CORRELATION ENERGY OF THE $(1s)^2 2s$ STATE OF THE Be^{+1} AND B^{+2} IONS

Mohammed Abdulhussain Al-Kaabi
Department of Physics, College of Science, Kerbala University

ABSTRACT:

A configuration interaction method is used to calculate the correlation energy of $(1s)^2 2s$ state for the Beryllium and Boron ions. The specific form of the configurations used for the systems studied here is linear combination of Slater determinants taken from Weiss with expansion lengths equal to (18). The difference between correlated energy and HF energy (correlation energy) was found to be (-0.01476 a.u) to Beryllium ion,(-0.00787a.u) to Boron ion. Our calculations were also made on the expectation values for the two above ions.

الخلاصة :-

تم استخدام الطريقة التقريبية (Configuration Interaction) لحساب طاقة الترابط الفراغي لايونات البرليوم والبورون عند المستوى الارضي اعتمادا على الدالة الموجية المقدمة من قبل الباحث Weiss والمتضمنة 18 شكل من اشكال الدالة الموجية . لقد وجد ان قيمة طاقة الترابط المحسوبة من الفرق بين الطاقة المتضمنة للترابط الفراغي (.E_{corr}) وطاقة هارتري فوك (HF) مساوية لـ - 0.01476 و 0.00787- بالوحدات الذرية لايوني البريليوم والبورون على التوالي . اضاف الى ذلك فقد عرضت القيم المتوقعة لكلا الايونين .

INTRODUCTION :

For many electron system, the anti-symmetric nature of the total wave function written as a determinant gives rise to the so-called "Fermi hole " which is a measure of a correlation effect between any pair of electrons possessing parallel spin components[1]. This means that the many electron system (represented by HF approximation) leaves much of the electron correlation out [2, 3], furthermore, the excited states are difficult to calculate. The essential problem is the construction of a wave function which also allows for spatial correlation between electrons with anti-parallel spins and capable calculate the excited states. Such wave function is formed by many method[1] such configuration interaction (CI)[4], the explicit interaction of correlation factors involving r_{ij} for any pair of electrons i and j such Hylleraas method [5,6], Cluster expansion [7] , Moller-Plesset perturbation theory [8], $Hy-CI$ method[9] and Full CI [10].The CI method is often employed by chemists when studying atom or small molecules, in this method the energy is minimized by searching through all Ψ which are linear combinations of N-electron determinants.In present work the electron correlation examined in terms of the correlation energy, which is the difference between the correlated energy and HF energy.Banyard and Al-Bayati[11] used the many electron theory (MET) proposed by Sinanglu to partition the two-particle difference density required for the evaluation the correlation energy and we used this density here to determine the correlation energy for the individual shells for Be^{+1} and B^{+2} ions by using the correlated wave function of Weiss with 18 configurations [12] and the HF functions of Weiss[13] .

THEORY AND WAVE FUNCTION

In the method of the configuration interaction, the wave function is proposed as a linear combination of many-electron system [12]:

$$\Psi_{corr.} = \Sigma_i c_i \Phi_i \qquad (1)$$

where Φ is an anti-symmetrized product of one –electron functions, and the coefficient c is taken to minimize the total energy.

According to forms of Weiss every Φ (every configuration) for three-electron system given by the following linear combinations of Slater determinants [12]:

$$(\varphi\chi)\psi = (6D_\lambda)^{-1/2} \sum_\mu \{ |\bar{\varphi}_{\lambda\mu}(1)\alpha\chi_{\lambda\mu}(2)\beta\psi(3)\alpha| + |\bar{\chi}_{\lambda\mu}(1)\alpha\varphi_{\lambda\mu}(2)\beta\psi(3)\alpha| \} \qquad (2)$$

Each single electron function φ, χ and ψ is a Slater-type orbital that is normalized but not orthogonal and consist of radial and angular $Y_{lm}(\theta, \vartheta)$ parts :

$$\chi_{nlm}(\zeta) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \vartheta) , \qquad (3)$$

The α and β spin functions represent the two components of spin and the sum over the azimuthal quantum index μ ensures that the electron pair forming the $K-shell$ core will be of ^1S symmetry. The orbital angular momentum index λ specifies the spin –orbital symmetry, while D_λ designates the degeneracy. The bar over the spin-orbital denotes complex conjugate with the phase of spherical harmonic chosen such that $\bar{Y}_{\lambda,\mu} = Y_{\lambda,-\mu}$.

