Correlation Energy of an Electron Gas at Metallic Densities

M. S. BHATIA* AND G. SPEISMAN
Department of Phsyics, Florida State University, Tallahassee, Florida
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A combined variational and perturbation-theoretic procedure is employed to obtain an upper limit to the ground-state energy of an electron gas at intermediate metallic densities within the accuracy of the perturbation-theory calculation of the ground-state energy. The Bohm-Pines auxiliary-variable theory of electron interactions is used. The Bohm-Pines intermediate transformation is modified so that it minimizes the ground-state energy at the intermediate stage. Further corrections are computed by perturbation theory following a procedure similar to that of Nozières and Pines. The final results for the correlation energy at intermediate densities are up to 20% lower than those of the earlier investigators. In the Appendix, it is shown that the intermediate transformation used in this paper is an extremum for its type.

I. INTRODUCTION

THE ground-state energy of a system of a large number of electrons moving in a background of uniform distribution of positive charge, so that the entire system is neutral, has been calculated quite accurately both in the high- and the low-density limits. The results of these calculations are usually expressed in terms of the extent to which they represent improvements over the Hartree-Fock calculation of the ground-state energy. If r_s is the mean interelectronic spacing measured in Bohr units, then one can write,

$$\epsilon_0=\left(\frac{2.21}{r_s^2}-\frac{0.916}{r_s}+\epsilon_c\right)\mathrm{Ry},$$

where ϵ_0 is the ground-state energy per electron, the first two terms on the right are that quantity calculated in the Hartree-Fock approximation and ϵ_c is the correlation energy.

Gell-Mann and Brueckner[1] have shown that in the high-density limit, the correlation energy may be written as the following series:

$$\epsilon_c=A\ln r_s+C+Dr_s\ln r_s+Er_s+O(r_s^2\ln r_s).$$

They explicitly calculated the constants A and C. Dubois[2] and Carr and Maradudin[3] have recently calculated the constants D and E.

In the low-density limit $r_s\gtrsim 10$ it was first shown by Wigner[4] that the correlation energy may be written as a power series in $r_s^{-1/2}$

$$\epsilon_c=ar_s^{-1/2}+br_s^{-3/2}+cr_s^{-2}+\cdots.$$

The densities actually found in metals lie in the intermediate density region $1.8<r_s<5.6$. There is no known rigorous expression for the correlation energy at these densities. Utilizing the collective description of the electron gas developed by Bohm and Pines,[5] Pines,[6] Nozières and Pines[7] have suggested an interpolation procedure by which the correlation energy may be obtained approximately. Hubbard[8] has obtained approximate results for the correlation energy at the intermediate densities by a different interpolation procedure which agrees within the accuracy of the calculations with those of Nozières and Pines.[7] More recently, Carr and Maradudin[3] have estimated the correlation energy at the intermediate densities by interpolating between the rigorous results for the correlation energy in the high-density and the low-density limits. Their results are again in agreement with those of Refs. 7 and 8 within the accuracy of the calculations.

However, all the above quoted results for the correlation energy are approximate. Since there is so far no rigorous expression for the correlation energy at metallic densities, it is of some interest to see if one can compute the correlation energy to a better degree of approximation than that of the previous investigators.

In this paper we propose to employ a combined variational and perturbation theoretic approach to obtain an upper limit on the ground-state energy of an electron gas at the intermediate densities within the accuracy of the perturbation-theory calculation of the ground-state energy. We shall use the auxiliary variable theory of electron interactions of Bohm and Pines.[5,6]

II. INTERMEDIATE TRANSFORMATION

The Hamiltonian for a system of N electrons in a cubical box of volume L^3 with uniform background of an equal amount of positive charge, subject to periodic boundary conditions may be written as

$$H=\sum_i\frac{p_i^2}{2m}+\tfrac{1}{2}\sum_{k\neq 0}(\rho_k^*\rho_k-N)v_k,$$

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[2] D. F. Dubois, Ann. Phys. (N. Y.) **7**, 174 (1959).

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[6] D. Pines, Phys. Rev. **92**, 625 (1953); in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 373.

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where

$$\mathbf{p}_i=(\hbar/i)\nabla, \quad \rho_k=\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \tag{1}$$

and

$$v_k=4\pi e^2/L^3k^2.$$

If we add to H,

$$H_{\text{add}}=\tfrac{1}{2}\sum_{k<k_c}(\pi_k^*\pi_k-2v_k^{1/2}\pi_k^*\rho_k), \tag{2}$$

we obtain the extended Hamiltonian of Bohm and Pines, H_{ext},

$$H_{\text{ext}}=H+H_{\text{add}}. \tag{3}$$

The operators π_k are such that they commute with all the particle operators and there exist conjugate coordinate operators η_k (which also commute with the particle operators) satisfying the commutation relations,

$$[\pi_k,\eta_{k'}]=-i\hbar\delta_{kk'},$$
$$[\pi_k,\pi_{k'}]=[\eta_k,\eta_{k'}]=0,$$
$$\pi_k^*=\pi_{-k},$$

and

$$\eta_k^*=\eta_{-k}.$$

The extended Hamiltonian H_{ext} then has $3N+N'$ degrees of freedom, where

$$N'=\left(\frac{L}{2\pi}\right)^3\int_{k<k_c}d^3k=\frac{k_c^3L^3}{6\pi^2}.$$

It has been shown[9] that within the random-phase approximation, the net effect of the added terms H_{add} is to change the ground-state energy by

$$\tfrac{1}{2}\sum_{k<k_c}\frac{\pi_k^*\pi_k}{\epsilon(k,0)},$$

where $\epsilon(k,0)$ is the static dielectric constant of the system. Since[10] $\epsilon(k,0)\geq 0$, the ground-state energy of the system is greater than or equal to that of the original system. Thus, if we use some trial vector $|\phi\rangle$, it is guaranteed in the random-phase approximation that $E_0^{\text{inter}}=\langle\phi|H_{\text{ext}}|\phi\rangle/\langle\phi|\phi\rangle\geq E_0$, where E_0 is the exact ground-state energy of the original system. Since the random-phase approximation leads to the exact answer for the ground-state energy in the high-density limit, the above equation holds in that limit. We assume that it holds at intermediate densities also. We can then use trial vectors containing some parameters to compute E_0^{inter} and then minimize E_0^{inter} with respect to these parameters to obtain an upper limit on the ground-state energy of the original system.

