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INFLUENCE OF CORRELATION FUNCTION ON EVALUATION OF THE CORRELATION ENERGY FOR THE PAIR ($1s\uparrow 1s\downarrow$) OF THE Be ATOM AND ITS ISOELECTRONIC SERIES

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The influence of various correlation functions is studied and applied to the pair ($1s\uparrow 1s\downarrow$) of Be atom and its isoelectronic series in ground states. Two-particle approximation is used for the evaluation of the correlation energies E_c. This method allows the evaluation of E_c for different pairs separately. In the ground state of Be atom, values of E_c obtained using functions of the type $\chi = \beta(r_1 + r_2)\varphi$, $\chi = (\alpha r_{12} + \beta(r_1 + r_2))\varphi$ and $\chi = (\alpha r_{12} + \gamma r_{12}(r_1 + r_2))\varphi$ agree with the exact values. Results approaching 96% of the exact values are obtained using functions of the type $\chi = [\alpha r_{12} + \beta(r_1 + r_2) + \gamma r_{12}(r_1 + r_2)]\varphi$.

1. Introduction

Two particle approximation represents one of the most important methods in the theory of many electron systems. Two particle approximation is a generalization of one electron Hartree-Fock approximation, in which every two electrons move in the potential of the other electrons of the system. In this method the pair correlation energy is taken into consideration. This method was first proposed by Fock et al.[1] in 1940 and continued by Jusys[2] and Arai[3]. It was derived theoretically by Sinanoglu[4-5] and then tested by different authors[6-14]. In Sinanoglu's method, the solution of the two-electron problem is correct only within the limits of the second order perturbation theory. The two-electron correlation without using perturbation theory can be calculated using Brenig's method[15].

Brenig's expression for the correlation energy in the two particle approximation can be divided exactly into different pair contributions[16]. In this paper Brenig's method is used for the calculation of the correlation energy for the pair ($1s\uparrow\ 1s\downarrow$) of Be atom and their isoelectronic series. The influence of various correlation functions on the correlation energy is studied.

2. *Theoretical aspects and considerations*

Brenig's expression for the correlation energy for N electron atom can be written in the form

$$E_c = \frac{1}{2} \sum_{i \neq j}^{N} \left\{ \frac{2}{N-1} \varphi_i(x_1)\, \varphi_j(x_2)\, [h(x_1) + h(x_2)]\, \chi_{ij}(x_1 x_2) + \right.$$

$$\left. + \varphi_i(x_1)\, \varphi_j(x_2)\, U(x_1 x_2)\, \chi_{ij}(x_1 x_2) \right\}. \tag{1}$$

The correlation energy for ($1s\uparrow\ 1s\downarrow$) pair in Be atom and its isoelectronic series in ground state can be written in the form

$$E_c^{1s\uparrow 1s\downarrow} = \frac{1}{3} [\varphi_{1s\uparrow}(x_1)\, \varphi_{1s\downarrow}(x_2)\, [h(x_1) + h(x_2)]\, \chi_{1s\uparrow 1s\downarrow}(x_1 x_2)] +$$

$$+ \frac{1}{2} [\varphi_{1s\uparrow}(x_1)\, \varphi_{1s\downarrow}(x_2)\, U(x_1 x_2)\, \chi_{1s\uparrow 1s\downarrow}(x_1 x_2)] \tag{2}$$

where

$$h(x_i) = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}$$

and

$$U(x_1 x_2) = \frac{1}{r_{12}}.$$

r_i is the distance of electron i from the nucleus, and r_{12} is the interelectronic distance. $\chi_{1s\uparrow 1s\downarrow}(x_1 x_2)$ is the correlation part of the two-particle wave function $\varphi^{1s\uparrow 1s\downarrow}(x_1 x_2)$, which is taken in the form[17]

$$\varphi^{1s\uparrow 1s\downarrow}(x_1 x_2) = \varphi_{1s\uparrow 1s\downarrow}(x_1 x_2)\, [1 + \alpha r_{12} + \beta(r_1 + r_2) +$$