For the partitioning technique, the correlated two-particle density for each shell can give by [11]:

$$\Gamma_{ij}^{corr.} = \sum_{i<j} (\phi_i\phi_j - \phi_j\phi_i) \left(\frac{\langle \Psi_{corr.} | \pi_{ij} \rangle}{\langle \Psi_{corr.} | \pi \rangle} - \Gamma_{ij}^{HF} \right) \qquad (4)$$

Where π is the product of all occupied HF spin- orbitals, and similarly for π_{ij} but with the omission of ϕ_i and ϕ_j. Γ_{ij}^{HF} is a two-particle density into pair wise components (i, j) in HF-system , defined as [14] :

$$\Gamma_{ij}^{HF} = \frac{1}{2} \sum_{i<j} (\phi_i\phi_j - \phi_j\phi_i)^2 \qquad (5)$$

Where the $(1/2)$ comes from normalization factor .The basis set of one-electron wave functions (ϕ_i and ϕ_j) chosen consisted of the normalized Slater-type orbital as in eq. (3).

The radial correlation contained within a correlated wave function may be investigated by evaluating the two-particle radial density distribution $D_{ij}^{corr.}(r_1, r_2)$, which defined as [15]:

$$D_{ij}^{corr.}(r_1, r_2) = \iint \Gamma_{ij}'^{corr.} r_1^2 r_2^2 d\Omega_1 d\Omega_2 \qquad (6)$$

Where $d\Omega$ refer to solid angles, r is the distance between electrons and nucleus. $\Gamma_{ij}'^{corr.}$ defined as:

$$\Gamma_{ij}'^{corr.} = \iint \Gamma_{ij}^{corr.} d\sigma_1 d\sigma_2 \qquad (7)$$

Here $d\sigma$ denotes spin-part (α spin up, β spin down).

The determination of expectation value $\langle r_1^m \rangle$ requires evaluation of one particle radial density distribution $D_{ij}^{corr.}(r_1)$ which is defined as [1]:

$$D_{ij}^{corr.}(r_1) = \int_0^\infty D_{ij}^{corr.}(r_1, r_2)\, dr_2 \qquad (8)$$

Then the expectation value $\langle r_1^m \rangle$, where $-2 \le m \le 2$, is determined from the expression [15]:

$$\langle r_1^m \rangle = \int_0^\infty D_{ij}^{corr.}(r_1)\, r^m\, dr_1 \qquad (9)$$

Also the expectation value $\langle r_{12}^m \rangle$ is obtained from [16]:

$$\langle r_{12}^m \rangle = \int_0^\infty f_{ij}^{corr.}(r_{12})\, r_{12}^m\, dr_{12} \qquad (10)$$

Where, $f_{ij}^{corr.}(r_{12})$, defined as [17]:

$$f_{ij}^{corr.}(r_{12}) = 1/2 \left(\int_0^{r12} r_1\, dr_1 \int_{r12-r1}^{r12+r1} \Gamma_{ij}^{\prime\prime corr.}\, r_2\, dr_2 + \int_{r12}^\infty r_1\, dr_1 \int_{r1-r12}^{r1+r12} \Gamma_{ij}^{\prime\prime corr.}\, r_2\, dr_2 \right) \qquad (11)$$

is the radial electron $-$ electron distribution function ,such that :

$$\Gamma_{ij}^{\prime\prime corr.} = \iint \Gamma_{ij}^{\prime corr.}\, d\Omega_1\, d\Omega_2 \qquad (12)$$

Now, the correlated energy in terms of expectation value is given by [18]:

$$V_{ij}^{corr.} = \left(-Z \langle r_1^{-1} \rangle + \langle r_{12}^{-1} \rangle \right) = 2 E_{ij}^{corr.} \qquad (13)$$

Where Z is atomic number for the ions and V is the potential energy, then the correlation energy E_{ij} defined as [12]:

$$E_{ij} = E_{ij}^{corr.} - E_{ij}^{HF} \qquad (14)$$

We can find all the above properties for HF-system by replacing only the $\Gamma_{ij}^{corr.}$ with Γ_{ij}^{HF}.

Our system consisted of three shell are intra-shell $K_\alpha K_\beta$ (for $i=1, j=2$), inter-shell $K_\alpha L_\alpha$ ($i=1, j=3$) and inter-shell $K_\beta L_\alpha$ ($i=2, j=3$).

