*Acta Physica Academiae Scientiarum Hungaricae, Tomus 27, pp. 161—168 (1969)*

# QUANTUM AND CORRELATION CORRECTIONS TO THE THOMAS–FERMI POTENTIAL*

By

T. TIETZ and S. KRZEMIŃSKI

DEPARTMENT OF THEORETICAL PHYSICS, UNIVERSITY OF ŁÓDZ, ŁÓDZ, POLAND

(Received 13. I. 1969)

This paper studies the correction to the Thomas—Fermi potential arising from the exichange inhomogeneity and correlation effects. Using the BARAFF equation and the approximate solution of the Thomas—Fermi equation for free neutral atoms, given by one of the authors there has been considered the low and high density approximation. It is found that the main contribution to the solution of the BARAFF equation arises from the inhomogeneity, screening and exchange terms.

Lastly the study of correlation effects in many-body systems has attracted the attention of a number of scientific workers [1]. This paper studies the correction of the Thomas—Fermi potential for free neutral atoms from the exchange, inhomogeneity and correlation effects by using the differential equation of BARAFF and a simple analytic expression of the Thomas—Fermi potential with a correct asymptotic behaviour for large distances.

It has been shown by BARAFF [2] that the first nonzero correction $\Phi_2$ to the Thomas—Fermi potential [3] $\Phi_0$ is given by the solution of the differential equation

$$\nabla^2 \Phi_2 - \left(\frac{4me^2}{\pi\hbar^3}\right) p_F \Phi_2 = \frac{4_m e^2}{\pi\hbar^5} p_F (E_{\text{ex}} + E_{\text{corr}}) + \frac{me^2}{12\pi \hbar^3 p_F} \cdot \left[4\nabla^2 \Phi_0 + \frac{2m}{(p_F)^2}\left(\frac{d\Phi_0}{dr}\right)^2\right], \tag{1}$$

where $p_F$ denotes the Thomas—Fermi momentum, $E_{\text{ex}} = -e^2 p_F/\pi\hbar$ and $E_{\text{corr}}$ denote the exchange and correlation energies of the system, respectively. The first term on the right-hand side of Equ. (1) represents the contribution arising from exchange and correlation effects and the second term gives the inhomogeneity correction. The second term on the left-hand side introduces the screening effect, which is one of the important consequences of the long-range Coulomb interaction of electrons. The right-hand side of Equ. (1) depends on $\Phi_0$, the Thomas—Fermi potential, and in solving the differential Equ. (1)

* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

we shall use the simple analytic solution of the Thomas—Fermi equation given by one of the authors [4]

$$\Phi_0(r) = -\frac{Ze^2}{r(1+Ax)^2(1+Bx)}, \tag{2}$$

where $x=r/\mu$ and $\mu=0.88534a_0/Z^{1/3}$. $Z$ is the atomic number and $a_0$ is the first radius of the hydrogen atom. The numerical values of the constants $A$, $B$ appearing in Equ. (2) are given by: $A = 0.05367\ Z^{1/3}$, $C = 0.035\,Z^{1/3}$. In the following we use atomic units and so put $e = \hbar = m = a_0 = 1$. The correlation energy of an electron gas has been investigated by several authors and it depends on the density of the system.

Let $r_s$ denote the mean spacing between two electrons measured in units of Bohr radii in the system. We then say that the system has high or low density according to $r_s \lesssim 1$ or $r_s \gg 1$. According to GELLMAN and BRUECKNER [5] the correlation energy of a high density gas is given by

$$E_{\rm corr} = G - E\ln p_F, \quad \text{where} \quad G = -0.05546 \quad \text{and} \quad E = 0.0622. \tag{3}$$

For an electron gas for low density the correlation energy in atomic units is given by the WIGNER [6] formula

$$E_{\rm corr} = -(0.89\,\bar{\alpha}\,\pi - 1)\,\frac{p_F}{\pi}, \text{ [where } \bar{\alpha} = \left(\frac{4}{9\pi}\right)^{1/3}. \tag{4}$$

First we shall solve the BARAFF equation for $\Phi_0$ given by Equ. (2) in the case of high density; this means we use $E_{\rm corr}$ given by Equ. (3). Then we solve the BARAFF equation for $\Phi_0$ in the case of low density when $E_{\rm corr}$ is given by the last formula.

