[1]See, e.g., K. Huang, Statistical Mechanics (John Wiley & Sons, Inc., New York, 1963).
[2]Ref. 1, p. 226.
[3]See, e.g., E. T. Copson, Theory of Functions of a Complex Variable (Oxford University Press, London, 1935).
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# A Parametric Approach to the Ground-State Energy of an Electron Gas

M. S. Becker, A. A. Broyles, and Tucson Dunn

*Physics Department, University of Florida, Gainesville, Florida*
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A parametric form is chosen for the ground-state wave function of an electron gas. The expression for the energy of the system is derived and then minimized with respect to the unknown parameters. The energies thus obtained agree well with the results of other authors.

## I. INTRODUCTION

The problem of obtaining the ground-state energy of a quantum electron gas has been approached in a number of ways. The original work on this subject was done by Wigner,[1] who calculated the "correlation energy" of an electron gas for very high densities ($r_s < 1$) and then extended the results in such a way as to obtain the correct value at very low densities ($r_s \gg 1$). He estimated his results to be correct everywhere to within 20%. Later calculations employing perturbation-expansion techniques[2-5] gave improved results for high densities while improved calculations for low densities[6] were carried out using Wigner's lattice model. In addition to Wigner's treatment, the region of metallic densities ($1 \lesssim r_s \lesssim 5$) has been treated[7] by truncating the Martin-Schwinger equations and using a random-phase approximation.[5] Finally, a recent paper[8] has shown how the problem may be treated by approximating the Slater sum for the system by an effective Boltzmann factor. The aim of this paper is to improve upon these calculations for the metallic density region, and also, to find a method which will give good agreement with the above-mentioned results in their respective regio gions of validity. It is further desirable that the method used for the electron gas be of sufficient flexibility so that it may later be generalized to include multicomponent systems. In accordance with these ideas, we shall present a parametric Rayleigh-Ritz variational method for calculating the ground-state energy, using a trial wave function of the form

$$\psi = D \exp\left(-\tfrac{1}{2}\sum_{i<j} u(r_{ij})\right), \tag{1.1}$$

where $u(r)$ is an unknown function to be determined by variation and $D$ is the wave function for an ideal gas of spin-$\frac{1}{2}$ particles.

## II. DERIVATION OF THE BASIC EQUATION

The Hamiltonian operator $H$ for an electron gas can be written as

$$H = -(\hbar^2/2m)\Delta^2 + V(\vec{r}_1 \cdots \vec{r}_N) \ , \tag{2.1}$$

where $\Delta^2 = \sum_{a=1}^{N} \nabla_a^2$ (2.2)

and $V(\vec{r}_1 \cdots \vec{r}_N)$ represents the Coulomb potential. The expectation value of the energy $\langle E \rangle$, is then

$$\langle E \rangle = Q^{-1} \int \psi^* [-(\hbar^2/2m)\Delta^2 + V] \psi d\tau \ , \tag{2.3}$$

where $Q = \int \psi^* \psi d\tau$ , (2.4)

and $d\tau \equiv d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N$ . (2.5)

We must now reduce this expression to a more tractable form in order to apply the variational principle.

First, we will treat the potential-energy term given by

$$\langle PE \rangle = Q^{-1} \int \psi^* V \psi d\tau \ . \tag{2.6}$$

Since $V(\vec{r}_1 \cdots \vec{r}_n)$ represents the Coulomb potential, we may define a two-body term $v(r_{ij})$ in the following manner:

$$V(\vec{r}_1 \cdots \vec{r}_n) = \sum_{i<j} v(r_{ij}). \tag{2.7}$$

Thus we may write

$$\langle \mathrm{PE} \rangle = \tfrac{1}{2} N\rho \int v(r) g(r) d\vec{r}, \tag{2.8}$$

where the radial distribution function $g(r)$ is given by

$$g(r) = N(N-1)\rho^{-2} Q^{-1} \int \psi^* \psi d\vec{r}_3 \cdots d\vec{r}_N. \tag{2.9}$$

The function $v(r)$ can be expressed as[5]

$$v(r) = \Omega^{-1} \sum_{\vec{k}}{}' \nu_k e^{i\vec{k}\cdot\vec{r}}, \tag{2.10}$$

where the prime indicates that the $k$ equal to zero is not included in the summation. This occurs because of the presence of the uniform positive background. Thus

$$\int v(r_{12}) dr_1 dr_2 = \sum_{\vec{k}}{}' \nu_k \delta(\vec{k})\delta(-\vec{k}) = 0. \tag{2.11}$$