Instead of making the trial vectors a function of parameters, we use a trial unitary transformation $e^{(i/\hbar)U(c_k)}$ containing parameters c_k to transform the Hamiltonian; the variational parameters c_k in the transformation operator $U(c_k)$ then appear in the transformed Hamiltonian. We then compute E_0^{inter} using a suitably tractable trial vector $|\psi_0\rangle$ and minimize E_0^{inter} with respect to the parameters c_k to obtain the "best" unitary transformation. Evidently this procedure is equivalent to using

$$e^{-(i/\hbar)U(c_k)}|\psi_0\rangle$$

as the trial vector.

Our transformation operator $U(c_k)$ is

$$U(c_k)=\sum_{k<k_c}v_k^{1/2}c_k\eta_k\rho_k. \tag{4}$$

(If we put $c_k=1$ for all k, we get the Bohm-Pines intermediate transformation operator.) The transformed Hamiltonian (to be referred to as the intermediate Hamiltonian, denoted by H_{inter}) is given by

$$H_{\text{inter}}=e^{iU/\hbar}H_{\text{ext}}e^{-iU/\hbar},$$
$$H_{\text{inter}}=T+H_{\text{osc}}+H_{\text{sr}}+H_{\text{rlr}}+H_{\text{I}}+H_{\text{II}}, \tag{5}$$

where

$$T=\sum_i(p_i^2/2m), \tag{5a}$$

$$H_{\text{osc}}=\tfrac{1}{2}\sum_{k<k_c}(\pi_k^*\pi_k+\omega_p^2|c_k|^2\eta_k^*\eta_k), \tag{5b}$$

$$H_{\text{sr}}=\tfrac{1}{2}\sum_{k<k_c}(\rho_k^*\rho_k-N)v_k, \tag{5c}$$

$$H_{\text{rlr}}=\tfrac{1}{2}\sum_{k<k_c}[(c_k^*-1)(c_k-1)v_k\rho_k^*\rho_k-Nv_k], \tag{5d}$$

$$H_{\text{I}}=\frac{i}{m}\sum_{k<k_c}v_k^{1/2}c_k\mathbf{k}\cdot(\mathbf{p}_i-\tfrac{1}{2}\hbar\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}_i}$$
$$+\tfrac{1}{2}\sum_{k<k_c}v_k^{1/2}[(c_k-1)\rho_k\pi_k^*+\text{c.c.}], \tag{5e}$$

$$H_{\text{II}}=(1/2m)\sum_{\substack{k\neq l\\ k,l<k_c}}\sum_i(v_kv_l)^{1/2}c_kc_l^*\eta_k^*\eta_l\mathbf{k}\cdot\mathbf{l}e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{r}_i}, \tag{5f}$$

$$\omega_p^2=4\pi Ne^2/L^3m.$$

If we set $c_k=1$, for all k, we obtain the Bohm-Pines intermediate Hamiltonian, $H_{\text{inter}}^{\text{BP}}$, as, indeed, we should. We note that H_{inter}, although similar to $H_{\text{inter}}^{\text{BP}}$, has the following new features: (1) The frequency of the oscillators is already k-dependent. (2) The interaction term linear in the field variables, H_{I} is more complicated by the presence of the second term in H_{I}. (3) There is a new term H_{rlr} which we call the residual long-range interaction, and which represents the particle interaction for $k<k_c$. In the Bohm-Pines work features (1) and (3) appear only after their final transformation.

Now choosing $|\psi_0\rangle$ to be the ground-state eigenvector of $T+H_{\text{osc}}$,

$$|\psi_0\rangle=|\psi_p\rangle|\psi_{\text{osc}}\rangle, \tag{6}$$

where $|\psi_p\rangle$ is a Slater determinant of single-electron momentum eigenvectors with minimum kinetic energy

[9] D. Pines, in *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 166.
[10] Reference 9, p. 292.

and $|\psi_{\rm osc}\rangle=\Pi_{k<k_c}|\psi_{\rm osc}{}^k\rangle$, $|\psi_{\rm osc}{}^k\rangle$ being the lowest energy eigenvector of the kth oscillator, we compute $E_0{}^{\rm inter}$. We obtain

$$E_0{}^{\rm inter}=\tfrac{3}{5}E_F+\tfrac{1}{2}\sum_{k<k_c}|c_k|\hbar\omega_p+\tfrac{1}{2}\sum_{k<k_c}[\langle v_k\rho_k{}^*\rho_k\rangle-Nv_k]$$
$$+\tfrac{1}{2}\sum_{k<k_c}[(c_k{}^*-1)(c_k-1)\langle v_k\rho_k{}^*\rho_k\rangle-Nv_k], \quad (7)$$

where

$$\langle v_k\rho_k{}^*\rho_k\rangle=\langle\psi_p|v_k\rho_k{}^*\rho_k|\psi_p\rangle \quad (8)$$
$$=(2e^2/3\pi)(3k_0{}^2/2k-k/8),$$

and k_0 is the Fermi wave vector, given by $k_0{}^3=3\pi^2NL^{-3}$.