## Solution of Baraff equation for high density

In the high density limit the BARAFF equation according to Equ. (3) in atomic units is

$$\begin{aligned}\nabla^2\Phi_2 - \left(\frac{4}{\pi}\right)\sqrt{-2\Phi_0\Phi_2} = \left\{\frac{4\sqrt{-2\Phi_0}}{\pi} + A - B\ln\sqrt{-2\Phi_0}\right\} + \\ + \frac{1}{12\pi\sqrt{(-2\Phi_0)}}\left\{4\nabla^2\Phi_0 - \frac{1}{\Phi_0}\left(\frac{d\Phi_0}{dr}\right)^2\right\},\end{aligned} \tag{5}$$

where $\Phi_0$ is given in atomic units by Equ. (2). The general solution of $\Phi_2$ given by the last differential equation is the sum of the solution of the homogeneous equation and the particular integral. Denoting the solution of the homogeneous equation by $\Phi$ and putting a series of the form

$$\Phi = \frac{1}{r} \sum_{k=1}^{\infty} \alpha_k t^{k+s}, \text{ where } t = r^{1/2} \tag{6}$$

for $\Phi$ we obtain after respecting the initial equation $s = 0$, when $\alpha_0 \neq 0$ and $\alpha_1 = \alpha_2 = 0$ for the expansion coefficient $\alpha_k$ the following recurrence formula:

$$n(n-2)\alpha_n - \frac{16}{\pi} \sqrt{2Z} \sum_{j=0}^{l} (-1)^j D_j \alpha_{n-3-2j}, \tag{7}$$

where

$$D_j = A^j + \sum_{k=1}^{j} \frac{(2k-1)!!}{2k!!} A^{j-k} C^k, \quad D_0 = 1. \tag{8}$$

The number $l$ takes the following values: $l = n - 1/2$ for even $n$ and $l = n - 3/2$ for odd $n$, where $n = 3, 4, 5, \ldots$ Setting $\Phi_2 = \Phi + \psi$, where $\psi$ is the particular solution of Equ. (5) we see that the particular solution $\psi$ after some simplification satisfies the following differential equation

$$\frac{d^2 \Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} - \frac{4\sqrt{2Z}}{r^{1/2}(1+Ar)(1+Cr)^{1/2}\pi} \Psi = f(r), \tag{9}$$

where

$$\Psi = \Phi_2 + G - E \ln \sqrt{2Z} + \frac{1}{2} E \ln r + E \ln(1+Ar) - \frac{1}{2} E \ln(1+Cr) +$$
$$+ \frac{1}{96} \left[ \frac{1}{r^2} + \frac{4A}{r(1+Ar)} + \frac{2C}{r(1+Cr)} - \frac{20A^2}{(1+Ar)^2} - \right.$$
$$\left. - \frac{7C^2}{(1+Cr)^2} - \frac{12AC}{(1+Ar)(1+Cr)} \right] \tag{10}$$

and $f(r)$ can be expanded in ascending powers of $r$, and one has

$$f(r) = \sum_{n=-4}^{\infty} \beta_{2n} r^n, \tag{11}$$

where the expansion coefficients $\beta_{2n}$ are given by the following recurrence relations

$$\beta_{-8} = \frac{1}{48}, \qquad \beta_{-6} = 0, \qquad \beta_{-4} = \frac{E}{2},$$

$$\beta_{-2} = 2EA + EC - \frac{8Z}{\pi^2} + \frac{11}{12}A^3 + \frac{1}{4}A^2C + \frac{1}{4}AC^2 + \frac{1}{3}C^3$$

$$\beta_{2n} = (-1)^{n+1}\Bigg\{(n+3)EA^{n+2} + \frac{n+3}{2}EC^{n+2} - \frac{8Z}{\pi^2}\sum_{k=0}^{n+1}(k+1)C^{n\pm 1-k}A^k$$

