Study of the Singlet and the Triplet States of Two Electron Systems in the First Excited State

*Khalil H. Al Bayati** *Maysoon A. Mahmood **

Date of acceptance 28 / 2/ 2010

Abstract

A study of the singlet and triplet states of two electron systems in the first excited state was performed using a simple quantum mechanical model, which assigns the 1s,and 2s orbital with two different variational parameters. Our results agree with a high level calculation used by Snow and Bills.

Key word: atomic properties/structure, quantum chemistry.

Introduction:

Quantum theory used a discussion of the excited states of the Helium atom to demonstrate the importance of the Pauli Principle in determining electronic repulsions [1].

The argument goes as follows:

1-Zeroth order wave functions for excited state of helium are:[2]

$$\psi_S = \frac{1}{\sqrt{2}}[1s(1)2s(2)+2s(1)1s(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \quad \text{……….} (1)$$

$$\psi_T = \frac{1}{\sqrt{2}}[1s(1)2s(2)-2s(1)1s(2)]\alpha(1)\alpha(2) \quad \text{…...} (2)$$

$$\psi_T = \frac{1}{\sqrt{2}}[1s(1)2s(2)-2s(1)1s(2)]\beta(1)\beta(2) \quad \text{……….} (3)$$

$$\psi_T = \frac{1}{\sqrt{2}}[1s(1)2s(2)-2s(1)1s(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)] \quad \text{……….} (4)$$

where ψ_S and ψ_T are the wave functions for singlet and triplet states respectively.

2-These wave functions are used with the electronic repulsion, $\frac{1}{r12}$ (in atomic units),to calculate the first order correction(E^1) to the zeroth order energies [1]

.

$$E^1(2^3S) = \frac{137}{729}\alpha \quad \text{………} (5)$$

$$E^1(2^1S) = \frac{169}{729}\alpha \quad \text{……….} (6)$$

where α is the screening parameter. It is concluded that the triplet have a lower energy than the corresponding singlet because the electronic repulsion $E^{(1)}$ is less for the triplet. The decreased in repulsion of triplet relative to singlet is explained by stating that "Pauli Forces" require that electrons with parallel spins be farther apart on the average than electrons with antiparallel spins [3].

---

* Physics Department, College of Science for Women, University of Baghdad.

Snow and Bills calculate the optimum value of the screening parameter α instead of the usual α =2, a similar result will be obtained by variational calculations as in table (1). The triplet has lower energies than the corresponding singlet, for the same reason mentioned above.

An obvious improvement to the first-order perturbation theory calculation is to add a variational parameter α to the 1s and 2s wave functions as in table (2) [1].

$$\psi_{1s}=\sqrt{\frac{\alpha^3}{\pi}}e^{-\alpha r} \qquad \ldots(7)$$

Calculations

$$\psi_{2s}=\sqrt{\frac{\alpha^3}{32\pi}}(2-\alpha r)e^{-\frac{\alpha r}{2}} \qquad \ldots.(8)$$

The most accurate calculations(for practical purposes exact)available for the Helium 1s2s excited state are shown in table (3).

Shenkuan[4] previously performed a similar analysis on the basis of the fourth-order perturbation theory calculations.

Table 1: One parameter variational calculations on Helium atom and Li^+ Singlet and Triplet states [1]

property	Helium atom			Lithium atom		
	^1S	Δ	^3S	^1S	Δ	^3S
α	1.815	0.035	1.85	2.185	0.035	2.85
<E>	-2.058	-0.08	-2.1382	-4.951	-0.124	-5.075
<T>	2.058	0.08	2.138	4.951	0.124	5.075
$<V_{ne}>$	-4.536	-0.088	-4.624	-10.555	-0.131	-10.686
$<V_{ee}>$	0.421	-0.106	0.315	0.653	0.117	0.536

$\Delta={}^3S-{}^1S$

Table 2:Expectation values for the Singlet and Triplet states of Helium 1s2s excited state calculated using the zero-order wave functions [1]

property	Helium atom		
	^1S	Δ	^3S
<E>	-2.036	-0.08	-2.124
<T>	2.500	0	2.500
$<V_{ne}>$	-5.000	0	-5.000
$<V_{ee}>$	0.464	-0.088	0.376
$<r_{12}>$	3.085	0.046	3.131

$\Delta={}^3S-{}^1S$

Table 3: Expectation value for the Singlet and Triplet states of the

property	^1S	Δ	^3S
<E>	-2.146	-0.029	-2.175
<T>	2.146	0.029	2.175
$\langle V_{ne} \rangle$	-4.541	-0.078	-4.619
$\langle V_{ee} \rangle$	0.25	0.018	0.268
$\langle r_{12} \rangle$	5.27	0.822	4.488

$\Delta = {}^3S - {}^1S$

Present calculations

In the present work the optimized values of the two parameters wave function in equation(7,8) used to calculate the different expectation values with result shown in (table 4). Our results give different values from those shown in the previous work (table 1, 2, 3 above).

The total wave functions for the singlet and triplet states are

$$\psi_S = \frac{1s(1)2s(2)+1s(2)2s(1)}{\sqrt{2+2s^2_{1s2s}}} \quad \ldots\ldots (9)$$

$$\psi_T = \frac{1s(1)2s(2)-1s(2)2s(1)}{\sqrt{2-2s^2_{1s2s}}} \quad \ldots\ldots\ldots (10)$$

The total energies and the individual terms in the total energies for the two parameters wave function are remarkably similar to those calculated using the accurate wave function.