Therefore,

$$\tfrac{1}{2}\rho \int v(r) g(r) d\vec{r} = \tfrac{1}{2}\rho \int v(r)[g(r)-1] d\vec{r}. \tag{2.12}$$

For the case under consideration, $v(r)$ may be expanded as[9]

$$v(r) = e^2(r^{-1} - a_0 L^{-1} - a_1 r^{-2} L^{-3} \cdots). \tag{2.13}$$

Since the factor $g(r)-1$ approaches zero rapidly as $r$ becomes large, we find that, in the limit as $L$ approaches $\infty$, we have

$$\begin{aligned}\langle \mathrm{PE} \rangle &= \tfrac{1}{2} N\rho \int v(r) g(r) d\vec{r} \\ &= \tfrac{1}{2} N\rho e^2 \int [g(r)-1] r^{-1} d\vec{r}.\end{aligned} \tag{2.14}$$

In order to reduce the kinetic-energy term in Eq. (2.3), we first note that integration by parts yields the following relationship:

$$-\int \psi^* \nabla^2 \psi d\tau = \int \nabla\psi^* \cdot \nabla\psi d\tau, \tag{2.15}$$

where the surface terms cancel as a result of the periodic boundary conditions imposed upon $\psi$. Substituting our chosen form for the wave function given by Eq. (1.1) into the above equation, and performing some manipulations, we find that the kinetic energy may be written as

$$\langle \mathrm{KE} \rangle = (\hbar^2/2m) Q^{-1} \int \nabla\psi^* \cdot \nabla\psi d\tau = \tfrac{3}{5} N\epsilon_F + J \tag{2.16}$$

where $J = (\hbar^2/2m) Q^{-1} \int \psi^* I \psi d\tau$; (2.17)

and $I = \sum_{i,j,k} \nabla_i u(r_{ij}) \cdot \nabla_i u(r_{ik})$. (2.18)

In obtaining the above result, use was made of the relationship

$$\begin{aligned}(\hbar^2/2m)(D^* \nabla^2 D) &= (\hbar^2/2m) \sum_j k_j^2 (D^* D) \\ &= \tfrac{3}{5} N\epsilon_F (D^* D),\end{aligned} \tag{2.19}$$

where $\epsilon_F$ denotes the Fermi energy. The last term in Eq. (2.16) can be written in terms of the radial distribution function $g(r)$ and the three body distribution function given by

$$\begin{aligned}&g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) \\ &\quad = N(N-1)(N-2)\rho^{-3} Q^{-1} \int \psi^* \psi d\vec{r}_4 \cdots d\vec{r}_N.\end{aligned} \tag{2.20}$$

Doing this, and adding the expression obtained for the potential energy in Eq. (2.14), we find that

$$\begin{aligned}\langle \mathrm{E} \rangle / N &= \tfrac{3}{5}\epsilon_F + \tfrac{1}{2}\rho e^2 \int [g_I(r) - 1] r^{-1} d\vec{r} \\ &\quad + (\hbar^2\rho/8m) \int [du(r)/dr]^2 g(r) d\vec{r} + (\hbar^2\rho^2/8m) L \\ &\quad + \tfrac{1}{2}\rho e^2 \int [g(r) - g_I(r)] r^{-1} d\vec{r},\end{aligned} \tag{2.21}$$

where

$$L = \int \nabla_1 u(r_{12}) \cdot \nabla_1 u(r_{13}) g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) d\vec{r}_{12} d\vec{r}_{13}, \tag{2.22}$$

and where we have added and subtracted a term involving the ideal-gas radial distribution function $g_I(r)$ in order that the first two terms of the above equation constitute the familiar Hatree-Fock solution[2] to the problem. The last three terms contain the unknown quantity $u(r)$, and their sum is called the correlation energy. It is this quantity that we are primarily concerned with here.

## III. APPLICATION OF APPROXIMATIONS

In order to proceed further, we now resort to some approximations.

### (A)

First, the energy expression is simplified by the application of either a random-phase approximation or a superposition approximation.[10] The random-phase approximation is used for the high-density calculations while the superposition approximation is used for the metallic region.