$$\frac{1}{4}A^2C^2\sum_{k=0}^{n}(n-k+1)(k+1)A^{n-k}C^k + \frac{1}{4}AC$$

$$\left[A^2\sum_{k=0}^{n}\frac{(k+1)(k+2)}{2}C^{n-k}A^k + C^2\sum_{k=1}^{n}\cdot\frac{(k+1)(k+l)}{2}A^{n-k}C^k\right]$$

$$+\frac{1}{4}AC\left[A\sum_{k=0}^{n+1}\cdot(k+1)\,C^{n+1-k}A^k + C\sum_{k=0}^{n+1}(k+1)A^{n+1-k}C^k + \right]$$

$$+\frac{(n+2)(n+3)}{2\cdot 3}C^{n-4} + \frac{7}{16}\frac{(n+1)(n+2)(n+3)}{1\cdot 2\cdot 3}C^{n+4}$$

$$+\frac{15}{12}\frac{(n+1)(n+2)(n+3)}{1\cdot 2\cdot 3}A^{n+4} + \frac{11}{12}\frac{(n+2)(n+3)}{2}A^{n+4}\Bigg\}$$

and $n = 0, 1, 2, 3, \ldots$.

Equ. (9) cannot be satisfied by a power series alone, and a complete solution of it should also contain a term involving $\ln t$. Therefore in order to solve Equ. (9) we put $\psi$ in the form

$$\psi = \sum_{k=-4}^{\infty} a_k t^k + \sum_{s=0}^{\infty} b_s t^s \cdot \ln t,$$

where $t = r^{1/2}$. Substituting this in Equ. (9) and comparing different powers of $t^k$ and $t^s \ln t$ on both sides of the differential equation we obtain for the expansion coefficients $a_k$ and $b_s$ the following recurrence formulae

$$a_{-4} = \frac{1}{2}\beta_{-8}, \quad a_{-3} = a_{-2} = a_0 = 0, \quad a_{-1} = -\frac{16\sqrt{2Z}}{\pi}a_{-4}$$

$$b_0 = 2\beta_{-4}, \quad b_1 = b_2 = b_4 = 0, \tag{12}$$

$$n(n+2)\,b_n - \frac{16\sqrt{2Z}}{\pi}\sum_{j=0}^{l}(-1)^j D_j b_{n-3-2j} = 0,$$

where $l = \dfrac{n-4}{2}$ for even $n$, $l = \dfrac{n-3}{2}$ for odd $n$, and $n = 3, 4, 5, \ldots$ also

$$n(n+2)\,a_n + 2(n+1)\,b_n - \frac{16\sqrt{2Z}}{\pi}\sum_{j=0}^{l}(-1)^j D_j\, a_{n-3-2j} = 4\beta_{n-4}\,, \qquad (13)$$

where $l = \dfrac{n}{2}$ for even $n$, $l = \dfrac{n+1}{2}$ for odd $n$,

$$\beta_{2n+1} = 0 \text{ and } n = 1, 2, 3, \ldots .$$

The symbols $D_j$ appearing in formulae (12) and (13) are given by Equ. (8). The solution of Equ. (9) still contains one arbitrary constant $\alpha_0$. This can be

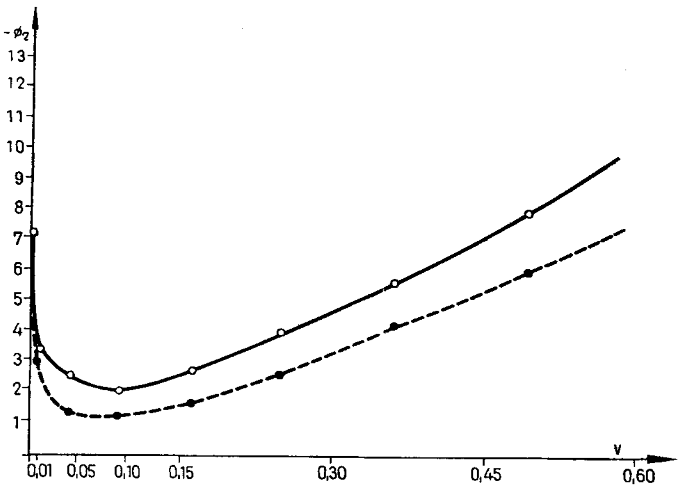


*Fig. 1.* Graph of $-\Phi_2$ against $r$ for $Z = 28$. —— the results of P. VENKATARANGAN; ---- the results of the authors

