

Self-Consistent Pair-Correlation Approach to Many-Body Effects in Metals*

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A self-consistent many-body procedure capable of handling the problem of correlation among Bloch electrons in metals is developed. Application to the uniform electron gas for several densities, in the range $r_s = 1.0a_0$ to $6.0a_0$, leads to correlation energies and compressibilities in good agreement with results from recent sophisticated dielectric treatments. The space pair-correlation function for parallel spins obtained by this treatment is positive over the entire range of r_s .

I. INTRODUCTION

Substantial progress has been made in recent years in the many-body theory of the electron gas through self-consistent treatments¹⁻³ of the influence of pair correlations on the dielectric function. These treatments are able to handle correlation effects from high densities, that is small values of r_s , the average interelectron separation, to low densities, that is large r_s , including the region of r_s that is prevalent in most metals. However, these analyses are best suited for a uniform electron gas, and its extension to real electron gas with associated inhomogeneities is rather complicated, although efforts have recently been made⁴ in this direction. The aim of the present work is to present a different approach to the pair-correlation problem which puts the uniform electron gas and the Bloch-electron problem in real metals on the same footing and therefore can be utilized for the latter without any theoretical modifications. This procedure uses the ideas of many-body perturbation⁵ and pair-excitation theories⁶ as developed in applications to atomic and molecular systems. The accuracy and practicability of the procedure will be tested by application to the problems of correlation energies, compressibilities and pair-correlation functions for the uniform electron gas at various densities. It will be shown that one obtains in this way results which compare very favorably with corresponding ones^{2,3} from the dielectric function approach.

In the many-body perturbation-theory (MBPT) procedure as applied to atoms,⁵ pair-correlation effects are handled through perturbation diagrams involving matrix elements between ground and pair excited states in the numerator and energy differences in the denominator. In the electron-gas problem, the latter can go to zero for electrons near the Fermi surface indicating that there are sizable correlation energies for these electrons. One has, therefore, to handle pair correlation to all orders. This can be done through the adaptation to the present problem of a self-consistent treat-

ment of pair correlations, following methods suggested by Sinanoğlu⁷ and applied to molecular systems by Čížek.⁸ The work in these references forms the starting point of the formulation of the procedure we have used for our present work on conduction electrons in metals.

Section II deals with the formulation of the self-consistent pair-correlation approach for the problem of conduction-electron wave functions in metals. Section III presents and discusses the results for the corrections to the one-electron energies, the correlation energy, the compressibility, density of states, and the space pair-correlation function.

II. THEORY

The basic ideas and steps in the formulation of the pair-correlation method are reviewed elsewhere^{7,8} and shall not be elaborated upon here. Only a few of the initial steps will be included for completeness and we shall concentrate instead on those features of the procedure that are special for the conduction-electron problem with its continuum energy distribution and Fermi surface.

Thus, following Čížek,⁸ the wave function of the ground-state eigenvector of the system may be written as

$$|\Psi\rangle = e^{\langle\hat{T}\rangle} |\Phi\rangle, \quad (1)$$

where $|\Phi\rangle$ is the eigenfunction for a one-electron Hamiltonian which may be conveniently chosen as the Hartree-Fock (HF) Hamiltonian. The operator \hat{T} may be expanded in terms of zero-, one-, two-, and more particle excitations as

$$\hat{T} = \sum_j \hat{T}_j \quad (2)$$

with

$$\hat{T}_j = \frac{1}{j!} \sum_{\substack{k_1, k_2, \dots, k_j \\ p_1, p_2, \dots, p_j}} f_j(k_1, k_2, \dots, k_j, p_1, p_2, \dots, p_j) \times \prod_{i=1}^j \eta_{k_i}^\dagger \eta_{p_i}, \quad (3)$$

where the p_i represent occupied states in the HF

approximation and k_i the unoccupied excited states, referred to, respectively, as hole and particle states in the MBPT language which we shall adopt here; $\eta_{k_i}^\dagger$ and η_{p_i} represent the usual creation and destruction operators and the excitation functions f_j in Eq. (3) are to be determined self-consistently by substituting (1) in the Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle, \quad (4)$$

where H , the total Hamiltonian, can be written in the usual form

$$H = H_0 + \frac{1}{2} \sum_{\substack{k_1 k_2 \\ p_1 p_2}} \langle k_1 k_2 | \frac{1}{r_{12}} | p_1 p_2 \rangle \eta_{k_1}^\dagger \eta_{k_2}^\dagger \eta_{p_2} \eta_{p_1} \\ - \sum_{k_1 p_1} \langle k_1 | V_0 | p_1 \rangle \eta_{k_1}^\dagger \eta_{p_1}. \quad (5)$$

In the present work, we shall follow Čížek's approximation of keeping only terms involving various powers of \hat{T}_0 and \hat{T}_2 in Eq. (2). With this approximation, one can equate coefficients of terms involving excitations of different numbers of particles, as represented by $\prod_{i=1}^l \eta_{k_i}^\dagger \eta_{p_i}$, on either side of Eq. (4).