We now choose c_k so that $E_0{}^{\rm inter}$ is a minimum. It can easily be seen that the values of c_k that minimize $E_0{}^{\rm inter}$ are

$$c_k=1-\frac{\frac{1}{2}\hbar\omega_p}{\langle v_k\rho_k{}^*\rho_k\rangle}, \quad \text{for} \quad 0\leq k\leq k_c$$
$$=0 \text{ for all other } k, \quad (9)$$

where $k_c=-\alpha+[\alpha^2+12k_0{}^2]^{1/2}$,

$$\alpha=3\pi\hbar\omega_p/e^2. \quad (10)$$

Substituting (8) and (9) into (7), converting the sums into integrals, we can write the correlation energy per particle, at the intermediate stage, after some elementary integrations, as

$$\epsilon_c{}^I=(1/N)(E_0{}^{\rm inter}-E_{\rm HF})$$
$$=\tfrac{1}{4}\hbar\omega_p\beta_c{}^3+(9/4)\frac{\pi\hbar^2\omega_p{}^2}{e^2k_0}\left[\tfrac{1}{2}\beta_c+6\ln\frac{12-\beta_c{}^2}{12}\right]$$
$$-(3e^2k_0/4\pi)[\tfrac{1}{2}\beta_c{}^2-(1/48)\beta_c{}^4], \quad (11)$$

where we have set $\beta_c=k_c/k_0$.

For purposes of comparison, we give here the expression for the correlation energy as computed after the Bohm-Pines intermediate transformation. It is easily obtained by setting $c_k=1$ in Eq. (7) and carrying out the integrations.

$$\epsilon_c{}^{I({\rm BP})}=\tfrac{1}{4}\hbar\omega_p\beta_{cp}{}^3-\frac{3e^2k_0}{4\pi}[\tfrac{1}{2}\beta_{cp}{}^2-(1/48)\beta_{cp}{}^4].$$

Bohm and Pines chose[11] their cutoff momentum β_{cp} by minimizing $\epsilon_c{}^{I({\rm BP})}$ with respect to β_{cp}. One gets

$$\beta_{cp}=2\alpha+(4\alpha^2+12)^{1/2}.$$

In Table I below we give the values of β_c, β_{cp}, $\epsilon_c{}^I$, $\epsilon_c{}^{I({\rm BP})}$, at typical metallic densities, together with the final value of the correlation energy, $\epsilon_c{}^{\rm NP}$ as estimated by Nozières and Pines.[7]

TABLE I. Correlation energy per particle at intermediate stage; the energy is given in Ry.

r_s	β_{cp}	β_c	$\epsilon_c{}^{I({\rm BP})}$	$\epsilon_c{}^I$	Gain	$\epsilon_c{}^{\rm NP}$
2	0.49	0.93	−0.018	−0.035	0.017	−0.093
3	0.59	1.09	−0.018	−0.034	0.016	−0.081
4	0.68	1.23	−0.018	−0.033	0.015	−0.072
5	0.75	1.34	−0.017	−0.032	0.015	−0.067

Thus we see that our simple modification of the Bohm-Pines intermediate transformation results in a gain in energy which is up to 20% of the final value as given by as given by Nozières and Pines.[7]

We shall demonstrate in the Appendix that if we make a small departure $\delta(\eta_k)$ from the linear form of $U(\eta_k)$, and then if we compute the ground-state energy at the intermediate stage, the terms linear in $\delta(\eta_k)$ do not give any contribution, thus showing that our transformation function is an extremum.

III. FINAL TRANSFORMATION

Introducing the creation and destruction operators, $a_k{}^*$ and a_k,

$$\eta_k=(\hbar/2\omega_pc_k)^{1/2}(a_k+a^*{}_{-k}),$$
$$\pi_k=i(\hbar\omega_pc_k/2)^{1/2}(a_k{}^*-a_{-k}),$$

together with their commutation relations which follow from Eqs. (4),

$$[a_k{}^*,a_k]=-\delta_{kk'},$$
$$[a_k{}^*,a_{k'}{}^*]=[a_k,a_{k'}]=0, \quad (12)$$

we can rewrite our Hamiltonian as

$$H_{\rm inter}=H_0+H_{\rm I}+H_{\rm II}+H_{\rm sr}+H_{\rm rlr}, \quad (13)$$

where

$$H_0=T+H_{\rm osc}$$

$$T=\sum_i\frac{p_i{}^2}{2m}, \quad H_{\rm osc}=\tfrac{1}{2}\sum_{k<k_c}\hbar\omega_pc_k(a_k{}^*a_k+a_ka_k{}^*), \quad (13a)$$

$$H_{\rm I}=i\sum_{\substack{k<k_c\\ i}}a_k[d_1\mathbf{k}\cdot(\mathbf{p}_i-\tfrac{1}{2}\hbar\mathbf{k})-d_2]e^{i\mathbf{k}\cdot\mathbf{r}_i}+\text{c.c.}, \quad (13b)$$

$$d_1=\tfrac{1}{2}\hbar v_k{}^{1/2}(c_k{}^{1/2}/m\omega_p),$$
$$d_2=(\tfrac{1}{2}\hbar v_k)^{1/2}(c_k-1)c_k{}^{1/2}\omega_p{}^{1/2}, \quad (13c)$$

and $H_{\rm II}$, $H_{\rm sr}$ and $H_{\rm rlr}$ are given by the Eqs. (5f), (5c), and (5d), respectively.