RESULTS AND DISCUSSION :

Our system consist of three-electron, two in K-shell with same quantum number except spin component, where the first electron with spin up (α) and the other spin–down (β),and the third electron puts in L-shell with spin -up ,this is general distribution of electrons in orbitals for ground state of present system.. For partitioning technique we deal with pair of electrons only, therefore intra and inter shells will arise, the intra shells represented by K-shell and the inter shells represented by $K_\alpha L_\alpha$ and $K_\beta L_\alpha$ shells. Now each shell have two electrons with parallel or anti-parallel spin direction, each of the electrons interact with nucleus by coulomb interaction (attractive interaction), expressed here by $\langle r_1^{-1} \rangle$.Both approximations HF and CI take into account this interaction, the problem is calculation of the interaction between the two-electrons (repulsive interaction $\langle r_{12}^{-1} \rangle$). Because HF-wave function leave much of correlation out when the two electrons with opposite direction, this will causes an accumulation electrons and this yield incorrect energy. The losing amount of correlation calculates by CI ,where the last prevent an accumulation of electrons by taken the electron from

ordinary orbital to be put in orbital with sufficient distance to prevent an accumulation and allows for correlation, as sequence, the energy approach to the experimental value of energy. The effect of this correlation appear in one and inter-particle expectation values ($\langle r_1^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$) for all shell and for two ions , For K-shell(Be^{+1})the effect of correlation causes increasing the one-particle expectation value for negative and positive exponent (m) as shown in table(1),but for inter-particle expectation value the effect decreasing the expectation values for negative (m) and increasing the values for positive (m) , as in table (2). When we go to the B^{+2} ion for same shell, we see that the correlation causes in decreasing one and inter-electron expectation values for negative (m) and increasing the values for positive (m), see tables (3 and 4). The correlation effect on expectation values in other shells clear in above tables.Because of correlation effect, the total energies for both ions are decreasing relative to HF- system and go toward the experimental values (exact values). This is come from the prevention of accumulation of electrons by CI , and the separation of electrons causes decreasing the expectation values relative to HF then the energies are decreases. This is clear from tables (5, 6). Our results agreement with those calculated by other workers [12, 16, 19, 20, 21] for different methods (see tables 1-6) which used to treat the correlation problem. It is worth to mention that the electron correlation oscillates between increasing and decreasing the value of HF-system in the different individual shells, this depend on nature of the wave function ,but the total effect is yield a minimize in total energy (it is the goal from the work). Also our calculations achieved by Mathcad program. The fractions of energy (correlation energy) that found from electron correlation for both ions listed in table (7), where appear that the correlation energy for Be^{+1} and B^{+2} are -0.01476 and 0.00787 (in atomic unit) which corresponding to E_{CI} (-14.29206, -23.38396) respectively. These results are good for our 18-configuration wave function. When compare with those obtained(for example)from Ref.19(-14.324751, -23.424596) find that the last values are best, this is attributes to the number of terms in wave function and the type of wave function, where the number of terms (configurations) for Ref.19 are (164) for Be^{+1} and (201) for B^{+2} .

Finally, our result close to the results of others workers and we do to improve our terms to obtain more amount of correlation.

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Table (1): The one-particle expectation value $\langle r_1^m \rangle$, $-2 \leq m \leq 2$, for Be^{+1} ion.

[a] Value from ref. 19 for Hylleraas-type wave function.
[b] Value from ref.20 for Hartree-Fock wave function.

shell	$\langle r_1^{-2} \rangle$ (a.u)		$\langle r_1^{-1} \rangle$ (a.u)		$\langle r_1^1 \rangle$ (a.u)		$\langle r_1^2 \rangle$ (a.u)	
	HF	CI	HF	CI	HF	CI	HF	CI
$K_\alpha K_\beta$	27.76307	27.77803	3.68243	3.68251	0.4150	0.41512	0.23304	0.23318
$K_\alpha L_\alpha$	14.6062	14.62566	2.1449	2.14642	1.3483	1.34712	3.1670	3.16116
$K_\beta L_\alpha$	14.60662	14.58453	2.1449	2.14388	1.3483	1.34532	3.16700	3.15001
Total	56.97589	56.98822	7.97223	7.97281	3.1116	3.10756	6.56704	6.54435
	56.9865[b]	56.99557[a]	7.97247[b]	7.973875[a]	3.1101[b]	3.101439[a]		6.508210[a]

shell	$\langle r_{12}^{-2} \rangle$ (a.u)		$\langle r_{12}^{-1} \rangle$ (a.u)		$\langle r_{12}^1 \rangle$ (a.u)		$\langle r_{12}^2 \rangle$ (a.u)	
	HF	CI	HF	CI	HF	CI	HF	CI
$K_\alpha K_\beta$	8.91721	8.59825	2.27324	2.24486	0.60717	0.60943	0.46608	0.46636
$K_\alpha L_\alpha$	0.3270	0.32785	0.51275	0.51333	2.33131	2.32916	6.3339	6.32221
$K_\beta L_\alpha$	0.59024	0.57949	0.54832	0.54893	2.32484	2.31881	6.33403	6.29991
Total	9.83445	9.50559	3.33431	3.21308	5.26332	5.25740	13.13401	13.08848
		9.090[c]		3.254[c]		5.270[c]		13.090[c]