From the coefficients of the $l=0$ terms, one obtains in this way:

$$P = \sum_{k_3 k_4} \langle k_1 k_2 | \frac{1}{r_{12}} | k_3 k_4 \rangle_{\text{ex}} f_2(k_3 k_4; p_1 p_2) + \sum_{k_3 p_3} \langle p_3 k_2 | \frac{1}{r_{12}} | k_3 p_2 \rangle_{\text{ex}} f_2(k_1 k_3; p_1 p_3) \\ + \sum_{k_3 p_3} \langle p_3 k_2 | \frac{1}{r_{12}} | k_3 p_1 \rangle_{\text{ex}} f_2(k_1 k_3; p_3 p_2) + \sum_{k_3 p_3} \langle p_3 k_1 | \frac{1}{r_{12}} | k_3 p_2 \rangle_{\text{ex}} f_2(k_3 k_2; p_1 p_3) \\ + \sum_{k_3 p_3} \langle p_3 k_1 | \frac{1}{r_{12}} | k_3 p_1 \rangle_{\text{ex}} f_2(k_3 k_2; p_3 p_2) + \sum_{p_3 p_4} \langle p_3 p_4 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} f_2(k_1 k_2; p_3 p_4) \quad (10)$$

that is seen to involve the pair excitation functions f_2 which are different from $f_2(k_1 k_2; p_1 p_2)$. These nondiagonal terms can however be shown (as in the Appendix) to be represented approximately by constant factors times $f_2(k_1 k_2; p_1 p_2)$ near the Fermi surface where most of the correlation effects originate. Consequently, one can consider the influence of these nondiagonal terms to be incorporated in the self-consistent parameters $\epsilon_{p_i}^c$ and $\mu_{k_i}^c$ in Eq. (7).

On solving for $f_2(k_1 k_2; p_1 p_2)$ from Eq. (7), one then gets

$$f_2(k_1 k_2; p_1 p_2) = \frac{1}{D} \langle k_1 k_2 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}}, \quad (11)$$

where

$$D = \epsilon_{p_1} + \epsilon_{p_2} - \epsilon_{k_1} - \epsilon_{k_2} + \epsilon_{p_1}^c + \epsilon_{p_2}^c + \mu_{k_1}^c + \mu_{k_2}^c. \quad (12)$$

Substituting Eq. (8) in Eq. (6) for $E - E_{\text{HF}}$, one ob-

$$E - E_{\text{HF}} = \frac{1}{2} \sum_{\substack{k_1 k_2 \\ p_1 p_2}} f_2(k_1 k_2; p_1 p_2) \langle p_1 p_2 | \frac{1}{r_{12}} | k_1 k_2 \rangle_{\text{ex}}, \quad (6)$$

where

$$\langle p_1 p_2 | \frac{1}{r_{12}} | k_1 k_2 \rangle_{\text{ex}} = \langle p_1 p_2 | \frac{1}{r_{12}} | k_1 k_2 \rangle \\ - \langle p_1 p_2 | \frac{1}{r_{12}} | k_2 k_1 \rangle$$

involves both direct and exchange terms. From the coefficients of the $l=2$ term in the Eq. (4) on either side, one obtains^{10,11} the more elaborate equations

$$\langle k_1 k_2 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} + (\epsilon_{k_1} + \epsilon_{k_2} - \epsilon_{p_1} - \epsilon_{p_2}) f_2(k_1 k_2; p_1 p_2) \\ - (\epsilon_{p_1}^c + \epsilon_{p_2}^c + \mu_{k_1}^c + \mu_{k_2}^c) f_2(k_1 k_2; p_1 p_2) + P = 0, \quad (7)$$

where

$$\epsilon_{p_1}^c = \sum_{p_3, k_3 k_4} \langle p_3 p_1 | \frac{1}{r_{12}} | k_3 k_4 \rangle_{\text{ex}} f_2(k_3 k_4; p_3 p_1) \quad (8)$$

and

$$\mu_{k_1}^c = \sum_{p_3 p_4, k_3} \langle p_3 p_4 | \frac{1}{r_{12}} | k_1 k_3 \rangle_{\text{ex}} f_2(k_1 k_3; p_3 p_4). \quad (9)$$