$$+ \gamma r_{12}(r_1 + r_2) + \delta(r_1 - r_2)^2 + \varepsilon(r_1 + r_2)^2 + \xi r_{12}^2] \tag{3}$$

where

$$\varphi^{1s\uparrow 1s\downarrow}(x_1 x_2) = \varphi_{1s\uparrow 1s\downarrow}(x_1 x_2) + \chi_{1s\uparrow 1s\downarrow}(x_1 x_2) \tag{4}$$

and $\varphi_{1s\uparrow 1s\downarrow}(x_1x_2)$ is chosen in the antisymmetric form

$$\varphi_{1s\uparrow 1s\downarrow}(x_1x_2) = \frac{1}{\sqrt{2}}[\varphi_{1s\downarrow}(r_1)\varphi_{1s\downarrow}(r_2) - \varphi_{1s\uparrow}(r_2)\varphi_{1s\downarrow}(r_1)]. \tag{5}$$

α, β, γ, δ, ε and ξ in Eq. (3) are variational parameters and can be determined using variational procedure which leads to the equation.

$$|H_{KL} - EN_{KL}| = 0 \tag{6}$$

where

$$N_{KL} = \int \psi_K^* \psi_L \, dx_1 dx_2$$

$$H_{KL} = \int \psi_K^* H \psi_L \, dx_1 dx_2$$

$$\psi_K = f_K(x_1x_2)\varphi_{1s\uparrow 1s\downarrow}(x_1x_2)$$

$$f_1(x_1x_2) = r_{12}, \qquad f_2(x_1x_2) = (r_1 + r_2),$$

$$f_3(x_1x_2) = r_{12}(r_1 + r_2), \qquad f_4(x_1x_2) = (r_1 - r_2)^2,$$

$$f_5(x_1x_2) = (r_1 + r_2)^2, \qquad f_6(x_1x_2) = r_{12}^2$$

while $f_0(x_1x_2)$ is taken as unity.

In all above calculations we have used the analytic ion-electron function[18].

3. *Results and discussions*

On the basis of the two particle approximation method, the correlation energy for the pair ($1s\uparrow$ $1s\downarrow$) of the beryllium atom and its isoelectronic series were calculated. The variational parameters for various correlation functions used are given in Table 1. The corresponding values of the correlation energy E_c are given in Table 2. Comparison of our results and those obtained by different workers for Be atom and its isoelectronic series are given in Table 3. This comparison indicates that the choice of a good correlation function allows in principle the exact calculation of the correlation energy. As an example, the results obtained by Kamel and Labzovsky[16] using the same method but with the function

$$\chi_{1s\uparrow 1s\downarrow}(x_1x_2) = \varphi_{1s\uparrow 1s\downarrow}(x_1x_2)[\alpha r_{12} + \beta(r_1 + r_2) + \varepsilon(r_1 + r_2)^2]$$

give a result smaller than that obtained in the present work using the function

$$\chi_{1s\uparrow 1s\downarrow}(x_1x_2) = \varphi_{1s\uparrow 1s\downarrow}(x_1x_2)[\alpha r_{12} + \beta(r_1 + r_2) + \gamma r_{12}(r_1 + r_2)].$$

TABLE 1.

Function used	Parameter	Z : 4	5	6	7	8
$f_0 f_1$	α	0.0137	0.0110	0.0091	0.0079	0.0070
$f_0 f_2$	β	0.0126	0.0102	0.0087	0.0077	0.0070
$f_0 f_3$	γ	0.0136	0.0139	0.0140	0.0142	0.0144
$f_0 f_5$	ε	0.0870	0.0088	0.0090	0.0090	0.0090
$f_0 f_6$	ξ	0.0130	0.0136	0.0138	0.0139	0.0140
$f_0 f_1 f_2$	α	0.0092	0.0071	0.0062	0.0054	0.0049
	β	0.0072	0.0060	0.0049	0.0043	0.0039
$f_0 f_1 f_3$	α	0.0115	0.0099	0.0089	0.0081	0.0076
	γ	0.0090	0.0082	0.0075	0.0068	0.0062
$f_0 f_1 f_2 f_3$	α	0.0086	0.0074	0.0067	0.0061	0.0058
	β	0.0070	0.0056	0.0048	0.0043	0.0038
	γ	0.0052	0.0040	0.0032	0.0027	0.0023

Calculated values of the variational parameters.