We adopt the random-phase approximation and neglect $H_{\rm II}$ and then perform a perturbation-theoretic unitary transformation on our intermediate Hamiltonian $H_{\rm inter}$ which eliminates $H_{\rm I}$ [Eq. (13b)] to first order in perturbation theory. The required unitary transformation can be shown to be $V=e^{iS/\hbar}$ where the

[11] In their subsequent papers, Pines and Nozières chose the cutoff momentum from different considerations (see Ref. 7). But since β_{cp} is the cutoff momentum which minimizes $\epsilon_c{}^{I({\rm BP})}$, any other choice of cutoff momentum increases the intermediate energy $\epsilon_c{}^{I({\rm BP})}$.

Hermitian operator S is given by

$$S=\sum_{\substack{k<k_c\\ i}}\frac{[d_1\mathbf{k}\cdot(\mathbf{p}_i-\frac{1}{2}\hbar\mathbf{k})-d_2]e^{i\mathbf{k}\cdot\mathbf{r}_i}}{\omega_p c_k-\mathbf{k}\cdot\mathbf{p}_i/m+\hbar k^2/2m}+\text{c.c.}$$

The old Hamiltonian H_{inter} goes into the new Hamiltonian H_{new}

$$H_{\text{inter}}\rightarrow e^{+is/\hbar}H_{\text{inter}}e^{-is/\hbar}\equiv H_{\text{new}}$$
$$=H_{\text{inter}}+\sum_{n=1}^{\infty}\left(\frac{i}{\hbar}\right)^n\frac{1}{n!}\cdot[H_{\text{inter}},S]_n$$

where $[H_{\text{inter}},S]_n$ is the nth-order commutator.

A direct calculation shows that

$$\frac{i}{\hbar}[H_0,S]=-i\sum_{\substack{k<k_c\\ i}}a_k[d_1\mathbf{k}\cdot(\mathbf{p}_i-1/2\hbar\mathbf{k})-d_2]+\text{c.c.}$$
$$=-H_{\text{I}}.$$

Thus, the first-order commutator of H_0 cancels exactly the zeroth-order commutator of H_{I}. Because of the way the higher order commutators are generated from the first-order commutator, there exists a relationship between the commutators of H_0 and H_1 which can be stated as

$$(H_0+H_1)_{\text{new}}=T+H_{\text{osc}}$$
$$+\sum_{n=1}^{\infty}[H_{\text{I}},S]_n\left(\frac{1}{n!}-\frac{1}{(n+1)!}\right)\left(\frac{1}{\hbar}\right)^n.$$

Retaining only the $n=1$ term, we have

$$H_{\text{new}}=T+H_{\text{osc}}+H_{\text{rp}}+H_{\text{rlr}}+H_a+H_{\text{sr}}, \tag{14}$$

where

$$H_{\text{osc}}'=H_{\text{osc}}+H_{\text{osc}}{}^c, \tag{14a}$$

$$H_{\text{osc}}{}^c=\tfrac{1}{2}\sum\left(\frac{2\pi e^2\hbar}{m\omega_p}\right)c_k\frac{[2(\mathbf{k}\cdot\mathbf{p}_i)/m]\omega_p c_k-(\mathbf{k}\cdot\mathbf{p}_i/m)^2+\hbar^2k^4/4m^2}{(c_k\omega_p-\mathbf{k}\cdot\mathbf{p}_i)^2/m-\hbar^2k^4/4m^2}(a_k{}^*a_k+a_ka_k{}^*), \tag{14b}$$

$$H_{\text{rp}}=-\frac{1}{\hbar}\sum_{\substack{i,j\\ k<k_c}}e^{-i\mathbf{k}\cdot\mathbf{r}_j}\frac{[d_1\mathbf{k}\cdot(\mathbf{p}_i-\frac{1}{2}\hbar\mathbf{k})-d_2][d_1\mathbf{k}\cdot(\mathbf{p}_j-\frac{1}{2}\hbar\mathbf{k})-d_2]e^{i\mathbf{k}\cdot\mathbf{r}_i}}{(\omega_p c_k-\mathbf{k}\cdot\mathbf{p}_j/m-\hbar k^2/2m)}$$
$$+\frac{[d_1\mathbf{k}\cdot(\mathbf{p}_j-\frac{1}{2}\hbar\mathbf{k})-d_2]e^{i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_i)}[d_1\mathbf{k}\cdot(\mathbf{p}_i-\frac{1}{2}\hbar\mathbf{k})d_2]}{(\omega_p c_k-(\mathbf{k}\cdot\mathbf{p}_j/m)+\hbar k^2/2m)}, \tag{14c}$$

$$H_a=-\frac{\hbar^2}{2m}\sum_{\substack{k>k_c\\ i}}\left(\frac{v_k k^2}{\omega_p}\right)\frac{c_k[2\omega_p c_k(\mathbf{k}\cdot\mathbf{p}_i/m)+(\mathbf{k}\cdot\mathbf{p}_i/m)^2-\hbar^2k^4/4m^2]+(c_k-1)^2\omega_p c_k}{(\omega_p c_k+\mathbf{k}\cdot\mathbf{p}_i/m)^2-\hbar^2k^4/4m^2}(a_ka_{-k}+a_{-k}{}^*a_k{}^*), \tag{14d}$$

and T, H_{osc}, H_{sr}, H_{rlr} are given by Eqs. (13a), (5c), and (5d), respectively. We have neglected the effect of the final transformation on H_{sr} and H_{rlr}.

IV. CORRELATION ENERGY

We now compute the correlation energy using the Hamiltonian as given by the Eqs. (14). As one should expect, H_{osc}' is diagonal with respect to eigenfunctions (6). The computation of the first-order correction to the energy with $H_{\text{osc}}{}^c+H_{\text{rp}}+H_a$ as a perturbation is entirely equivalent to computation of the second-order perturbation correction with H_{I} as a perturbation, together with the random-phase approximation.