The quantity P is given by

tains for the correlation energy,

$$E - E_{\text{HF}} = \frac{1}{2} \sum_i \epsilon_{p_i}^c = \frac{1}{2} \sum_j \mu_{k_j}^c. \quad (13)$$

The parameters $\epsilon_{p_i}^c$ can best be understood by examining Eq. (8). They can be seen to correspond¹² to taking a pair-correlation diagram involving two-hole states p_1 and p_2 with summation carried out over the p_2 states, the excited-state summation over $k_1 k_2$ being an intrinsic part of the evaluation of the diagram. One could thus regard $\epsilon_{p_1}^c$ as a change in the energy of state p_1 due to pair correlation with all the other occupied states. However, since we have incorporated the effect of the terms in Eq. (10) in the parameter $\epsilon_{p_i}^c$ and $\mu_{k_i}^c$, $\epsilon_{p_i}^c$ in fact contains both pair-correlation corrections as well as the higher-order correlation effects. The quantitative importance of these higher-order effects will be discussed in Sec. III. The factor of

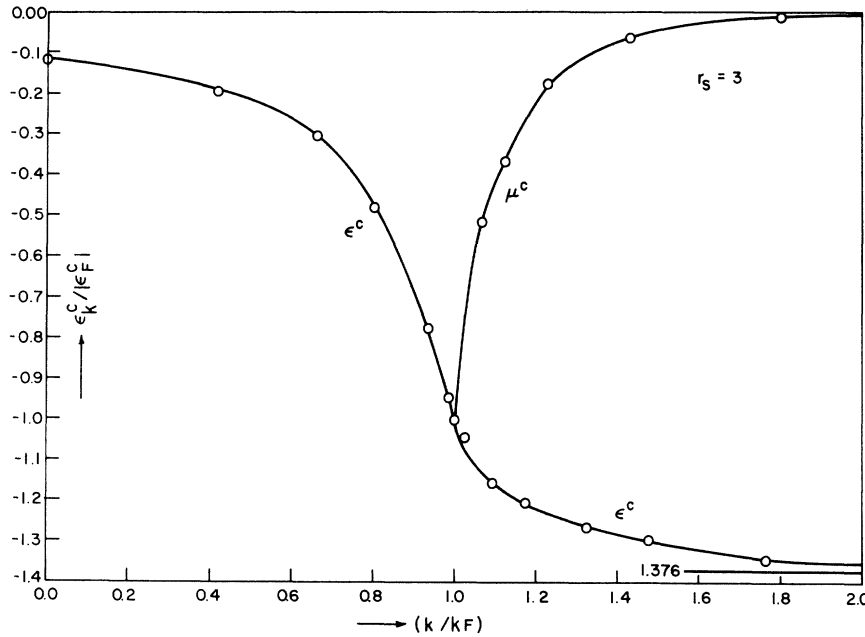


FIG. 1. Variation of ϵ_k^c and μ_k^c with k .

$\frac{1}{2}$ in the right-hand side of Eq. (13) ensures that the contribution from pairs of states p_1 and p_2 is not counted twice. The parameters $\mu_{k_1}^c$, however, cannot be interpreted as excited-state energy corrections as was the case for the $\epsilon_{p_1}^c$.

Before proceeding to present and discuss results of actual calculation in Sec. III, we would like to comment briefly on the relationship between the ideas involved in the present work and the earlier work of Bohm and Pines.¹³ Thus, we find from the values of our correlation parameters in Fig. 1, that the pair-correlation function $f_2(k_1 k_2; p_1 p_2)$ gets strongly screened with respect to the bare result [in the absence of the $\epsilon_{p_1}^c$ -type terms in denominator of Eq. (11)], due to the rapid increase in the correlation parameters $\epsilon_{p_1}^c$ as the momentum transfer $|\vec{k}_1 - \vec{p}_1|$ gets smaller on approaching the Fermi surface. This screening is equivalent to the cutoff approximation for small q used by Bohm and Pines,¹³ except that the screening we get is more general since it is a function of both \vec{k}_1 and \vec{p}_1 .

It should be pointed out that both the present procedure and the dielectric function procedure do involve self-consistency, although in quite different ways. We feel that the main advantage of the procedure proposed here is that, unlike the dielectric formalism which is best suited for a homogeneous system such as a free-electron gas, the present procedure can be applied directly to Bloch electrons by solving Eqs. (8) and (11) self-consistently using matrix elements involving Bloch wave functions. However, in our application here, where our main motivation is to test the present procedure by comparison with available results by other procedures, we shall

confine ourselves to a free-electron system.