#### 1. *Random-Phase Approximation*

In Eq. (2.16) we saw that the kinetic energy contained a term labeled $J$ which we defined in Eq. (2.17). We want to apply the random-phase approximation to this term. First, we assume that the unknown function $u(r)$ may be written as

$$u(r) = \Omega^{-1} \sum_{\vec{k}}{}' \phi(k) e^{i\vec{k}\cdot\vec{r}}. \tag{3.1}$$

Using Eq. (3.1) in Eq. (2.18) yields

$$I = \Omega^{-2} \sum_{i,j} \sum_{\vec{m},\vec{k}} -(\vec{k}\cdot\vec{m}) \phi(k)\phi(m) e^{i\vec{k}\cdot\vec{r}_i} e^{-i\vec{m}\cdot\vec{r}_j} \sum_a e^{i(\vec{k}+\vec{m})\cdot\vec{r}_a}. \tag{3.2}$$

The random-phase approximation (R.P.A.) assumes that the $\vec{r}_a$, which appears in the above equation, is distributed at random so that the factor $\sum_a \exp[i(\vec{k}+\vec{m})\cdot\vec{r}_a]$ may be replaced by $N\delta_{\vec{k},-\vec{m}}$. Performing this substitution in Eq. (3.2) and summing over $\vec{m}$ gives

$$I \simeq N\Omega^{-2}\sum_{i,}\sum_{jk}{}' k^2\phi^2(k)e^{i\vec{k}\cdot\vec{r}_{ij}}. \tag{3.3}$$

Thus Eq. (2.17) may be written as

$$J \simeq (\hbar^2\rho/8m)Q^{-1}\int_\tau \psi^*\psi\left[\rho\sum_k{}' k^2\phi^2(k)+\Omega^{-1}\sum_{i\neq j}\sum_k{}' k^2\phi^2(k)e^{i\vec{k}\cdot\vec{r}_{ij}}\right]d\tau \ . \tag{3.4}$$

Using the definition of $g(r)$ as given by Eq. (2.9), converting the summations to integrals, and adopting the same procedure used to obtain the factor $g(r)-1$ in Eq. (2.12), we finally obtain

$$J \simeq (N\hbar^2\rho/8m)(2\pi)^{-3}\int_{\vec{k}} k^2\phi^2(k)d\vec{k} + (N\hbar^2\rho^2/8m)\int_{\vec{r}}[g(r)-1]\int_{\vec{k}} k^2\phi^2(k)e^{i\vec{k}\cdot\vec{r}}d\vec{k}\,d\vec{r} \ . \tag{3.5}$$

Substituting this result into Eq. (2.16) and combining with Eq. (2.14), we find that

$$\frac{E_{\text{RPA}}}{N\epsilon_F} = \frac{3}{5}+\frac{\gamma^2}{16\pi}\int[g_I(R)-1]\frac{d\vec{R}}{R}+\frac{1}{96\pi^5}\int x^2\phi^2(x)d\vec{x}$$
$$+\frac{1}{288\pi^7}\int_{\vec{R}}[g(R)-1]\int_{\vec{x}} x^2\phi^2(x)e^{i\vec{x}\cdot\vec{R}}d\vec{x}\,d\vec{R}+\frac{\gamma^2}{16\pi}\int[g(R)-g_I(R)]\frac{d\vec{R}}{R} \ , \tag{3.6}$$

where $\gamma^2 = 8e^2K_F/3\pi\epsilon_F$ , (3.7)

and where the Fermi units have been used (see Appendix). As before in Eq. (2.21), the last three terms represent correlation energy.

### 2. *Superposition Approximation*

Equation (2.21) contains an integral involving the three-body distribution function $g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)$. This integral is labeled $L$ and is defined by Eq. (2.22). In order to simplify $L$, we will apply the Kirkwood superposition approximation (S.A.) given by replacing the function $g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ by the product $g(r_{12})g(r_{13})g(r_{23})$. Performing this substitution in $L$ yields

$$L \simeq \int \nabla_1 u(r_{12})\cdot\nabla_1 u(r_{13})g(r_{12})g(r_{13})g(r_{23})d\vec{r}_{12}d\vec{r}_{13} \ . \tag{3.8}$$

A brief consideration of the above shows that

$$L \simeq \int \nabla_1 u(r_{12})\cdot\nabla_1 u(r_{13})g(r_{12})g(r_{13})[g(r_{23})-2]d\vec{r}_{12}d\vec{r}_{13} \ . \tag{3.9}$$

In order to uncouple the variables in the above, we now introduce a $\delta$ function as follows:

$$L \simeq \int \nabla_1 u(r_{12})\cdot\nabla_1 u(r_{13})g(r_{12})g(r_{13})[g(r_{23})-1]\times\delta(\vec{r}_{23}-\vec{r}_{13}+\vec{r}_{12})d\vec{r}_{12}d\vec{r}_{13}d\vec{r}_{23} \ . \tag{3.10}$$

