate than the RPA result.

In Table I we compare our numerical results for the correlation energy with those obtained by Hubbard. In Fig. 1 we plot $E_c(k)$ for $r_s=4$ as calculated by us and by

TABLE I. A comparison between the revised BP calculation of the correlation energy and that of Hubbard; the energies are given in ry.

r_s	2	3	4	5
E_{BP}	−0.094	−0.081	−0.072	−0.065
E_{Hubbard}	−0.099	−0.086	−0.074	−0.067

Hubbard. The close agreement of the two interpolation procedures is not surprising, since they agree in both the high and low momentum limits.

It is difficult to set any exact limit on the accuracy of either interpolation procedure. We can estimate rather well the accuracy of $E_c^{\mathrm{lr}}(\beta)$ in our scheme, but we do not know the accuracy of our perturbation theory expression for $E_c^{\mathrm{sr}}(\beta)$. Hubbard's interpolation procedure is sufficiently close to ours that it suffers from the same defect, an inadequate knowledge of the behavior of $E_c(k)$ in the region between $\beta=0.47r_s^{\frac{1}{2}}$ and that value of β for which the perturbation theory calculation of $E_c^{\mathrm{sr}}(\beta)$ becomes accurate. It is perhaps encouraging that there is such good agreement between Hubbard's estimate of $E_c(k)$ and the perturbation theory calculation for $\beta\gtrsim 1$; however both could be somewhat inaccurate in the region of $\beta\cong 1$. If one is content with 15% accuracy in the correlation energy, it is quite likely that both schemes may be regarded as satisfactory. On the other hand, if one demands a value of the correlation energy which is accurate to within 5%, it is doubtful that either scheme is that accurate except, perhaps, through a fortunate cancellation of rather larger errors.

We conclude that the Hubbard scheme is mathematically more satisfying, since it yields a smooth curve for $E_c(k)$. On the other hand, our modified SSP interpolation procedure is simpler, and rather closely tied to the physical behavior of the electron gas. It may also be more flexible, in that it permits straightforward calculation of other metallic properties, such as the one-electron energies, specific heats, etc.[29]

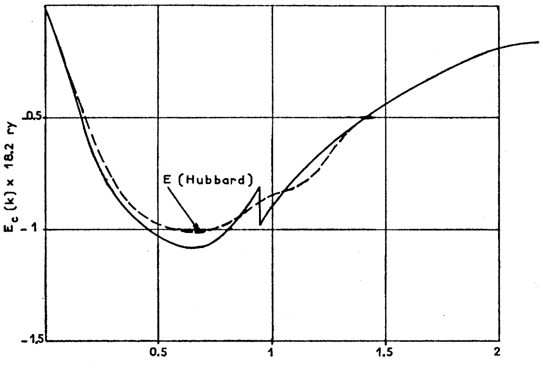

FIG. 1. $E_c(k)$ in the present calculation and according to Hubbard for $r_s=4$.

APPENDIX I

The GB result for the correlation energy may be written as

$$E_{\mathrm{corr}}=-\frac{3}{4\pi\alpha^2r_s^2}\int k^3dk \times\int_{-\infty}^{+\infty}du\sum_{n=}^{n=\infty}\left\{\frac{(-1)^n}{n}[Q_k(u)]^n\right\}, \quad \text{(A1)}$$

where the function $Q_k(u)$ is given by

$$Q_k(u)=\frac{\alpha r_s}{\pi^2k^2}\int_{\substack{|p|<1\\ |\mathbf{p}+\mathbf{k}|>1}} d^3p \times\int_{-\infty}^{+\infty}\exp\{ituk-|t|(\tfrac{1}{2}k^2+\mathbf{k}\cdot\mathbf{p})\}dt. \quad \text{(A2)}$$

The total change in energy due to the Coulomb interaction, $E_{\mathrm{tot}}=E_{\mathrm{corr}}+E_{\mathrm{exch}}$, is given by

$$E_{\mathrm{tot}}=-\frac{3}{4\pi\alpha^2r_s^2}\int_0^{\infty}dk\,k^3\int_{-\infty}^{+\infty}du \times\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[Q_k(u)]^n-\sum_k\left(\frac{2\pi e^2}{k^2}\right). \quad \text{(A3)}$$