III. RESULTS AND DISCUSSION

Equations (8) and (11) were solved self-consistently for $r_s = 1.0a_0$ through $6.0a_0$ at intervals of $1.0a_0$, r_s representing the radius per electron appropriate to the density. The initial choices of the ϵ_p^c and μ_k^c were all taken to be zero in the first cycle and the values for them after each cycle, as well as those at ultimate convergence, were negative. For the typical case of $r_s = 3a_0$, the value of ϵ_p^c is seen from Fig. 1 to steadily decrease from -0.033 Ry at $|\vec{p}|=0$ to -0.288 Ry at the Fermi surface. The parameter μ_k^c steadily increases from the Fermi-surface value of -0.288 Ry to zero at about $k = 2.5k_F$ and beyond. We have also studied the correlation correction ϵ_p^c for energies of electrons excited above the Fermi surface. These parameters, which should be distinguished from μ_k^c , represent the influence of correlation with the other electrons on the energy of an excited electron. The same equations (8) and (11) were solved iteratively for this purpose with one of the two states p_1 in the two equations being taken above the Fermi surface and one below. For $r_s = 3a_0$, for example, the values of ϵ_p^c above the Fermi surface appear to approach an asymptotic value of about a factor 1.38 times the value of ϵ_p^c at the Fermi surface. This ratio actually varies very slightly with r_s , being about 1.40 for $r_s = 2a_0$.

The study of ϵ_p^c as a function of p near the Fermi surface, both above and below permits us to evaluate $d\epsilon_p^c/dp$ as a function of p through the Fermi surface. This function is important because the

TABLE I. Correlation energy (Ry per electron).

$r_s(a_0)$	Present theory	Singwi <i>et al.</i> (Ref. 2)	Singwi <i>et al.</i> (Ref. 14)	Toigo-Woodruff ^a
1	-0.148 ± 0.002	-0.112	-0.125	-0.103
2	-0.098 ± 0.002	-0.089	-0.097	-0.083
3	-0.074 ± 0.002	-0.075	-0.080	-0.071
4	-0.062 ± 0.002	-0.065	-0.070	-0.063
5	-0.050 ± 0.002	-0.058	-0.063	-0.057
6	-0.042 ± 0.003	-0.052	-0.057	-0.052

^aThe values in this column are those calculated by Vashishta and Singwi (Ref. 2) using the formulation of Toigo-Woodruff.

density of states is proportional to the inverse of $d\epsilon/dp$. The latter is known to blow up near the Fermi surface in the Hartree-Fock theory for the uniform electron gas. Our results for $d\epsilon_F^c/dp$, as plotted in Fig. 2, indicate a negative infinity at the Fermi surface indicating that it is capable of canceling the positive infinity from Hartree-Fock theory to give a finite net result.

We shall now present and compare our results for the correlation energy, compressibility, and pair-correlation function with those from the earlier work. Considering the correlation energy first, this can be obtained from Eq. (13) using the values of ϵ_F^c . In Table I, we have listed our results for the correlation energy per electron for $r_s = a_0$ through $6a_0$ at intervals of a_0 . Also listed for reference are the corresponding results of three recent investigations using the dielectric function approach, two by Singwi and collaborators^{2,14} and one by Toigo and Woodruff.³ The errors we have quoted for our theoretical results are composed of estimated errors in convergence and of finite mesh size for integration. It is clear from Table I that the present self-consistent pair-correlation approach gives correlation energy results that agree well with those from recent dielectric function procedures for the range $r_s = 2.0a_0$ to $6.0a_0$, which spans the physical range, the agreement being somewhat better with the latest results of Vashishta and Singwi.²

For $r_s = 1.0a_0$, our procedure seems to overestimate the correlation energy as compared to the dielectric approach. In fact, there seems to be a trend towards an overestimation of the correlation energy for small r_s . This trend could perhaps be understood as follows: The nondiagonal terms in Eq. (10) represent mainly the influence of ring diagrams or what are called in atomic many-body perturbation theory literature, the pair-pair-correlation diagrams.¹² As argued in the Appendix, while their influence could be approximately included through the self-consistently calculated parameters ϵ_F^c and μ_k^c , the approximation appears to break down at very high densities where the ring diagrams are expected to be quite important. An

examination of the role of the extra term $-4k_F^2/(\pi|\vec{k}_1 - \vec{p}_1|)$ due to the ring diagrams in Eq. (A13) however indicates that it would serve to produce a decrease in the magnitude of the correlation energy which is a change in the right direction.

