REFINEMENT OF SEMICLASSICAL METHOD FOR EVALUATING ELECTRONIC CORRELATION ENERGY

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In this work, we have studied the ground state energy of atomic systems using electron gas approximation. We evaluate the correlation energy for neutral atoms using a semiclassical method including the Dirac's exchange-term in the energy functional. The results obtained show good agreement compared with exact values specially for $Z = 2$ to 18.

1. Introduction

The energy of the ground state for many electron systems is of greatest interest and importance. Taking into account the electronic correlation a good agreement between the theoretical and experimental results can be obtained. The correlation energy of electronic system is a purely theoretical entity. It is commonly defined as the difference between the exact nonrelativistic energy and the Hartree-Fock energy[1].

It is well known that there are, in principle, several methods available in order to calculate electronic correlation energies (E_c). The most important methods for calculating E_c are configuration interaction[2,3], cluster expansion method[4,5], a synthesis of these two methods[6], many body perturbation theory[7-9] and Thomas-Fermi statistical method[10-13]. An approximate estimation of the electronic correlation energy for atomic systems was discussed by Kamel and Labzowsky[14] and then by Kamel et al.[15].

This method is based on the variational evaluation for the correlation energy using the second order perturbation theory together with a Thomas-Fermi statistical expression for the electron density. The idea of approximating the behaviour of various electronic systems by that of the uniform electron gas has recieved much attention from many investigators due to its relative simplicity. The statistical method has proved to be a valuable tool for evaluating a large number of physical parameters. In the earlier days of quantum mechanics[16], this approximation was mainly used to obtain the electronic density distributions.

The aim of this work is to evaluate the correlation energy for atomic systems using the method proposed by Kamel and Labzowsky taking into account the exchange term in the expression of energy.

2. Total energy and separate energy contributions

On the basis of the electron-gas approximation, the energy of an atom with electron density distribution $\varrho(r)$ around the nucleus of atomic number Z is given by[17,18]

$$E = C_k \int [\varrho(r)]^{5/3} \, dr + C_e \int [\varrho(r)]^{4/3} \, dr$$

$$- Z \int [\varrho(r)/r] \, dr + \frac{1}{2} \int\int [\varrho(r_1)\, \varrho(r_2)/r_{12}] \, dr_1 dr_2 \tag{1}$$

which can be written as

$$E = E_k + E_e + E_{p'} + E_{p''}, \tag{2}$$

$$C_k = \frac{3}{10}(3\pi^2)^{2/3}, \qquad C_e = -\frac{3}{4}(3/\pi)^{1/3}.$$

E is the Hartree-Fock part of electron gas approximation which includes kinetic energy E_k, exchange energy E_e and coulombic energy $(E_{p'} + E_{p''})$, which are the first, second, third and fourth terms in Eq. (1), respectively.

$\varrho(r)$ in Eq. (1) satisfies the condition.

$$\int \varrho(r) \, dr = Z \tag{3}$$

$\varrho(r)$ can be chosen in the following form[19]

$$\varrho(r) = A \, e^{-\lambda r}/r^{3/2} \tag{4}$$

where λ represents a variational parameter and A is a normalization factor which can be obtained using Eq. (3) in the form

$$A = \frac{Z}{2}\left(\frac{\pi}{\lambda}\right)^{3/2}. \tag{5}$$

The variational parameter λ, determined from the condition of minimum energy, takes the form

$$\lambda \doteq 0.91743\, Z^{1/3} + 0.15690\, Z^{-1/3}. \tag{6}$$

The H-F part of the electron gas approximation given by Eq. (1) is evaluated as

$$E = -0.75080\, Z^{7/3} - 0.25678\, Z^{5/3} - 0.02190\, Z. \tag{7}$$

3. The correlation energy of neutral atoms

The correlation energy can be taken as the second order perturbation of energy which can be written in the form[20]

$$E_c = -\frac{1}{2} \sum_{m,n}^{\leqslant N} \langle mn| \, U(q_1 q_2) \frac{1}{H(q_1) + H(q_2) - \varepsilon_m - \varepsilon_n} \, U(q_1 q_2) \, |nm\rangle \tag{8}$$

where,

$H(q)$ is the one electron Hartree-Fock Hamiltonian,

$U(q_1 q_2)$ is the electron-electron interaction operator,

N is the number of electrons and

q_1, q_2 are the space and spin variables.

