

Ground-State Energy of a High-Density Electron Gas

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The terms of $O(r_s \ln r_s)$ and $O(r_s)$ in the expansion of the ground-state energy of the high-density electron gas are studied in this paper. The value of the coefficient of $r_s \ln r_s$ is evaluated, and it is found to differ from the value obtained by DuBois. The result of the present calculation for the energy per electron is

$$E = 2.21r_s^{-2} - 0.916r_s^{-1} + 0.0622 \ln r_s - 0.096 + 0.018r_s \ln r_s + (E_3' - 0.036)r_s + O(r_s^2 \ln r_s),$$

where E_3' is a sum of twelve dimensional integrals. Although E_3' has not been evaluated it is shown with the aid of the virial theorem that no reasonable value of E_3' can make the series expansion rapidly convergent beyond $r_s \sim 1$. Under the rather arbitrary assumption that $E_3'r_s$ as well as higher order terms can be neglected below $r_s = 1$, an interpolation between the present result and the low-density expansion is carried out, and values of the correlation energy in the region of metallic densities are estimated.

FOR a large number of electrons moving in a fixed uniform distribution of positive charge, expansions exist for the exact ground-state energy in the limits of both high and low density. The principal assumption in these calculations is that the particular perturbation series converge. A considerable importance is attached to the question of whether these series contain physical meaning at intermediate densities, and to the possibility that the two expansions might cover the complete range. There is particular interest in knowing if the expansion for the high-density case, which resembles a metal, holds in the range of actual metallic densities, i.e., for r_s between 2 and 5, where r_s is, in Bohr units, the radius of the equivalent sphere which each electron occupies.

In low densities the electrons crystallize into a lattice¹ and therefore have the electrical properties of an insulator.² Thus, an additional question arises, which was investigated by Mott³ in a qualitative way, concerning the transition from metallic to nonmetallic behavior.⁴

In a previous series of calculations⁵⁻⁷ the problem of the low-density electron gas has been treated in some detail^{7a}; in particular, it appears that the expression obtained may be valid down to the neighborhood of r_s equal to eight or nine, and an estimate of the next term in the expansion gives a reasonable result down to an r_s of about six. Because of this result it seems profitable

to carry the high-density calculation one step further, which means evaluating the r_s and $r_s \ln r_s$ terms. The $r_s \ln r_s$ term has in fact already been evaluated by Du Bois.⁸ We obtain a considerably different result however, and have uncovered a number of errors in the original calculation (which may not seem too surprising considering the length and tedious nature of the problem).

We shall review the calculation along the lines originally developed by Gell-Mann and Brueckner.⁹ The kinetic energy operator T is the unperturbed Hamiltonian and V , the total Coulomb interaction, is the perturbing part.

Up through second order in the Rayleigh-Schrödinger perturbation series the energy terms are known, the result in Rydberg units being

$$E_0 = \epsilon_0 = 2.21Nr_s^{-2}, \quad (1)$$

$$E_1 = V_{00} = -0.916Nr_s^{-1}, \quad (2)$$

$$E_2 = \sum_{j \neq 0} \frac{V_{0j}V_{j0}}{\epsilon_0 - \epsilon_j} = E_{24} + (0.046 \pm 0.002)N, \quad (3)$$

where

$$E_{24} = \frac{-3N}{8\pi^5} \int \frac{dq}{q^4} \int d\mathbf{p}_1 \int d\mathbf{p}_2 \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2)}, \quad (4)$$

where the region of integration is

$$p_1 < 1, \quad p_2 < 1, \quad |\mathbf{p}_1 + \mathbf{q}| > 1, \quad |\mathbf{p}_2 + \mathbf{q}| > 1,$$

and where N is the number of electrons, ϵ the unperturbed energy, \mathbf{q} a momentum transfer between electrons, and \mathbf{p} a momentum within the Fermi sphere. The subscript zero indicates the unperturbed ground-state wave function and j indicates an unperturbed excited state, each state being a Slater determinant of plane waves. The value of the second, or exchange term, in (3) is the result of the computation of Marcum and Kahn, given by Gell-Mann and Brueckner.⁹

⁸ D. F. Du Bois, *Ann. Phys. (N.Y.)* **7**, 174 (1959).