For obtaining the compressibility K including correlation, we have made use of the relation (14) obtained from thermodynamic considerations,¹⁴

$$\frac{K_{\text{free}}}{K} = 1 + \left(\frac{4}{9\pi}\right)^{2/3} \left[-\frac{r_s}{\pi} + \frac{1}{6} r_s^4 \left(\frac{d^2 E_c}{dr_s^2} - \frac{2}{r_s} \frac{dE_c}{dr_s} \right) \right] \quad (14)$$

the correlation energy $E_c = E - E_{\text{HF}}$ being expressed in rydbergs. The compressibility can also be obtained from the static dielectric function at the large-wavelength limit.¹⁴ This is not important for our work but has been utilized earlier by some investigators using the dielectric function approach. In Fig. 3, we have plotted our values of K_{free}/K as a function of r_s and made comparisons with those of Singwi and collaborators^{2,14} and Toigo and Woodruff.³ From Fig. 3, we can see that our results for K_{free}/K are always positive while those of Toigo and Woodruff³ and Vashishta and Singwi become negative beyond $r_s = 5a_0$. Singwi *et al.*'s earlier result¹⁴ using the large-wavelength limit of the dielectric function did not go negative. However,

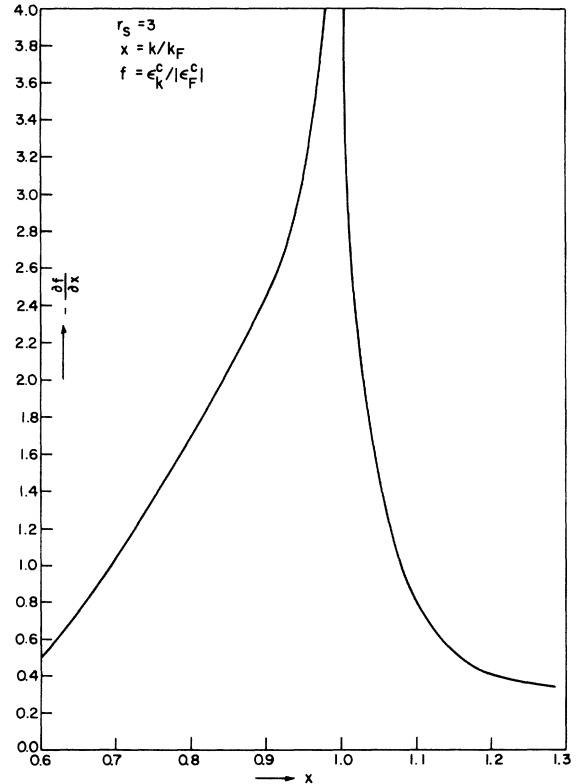


FIG. 2. Variation of derivative of ϵ_F^c near Fermi surface

they were unhappy with their earlier result because it did not agree with that from Eq. (14).

Finally, we would like to remark on the space pair-correlation function from the present analysis. We shall confine our attention only to the parallel-spin pair-correlation function $g_{++}(r)$, because in the Hartree-Fock approximation, $g_{++}(0) = 0$ while $g_{+-}(0) = 1$. The sign of $g_{++}(0)$ is therefore a more crucial test of the correlation correction. To do this, one can use the equation

$$g_{++}(r) = \langle \Psi | \sum_{i,j} \delta_{\sigma_i, \sigma_j} \delta(\vec{r} - \vec{r}_i + \vec{r}_j) | \Psi \rangle \frac{V}{\frac{1}{2}N(\frac{1}{2}N - 1)}, \quad (15)$$

where $|\Psi\rangle$ is given by Eq. (1), \vec{r}_i and \vec{r}_j refer to the position vectors of the i th and j th electrons, N is the number of electrons, and V is the volume. The Kronecker $\delta_{\sigma_i, \sigma_j}$ is introduced to take account of only parallel-spin pairs. One then gets, on introducing f_2 from Eq. (11) in Eq. (1),

$$\begin{aligned} g_{++}(r) = & 1 - \left(\frac{3}{(k_F r)^3} (\sin k_F r - k_F r \cos k_F r) \right)^2 \\ & + \frac{1}{\frac{4}{3} \pi k_F^3} \frac{4\pi e^2}{2(2\pi)^6} \int \int \int d^3 p_1 d^3 p_2 d^3 k_1 \\ & \times \left(\frac{1}{|\vec{p}_1 - \vec{k}_1|^2} - \frac{1}{|\vec{p}_2 - \vec{k}_1|^2} \right) \\ & \times [e^{-i\vec{k}_1 \cdot \vec{r}} (e^{i\vec{p}_1 \cdot \vec{r}} - e^{i\vec{p}_2 \cdot \vec{r}}) + \text{c. c.}]. \quad (16) \end{aligned}$$

An examination of the third term in Eq. (16) representing the correlation correction, indicates that for $r=0$, independent of the value of r_s , the correlation correction always goes to zero. Thus $g_{++}(0) = 0$ for all r_s and does not go negative.