The first term on the right-hand side of (A3) may therefore be viewed as the energy change brought about by a perturbation

$$\sum_k\left(\frac{2\pi e^2}{k^2}\rho_k\rho_{-k}\right). \quad \text{(A4)}$$

The GB result is now in a form well suited for its application to the calculation of the long-range correlation energy arising from H_{rp}, E_{rp}. To lowest order in k^2, we may write

$$H_{\mathrm{rp}}=\sum_k\frac{2\pi e^2}{k^2}\rho_k{}^s\rho_{-k}{}^s, \quad \text{(A5)}$$

where $\rho_k{}^s$ is a screened density fluctuation defined by

$$\rho_k{}^s=\sum_i\left(\frac{-\mathbf{k}\cdot\mathbf{p}_i}{m\omega_p}\exp(-i\mathbf{k}\cdot\mathbf{x}_i)\right).$$

Thus (A5) and (A4) differ only in the replacement of ρ_k by $\rho_k{}^s$. E_{rp} is therefore given by

$$E_{\mathrm{rp}}=-\frac{3}{4\pi\alpha^2r_s^2}\int_0^{\beta}dk\,k^3 \times\int_{-\infty}^{+\infty}du\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[Q_k{}^s(u)]^n, \quad \text{(A6)}$$

where $Q_k{}^s(u)$ is the screened version of $Q_k(u)$ arising

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[29] An investigation of the way in which one-electron properties are influenced by H_{sr} has recently been carried out by J. Fletcher and D. C. Larson, following paper [Phys. Rev. **110**, 455 (1958)]. They have considered only the second-order interaction between electrons of antiparallel spin, and obtain thereby not unreasonable values for the specific heat, etc.

from the replacement of ρ_k in (A4) by $\rho_k{}^s$ in (A5). Inspection of the matrix elements arising from (A4) and (A5) shows that the change from ρ_k to $\rho_k{}^s$ introduces a multiplicative factor in the integration over p in (A2) which is simply

$$-(3\pi/4\alpha r_s)(\mathbf{k}\cdot\mathbf{p})^2,$$

that is, $-g_k{}^2(p)$ (to lowest order in k^2). The minus sign corresponds to the fact that H_{rp} induces attractive electron correlations.

We have therefore

$$Q_k{}^s(u)=-\frac{3}{4\pi}\int_{\substack{p<1\\|\mathbf{p}+\mathbf{k}|>1}} d^3p\,\frac{(\mathbf{k}\cdot\mathbf{p})^2}{k^2}\times\int_{-\infty}^{+\infty}dt\,\exp\left\{ituk-|t|\left(\frac{k^2}{2}+\mathbf{k}\cdot\mathbf{p}\right)\right\}$$
$$=3u^2R(u)-1, \tag{A7}$$

where

$$R(u)=1-u\arctan(1/u),$$

and we have carried out the integration in the first of Eqs. (A7) to lowest order in k. On substituting (A7) into (A6) and summing the series there, we find

$$E_{\mathrm{rp}}=\frac{3}{4\pi\alpha^2 r_s{}^2}\int_0^\beta dk\,k^3\int_{-\infty}^{\infty}du\,\ln[3u^2R(u)]. \tag{A8}$$

The latter integral may be computed numerically, and yields the result

$$E_{\mathrm{rp}}=-0.98(\beta^4/r_s{}^2)\text{ ry}. \tag{A9}$$

We now show that the GB result, (A1), when restricted to sufficiently long wavelength momentum transfers β, may be expanded as a power series in β. Let us return to the expression (A2) for $Q_k(u)$. A careful examination of (A2) shows that $Q_k(u)$ may be expanded in powers of k, and contains only even powers of k. The leading contribution is

$$Q_k(u)=(4\alpha r_s/\pi k^2)R(u).$$

On substituting this value in (A1) and carrying out the sum there, we get

$$E_c{}^{\mathrm{lr}}(\beta)=-\frac{3}{4\pi\alpha^2 r_s{}^2}\int_0^\beta dk\,k^3\int_{-\infty}^{\infty}du\left\{\left[\frac{4\alpha r_s}{\pi k^2}R(u)\right]-\ln\left[1+\frac{4\alpha r_s}{\pi k^2}R(u)\right]\right\}. \tag{A10}$$