Noting that $\delta(\vec{r}) = (2\pi)^{-3}\int e^{i\vec{k}\cdot\vec{r}}d\vec{k}$ , (3.11)

we see that, after some manipulation, Eq. (3.10) can be written as

$$L \simeq \left(\frac{1}{2\pi}\right)^3\int_{\vec{k}} d\vec{k}\left[\left(\int_{\vec{r}}[g(r)-1]e^{i\vec{k}\cdot\vec{r}}d\vec{r}\right)\left(\frac{d}{dk}\int_{\vec{r}}\frac{du(r)}{dr}\frac{g(r)}{r}e^{i\vec{k}\cdot\vec{r}}d\vec{r}\right)^2\right]. \tag{3.12}$$

Substituting this result into Eq. (2.21) and changing to Fermi units (see Appendix), we obtain

$$\frac{E_{\text{S.A.}}}{N\epsilon_F} = \frac{3}{5}+\frac{\gamma^2}{16\pi}\int[g_I(R)-1]\frac{d\vec{R}}{R}+\frac{1}{12\pi^2}\int\left(\frac{du(R)}{dR}\right)^2 g(R)d\vec{R}$$
$$+\frac{1}{288\pi^7}\int_x d\vec{x}\left[\left(\int[g(R)-1]e^{i\vec{x}\cdot\vec{R}}d\vec{R}\right)\left(\frac{d}{dx}\int\frac{du(R)}{dR}\frac{g(R)}{R}e^{i\vec{x}\cdot\vec{R}}d\vec{R}\right)^2\right]+\frac{\gamma^2}{16\pi}\int[g(R)-g_I(R)]\frac{d\vec{R}}{R} \ , \tag{3.13}$$

where, once again, the last three terms constitute the correlation energy.

(B)

Next, we must calculate the radial distribution function $g(r)$ as a functional of the unknown quantity $u(r)$. To do this, we note that the product $D^*D$ can be approximated by writing

$$D^*D \simeq \exp\left(-\sum_{i<j}\theta(r_{ij})\right) , \tag{3.14}$$

where $\theta(r)$ has been determined from the ideal-gas calculations of Lado.[11] This enables us to write $g(r)$ as

$$g(r) \simeq N(N-1)\rho^{-2}\int \exp\{-\sum_{i<j}[\theta(r_{ij})+u(r_{ij})]\}\, d\vec{r}_3\cdots d\vec{r}_N \Big/ \int \exp\{-\sum_{i<j}[\theta(r_{ij})+u(r_{ij})]\}\, d\vec{r}_1\cdots d\vec{r}_N . \tag{3.15}$$

Radial distribution functions of this form may be readily calculated by several methods. We have chosen to use the Percus-Yevick integral equation[12] for the metallic densities and a perturbation formula[13] for the high-density points. Let us now define the structure factor $S(x)$ in the usual manner by writing

$$S(x) = \rho G(x) - 1 , \tag{3.16}$$

where $G(x)$ is the Fourier transform of $[g(R)-1]$. The perturbation approximation referred to above tells us that

$$S(x) \simeq S_I(x)/[1+\rho\phi(x)S_I(x)] , \tag{3.17}$$

where $\phi(x)$ is the Fourier transform of the effective potential as shown in Eq. (3.1), and the ideal-gas structure factor $S_I(x)$ is given by

$$S_I(x) = \rho G_I(x) + 1 = \tfrac{3}{4}x - (x^3/16), \quad x \leq 2; \quad \text{or} \quad 1, \quad x \geq 2. \tag{3.18}$$

Substituting this result into Eq. (3.6) and simplifying, we find that for high densities the correlation energy may be written as

$$\epsilon_c \simeq (1/24\pi^4)\int x^4\phi^2(x)S(x)dx + (3\gamma^2/8)\int [S(x) - S_I(x)]dx. \tag{3.19}$$

(C)

Finally, although the function $u(r)$ is unknown, some information about its form is already available. Specifically, as $r$ becomes infinitely large, $u(r)$ must vanish, and the work of Dunn and Broyles indicates that $u(0)$ is finite and nonzero. This can be expected since the electrons can tunnel into the classical Coulomb barrier. The work of Dunn and Broyles and others[14] further indicates that the function $u(r)$ falls off as $(r)^{-1}$ in the large-$r$ limit. A simple functional form of $u(r)$ which obeys these conditions is given by

$$u_2(r) = ar^{-1}(1-e^{-br}) , \tag{3.20}$$

where $a$ and $b$ are unknown parameters to be determined. If this form of $u(r)$ is adopted, one can express the wave function, and consequently, also the energy for the system, as a function of the two parameters alone. Thus the ground-state energy may be calculated simply by computing the energy for various values of the two parameters and determining which values give the lowest energy. The accuracy of the minimum energy obtained in this manner depends rather heavily on how well the parametric form chosen for $u(r)$ agrees with the true form of $u(r)$. In the hopes of obtaining better numerical results, the calculations were repeated with a form more flexible than that given by Eq. (3.20). It is given by

$$u_4(r) = ar^{-1}(1-e^{-br}) + \alpha(\beta^2+r^2)^{-1} , \tag{3.21}$$

where $a, b, \alpha$, and $\beta$ are all unknown parameters to be determined by variation.