In conclusion, the present procedure of carrying out a self-consistent solution of the influence of pair correlation on one-electron energies gives results in good agreement with total correlation energies obtained by recent sophisticated dielectric-function procedures. Also, it gives positive results for the compressibility and pair-correlation function as expected from physical considerations. In addition, it has the merit of being applicable to Bloch electrons without any theoretical modifications.

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APPENDIX

The purpose of this appendix is to show that the nondiagonal terms in Eq. (10) can be approximately expressed as proportional to $f_2(k_1 k_2; p_1 p_2)$ and consequently, their influence can be included through the parameters $\epsilon_{p_i}^c$ and $\mu_{k_i}^c$ in the denominator in Eq. (11). Since correlation corrections occur

mainly from occupied and empty states near the Fermi surface, we shall consider only small momentum transfers in our analysis.

In the first term on the right-hand side of Eq. (10); namely,

$$\sum_{k_3 k_4} \langle k_1 k_2 | \frac{1}{r_{12}} | k_3 k_4 \rangle_{\text{ex}} f_2(k_3 k_4; p_1 p_2) \quad (A1)$$

the momentum transfer involved in the matrix element of $1/r_{12}$ is $|\vec{k}_3 - \vec{k}_1| = |\vec{p}|$. So this term will give its most divergent behavior for $\vec{p} \rightarrow 0$. The major part of the variation of this term with \vec{p} is then being produced by $\langle k_1 k_2 | 1/r_{12} | k_3 k_4 \rangle_{\text{ex}}$ rather than $f_2(k_3 k_4; p_1 p_2)$ the latter being nearly independent of \vec{p} . Consequently, (A1) can be written as

$$\left(\sum_{k_3 k_4} \langle k_1 k_2 | \frac{1}{r_{12}} | k_3 k_4 \rangle_{\text{ex}} \right) f_2(k_1 k_2; p_1 p_2). \quad (A2)$$

Through analogous arguments, the closely similar sixth term can be approximated as

$$\left(\sum_{p_3 p_4} \langle p_3 p_4 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} \right) f_2(k_1 k_2; p_1 p_2). \quad (A3)$$

We consider next the second term in the Eq. (10). The most divergent part here is for small $\vec{q} = \vec{k}_1 - \vec{p}_1$ and for this all of the momenta k_1, k_2, k_3, p_1, p_2 , and p_3 have to be close to the Fermi surface. From the expression for $f_2(k_1 k_2; p_1 p_2)$ given by Eq.

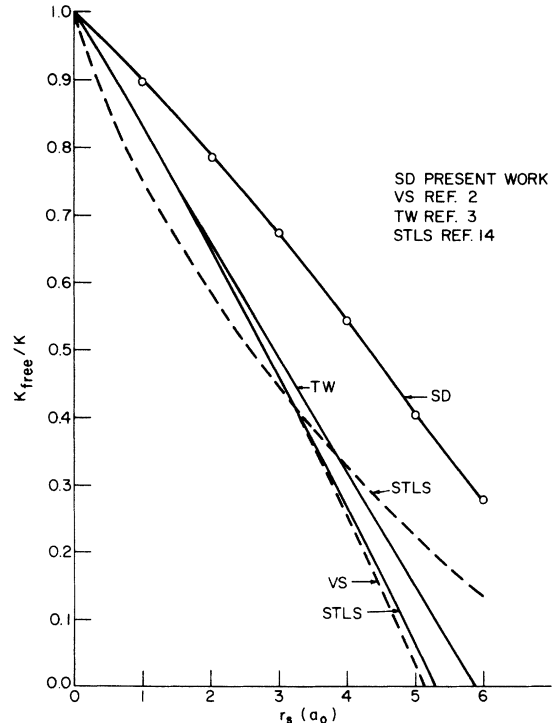


FIG. 3. K_{free}/K as a function of r_s . Full curve is from differentiation of total energy and dashed curve from the long-wavelength limit of the static dielectric function.