The correction arising from $H_{\text{osc}}{}^c$ is $\langle\psi|H_{\text{osc}}{}^c|\psi\rangle$,

$$\langle\psi|H_{\text{osc}}{}^c|\psi\rangle=\sum_{k<k_c}\langle\psi|H_{\text{osc}}{}^c(k)|\psi\rangle,$$

with

$$\langle\psi|H_{\text{osc}}{}^c(k)|\psi\rangle=\frac{2\pi\hbar e^2}{m\omega_p}c_k\sum_i\frac{2(\mathbf{k}\cdot\mathbf{p}_i/m)\omega_p c_k-(\mathbf{k}\cdot\mathbf{p}_i/m)^2+\hbar^2k^4/4m^2+(1-c_k{}^2)\omega_p{}^2}{(\omega_p c_k-\mathbf{k}\cdot\mathbf{p}_i/m)^2-\hbar^2k^4/4m^2}.$$

Changing the sums to integrals, and carrying out the integrations, we obtain

$$\langle\psi|H_{\text{osc}}{}^c(k)|\psi\rangle=\tfrac{1}{4}\hbar\omega_p c_k-\frac{e^2m\omega_p k_0}{2\pi\hbar k^2}c_k+\frac{e^2m^3\omega_p}{4\pi\hbar^3k^5}c_k\left\{\left[\left(c_k\omega_p-\frac{\hbar k^2}{2m}\right)^2-\left(\frac{\hbar k_0k}{m}\right)^2\ln\frac{\omega_p c_k-\hbar k_0k/m-\hbar k^2/2m}{\omega_p c_k+\hbar k_0k/m-\hbar k^2/2m}\right]\right.$$
$$\left.+\left[\left(\omega_p c_k+\frac{\hbar k^2}{2m}\right)^2-\left(\frac{\hbar k_0k}{m}\right)^2\right]\times\ln\frac{\omega_p c_k+\hbar k_0k/m+\hbar k^2/2m}{\omega_p c_k-\hbar k_0k/m+\hbar k^2/2m}\right\}.$$

Similarly, we obtain the correction arising from $H_{\rm rp}$,

$$\langle\psi|H_{\rm rp}|\psi\rangle=\sum_{k<k_c}\langle\psi|H_{\rm rp}{}^k|\psi\rangle,$$

where $\langle\psi|H_{\rm rp}{}^k|\psi\rangle$, after elementary integrations, is given by

$$\langle\psi|H_{\rm rp}(k)|\psi\rangle=-\frac{1}{2\hbar}\Bigg\{-\frac{e^2m^2\omega_p{}^2}{2\pi\hbar^2k^3}c_k{}^2-\frac{e^2p_F{}^2}{2\pi\hbar^2k}c_k{}^2+\frac{e^2p_F{}^2}{\pi\hbar^2k}c_k-\frac{e^2k}{12\pi}c_k+\frac{1}{24}\frac{e^2k}{\pi}c_k{}^2$$

$$-\frac{e^2m^2}{4\pi\hbar^3}\frac{\omega_p}{k^5}c_k\left[\left(\omega_pc_k-\frac{\hbar k^2}{2m}\right)^2-\left(\frac{kp_F}{m}\right)^2\right]\ln\frac{[\omega_pc_k-\hbar k^2/2m-kp_F/m][\omega_pc_k-\hbar k^2/2m+kp_F/m]}{\omega_p{}^2c_k{}^2}$$

$$+\left[\left(\omega_pc_k+\frac{\hbar k^2}{2m}\right)^2-\left(\frac{kp_F}{m}\right)^2\right]\ln\frac{\omega_p{}^2c_k{}^2}{(\omega_pc_k+\hbar k^2/2m+kp_F/m)(\omega_pc_k+\hbar k^2/2m-kp_F/m)}.$$

Then

$$\langle\psi|H_{\rm rp}(k)+H_{\rm osc}{}^c(k)|\psi\rangle=-\tfrac{1}{4}\hbar\omega_pc_k-\frac{e^2m\omega_pp_F}{2\pi\hbar^2k^2}c_k-\frac{e^2p_F{}^2c_k}{2\pi\hbar^2k}-\frac{e^2kc_k}{12\pi}+\frac{e^2p_F{}^2c_k}{\pi\hbar^2k}+\frac{e^2kc_k{}^2}{24\pi}-\frac{e^2m^2\omega_p{}^2c_k{}^2}{2\pi\hbar^2k^3}+\frac{e^2m^3\omega_pc_k}{4\pi\hbar^3k^5}$$

$$\times\left[\left(\omega_pc_k-\frac{\hbar k^2}{2m}\right)^2-\left(\frac{kp_F}{m}\right)^2\right]\ln\frac{\omega_pc_k}{\omega_pc_k-\hbar k^2/2m+kp_F/m}+\left[\left(\omega_pc_k+\frac{\hbar k^2}{2m}\right)^2-\left(\frac{kp_F}{m}\right)^2\right]\ln\frac{\omega_pc_k+\hbar k^2/2m+kp_F/m}{\omega_pc_k}\Bigg\}.$$

The correction per particle due to $H_{\rm osc}{}^c$ and $H_{\rm rp}$ can then be written as

$$\begin{aligned}\epsilon^1&=\frac{1}{N}\langle\psi|H_{\rm osc}{}^c+H_{\rm rp}|\psi\rangle\\&=\frac{1}{2\pi^2n}\int_0^{k_c}k^2dk\langle\psi|H_{\rm osc}{}^c(k)+{\rm H}_{\rm rp}(k)|\psi\rangle.\end{aligned}\tag{15}$$

This integration can be carried out numerically.