⁹ M. Gell-Mann and K. A. Brueckner, *Phys. Rev.* **106**, 364 (1957).

¹ E. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).

² More precisely, they would have these properties if small irregularities were placed in the positive charge to break up the translational degeneracy.

³ N. F. Mott, *Phil. Mag.* **6**, 287 (1961).

⁴ Some authors have speculated that a transition occurs at low density from a lattice to a "liquid" arrangement in analogy to the melting of a solid. Since a solid melts largely because of entropy considerations, and only the ground-state energy is involved here, the analogy is not a close one, however. Nevertheless, the possibility remains that other transitions might occur within the metallic or nonmetallic range.

⁵ W. J. Carr, Jr., *Phys. Rev.* **122**, 1437 (1961).

⁶ R. Coldwell-Horsfall and A. A. Maradudin, *J. Math. Phys.* **1**, 395 (1960).

⁷ W. J. Carr, Jr., Rosemary A. Coldwell-Horsfall, and A. E. Fein, *Phys. Rev.* **124**, 747 (1961).

^{7a} Note added in proof. Some recent work on the low-density gas has been done by F. W. de Wette, Dept. of Physics, University of Illinois and Argonne National Laboratories (private communication).

The third-order expression for the energy may be written as

$$E_3 = \sum_{i \neq 0} \sum_{j \neq 0} \frac{V_{0i}(V - V_{00})_{ij} V_{j0}}{(\epsilon_0 - \epsilon_i)(\epsilon_0 - \epsilon_j)}. \quad (5)$$

After a rather lengthy calculation we have reduced (5) to the following expressions:

$$E_3 = E_{36} + E_{34} + E_{3'}, \quad (6)$$

where

$$E_{36} = \frac{3 \alpha r_s N}{4 \pi^7} \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{q}}{q^6} \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2))} \times \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_3))}, \quad (7)$$

and where the region of integration is: $|\mathbf{p}_i + \mathbf{q}| > 1$, $|\mathbf{p}_i| < 1$.

$$E_{34} = \frac{-3 \alpha r_s N}{8 \pi^7} \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{q}}{q^4 |\mathbf{p}_1 - \mathbf{p}_2|^2} \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_3))} \frac{3 \alpha r_s N}{4 \pi^7} \times \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{q}}{q^4 |\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{q}|^2} \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2))} \frac{3 \alpha r_s N}{8 \pi^7} \times \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{q}}{q^4} \left[\frac{1}{|\mathbf{p}_1 - \mathbf{p}_2|^2} - \frac{1}{|\mathbf{p}_1 - \mathbf{p}_2 + \mathbf{q}|^2} \right] \times \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_3))^2}, \quad (8)$$

where the regions of integration are $|\mathbf{p}_i| < 1$ and $|\mathbf{p}_i + \mathbf{q}| > 1$ for the first two integrals and $|\mathbf{p}_i| < 1$, $|\mathbf{p}_1 + \mathbf{q}| > 1$, $|\mathbf{p}_3 + \mathbf{q}| > 1$, for the last one. And

$$E_{3'} = \frac{3 \alpha r_s N}{32 \pi^7} \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{q}_1 d\mathbf{q}_2}{q_1^2 q_2^2} \left[\frac{2}{|\mathbf{q}_1 - \mathbf{q}_2|^2} - \frac{1}{|\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{q}_1 + \mathbf{q}_2|^2} \right] \frac{1}{(q_1^2 + \mathbf{q}_1 \cdot (\mathbf{p}_1 + \mathbf{p}_2))} \frac{1}{(q_2^2 + \mathbf{q}_2 \cdot (\mathbf{p}_1 + \mathbf{p}_2))} - \frac{3 \alpha r_s N}{16 \pi^7} \int \frac{d\mathbf{p}_1 d\mathbf{q}_2 d\mathbf{q}_1 d\mathbf{q}_2}{q_1^2 q_2^2} \left[\frac{2}{|\mathbf{q}_1 - \mathbf{q}_2|^2} - \frac{1}{|\mathbf{p}_1 - \mathbf{p}_2|^2} \right] \times \frac{1}{\mathbf{q}_1 \cdot (\mathbf{p}_2 - \mathbf{p}_1) \mathbf{q}_2 \cdot (\mathbf{p}_2 - \mathbf{p}_1)} + \frac{3 \alpha r_s N}{8 \pi^7} \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{q}}{q^2 |\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{q}|^2} \frac{1}{|\mathbf{p}_2 - \mathbf{p}_3|^2} \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2))} \times \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_3))} + \frac{3 \alpha r_s N}{16 \pi^7} \int \frac{d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{q}}{q^2 |\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{q}|^2} \left[\frac{1}{|\mathbf{p}_1 - \mathbf{p}_3 + \mathbf{q}|^2} - \frac{1}{|\mathbf{p}_1 - \mathbf{p}_3|^2} \right] \times \frac{1}{(q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2))^2}; \quad (9)$$