(11), we can see that $f_2(k_1 k_3; p_1 p_3) = \text{const} \times (1/q^2)$ and is independent of the individual values of the k_1 and p_1 . Thus, one can make the replacements $k_3 \rightarrow k_2$ and $p_3 \rightarrow p_2$ in the factor f_2 in the second term of Eq. (10) and obtain

$$\left(\sum_{k_3 p_3} \langle p_3 k_2 | \frac{1}{r_{12}} | k_3 p_2 \rangle_{\text{ex}} \right) f_2(k_1 k_2; p_1 p_2). \quad (\text{A4})$$

Considering next the third term in (10), from an examination of the $1/r_{12}$ matrix element, the most divergent behavior for fixed k_1 , k_2 , p_1 , and p_2 appears to arise from the exchange term in the region of p_3 close to p_1 and consequently of k_3 close to k_2 . In that case, again, as for the second term, f_2 is

nearly proportional to $1/q^2$ and so we get the third term in (10) equal to

$$\left(\sum_{k_3 p_3} \langle p_3 k_2 | \frac{1}{r_{12}} | k_3 p_1 \rangle_{\text{ex}} \right) f_2(k_1 k_2; p_1 p_2). \quad (\text{A5})$$

Proceeding similarly, the fifth and the sixth terms can be written as

$$\left(\sum_{k_3 p_3} \langle p_3 k_1 | \frac{1}{r_{12}} | k_3 p_2 \rangle_{\text{ex}} \right) f_2(k_1 k_2; p_1 p_2) \quad (\text{A6})$$

and

$$\left(\sum_{k_3 p_3} \langle p_3 k_1 | \frac{1}{r_{12}} | k_3 p_1 \rangle_{\text{ex}} \right) f_2(k_1 k_2; p_1 p_2). \quad (\text{A7})$$

Combining all these terms, Eq. (7) leads to

$$f_2(k_1 k_2; p_1 p_2) = \frac{1}{D} \langle k_1 k_2 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} + \frac{1}{D} f_2(k_1 k_2; p_1 p_2) \left[\sum_{k_3 k_4} \langle k_1 k_2 | \frac{1}{r_{12}} | k_3 k_4 \rangle_{\text{ex}} \right. \\ \left. + \sum_{k_3 p_3} \left(\langle p_3 k_2 | \frac{1}{r_{12}} | k_3 p_2 \rangle_{\text{ex}} + \langle p_3 k_2 | \frac{1}{r_{12}} | k_3 p_1 \rangle_{\text{ex}} + \langle p_3 k_1 | \frac{1}{r_{12}} | k_3 p_2 \rangle_{\text{ex}} + \langle p_3 k_1 | \frac{1}{r_{12}} | k_3 p_1 \rangle_{\text{ex}} \right) \right. \\ \left. + \sum_{p_3 p_4} \langle p_3 p_4 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} \right]. \quad (\text{A8})$$

The matrix elements of $1/r_{12}$ in Eq. (A8) involve both direct and exchange terms. For the terms in the square brackets, we keep only the most divergent parts (direct or exchange, as the case may be), which reduces (A8) to the form

$$f_2(k_1 k_2; p_1 p_2) = \frac{1}{D} \langle k_1 k_2 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} + \frac{1}{D} \frac{1}{V} f_2(k_1 k_2; p_1 p_2) \left[\sum_{k_3 k_4} \frac{4\pi}{|\vec{k}_3 - \vec{k}_1|^2} \delta_{\vec{k}_1 + \vec{k}_2, \vec{k}_3 + \vec{k}_4} \right. \\ \left. + \sum_{k_3 p_3} \left(\frac{4\pi}{q^2} \delta_{\vec{k}_3, \vec{p}_3 - \vec{q}} - \frac{4\pi}{|\vec{p}_3 - \vec{p}_1|^2} \delta_{\vec{k}_3 + \vec{p}_1, \vec{k}_2 + \vec{p}_3} - \frac{4\pi}{|\vec{k}_3 - \vec{k}_1|^2} \delta_{\vec{p}_3 + \vec{k}_1, \vec{k}_3 + \vec{p}_2} + \frac{4\pi}{q^2} \delta_{\vec{k}_3, \vec{p}_3 + \vec{q}} \right) \right. \\ \left. + \sum_{p_3 p_4} \frac{4\pi}{|\vec{p}_3 - \vec{p}_1|^2} \delta_{\vec{p}_3 + \vec{p}_4, \vec{p}_1 + \vec{p}_2} \right]. \quad (\text{A9})$$