Table 4: Singlet and Triplet states using two parameters wave function

Hand rule property	Helium singlet	Δ	Helium Triplet	Li^{+1} Singlet	Δ	Li^{+1} Triplet	Be^{+2} Singlet	Δ	Be^{+2} Triplet
α	2.0127	-0.0191	1.99363	3.01861	-0.01927	2.9993	4.02311	-0.0211	4.002
β	0.9247	0.6263	1.5509	1.68125	0.88914	2.5704	2.46544	1.1125	3.5779
$\langle E \rangle$	-2.1705	0.0039	-2.1666	-5.0906	-0.0120	-5.1026	-9.257	-0.0322	-9.2892
$\langle T \rangle$	2.1705	-0.0039	2.1666	5.0906	0.0120	5.1026	9.257	0.0322	9.2892
$\langle V_{ne} \rangle$	-4.594	-0.0264	-4.62038	-10.6294	-0.05476	-10.6842	-19.1597	0.0862	-19.246
$\langle V_{ee} \rangle$	0.2535	0.0336	0.28709	0.4482	-0.4003	0.4790	0.6456	0.0229	0.6685
$\langle r_{1s} \rangle$ *	0.7452	0.0071	0.75239	0.4969	0.0032	0.5001	0.37284	0.0019	0.3748
$\langle r_{2s} \rangle$	6.4887	-2.620	3.8686	3.5688	-1.2345	2.3343	2.43363	-0.7567	1.6769
$\lvert\langle 1s \vert 2s \rangle\rvert$	0.232	0.072	0.304	0.251	0.077	0.328	0.263	0.077	0.34
<r12>	6.3098	-2.2713	4.0385	3.4912	-1.0566	2.4346	2.3928	-0.644	1.7488

Discussion and Conclusions

Table (4) Shows the results of calculations of Singlet and Triplet states for He, Li^+, and Be^{+2} using two parameters wave functions. From this table one can conclude the following:

1-: $<V_{ne}>$ and $<V_{ee}>$ increase as Z increases for both singlet and Triplet states due to the increase of the attraction force of the nucleus.

2- The triplet state gives lower energy than the singlet state because the electron-nuclear attraction out weights the electron-electron repulsion.

3- Atomic size $<r_{2s}>$ decreases in the triplet state for (He,Li^+,Be^{+2}) due to the large decrease in the size of the 2s orbital whereas the 1s orbital size $<r_{1s}>$ is basically nearly the same in the singlet and triplet states.

4- The decrease in the size of the 2s orbital could be responsible for the increase in the electron-nuclear attraction, electron-electron repulsion and the absolute magnitude of the 1s-2s orbital overlap.

5- Two parameters calculation in table (4) does not show the Helium triplet state to be lower in energy than the singlet state but the absolute magnitudes of $<V_{ne}>$ and $<V_{ee}>$ are greater in the triplet state.

The calculations for the Lithium and Berilium ions show that the Triplet state is lower in energy and the same trend in $<V_{ne}>$ and $<V_{ee}>$ as for the Helium atom and the exact calculation. In other words, both electron-electron repulsion and electron-nuclear attraction are stronger in the Triplet state. Thus, the common explanation that the triplet state is favored because of the reduced electron-electron repulsion may be without merit

6-For He ,Li^+, and Be^{+2} the optimized two parameter wave function {table (4)} gives results which are very different from those shown for the optimized one-parameter wave function, and zero-order wave function as in tables (1)and(2). The total energies and the individual terms in total energies for the two parameters wave function are remarkably similar to those calculated using the accurate wave function.

These fairly accurate calculations {table(3)} give an electronic repulsion in the triplet state which is greater than the repulsion in the corresponding singlet state, rather than less as implied by the usual argument. The triplet energy is lower due to the greater nuclear attraction, which is more than compensate for greater repulsion .The average inter-electronic distance in tables (3) and (4) also confirms that electrons are closer in the triplet state than in the corresponding singlet state. This leads us to say that $<V_{ne}>$ decreases more than $<V_{ee}>$ and T increases leading to a more stable triplet state[1].

References

1-Frank Rioux, J. Chem. Educ., 84, No.2, 358 (2007).
2-Physics of Atoms and Molecules, B. H. Bransden & C. J. Joachain, second edition, England (2003).
3-R. L. Snow and J. L .Bills. Chem.Educ.Vol.51,No. 9, 585 (1974)
4-Ni Shenkuan, J. Chem. Educ., 69, No.10, 803 (1992).

دراسة الحالات المفردة والثلاثية للانظمة ذات الالكترونين في الحالة المتهيجة الاولى

ميسون عبد الحميد *** ***خليل هادي البياتي*

**قسم الفيزياء، كلية العلوم للبنات،جامعة بغداد*

الخلاصة:

تم دراسة الحالة الفردية والثلاثيه لذرة الهليوم وايوناتها في الحالة المتهيجة الاولى باستعمال موديل بسيط في ميكانيك الكم حيث اعطي المدار الاول متغير يختلف عن المدار الثاني وكانت النتائج مطابقة لحسابات Snow وBills حيث استخدما حسابات عالية المستوى.