where the first integral is the sum of two parts, one over the region: $|\mathbf{p}_1 + \mathbf{q}_1| > 1$, $|\mathbf{p}_1 + \mathbf{q}_2| > 1$, $|\mathbf{p}_1| < 1$; $|\mathbf{p}_2 + \mathbf{q}_1| > 1$, $|\mathbf{p}_2 + \mathbf{q}_2| > 1$, $|\mathbf{p}_2| < 1$; the second over the region with the opposite inequalities; the next integral is over the region: $|\mathbf{p}_1 + \mathbf{q}_1| > 1$, $|\mathbf{p}_1 + \mathbf{q}_2| > 1$, $|\mathbf{p}_1| < 1$, $|\mathbf{p}_2 + \mathbf{q}_1| < 1$, $|\mathbf{p}_2 + \mathbf{q}_2| < 1$, $|\mathbf{p}_2| > 1$; the next to last over: $|\mathbf{p}_i + \mathbf{q}| > 1$, $|\mathbf{p}_i| < 1$; and the final one over $|\mathbf{p}_1 + \mathbf{q}| > 1$, $|\mathbf{p}_2 + \mathbf{q}| > 1$, $|\mathbf{p}_i| < 1$.

The perturbation expansion is one in increasing powers of r_s ; however, as is well known, the expression E_{24} is a divergent integral as are E_{36} , E_{34} , and corresponding terms in higher orders. To circumvent these infinities, the series must be reordered, as first pointed out by Macke¹⁰ and done in a precise manner by Gell-Mann and Brueckner.⁹ The sum $E_{24} + E_{36} + E_{34} + \dots$, which contains the most divergent integrals in each order, represents a well-behaved function of q and is given in Ref. 9. In the notation of these authors the

energy per electron coming from this sum is

$$\epsilon' = \frac{-3(\alpha r_s)^{-2}}{16\pi^2} \int q d\mathbf{q} \int_{-\infty}^{\infty} d\mu \times \left[\frac{\alpha r_s}{\pi^2 q^2} Q_q(\mu) - \ln \left(1 + \frac{\alpha r_s}{\pi^2 q^2} Q_q(\mu) \right) \right], \quad (10)$$

where $\alpha = (4/9\pi)^{1/3}$ and $Q_q(\mu)$ is a function defined by a fourfold integration as given in Eq. (18) of the same reference. After performing the integration we obtain

$$Q_q(\mu) = 2\pi \left\{ \frac{1}{2q} \left[1 + \mu^2 - \frac{1}{4} q^2 \right] \ln \frac{(1 + \frac{1}{2} q)^2 + \mu^2}{(1 - \frac{1}{2} q)^2 + \mu^2} + 1 - \mu \tan^{-1} \frac{1 + \frac{1}{2} q}{\mu} + \mu \tan^{-1} \frac{\frac{1}{2} q - 1}{\mu} \right\}. \quad (11)$$

¹⁰ W. Macke, Z. Naturforsch. 5a, 192 (1950).