We next compute the second-order perturbation theory correction $\epsilon_{\rm sr}$ arising from $H_{\rm sr}$ [Eq. (5c)]. It can be seen to be

$$\epsilon_{\rm sr}=\epsilon_{\rm sr}{}^a+\epsilon_{\rm sr}{}^p,\tag{16}$$

where $\epsilon_{\rm sr}{}^a$, the correction for electrons with antiparallel spin and $\epsilon_{\rm sr}{}^p$ for electrons with parallel spin, are given by

$$\epsilon_{\rm sr}{}^a=\frac{1}{8\pi^3}\int_{\beta>\beta_c}d^3\beta J_a(\beta),\tag{16a}$$

$$\epsilon_{\rm sr}{}^p=\frac{1}{8\pi^3}\int_{\beta>\beta'}d^3\beta J_p(\beta),\tag{16b}$$

with

$$J_a(\beta)=-\frac{3}{2\pi^2}\frac{1}{\beta^4}\int_{\substack{|p_1|<1\\|\mathbf{p}_1+\boldsymbol{\beta}|>1}}d^3p_1\int_{\substack{|p_2|<1\\|\mathbf{p}_2+\boldsymbol{\beta}|>1}}d^3p_2\frac{1}{\beta^2+\boldsymbol{\beta}\cdot(\mathbf{p}_1+\mathbf{p}_2)}$$

and

$$J_p(\beta)=-\frac{3}{2\pi^2}\int_{\substack{|\mathbf{p}_1|<1\\|\mathbf{p}_1+\boldsymbol{\beta}|>1}}d^3p_1\int_{\substack{|p_2|<1\\|\mathbf{p}_2+\boldsymbol{\beta}|>1}}d^3p_2\left\{\frac{1}{\beta^4}-\frac{1}{\beta^2(\boldsymbol{\beta}+\mathbf{p}_1+\mathbf{p}_2)^2}\right\}.$$

($\mathbf{p}_1$, $\mathbf{p}_2$ are electron momenta measured in the units of Fermi momentum.)

Nozières and Pines[7] have argued that the contribution $\epsilon_{\rm sr}{}^p$ from the electrons with parallel spin is small. We have not shown that it will be small for our choice of cutoff momentum but we believe it is negligible; in any case the correction will be negative and will lead to further lowering of the ground-state energy. From here on we neglect this contribution.

For $\beta>2$, with $|p_1|$, $|p_2|<1$, the restrictions $|\mathbf{p}_1+\boldsymbol{\beta}|>1$ and $|\mathbf{p}_2+\boldsymbol{\beta}|>1$, are automatically satisfied. Furthermore, for $\beta>2$, $\boldsymbol{\beta}\cdot(\mathbf{p}_1+\mathbf{p}_2)/\beta^2<1$ and therefore we can write, for $\beta>2$,

$$J_a^{\text{out}}(\beta)=-\frac{3}{\pi^2}\sum_{n=0}^{\infty}\sum_{r=0}^{n}(-1)^n\beta^{-n-3n}C_r\int d^3p_1\int d^3p_2[(\boldsymbol{\beta}\cdot\mathbf{p}_1)^{n-r}(\boldsymbol{\beta}\cdot\mathbf{p}_2)^r]$$

(^nC_r are the coefficients in the binomial expansion)

$$=-48\sum_{m=0}^{\infty}\sum_{s=0}^{2m}\beta^{-2m-2}\frac{(2m)!}{(2s+3)(2s+1)!(2m-2s+3)(2m-2s+1)!}\quad\text{for}\quad\beta>2. \tag{17}$$

For $\beta<2$, on carrying out the integrations we obtain,

$$J_a^{\text{in}}(\beta)=-\frac{3}{2\beta^4}\Big[-\frac{1}{20}\beta^3+\frac{29}{15}\beta+\Big(\frac{-8}{3}\beta-\frac{32}{15}\frac{1}{\beta}\Big)\ln 2+\Big(-1+\frac{1}{6}\beta^2-\frac{1}{80}\beta^4+\frac{16}{15}\frac{1}{\beta}\Big)$$
$$\times\ln(2-\beta)+\Big(1-\frac{1}{6}\beta^2+\frac{1}{80}\beta^4+\frac{16}{15}\frac{1}{\beta}\Big)\ln(2+\beta)\Big]\quad\text{for}\quad\beta<2. \tag{18}$$

Substituting (17) and (18) in (16) we obtain

$$\epsilon_{\text{sr}}=\frac{1}{2\pi^2}\int_{\beta>2}\beta^2d\beta J_a^{\text{out}}(\beta)+\frac{1}{2\pi^2}\int_{\beta'<\beta<2}\beta^2d\beta J_a^{\text{in}}(\beta)$$

$$\epsilon_{\text{sr}}=\frac{-12}{\pi^2}\sum_{n=1}^{\infty}\frac{(2n-2)}{(2n+1)}\sum_{l=1}^{n}\frac{1}{2^{2n+1}}\frac{1}{(2l-1)!(2l+1)(2n-2l+1)!(2n-2l+3)}$$
$$-\frac{3}{4\pi^2}\Big[\Big(\frac{-4}{15}-\frac{8}{3}\ln 2\Big)\ln 2-\frac{1}{15}+\frac{1}{60}\beta_c^2-\frac{8}{3}(1-\ln 2)\ln\beta_c-\frac{16}{15}\frac{1}{\beta_c^2}\ln 2$$
$$+\Big(\frac{1}{240}\beta_c^2-\frac{1}{6}\beta_c-\frac{1}{\beta_c}+\frac{8}{15}\frac{1}{\beta_c^2}+\frac{2}{3}\Big)\ln(2-\beta_c)+\Big(-\frac{1}{240}\beta_c^3+\frac{1}{6}\beta_c+\frac{1}{\beta_c}+\frac{8}{15}\frac{1}{\beta_c^2}+\frac{2}{3}\Big)\ln(2+\beta_c)\Big]\text{Ry}.$$

The first term in the above expression can be evaluated numerically.