In (A10) the first term in brackets yields the β^2 term of (23); we integrate the remaining term by parts, obtaining

$$-\frac{3}{4\pi\alpha^2 r_s{}^2}\int_0^\beta k^3dk\,I(k), \tag{A11}$$

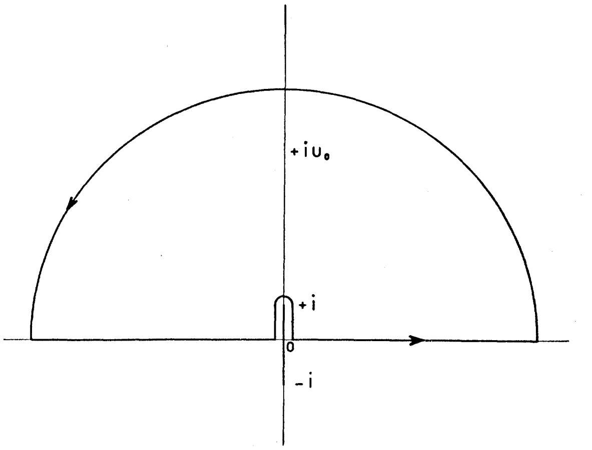

FIG. 2. The contour on which one must integrate $uR'(u)/[R(u)+\pi k^2/4\alpha r_s]$ in order to expand $I(k)$ in powers of k.

where

$$I(k)=\int_{-\infty}^{+\infty}du\,\frac{uR'(u)}{(\pi k^2/4\alpha r_s)+R(u)}. \tag{A12}$$

We wish to expand $I(k)$ in powers of k.

The function $R(u)$ is even and analytic. It has two branch points at $u=\pm i$, which we must join by a cut in the complex plane. Its only zero is at $u=\infty$, near which it behaves as

$$R(u)\sim 1/3u^2-1/5u^4\cdots.$$

For small enough k, the only poles of

$$\frac{uR'}{(\pi k^2/4\alpha r_s)+R(u)}$$

arise therefore at $\pm iu_0$, where u_0 is given by

$$u_0=i(4\alpha r_s/3\pi k^2)^{\frac{1}{2}}[1+O(k^2)].$$

The residue of the pole iu_0 is simply iu_0.

$I(k)$ may then be calculated by integrating over the contour shown on Fig. 2. We find

$$I(k)=2\pi i(iu_0)-\oint_c\frac{uR'(u)}{R(u)+\pi q^2/4\alpha r_s}, \tag{A13}$$

in which the contour c goes from -0 to i and then back to $+0$.

The first term of (A13) corresponds to the plasmon ground-state energy. It gives rise to the $\beta^3/r_s{}^{\frac{3}{2}}$, $\beta^5/r_s{}^{\frac{5}{2}}$, $\cdots$ terms. The coefficients determined with (A11) agree perfectly with those obtained by the plasma theory. Remark that we have kept only the first term in the expansion of $Q_k(u)$. Since $Q_k(u)$ contains only even powers of k, such corrections will always lead to corrections to the energy odd in β, such as $\beta^7/r_s{}^{\frac{5}{2}}$, $\cdots$.

The second term of (A13) corresponds to the energy of the individual particles. We can simplify it considerably by remarking that on the contour c, $R(u)$ is never small, being of order 1 or more. We may therefore expand the fraction in powers of k. The correlation energy arising from the individual particles is then given by

$$-\frac{3}{16\pi\alpha^2 r_s^2}\beta^4 \oint_c \frac{uR'(u)}{R}du + \frac{1}{32\alpha^3 r_s^3}\beta^6 \oint_c \frac{uR'}{R^2}du \cdots. \quad \text{(A14)}$$

It is easily shown that the inclusion of k^2 correction terms to $Q_k(u)$ will only introduce even powers of β.