As $q \rightarrow 0$ it may be readily established that

$$Q_q(\mu) = 4\pi R(\mu) + q^2 R_1(\mu) + 0(q^4), \quad (12)$$

with the definitions

$$R(\mu) = 1 - \mu \tan^{-1} 1/\mu \quad (13)$$

and

$$R_1(\mu) = -\frac{\pi}{3(1+\mu^2)^2}. \quad (14)$$

With (11) and (10) an expansion may be obtained for ϵ' in powers of r_s and in powers of r_s multiplied by $\ln r_s$, although some care is required in doing so to avoid divergent integrals. We obtain, using the previous evaluation of Gell-Mann and Brueckner for the first two terms,

$$\epsilon' = 0.0622 \ln r_s - 0.142 + r_s (A_{11} \ln r_s + C_{11}) + 0(r_s^2, r_s^2 \ln r_s), \quad (15)$$

where

$$A_{11} = \frac{-6\alpha}{\pi^5} \int_{-\infty}^{\infty} d\mu R^2(\mu) R_1(\mu) = 0.0054, \quad (16)$$

and¹¹

$$C_{11} = \frac{-8\alpha}{\pi^4} \int_{-\infty}^{\infty} d\mu R^3(\mu) - \frac{6\alpha}{\pi^5} \int_{-\infty}^{\infty} d\mu R^2(\mu) R_1(\mu) \ln \frac{4\alpha R(\mu)}{\pi} + \frac{\alpha}{4\pi^7} \int_{-\infty}^{\infty} d\mu \int_1^{\infty} \frac{dq}{q^3} Q_q^3(\mu) + \frac{\alpha}{4\pi^7} \int_{-\infty}^{\infty} d\mu \int_0^1 \frac{dq}{q^3} \times [Q_q^3(\mu) - (4\pi R(\mu))^3 - 3q^2 R_1(\mu) (4\pi R(\mu))^2]. \quad (17)$$

Numerical evaluation of the terms in (17) lead finally to

$$C_{11} = -0.018 - 0.0042 + 0.0072 - 0(10^{-4}) = -0.015. \quad (18)$$

SUMMATION OF THE NEXT MOST DIVERGENT TERMS

The next logical step in this approach is to sum the terms of next highest divergence in the perturbation series. We denote this sum, $E_{34} + \dots$ by $N\epsilon''$. According to Du Bois' results [his Eq. (C16)] an approximation for ϵ'' sufficient for obtaining the exact r_s and $r_s \ln r_s$ terms is given by¹²

¹¹ Du Bois obtains the expression

$$C_{11} = \delta_1 + \frac{6\alpha}{\pi^5} \int_{-\infty}^{\infty} d\mu R^2 R_1 \ln R + \frac{6\alpha_1}{\pi^5} \ln \frac{4\alpha}{\pi} + \frac{2\alpha}{\pi^4} \int_{-\infty}^{\infty} d\mu R^3$$

with

$$\delta_1 = (4\pi)^{-2} \frac{\alpha}{\pi^6} \int_{-\infty}^{\infty} d\mu \int_0^1 \frac{dq}{q^2} [Q_q^3 - (4\pi R)^3 - 3R_1 (4\pi R)^2] + \frac{\alpha}{\pi^6} \int_{-\infty}^{\infty} d\mu \int_1^{\infty} \frac{dq}{q^3} Q_q^3.$$

This expression is similar in form to ours but differs in sign, numerical factors, and a power of q^2 in one term (probably a misprint). Du Bois' expression for A_{11} and his value of R_1 also differ from ours, but the discrepancy here is obviously due to misprint since his numerical results for A_{11} are in approximate agreement with ours.

¹² More correctly, we have taken Du Bois' result with opposite sign.

$$\epsilon'' = \frac{-9}{16\pi^6} \frac{1}{r_s^2} \int_0^{r_s} dr_s' r_s' \int_{-\infty}^{\infty} d\mu \times \int \frac{d\mathbf{q}}{q} \frac{Q_q(\mu) Q_{r_s'^{10}}(q, iqu)}{[q^2 + (\alpha r_s' / \pi^2) Q_q(\mu)]}, \quad (19)$$

where $Q_{r_s'^{10}}$ is a function proportional to r_s' , defined by Eq. (A3) in Ref. 8. One check on the correctness of (19) may be made by expanding the denominator in powers of r_s . The first term should equal E_{34} ; i.e.,

$$E_{34} = \frac{-9}{16\pi^6} \frac{1}{r_s^2} \int_0^{r_s} dr_s' r_s' \int_{-\infty}^{\infty} d\mu \times \int \frac{d\mathbf{q}}{q^3} Q_q(\mu) Q_{r_s'^{10}}(q, iqu) \quad (20)$$

which can be shown to be the case.