TABLE 2.

Parameter used	Z : 4	5	6	7	8
α	262	268	270	275	281
β	328	332	338	345	355
γ	249	252	254	257	260
ε	208	211	211	213	214
ξ	177	177	184	187	189
α, β	365	370	376	384	395
α, γ	386	391	398	407	418
α, β, γ	430	436	443	453	466

Correlation energy for the pair ($1s\uparrow\ 1s\downarrow$) of Be atom and its isoelectronic series in the ground state (units of E_c in H with reversed sign; 1 H = 27.2 eV).

This function leads to about 96% of the exact value. It is pointed that the method used in this study follows a simple procedure for calculating the correlation energy and does not involve complicated calculations. Despite this, from Table 2 it is clear that reliable values of E_c are obtained using functions of the form

$$\chi_{1s\uparrow 1s\downarrow}(x_1 x_2) = \beta\, \varphi_{1s\uparrow 1s\downarrow}(x_1 x_2)(r_1 + r_2),$$

$$\chi_{1s\uparrow 1s\downarrow}(x_1 x_2) = \varphi_{1s\uparrow 1s\downarrow}(x_1 x_2)\,[\alpha r_{12} + \beta (r_1 + r_2)]$$

and

$$\chi_{1s\uparrow 1s\downarrow}(x_1 x_2) = \varphi_{1s\uparrow 1s\downarrow}(x_1 x_2)\,[\alpha r_{12} + r_{12}(r_1 + r_2)].$$

TABLE 3.

Method	E_c (in H with reversed sign)
1) Perturbation theory on the basis of Hartree-Fock function (second order)[19].	360
2) Two body approximation[10].	420
3) Two body approximation (Brenig's method f_0, f_1, f_2, f_3)[16].	390
4) Two body approximation (Brenig's method f_0, f_1)[20].	260
5) Semiempirical values of E[13].	418
6) Present work Brenig's method.	
a) f_0, f_6	117
b) f_0, f_5	208
c) f_0, f_3	249
d) f_0, f_1	262
e) f_0, f_2	328
f) f_0, f_1, f_2	365
g) f_0, f_1, f_3	386
h) f_0, f_1, f_2, f_3	430
7) Exact value	446

($1s\uparrow\ 1s\downarrow$) contribution for the correlation energy of Be atom in its ground state.

The function $[\varphi_{1s\uparrow 1s\downarrow}(x_1x_2)\,\delta(r_1 - r_2)^2]$ gives very small values of E_c and hence we do not report it. Moreover this method allows the evaluation of E_c for different pairs separately. This allows the calculation of the correlation energy for the pair ($1s\uparrow\ 1s\downarrow$) of the Be atom and its isoelectronic series.

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UTJECAJ IZBORA KORELACIJSKE FUNKCIJE NA VRIJEDNOST KORELACIJSKE ENERGIJE ZA PAR ($1s\uparrow\ 1s\downarrow$) U ATOMU Be I NJEMU IZOELEKTRONSKIMA

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Istražuje se utjecaj izbora raznih korelacijskih funkcija za par ($1s\uparrow\ 1s\downarrow$) u osnovnom stanju atoma Be i njemu izoelektronskima. Koristi se dvočestična aproksimacija za računanje korelacijske energije E_c. Metoda dozvoljava računanje E_c za svaki par posebno. Za osnovno stanje atoma Be vrijednosti E_c, koristeći funkcije oblika $\chi = \beta(r_1 + r_2)\varphi$, $\chi = [\alpha r_{12} + \beta(r_1 + r_2)]\varphi$ i $\chi = [\alpha r_{12} + \gamma r_{12}(r_1 + r_2)]\varphi$, dobro se slažu s točnom vrijednošću. Funkcija oblika $\chi = [\alpha r_{12} + \beta(r_1 + r_2) + \gamma r_{12}(r_1 + r_2)]\varphi$ daje rezultate koji odstupaju 96% od točne vrijednosti.