Kinetic and Potential Energies of an Electron Gas

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It is pointed out that the kinetic and potential energies of an electron gas may be obtained exactly in the high-density limit by using the virial theorem in conjunction with the results of Gell-Mann and Brueckner. For intermediate and low densities, the results obtained from Wigner's formula are also referred to, although for the intermediate region these are likely to be at best semiquantitative.

1. INTRODUCTION

FOLLOWING earlier investigations by Wigner,[1] there has recently been considerable progress in dealing with correlation effects in an electron gas.[2-4] In particular, the high-density limit has been examined rather thoroughly using perturbation theory, and the two leading terms in the correlation energy are now known exactly from the work of Macke[2] and Gell-Mann and Brueckner.[4] Unfortunately, all the methods so far applied successfully to the correlation problem have been of considerable complexity, and it is difficult therefore to follow in detail the physical nature of the correlation effects as the density is varied. Indeed, to do so completely would require explicit knowledge of the many-body wave function or, alternatively, the second-order density matrix, over the entire range of electron densities. There is one further, and very simple, method, however, of gaining some limited insight into the way in which the correlation energy arises. This is to follow the separate kinetic and potential energy terms as the electron density changes. As far as we are aware, this has not been attempted previously, and the purpose of this article is to point out that once the exact correlation energy is known, the separate kinetic and potential energy contributions can be obtained almost immediately by suitable application of the many-body virial theorem. Thus, from the results of Gell-Mann and Brueckner, the high-density forms of these energy terms are obtained exactly. We shall also make a very rough calculation for intermediate and low densities using Wigner's result, although we should stress that the separate energy terms obtained by applying the virial theorem to an approximate correlation energy will be much more seriously in error in general than the original total energy.

2. FORM OF THE VIRIAL THEOREM

For the present problem, with Coulombic interactions, the virial theorem may be written in the form

$$2T + V = -r_s(dE/dr_s), \qquad (1)$$

where T, V, and E are, respectively, kinetic, potential, and total energies per particle, and r_s is the radius of a sphere containing one electron.[5] Since $T + V = E$, we have

$$T = -E - r_s(dE/dr_s). \qquad (2)$$

As is customary, we now write the total energy E as

$$E = \epsilon_F + \epsilon_x + \epsilon_c, \qquad (3)$$

the three separate terms being, respectively, the Fermi energy, the exchange energy, and the correlation energy. Using the explicit results

$$\epsilon_F = \frac{3}{5}\left(\frac{9\pi}{4}\right)^{\frac{2}{3}}\frac{1}{r_s^2} \approx \frac{2.21}{r_s^2}, \qquad (4)$$

and

$$\epsilon_x = -\frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{1}{r_s} \approx -\frac{0.916}{r_s}, \qquad (5)$$

and introducing ΔT and ΔV as the changes in kinetic and potential energies due to correlation, we find

$$\Delta T = T - \epsilon_F = -\epsilon_c - r_s(d\epsilon_c/dr_s), \qquad (6)$$

$$\Delta V = V - \epsilon_x = 2\epsilon_c + r_s(d\epsilon_c/dr_s). \qquad (7)$$

These results are quite general, and once ϵ_c is known as a function of r_s we may easily obtain ΔT and ΔV from them.

3. RESULTS FOR HIGH-DENSITY LIMIT

The correlation energy in the high-density limit may be written, following Gell-Mann and Brueckner, as

$$\epsilon_c = A \ln r_s + C + \text{terms that vanish as } r_s \rightarrow 0, \qquad (8)$$

where $A = (2/\pi^2)(1 - \ln 2) = 0.0622$ and $C = -0.096 \pm 0.002$. Equations (6), (7), and (8) then yield immediately

$$\Delta T = -A \ln r_s - (A + C)$$
$$+ \text{terms that vanish as } r_s \rightarrow 0, \qquad (9)$$

and

$$\Delta V = 2A \ln r_s + (A + 2C)$$
$$+ \text{terms that vanish as } r_s \rightarrow 0. \qquad (10)$$

We note that for $r_s < 1$, both the leading terms in the

[1] E. P. Wigner, Phys. Rev. 46, 1002 (1934) and Trans. Faraday Soc. 34, 678 (1938).
[2] W. Macke, Z. Naturforsch. 5a, 192 (1950).
[3] D. Pines, Phys. Rev. 92, 626 (1953) and in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.
[4] M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).