Finally we evaluate the correction which arises from H_{rp} and H_{rlr} in second and higher order perturbation theory, ϵ_2, by the Gell-Mann–Breuckner selective summation method. In principle this can be done exactly but the computations become unmanageable. We are, therefore, forced to resort to an approximation.

Our approximation consists in making a series expansion in powers of k of the coefficients c_k

$$c_k=1-\frac{6\pi\hbar\omega_p}{e^2k_0}\frac{(k/k_0)}{12-(k/k_0)^2},$$
$$c_k=1-\frac{\pi\hbar\omega_p}{2e^2k_0}\Big(\frac{k}{k_0}\Big)\Big(1-\frac{(k/k_0)^2}{12}+\cdots\Big).$$

From Table I, we see that the series converges quite rapidly for the values of β at metallic densities. Retaining only the term linear in β, we have

$$c_k\simeq 1-\frac{\hbar\omega_p}{2e^2k_0}\frac{k}{k_0}=1-\gamma\frac{k}{k_0},$$

where

$$\gamma=2e^2k_0/\pi\hbar\omega_p.$$

Using this approximate value of c_k, one can write H_{rp}, expanding the denominator in powers of k and retaining the lowest order term in k, as

$$H_{\text{rp}}\simeq-\frac{2\pi e^2}{m^2\omega_p^2}\sum_{k<k_c,i\neq j}\frac{(\mathbf{k}\cdot\mathbf{p}_i)(\mathbf{k}\cdot\mathbf{p}_j)}{k^2}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}-\frac{2\pi e^2}{\gamma^2}\sum_{k<k_c,i\neq j}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)},$$

and in the same approximation,

$$H_{\rm rlr}\simeq\frac{2\pi e^2}{\gamma^2}\sum_{k<k_c,i\neq j}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}.$$

Thus

$$H_{\rm rp}+H_{\rm rlr}\simeq-\frac{2\pi e^2}{m^2\omega_p{}^2}\sum_{k<k_c,i\neq j}\frac{1}{k^2}(\mathbf{k}\cdot\mathbf{p}_i)(\mathbf{k}\cdot\mathbf{p}_j)e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}.$$

We can now write ϵ_2 as (see the Appendix of Ref. 7)

$$\epsilon_2=-\frac{3}{4\pi\alpha^2r_s{}^2}\int_0^{\beta_c}d\beta\beta^3\int_{-\infty}^{\infty}du\sum_{n=2}^{\infty}\frac{(-1)^n}{n}[Q_\beta(u)]^n\mathrm{Ry}, \tag{19}$$

where

$$Q_\beta(u)=\frac{-3}{4\pi}\int_{\substack{|\mathbf{p}|<1\\|\mathbf{p}+\boldsymbol{\beta}|>1}}d^3p\frac{(\boldsymbol{\beta}\cdot\mathbf{p})}{\beta^2}\int_{-\infty}^{\infty}dt\exp[itu\beta-|t|(\boldsymbol{\beta}\cdot\mathbf{p}+\tfrac{1}{2}\beta^2)]=-1+\tfrac{3}{2}\beta-\tfrac{3}{8}\beta^2-\tfrac{1}{8}\beta^3+\tfrac{3}{2}u^2+\tfrac{3}{2}\beta u^2$$

$$+(-3u^3+\tfrac{3}{4}\beta^2u)\arctan\frac{(1+\frac{1}{2}\beta)}{u}-\tfrac{3}{2}u\left[\arctan\frac{1+\frac{1}{2}\beta}{u}-\arctan\frac{(1-\frac{1}{2}\beta)}{u}\right]-\tfrac{3}{2}\beta u^2\ln\left[1+\frac{(1-\frac{1}{2}\beta)^2}{u^2}\right]$$

$$+\left[-\frac{3\beta}{16}+\frac{3}{4}\frac{u^2}{\beta}+\frac{3}{4}\frac{u^4}{\beta}+\frac{3}{64}\beta^3-\frac{9}{8}\beta u^2\right]\ln\frac{(1+\frac{1}{2}\beta)^2/u^2+1}{(1-\frac{1}{2}\beta)^2/u^2+1}.$$

{It is readily verified that the above expression for $Q_\beta(u)$ reduces to that of Nozières and Pines [Eq. (A7) of Ref. 7] for small β.}

Summing the series in (19), we obtain

$$\epsilon_2=-\frac{3}{4\pi\alpha^2r_s{}^2}\int_0^{\beta_c}d\beta\beta^3\int_{-\infty}^{\infty}du\{\ln[1+Q_\beta(u)]-Q_\beta(u)\}\mathrm{Ry}.$$

The above integrations can be carried out numerically.