evaluated from the boundary condition at the origin. For any neutral atom the potential near the origin is dominated by the nuclear attraction and this is equal to $-Ze^2/r$. Since the Thomas—Fermi potential $\Phi_0$ also tends to $-Ze^2/r$ as $r \to 0$, it is clear that the correlation to the Thomas— Fermi potential contains any $1/t^2$, so that $\alpha_0 = 2A + C/48$. When $\alpha_0 = 2A + C/48$ is substituted in Equ. (8) we get the correction $\Phi_2$ to the Thomas— Fermi potential.

We have studied the nature of variation of $\Phi_2$ with $r$ for the atoms silicon and nickel which have atomic numbers $Z = 14$ and $Z = 28$, respectively. Figs. 1 and 2 give the graphs of $\Phi_2$ as a function of $r$. Our results have been compared with those of VENKATARANGAN [7], which are based on another approximate solution of the Thomas—Fermi potential given by the author [8].

From the graphs it follows that $\Phi_2$ starts from infinity for very small values of $r$, decreases to a minimum value and again increases.

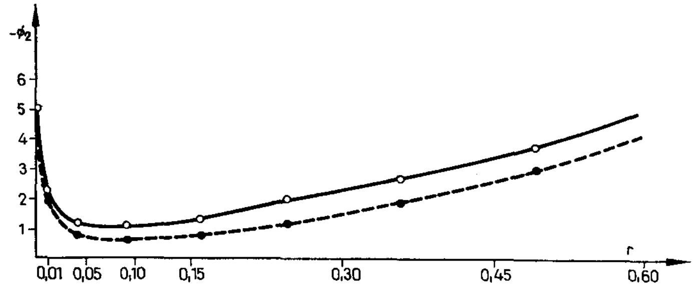


*Fig. 2.* Graph of $-\Phi_2$ against $r$ for $Z = 14$. —— the results of P. VENKATARANGAN, ---- the results of the authors

## Solution of the Baraff equation for low density

For an electron gas of low density the correlation energy is given by the WIGNER formula, i.e. by Equ. (4). The only difference in the differential equation (1) now arises from the term $(E_S - p_F^2/2m)$ which in this case is equal to $-0.89$ $\bar{\alpha}\pi(e^2 p_F/\pi\hbar)$.

After some calculation it can be shown that in this case the correction $\Phi_2$ to the Thomas—Fermi potential can be written as

$$\Phi_2 = r^{-2.676} \sum_{k=0}^{\infty} \gamma_k r^{-k} - \frac{1}{96}\left[\frac{1}{r^2} + \frac{4A}{r(1+Ar)} + \frac{2C}{r(1+Cr)} - \right.$$

$$\left. - \frac{20A^2}{(1+Ar)^2} - \frac{7C^2}{(1+Cr)^2} - \frac{12AC}{(1+AC)(1+Cr)}\right] + \sum_{p=0}^{\infty} d_{2p}\, r^{-\frac{2p+4}{2}},$$

where the expansion coefficients $d_{2p}$ are given by

$$d_0 = \frac{\delta_y}{2 - \frac{4}{\pi A}\sqrt{\frac{2Z}{C}}} \qquad d_1 = 0\,,$$

$$\left[(n+2)(n+4) - \frac{16}{\pi A}\sqrt{\frac{2Z}{C}}\right] d_n - \frac{16}{\pi A}\sqrt{\frac{2Z}{C}} \sum_{j=1}^{l} (-1)^j D_j' d_{n-2j} = 4\delta_{\frac{n}{2}+4} \tag{15}$$

for even $n$, and zero for odd $n$, where $l = n/2$ for even $n$, and $l = n - 1/2$ for odd $n$, and $n = 2, 3, 4, \ldots$, the expansion coefficient $\gamma_k$ satisfies the following formulae:

$$s = \frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{4}{\pi A}\sqrt{\frac{2Z}{C}}} \approx 2.676\,, \quad \text{when} \quad \gamma_0 \neq 0\,, \tag{16}$$

$$\left[(s+n-1)(s+n) - \frac{4}{\pi A}\sqrt{\frac{2Z}{C}}\right]\gamma_n - \frac{4}{\pi A}\sqrt{\frac{2Z}{C}} \sum_{j=0}^{n} (-1)^j D_j' \gamma_{n-j} = 0\,.$$