Upon isolating the r_s and $r_s \ln r_s$ terms in (19), we obtain

$$\epsilon'' = r_s (A_{1x} \ln r_s + C_{1x}) + 0(r_s^2, r_s^2 \ln r_s), \quad (21)$$

where¹³

$$A_{1x} = \frac{3\alpha}{2\pi^4} \int_{-\infty}^{\infty} d\mu R(\mu) R^{(1)}(i\mu) = 0.013 \quad (22)$$

and

$$C_{1x} = A_{1x} \left(\ln \frac{4\alpha}{\pi} - \frac{1}{3} \right) - \delta_{1x} + \frac{3\alpha}{2\pi^4} \times \int_{-\infty}^{\infty} d\mu R(\mu) R^{(1)}(i\mu) \ln R(\mu), \quad (23)$$

with

$$\delta_{1x} = \frac{3\alpha}{16\pi^6} \int_{-\infty}^{\infty} d\mu \left\{ \int_{q>1} \frac{d\mathbf{q}}{q^3} Q_q(\mu) Q_{r_s'^{10}}(q, iqu) \frac{1}{\alpha r_s} + \int_{q<1} \frac{d\mathbf{q}}{q^3} \left[Q_q(\mu) Q_{r_s'^{10}}(q, iqu) \frac{1}{\alpha r_s} - 4\pi R(\mu) R^{(1)}(i\mu) \right] \right\}. \quad (24)$$

The function $R^{(1)}(i\mu)$ is obtained from the limit of $(1/\alpha r_s) Q_{r_s'^{10}}(q, iqu)$ as $q \rightarrow 0$ and is given by Eq. (A5) in Ref. 8.

We find by numerical integration that

$$C_{1x} = -0.0097 - 0.008 - 0.0037 = -0.021. \quad (25)$$

RESULTS

Upon collecting terms we obtain a coefficient of 0.018 for the $r_s \ln r_s$ term (as compared with Du Bois' 0.0049) and the energy per electron becomes

$$E = 2.21 r_s^{-2} - 0.916 r_s^{-1} + 0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s + (E'_3 - 0.036) r_s + 0(r_s^2, r_s^2 \ln r_s), \quad (26)$$

¹³ Du Bois gives $A_{1x} = -0.00045$. However, our expressions for A_{1x} and C_{1x} are the same as his except for a factor of -4π .

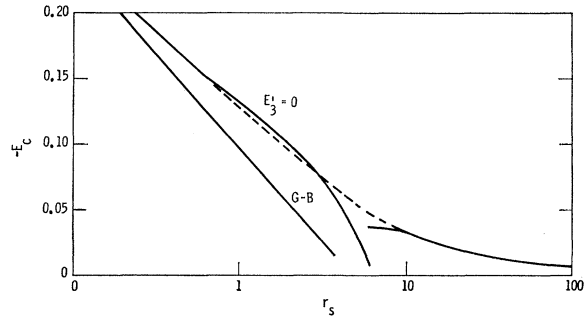


FIG. 1. Correlation energy plotted against r_s . The curve marked $E_3' = 0$ is a plot of Eq. (27) with E_3' neglected. The straight line is a plot of $0.0622 \ln r_s - 0.096$, the Gell-Mann and Brueckner expression for the correlation energy. The solid curve for large r_s was taken from Ref. 7, and the dashed curve is an interpolation.

where E_3' is the sum of the twelve-dimensional integrals given in Eq. (9). The individual terms in E_3' diverge. However, when the first three and the last two integrals are grouped together the result seems to be finite.

From (26) the correlation energy E_c , defined as $E - 2.21r_s^{-2} + 0.916r_s^{-1}$, is given in the first two orders of approximation by

$$E_c = (0.0622 \ln r_s - 0.096) + r_s(0.018 \ln r_s + E_3' - 0.036). \quad (27)$$

In Fig. 1, E_c is plotted against r_s , with E_3' arbitrarily taken to be zero. The first-order approximation for the correlation energy, $0.0622 \ln r_s - 0.096$ is shown on the same figure. By use of the virial theorem^{7,14} the kinetic and potential correlation energies T_c and V_c have also been plotted in Figs. 2 and 3.