In Table II, we list the numerical values of the various corrections at metallic densities. In Table III we give the final value of the correlation energy per particle $\epsilon_c=\epsilon_{\rm inter}+\epsilon_1+\epsilon_{\rm sr}+\epsilon_2$, as computed by us, together with the results as obtained by Nozières and Pines,[7] Hubbard,[8] and Carr and Maradudin.[3]

TABLE II. Numerical values of the corrections in Ry.

r_s	ϵ_1	$\epsilon_{\rm sr}$	ϵ_2
2	−0.004	−0.035	−0.036
3	−0.004	−0.027	−0.029
4	−0.004	−0.022	−0.027
5	−0.004	−0.020	−0.025

TABLE III. Comparison of the correlation energy by various estimates. The energies are in Ry units.

	r_s			
ϵ_c	2	3	4	5
Present	−0.106	−0.094	−0.086	−0.081
a	−0.093	−0.081	−0.072	−0.065
b	−0.099	−0.086	−0.074	−0.067
c	−0.096	−0.076	−0.064	−0.054

[a] P. Nozières and D. Pines, Phys. Rev. 111, 242 (1958).
[b] J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1958).
[c] W. J. Carr and A. A. Maradudin, Phys. Rev. 133, A374 (1964).

V. SUMMARY

We see from the Table III that our value of the correlation energy, at metallic densities, is up to 20% lower than that of the previous investigators. Thus, almost all of the gain in energy at the intermediate stage over the Bohm-Pines–Nozière's intermediate value of the energy is preserved through the final transformation. The gain arises from the use of the variational principle at the intermediate stage to find the "best" intermediate transformation. It is shown in the appendix that our intermediate transformation function

$$U=\sum_{k<k_c}v_k{}^{1/2}c_k\eta_k\rho_k$$

with c_k given by Eqs. (9) is an extremum.

We have obtained an upper (lower) limit to the ground-state (correlation) energy within the accuracy of the perturbation-theory calculation together with the random-phase approximation. The over-all accuracy of the results obtained by the above procedure has been discussed in great detail by Pines and Nozières[7] and is estimated to be 15%.

The validity of our result for the ground-state energy of an electron gas rests on the assumption that the ground-state energy of the extended system is greater than or equal to the ground-state energy of the actual physical system. As has been pointed out before, this assumption holds within the random-phase approximation which leads to the exact answer for the ground-state energy in the high-density limit. Furthermore Bohm, Huang, and Pines[12] have given physical arguments in support of the aforementioned assumption, which make it plausible.

APPENDIX

We wish to show in this Appendix that the intermediate transformation $e^{iU/\hbar}$, with $U=\sum_{k<k_c} v_k^{1/2} c_k \eta_k \rho_k$ with c_k given by Eqs. (8) and (9), is an extremum, i.e., if we make a small departure $\delta_k(\eta)$ from the linear form of the function U of η_k, i.e.,

$$U'=\sum_{k<k_c} v_k^{1/2}[c_k\eta_k+\delta_k(\eta)]\rho_k,$$

then the corrections to the ground-state energy are of the second order in δ_k.

The new intermediate Hamiltonian H'_{inter},

$$H_{\text{inter}}'=e^{iU'/\hbar}H_{\text{ext}}e^{-iU'/\hbar},$$

can be obtained as before using the commutation relations (4). We get

$$\begin{aligned}
H_{\text{inter}}'=&\sum_i \frac{p_i^2}{2m}+\tfrac{1}{2}\sum_{k<k_c}[\pi_k^*\pi_k+(c_k\omega_p)^2\eta_k^*\eta_k]+(i/m)\sum_{k<k_c} v_k^{1/2}(c_k\eta_k+\delta_k)\mathbf{k}\cdot(\mathbf{p}_i-\tfrac{1}{2}\hbar\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}_i}\\
&+\tfrac{1}{2}\sum_{k<k_c}(c_k-1)v_k^{1/2}[\pi_k^*\rho_k+\rho_k^*\pi_k]+(1/2\hbar)\sum_{k<k_c}(c_k-1)v_k\rho_k^*\rho_k[\pi_k\delta_k-\delta_k\pi_k]\\
&+(i/2\hbar)\sum_{k<k_c}(c_k-1)v_k\rho_k^*\rho_k[\pi_k^*\delta_k^*-\delta_k^*\pi_k^*]+(i/2\hbar)\sum_{\substack{l,k,<k_c\\ l\neq k}}(c_k-1)(v_kv_l)^{1/2}\rho_k^*\rho_l[\pi_k\delta_l-\delta_k\pi_l]\\
&+(i/2\hbar)\sum_{\substack{l,k<k_c\\ l\neq k}}(c_k-1)(v_kv_l)^{1/2}\rho_k^*\rho_l[\pi_k^*\delta_l^*-\delta_l^*\pi_k^*]+\tfrac{1}{2}\hbar^2\sum_{k<k_c}c_k\omega_p^2(\eta_k\delta_k^*+\delta_k\eta_k^*)\\
&+\tfrac{1}{2}\sum_{k<k_c}[(c_k-1)^2v_k\rho_k^*\rho_k-Nv_k]+(\hbar^2/2m)\sum_{\substack{k\neq l\\ k,l<k_c}}\sum_i(v_kv_c)^{1/2}|c_k|^2\eta_k\eta_l^*\mathbf{k}\cdot\mathbf{l}e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{r}_i}\\
&+\tfrac{1}{2}\sum_{k<k_c}[v_k\rho_k^*\rho_k-Nv_k]+O(\delta_k\delta_{k'}).
\end{aligned}$$

Taking the expectation value of H_{inter}' with $|\psi_0\rangle$ [Eq. (6)], we obtain

$$(E_0^{\text{inter}})_{\text{new}}=E_0^{\text{inter}}+O(\delta_k\delta_{k'}).$$

Thus, corrections to the ground-state energy because of a small variation δ from the transformation function U are of the second order in δ. The transformation function U is therefore an extremum.

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[12] D. Bohm, K. Huang, and D. Pines, Phys. Rev. **107**, 71 (1957).