The symbols $D_j'$ and $\delta_n$ appearing in the last formula are:

$$D_j' = A^{-j} + \sum_{k=0}^{j} \frac{(2k-1)!!}{2k!!} A^{k-j} C^{-k} \tag{17}$$

and

$$\delta_4 = \left(\frac{5}{16} - \frac{8Z}{\pi A^2 C} \cdot 0.89\,\bar{\alpha}\right)$$

$$\delta_n = (-1)^{n-4}\Bigg[\frac{11}{12}\,\frac{(n-3)(n-2)}{2} A^{-n+4} + \frac{1}{3}\,\frac{(n-3)(n-2)}{2} C^{-n+4} +$$

$$+ \frac{1}{4}\sum_{k=0}^{n-4}(k+1) C^{k-n+4} A^{-k} + \frac{1}{4}\sum_{k=0}^{n-4}(k+1) A^{k-n+4} C^{-k} -$$

$$+ \frac{1}{4}\sum_{k=0}^{n-4}\frac{(k+1)(k+2)}{2} A^{k-n+4} - C^{-k} -$$

$$- \frac{1}{4}\sum_{k=0}^{k-4}\frac{(k+1)(k+2)}{2} C^{k-n+4} A^{-k} - \frac{1}{4}\sum_{k=0}^{k-4}(n-k-3)(k+1)\cdot$$

$$A^{k-n+4} C^{-k} - \frac{15}{12}\,\frac{(n-3)(n-2)(n-1)}{1\cdot 2\cdot 3} A^{-n+4} -$$

$$- \frac{7}{16}\,\frac{(n-3)(n-2)(n-1)}{1\cdot 2\cdot 3} C^{-n+4} -$$

$$- \frac{8Z}{\pi A^2 C}\, 0.89\,\bar{\alpha} \sum_{k=0}^{n-4}(k+1) C^{k-n+4} A^{-k}\Bigg].$$

for $n = 5, 6, 7, \ldots$.

From Equ. (18) it follows that $\Phi_2$ asymptotically tends to zero as $r^{-2}$. This is an unsatisfactory feature of the BARAFF equation since one would expect the correction to converge more rapidly than the Thomas—Fermi potential

## REFERENCES

1. For reference see P. VENKATARANGAN, Can. J. Phys., **43**, 1157, 1965 and K. S. VISWANATHAN and B. N. NARAHARI, Achar, Can. J. Phys., **42**, 2332, 1964.
2. G. A. BARAFF, Phys. Rev., **123**, 2287, 1961.
3. P. GOMBÁS, Encyclopedia of Physics, Vol. 36, Springer Verlag, Berlin—Göttingen—Heidelberg, 1956.
4. T. TIETZ, Il N. Cim., **4**, 1192, 1956.
5. M. GELL-MANN and K. BRIECKNER, Phys. Rev., **106**, 364, 1957.
6. E. WIGNER, Phys. Rev., **46**, 1002, 1934.
7. For reference see [1].
8. T. TIETZ, J. Chem. Phys., **2**, 2094, 1954.

# КВАНТОВЫЕ И КОРРЕЛЯЦИОННЫЕ ПОПРАВКИ К ПОТЕНЦИАЛУ ТОМАСА—ФЕРМИ

Т. ТИТЦ и С. КРЗЕМИНСКИЙ

Резюме

В данной работе изучается корреляция к потенциалу Томаса—Ферми, обусловленная неоднородностью обмена и корреляционными эффектами. Применяя уравнение Бараффа и приближенное решение уравнения Томаса—Ферми для свободных нейтральных атомов, данное одним из авторов, рассматривается приближение малой и высокой плотности. Найдено, что основной вклад в решение уравнения Бараффа вносят неоднократные, экранирующие и обменные члены.