In Eq. (A9), the first term in the square bracket cancels the fourth, and the third term cancels the sixth. So we get for small momentum transfer $\vec{q} = \vec{k}_1 - \vec{p}_1 = \vec{p}_2 - \vec{k}_2$

$$f_2(k_1 k_2; p_1 p_2) = \frac{1}{D} \langle k_1 k_2 | \frac{1}{r_{12}} | p_1 p_2 \rangle_{\text{ex}} + \frac{1}{D} f_2(k_1 k_2; p_1 p_2) \left(\frac{1}{V} \sum_{k_3 p_3} \frac{4\pi}{q^2} (\delta_{\vec{k}_3, \vec{p}_3 - \vec{q}} + \delta_{\vec{k}_3, \vec{p}_3 + \vec{q}}) \right) \quad (\text{A10})$$

which leads to

$$f_2(k_1 k_2; p_1 p_2) = \frac{\langle k_1 k_2 | 1/r_{12} | p_1 p_2 \rangle_{\text{ex}}}{\epsilon_{p_1} + \epsilon_{p_2} - \epsilon_{k_1} - \epsilon_{k_2} + \epsilon_{p_1}^c + \epsilon_{p_2}^c + \mu_{k_1}^c + \mu_{k_2}^c - \sum_{k_3 p_3} V^{-1} (4\pi/|\vec{k}_1 - \vec{p}_1|^2) (\delta_{\vec{k}_3, \vec{p}_3 - \vec{q}} + \delta_{\vec{k}_3, \vec{p}_3 + \vec{q}})}$$

The summation in the denominators in (A11) can be shown to be equal to

$$-4k_F^2/\pi |\vec{k}_1 - \vec{p}_1| \quad (\text{A12})$$

giving finally

$$f_2(k_1 k_2; p_1 p_2) = \frac{\langle k_1 k_2 | 1/r_{12} | p_1 p_2 \rangle_{\text{ex}}}{(\epsilon_{p_1} + \epsilon_{p_2} - \epsilon_{k_1} - \epsilon_{k_2} + \epsilon_{p_1}^c + \epsilon_{p_2}^c + \mu_{k_1}^c + \mu_{k_2}^c - 4k_F^2/\pi |\vec{k}_1 - \vec{p}_1|)} \quad (\text{A13})$$

The term $R = 4k_F^2/|\vec{k}_1 - \vec{p}_1|$ in the denominator of (A13) is divergent for small q , but this divergence is weaker than that of the matrix element in the numerator (which goes as $1/q^2$). In fact, the divergence of R would disappear if the electron-electron interaction was screened. It thus appears that incorporation of the ring diagrams can in fact be carried out through the inclusion of a constant parameter which can be absorbed in the other self-consistent parameters in Eq. (12) of the text.

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¹J. Hubbard, Proc. R. Soc. A **240**, 539 (1957); Proc. R. Soc. A **243**, 336 (1957).

²P. Vashishta and K. S. Singwi, Phys. Rev. B **6**, 875 (1972), and several earlier references listed therein to the work of Singwi and collaborators.

³F. Toigo and T. O. Woodruff, Phys. Rev. B **2**, 3958 (1970); Phys. Rev. B **4**, 2799 (1972).

⁴See for example: K. J. Duff and A. W. Overhauser, Phys. Rev. B **5**, 2799 (1972).

⁵H. P. Kelly, Phys. Rev. A **3**, 578 (1971); T. S. Lee and T. P. Das, Phys. Rev. A **6**, 968 (1972); and references to earlier papers listed in these articles.

⁶O. Sinanoğlu and K. A. Brueckner, *Three Approaches to Electron Correlation in Atoms* (Yale U. P., New Haven, Conn., 1970). See also C. Nicolaides, O. Sinanoğlu, and P.

Westhaus, Phys. Rev. A **4**, 1400 (1971); C. M. Moser and R. K. Nesbet, Phys. Rev. A **6**, 1710 (1972); and earlier references listed in these articles.

⁷O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962); Adv. Chem. Phys. **6**, 315 (1964).

⁸J. Čížek, J. Chem. Phys. **45**, 4256 (1966).

⁹ T_1 can be shown to make negligible contribution through the Brillouin theorem, (see Ref. 8, p. 4263).

¹⁰See Eqs. (59)–(61) of Ref. 8.

¹¹Equations analogous to Eq. (7) have been obtained by H. P. Kelly [Phys. Rev. **134**, A1450 (1964)].

¹²T. S. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. A **4**, 1410 (1971).

¹³D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

¹⁴K. S. Singwi, A. Sjolander, M. P. Tosi, and R. H. Land, Phys. Rev. B **1**, 1044 (1970).