If the series expansion is rapidly convergent and Eq. (27) accurately represents the correlation energy in the region of metallic densities, we would expect that in this region, and especially at smaller densities, the second-order term would be quite small compared with the first. As observed in Eq. (27) and Fig. 1, however, such is not the case unless E_3' is positive. But according to Fig. 2 even with E_3' set equal to zero, Eq. (27) gives

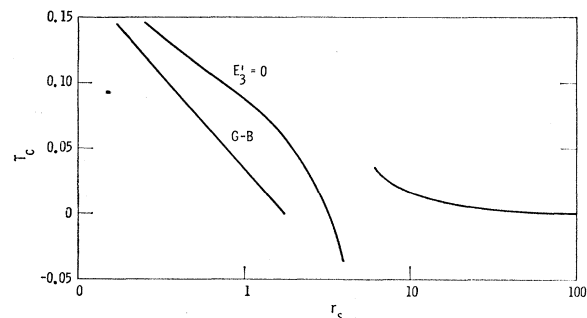


FIG. 2. The kinetic part of the correlation energy plotted against r_s . The meaning of the various curves is the same as in Fig. 1.

¹⁴ N. H. March, Phys. Rev. 110, 604 (1958).

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

E_c	2	3	r_s 4	5	6
Present	-0.096	-0.076	-0.064	-0.054	-0.048
a	-0.085	-0.068	-0.058	-0.051	-0.046
b	-0.090	-0.081	-0.075	-0.069	-0.064
c	-0.099	-0.086	-0.074	-0.067	
d	-0.094	-0.081	-0.072	-0.065	

^a W. J. Carr, Jr., Rosemary A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. 124, 747 (1961).

^b E. Wigner (corrected) D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 367.

^c J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1958).

^d P. Nozieres and D. Pines, Phys. Rev. 111, 442 (1958).

an absurd negative kinetic correlation energy over most of the range of metallic densities. A positive E_3' would make T_c go through zero at an even smaller value of r_s .

The conclusion is that regardless of the value of E_3' , Eq. (27) will not give an accurate account of the correlation energy in the interesting region of r_s between two and five, since in binding energy calculations the result is often desired to the order of 10^{-2} Ry or better. If the series (26) converges at all in this region of interest it does so rather slowly.

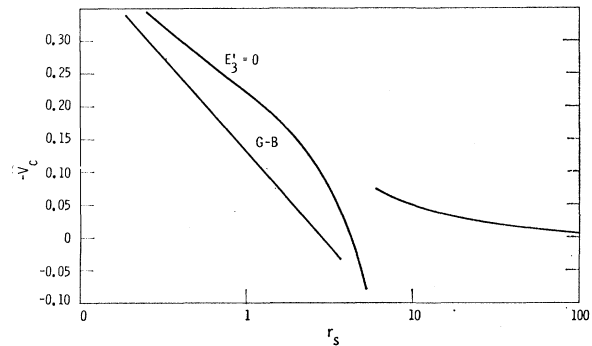


FIG. 3. The potential part of the correlation energy plotted against r_s . The meaning of the various curves is the same as in Fig. 1.

If the metal to nonmetal transition introduces no more than a small discontinuity in the slope of the ground-state energy as a function of r_s , then the high-density and low-density expressions for the energy might be expected to fit smoothly on to one another. Since E_3' has not been evaluated we have arbitrarily taken a value (specifically $E_3' \approx 0$) which allows a smooth connection between the high- and low-density results for the correlation energy and the kinetic and potential correlation energies. With $E_3'r_s$ neglected, a reasonably smooth connection can be made in Figs. 1-3 if it is assumed that the high-density curve is accurate only for r_s less than unity. Such an interpolation is shown by the dashed line of Fig. 1. The correlation energies estimated in this way are given in Table I. They are intermediate between the values of Ref. 7 and previous estimates. However, it is doubtful if any of the estimates in Table I can be relied upon to 10^{-2} Ry and to this order there is agreement.