## IV. RESULTS

The minimum correlation energies, for various densities, using Eq. (3.20) and Eq. (3.21), are given in the tables below. The notation used in Table I is the following: $r_S$ is the ion sphere radius in Bohr units, $\gamma^2 = 1.13r_S$, $E_2$ is the minimum correlation energy found by using Eq. (3.20), $E_4$ is the minimum correlation energy found by using Eq. (3.21). The results are presented in fermi units and, as mentioned before, the high-density points ($\gamma^2 = 0.01$ and $0.1$) were calculated using Eq. (3.19), while the lower density points ($\gamma^2 = 1.0$, $3.0$, and $5.0$) were done using the last three terms of Eq. (3.13) and the Percus-Yevick integral equation.

From a consideration of the Table I, it is apparent that, for metallic densities, the two-parameter effective potential given by Eq. (3.20) yields essentially the same results as the four-parameter form given by Eq. (3.21). It is possible, therefore, that for the metallic density region, the

TABLE I. The ground-state correlation energies in Fermi Units.[a]

| $r_s$ | $\gamma^2$ | $E_2$ | $E_4$ |
|---|---|---|---|
| 0.0113 | 0.01 | -0.000 012 1 | -0.000 012 7 |
| 0.113 | 0.1 | -0.000 85 | -0.000 88 |
| 1.13 | 1.0 | -0.041 | -0.041 |
| 3.39 | 3.0 | -0.31 | -0.31 |
| 5.65 | 5.0 | -0.69 | -0.69 |

[a]See Appendix.

TABLE III. Ground-state wave functions in Fermi units.[a]

| $\gamma^2$ | $a$ | $b$ | $\alpha$ | $\beta$ |
|---|---|---|---|---|
| 0.01 | 0.15 | 0.20 | 0.4 | 10.0 |
| 0.1 | 0.75 | 0.33 | 2.5 | 8.0 |
| 1.0 | 1.5 | 1.25 | | |
| 3.0 | 4.2 | 1.4 | | |
| 5.0 | 5.3 | 1.5 | | |

[a]See Appendix.

two-parameter function is quite a good approximation to the optimum two-body effective potential. A comparison with the results of other authors which seems to substantiate this hypothesis is given in Table II. Thus we conclude that the effective potential given by Eq. (3.20) may be rather good guess. The values obtained for the parameters $a$, $b$, $\alpha$, and $\beta$ are given in Table III.

In conclusion, let us discuss one final point. It may appear strange that the superposition approximation has been used for $g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ while the Percus-Yevick integral equation was used instead of the Born-Green-Yvonne (BGY) integral equation[15,16] for the purpose of computing the radial distribution function $g(r)$. The reason for this is that the work of Broyles, Chung, and Sahlin[17] indicates that the Percus-Yevick equation is superior to the BGY equation for computing $g(r)$, and a proper form of the Percus-Yevick equation for calculating $g_3$ was not readily available.

TABLE II. Comparison of ground-state correlation energies in Fermi units.[a]

| $\gamma^2$ | Variational method | Carr | Wigner | Dunn and Broyles |
|---|---|---|---|---|
| 0.01 | -0.000 012 7 | -0.000 013 | | |
| 0.1 | -0.000 88 | -0.000 82 | | |
| 1.0 | -0.041 | -0.044 | -0.034 | -0.051 |
| 3.0 | -0.31 | | -0.24 | -0.30 |
| 5.0 | -0.69 | | -0.57 | -0.62 |

[a]See Appendix.

## APPENDIX

### *Fermi Units*

Fermi units are based on the definition of the Fermi energy given by

$$\epsilon_F = \hbar^2 K_F^2/2m \quad ,$$

where $K_F = (3\pi^2\rho)^{1/3}$ .

The unit of length in these units is

$$a_F = 1/K_F \quad .$$

In order that the variables of integration in this paper will be dimensionless, the following transformations are made in the energy expressions:

$$\vec{r} = \vec{R}/K_F$$

and $\vec{K} = K_F \vec{x}$ ,

where $\vec{R}$ and $\vec{x}$ are dimensionless.


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