The summation in Eq. (8) is taken over all the occupied states.

Following the work of Kamel and Labzowsky[14] expression (8) takes the form

$$E_c = -\frac{1}{2} \frac{\left[\iint \frac{1}{U(r_1 r_2)} \varrho(r_1) \varrho(r_2) \, dr_1 \, dr_2\right]^2}{\int \frac{1}{U^2(r_1 r_2)} [H(r_1) + H(r_2) - 2\bar{\varepsilon}] \frac{1}{U^2(r_1 r_2)} \varrho(r_1) \varrho(r_2) \, dr_1 dr_2} \tag{9}$$

where

$$H(r_i) = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \int \frac{\varrho(r')}{|r_i - r'|} \, dr',$$

$$U(r_1, r_2) = \frac{1}{|r_1 - r_2|}$$

where $\varrho(r)$ is the Thomas-Fermi statistical expression for the electron density given by Eq. (4) and $\bar{\varepsilon} = E^{HF}/Z$, is the mean energy of one electron.

According to Eq. (9) it is clear that the calculation of the correlation energy E_c requires the evaluation of the following integrals

$$I_1 = \int \frac{1}{U(r_1 r_2)} \varrho(r_1) \varrho(r_2) \, dr_1 dr_2$$

$$= 7.2330 \, Z^2/\lambda \tag{10}$$

$$I_2 = -2\,\bar{\varepsilon} \int \frac{1}{U^4(r_1 r_2)} \varrho(r_1) \varrho(r_2) \, dr_1 dr_2$$

$$= -330 \, Z^2 \, \bar{\varepsilon}/\lambda^4 \tag{11}$$

$$I_3 = \int \frac{1}{U^2(r_1 r_2)} H(r_i) \frac{1}{U^2(r_1 r_2)} \varrho(r_1) \varrho(r_2) \, dr_1 dr_2,$$

where $i = 1, 2$.

A method explained by Kompaneets and Pavlovski[21] and then used by Kamel and Labzowsky[14] was applied to evaluate the integral I_3. The operator $H(r_i)$ was used in an integral form. The matrix element $H(r', r)$ and also $\varrho(r', r)$ expanded in the form of Fourier integrals in terms of $(r' - r)$. Finally the following expression for I_3 can be obtained

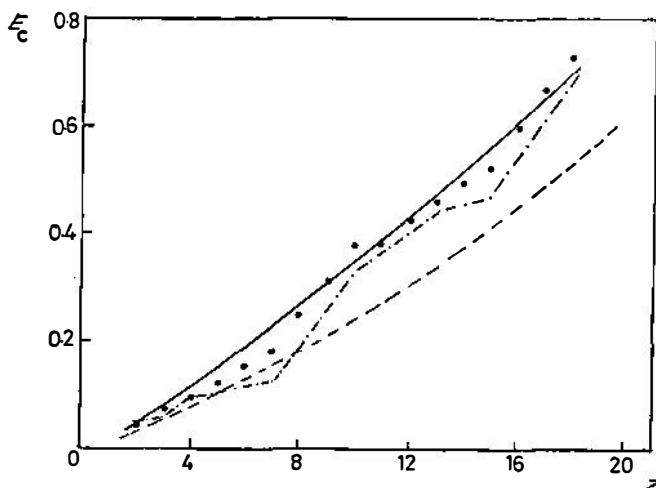$$I_3 = 56.4309 \, Z^{8/3}/\lambda^2 - 77.8289 \, Z^3/\lambda^3. \tag{12}$$

Fig. 1. The correlation energy E_c in atomic units (1 au $= 4.36 \cdot 10^{-18}$ J) for atomic systems with atomic number Z from 2 to 18.