[5] Throughout this article we shall measure lengths in atomic units and energies in Rydbergs.

kinetic energy are positive, while both the potential energy terms are negative, the decrease in the total energy of the electron gas coming from the gain in the potential energy due to the correlations keeping the electrons, on the average, further apart, this outweighing the associated increase in kinetic energy. Unfortunately, it seems necessary to have more information on the higher terms of the series (8) before deciding on the range of r_s over which the two available terms will yield reasonable numerical values for ϵ_c. For low densities, the results of Wigner are probably not seriously in error, and we therefore consider now whether we can obtain supplementary information on the kinetic and potential energies in this way.

4. USE OF WIGNER'S FORMULA

Wigner's formula may be written[6]

$$\epsilon_{cW} = -0.88/(r_s + 7.8). \quad (11)$$

To show the relation with the Gell-Mann and Brueckner work for the high-density limit, we have plotted both Eqs. (8) and (11) in Fig. 1. We have, somewhat arbitrarily, used Eq. (8) out to $r_s = 1$, and the Wigner formula over the range $1 < r_s < 2$, and we should emphasize that in doing so we have probably extended both formulas outside their proper range of validity. However, both formulas lead to practically the same energy at $r_s = 1$, although, as is only to be expected, they do not join smoothly here.

Let us now use the approximate result (11) in the Eqs. (6) and (7) which we derived from the virial theorem, although, as we have already remarked, errors in Eq. (11) will be very appreciably magnified in the separate terms thus obtained. We find then

$$\Delta T_W = 6.9/(r_s + 7.8)^2, \quad (12)$$

$$\Delta V_W = -(0.88r_s + 13.8)/(r_s + 7.8)^2, \quad (13)$$

and these results are again plotted in Fig. 1 for $1 < r_s < 2$, together with the values given by Eqs. (9) and (10) for $r_s < 1$. From Fig. 1 it then appears very likely that Eqs. (12) and (13) are considerably overestimating the separate energy changes due to correlation in the density range represented by $1 < r_s < 2$. From a qualitative point of view, however, ΔT_W is always positive and ΔV_W always negative according to Eqs. (12) and (13),

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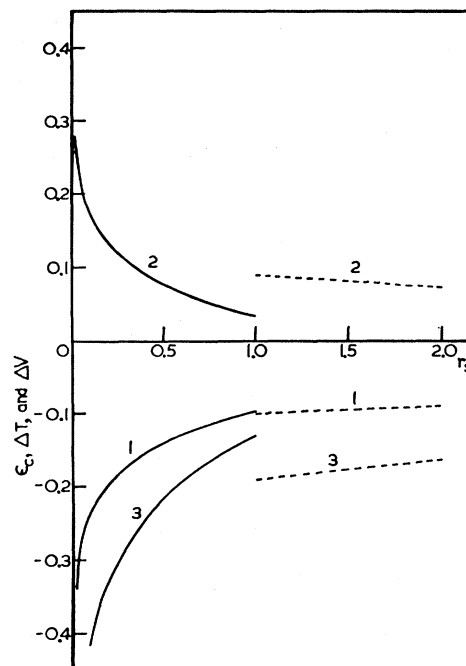[6] See, for example, the second article cited in reference 3.

FIG. 1. Energy changes due to correlation effects, as functions of r_s. The solid curves, for $r_s < 1$, are as follows: 1, ϵ_c from Eq. (8); 2, ΔT from Eq. (9); 3, ΔV from Eq. (10). The dashed curves, for $1 < r_s < 2$, are as follows: 1, ϵ_{cW} from Eq. (11); 2, ΔT_W from Eq. (12); 3, ΔV_W from Eq. (13).

agreeing with the conclusions drawn from Eqs. (9) and (10) for the high-density limit.

It is perhaps interesting to note also that in the low-density limit $r_s \to \infty$, the correlation energy is entirely potential energy in first order, but that according to Eqs. (4) and (12) the "correction" to the kinetic energy is about three times the Fermi energy. This kinetic energy "correction" may need quantitative modification later when a more accurate discussion of the low-density limit becomes available. However, it would appear that the present discussion establishes the general features of the separate energy curves and shows that over the entire range of densities it is the balance between an increased kinetic energy and a decreased potential energy of greater absolute value which yields the correlation energy, the ratio of kinetic to potential energy change going from $-\frac{1}{2}$, in the limit $r_s \to 0$, to 0 in the limit $r_s \to \infty$.