In order to establish the equivalence of the plasma and the GB calculation of the β^4 term, we have to show that

$$\int_{-\infty}^{+\infty} du \ln[3u^2 R(u)] = -\oint_c \frac{uR'(u)}{R}du. \quad \text{(A15)}$$

The integral on the left-hand side may be integrated by parts, yielding

$$-\int_{-\infty}^{+\infty}\left[2+\frac{uR'(u)}{R}\right]du.$$

Since the function $\{2+[uR'(u)/R]\}$ goes to zero as $1/u^2$ at infinity, we can again integrate on the contour of Fig. 2. The only contribution comes from the integration on the contour c. The term 2, being single valued, gives obviously zero, which establishes (A15).

We remark that it is simple to calculate the higher order terms in β by using (A14). In (A14) we give the explicit coefficient of β^6, which has been computed numerically. The contribution to the correlation energy from (A14) is thus

$$-0.98\frac{\beta^4}{r_s^2}-0.23\frac{\beta^6}{r_s^3}+\cdots \text{ ry}. \quad \text{(A16)}$$

APPENDIX II

In this appendix we discuss briefly the question of non-RPA corrections to the plasma frequency. In the BP approach such corrections occur for the following reason: when one eliminates the linear plasmon-electron coupling by a canonical transformation generated by S, the transformation acts also on H_{sr} and yields new terms coupling the plasmons with the individual particles. These new terms give rise to the extra "exchange" frequency shift of the plasmons. We shall restrict ourselves to a very limited class of such corrections, namely those of order k^2 which involve only one power of H_{sr}. Each power of H_{sr} introduces a factor e^2, i.e., a factor r_s: this discussion is therefore limited to the terms in $\beta^5/r_s^{\frac{3}{2}}$ in the correlation energy.

The canonical transformation gives rise to new terms of the form

$$\frac{i}{\hbar}[H_{\text{sr}},S]+\tfrac{1}{2}\left(\frac{i}{\hbar}\right)^2[[H_{\text{sr}},S],S]+\cdots. \quad \text{(A17)}$$

The first term of (A17) is an extra coupling term. It can be eliminated by a further canonical transformation: this would yield a frequency shift involving two powers of H_{sr}, and is therefore beyond the range of the study. The terms in which we are interested are in fact the second-order terms, or, more precisely, their expectation value with respect to the electronic wave function. Such terms are quadratic in the field coordinates and therefore represent a shift in the plasmon frequency.

If we limit ourselves to the leading order in k, the generating function of the canonical transformation performed in BP III can be written

$$S=\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}}\sum_i \frac{\mathbf{k}\cdot\mathbf{p}_i}{m\omega_p^2}\exp(-i\mathbf{k}\cdot\mathbf{x}_i)\pi_{-k}.$$

It is a straightforward matter to calculate the double commutator of (A17), and to take the corresponding expectation value for a Fermi distribution of independent particles. The final result is to add to the Hamiltonian a correction term given for small k by

$$-\sum_k \frac{3}{40}\frac{k^2}{k_0^2}\pi_k{}^*\pi_k.$$

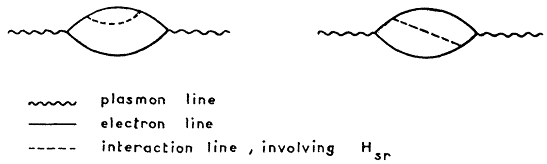

FIG. 3. The diagrams taken into account in the calculation of Appendix II.

This results in a shift of the frequency

$$\frac{\Delta\omega}{\omega_p}=-\frac{3}{40}\frac{k^2}{k_0^2}. \quad \text{(A18)}$$

The contribution to the long-range energy of the system may then be written as

$$-0.039(\beta^5/r_s^{\frac{3}{2}}) \text{ ry},$$

which is to be compared to the β^5 term occuring within the RPA

$$0.70(\beta^5/r_s^{\frac{5}{2}}) \text{ ry}.$$

It may be seen that, for actual metallic densities, the exchange correction to the plasma frequency is appreciably smaller than the RPA correction.

It is interesting to see what the foregoing procedure means in the language of diagrams. The diagrams which we take into account are those shown on Fig. 3. They involve first-order corrections to the excitation energy of the individual particles, *and* to the matrix elements for such excitations, $(\rho_k)_{0n'}$. Remark that in keeping only some of these diagrams, one can be led to a shift of the plasma frequency independent of k: such a result is obviously spurious, since it disappears when one takes consistently into account all diagrams of a given order.