Table (2): The inter-particle expectation value $\langle r_{12}^m \rangle$, $-2 \leq m \leq 2$, for Be^{+1} ion.

[c] Value from ref.16 for Hylleraas-type wave function.

Table (3): The one -particle expectation value $\left\langle r_1^m \right\rangle, -2 \le m \le 2$, for B^{+2} ion.

shell	$\left\langle r_1^{-2} \right\rangle$ (a.u)		$\left\langle r_1^{-1} \right\rangle$ (a.u)		$\left\langle r_1^1 \right\rangle$ (a.u)		$\left\langle r_1^2 \right\rangle$ (a.u)	
	HF	CI	HF	CI	HF	CI	HF	CI
$K_\alpha K_\beta$	44.63224	44.61230	4.68068	4.67864	0.32522	0.32546	0.14268	0.14294
$K_\alpha L_\alpha$	23.83811	23.80692	2.77385	2.77194	0.98033	0.98094	1.63467	1.63652
$K_\beta L_\alpha$	23.80692	23.75628	2.77194	2.76954	0.98094	0.97966	1.63652	1.63141
Total	92.27727	92.1755	10.22647	10.22012	2.28649	2.28606	3.41387	3.41087
	92.7550[b]	92.26189[a]	10.22466[b]	10.22552[a]	2.28672[b]	2.282859[a]		3.398147[a]

Table (4): The inter-particle expectation value $\left\langle r_{12}^m \right\rangle, -2 \le m \le 2$, for B^{+2} ion.

shell	$\left\langle r_{12}^{-2} \right\rangle$ (a.u)		$\left\langle r_{12}^{-1} \right\rangle$ (a.u)		$\left\langle r_{12}^1 \right\rangle$ (a.u)		$\left\langle r_{12}^2 \right\rangle$ (a.u)	
	HF	CI	HF	CI	HF	CI	HF	CI
$K_\alpha K_\beta$	14.44873	14.04559	2.89712	2.86856	0.47550	0.47707	0.28537	0.28587
$K_\alpha L_\alpha$	0.62136	0.62017	0.70853	0.70795	1.67891	1.67999	3.26935	3.27312
$K_\beta L_\alpha$	1.16954	1.14507	0.76555	0.76513	1.67375	1.67111	3.27312	3.26281
Total	16.23963	15.81076	4.3712	4.34164	3.82816	3.82817	6.82784	6.82180
		15.300[c]		4.287[c]		3.837[c]		6.829[c]

Table (5):The potential energy and total energy for Be^{+1} ion.

shell	V (a.u)		$E = V/2$ (a.u)	
	HF	CI	HF	CI
$K_\alpha K_\beta$	-12.45648	-12.48518	-6.22824	-6.24259
$K_\alpha L_\alpha$	-8.06685	-8.07235	-4.03342	-4.036175
$K_\beta L_\alpha$	-8.03128	-8.02659	-4.01564	-4.013295
Total	-28.55461	-28.58412	-14.2773	-14.29206
			-14.277393[d]	-14.319810[d]
	$E_{exper.} = -14.32479$ [e]			

[d]Value from ref.21 for CISD wave function. See also Ref 22.
[e] Experimental Value from ref.12

Table (6): The potential energy and total energy for B^{+2} ion.

shell	V (a.u)		$E = V/2$ (a.u)	
	HF	CI	HF	CI
$K_\alpha K_\beta$	-20.50628	-20.52464	-10.25314	-10.26232
$K_\alpha L_\alpha$	-13.15175	-13.16072	-6.575875	-6.58036
$K_\beta L_\alpha$	-13.09415	-13.08257	-6.547075	-6.54128
Total	-46.75218	-46.76793	-23.37609	-23.38396
				-23.340506[d]
$E_{exper.} = -23.42471$[e]				

Table (7): The correlation energy for Be^{+1} and B^{+2} ions.

ION	$E = E^{corr.} - E^{HF}$ (a.u)
Be^{+1}	-0.01476
B^{+2}	-0.00787