● ● Experimental[22];

————— Present work;

— — — — Results of Ref 14;

—·—·— Present work (spin dependent)

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Substituting Eqs. (10), (11) and (12) into Eq. (9) using λ as given by Eq. (6) we obtain the following formula for the electronic correlation energy.

$$E_c = - \frac{1.1154\, Z^{8/3} + 0.3815\, Z^2 + 0.0326\, Z^{4/3}}{4.0398\, Z^{2/3} - 23.8903\, Z^{4/3} + 1.3896 - 165\, E^{HF}/Z} \cdot \tag{13}$$

Fig. 1 shows the atomic correlation energy E_c as a function of the atomic number Z. It is clear that our results give a good agreement with the exact values of Veillard and Clementi[22] better than that calculated by Kamel and Labzowsky[14] using the same method without Dirac's exchange term in the energy.

4. The angular momentum dependence of electron correlation

To study the effect of the spin S of the atom on the electronic correlation energy, we use the generalized Thomas-Fermi statistical model, in which two different values for the density matrix are considered. ϱ_1 and ϱ_2 are the density matrices for electrons with different spin projections. These densities satisfy the conditions

$$\int (\varrho_1 + \varrho_2)\, \mathrm{d}\mathbf{r} = Z$$
$$\int |\varrho_1 - \varrho_2|\, \mathrm{d}\mathbf{r} = 2S. \tag{14}$$

ϱ_1, ϱ_2 can be chosen in the form

$$\varrho_{1,2} = A_{1,2}\, \frac{e^{-\lambda_{1,2} r}}{r^{3/2}}. \tag{15}$$

The variational parameters λ_1, λ_2, determined from the condition of minimum energy taking the exchange term E_e (Eq. (2)) into account, take the form

$$2A'(\gamma)\, B(\gamma) - A(\gamma)\, B'(\gamma) = 0, \tag{16}$$

where the primes denote differentiation with respect to γ,

$$A = -(\delta + 1)(1 + \delta\gamma) + 0.1817(1 + \delta^2\gamma) - 0.1398 \left(\frac{\delta + 1}{Z}\right)^{2/3}(1 + \delta^{4/3}\gamma) +$$
$$+ 0.6366\, \delta\, |-\sqrt{\gamma} + 1.57\gamma + (1 - \gamma)\tan^{-1}\sqrt{\gamma}|, \tag{17}$$
$$B = 1.416\,(1 + \delta^{5/3}\gamma^2)(1 + \delta)^{7/3}, \tag{18}$$
$$\lambda_2 = -Z^{1/3}\, A\,(1 + \delta)^2/B, \tag{19}$$

$$\gamma = \lambda_1/\lambda_2 \quad \text{and} \quad \delta = (Z - 2S)/(Z + 2S).$$

Using the iteration method a numerical solution for Eq. (16) was carried out to obtain the values of γ then λ_1 and λ_2. Using $\varrho = \varrho_1 + \varrho_2$ in Eq. (9) and calculating the required integrals the electronic correlation energies E_c were calculated for atoms with $Z = 2$ to 18 in ground states.

The results shown in Fig. 1 attained the same trend as that obtained by Veillard and Clementi[22].

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POBOLJŠANJE POLUKLASIČNE METODE ZA ODREĐIVANJE KORELATIVNE ENERGIJE ELEKTRONA

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U radu se proučava energija osnovnog stanja atomskog sistema koristeći aproksimaciju elektronskog plina. Određena je korelativna energija neutralnih atoma koristeći poluklasičnu metodu koja uključuje Dirac-ov član zamjene u funkcionalu energije. Postignuti rezultati pokazuju dobro slaganje s pravim vrijednostima, posebno za $Z = 2 - 18$.