Calculation Some Atomic Properties For Three and Four Electron Systems by Using Hartree- Fock Method

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Abstract. In this paper many physical properties evaluated like two particles radial density distribution function $D(r_1, r_2)$, one-particle radial density distribution function $D(r_1)$ has been evaluated by using Hartree-Fock type wave function for three and four electron systems (Li, Li$^-$, Be, Be$^+$, B$^{+2}$) and the inter particle expectation values $\langle r \rangle$ has been evaluated too. Also it was calculation the expectation values for all energies $\langle V_{en} \rangle$, $\langle \rho \rangle$, $\langle T \rangle$ and $\langle E_{HF} \rangle$. All the results and the behaviors obtained in this work have been discussed, interpreted and compared with those previously obtained. It was found that the maximum of one-particle density distribution is shifting to the origin by increasing the atomic number (Z), due to the attraction forces between the nucleus and the electron clouds. As atomic number is Z increase, all the total energies are increases because the increasing nuclear charge effect. The results also indicate that attraction energy expectation values $\langle V_{en} \rangle$ are larger than the repulsion energy expectation value $\langle V_{en} \rangle$.

Keywords: Hartree-Fock, Radial electronic density distribution .

1. Introduction

Any system can be described by a wave function $\Psi(r_1, r_2 ... r_N)$; it is a mathematical expression to describe the system properties as position, momentum, energy etc. The exact calculation of wave functions for many electron atoms becomes difficult because of the many electron-electron repulsions that should be ignored for simplicity. There are two main kinds of the wave function approximation methods which use in this research, the first one is the uncorrelated wave function approximation Hartree-Fock (HF), and the second one is the correlated wave function approximation Configuration Interaction (CI)[1] Alexei M. Frolov and David M. Wardlaw [2] studied state properties of the four-electron lithium ion Li$^-$ in its ground 2S−state and isotope substituted Li$^-$ and Li$^+$ ions in their ground 2S−state(s) are determined from the results of accurate. Mohammed A Al-Kaabi [3] Studied configuration interaction method is used to calculate the correlation energy of (1s)$^2$ 2s state for the Beryllium and Boron ions. The difference between correlated energy and energy (correlation energy) was found to be (-0.01476 a.u) to Beryllium ion,(-0.00787a.u) to Boron ion. The aim of the this work was studied and evaluated some physical properties for three and four electron systems (Li, Li$^-$, Be, Be$^+$, B$^{+2}$).

2. Theory

Schrödinger’s equation cannot be solved exactly for two-electron atoms or ions. So that an approximation method must be used. For atoms, such as Helium and Lithium the variational method is accurate enough, for atoms of higher atomic number, the best approach to find a good wave function
lies in first calculation an approximate wave function using the Hartree-Fock procedures which depends on the Central Field approximation. The basic idea of this approximation is that each of the atomic electrons moves in an effective spherically symmetric potential v(r) created by the nucleus and all the other electrons. The problem is the determination of the electron-electron repulsion term \[ \sum_{i<j} \frac{1}{r_{ij}} \] \[ \] [4].

There are two methods to calculate this term; first the simple semi-classical method of Thomas and Fermi, second the more precise Hartree-Fock or self consistent field approach. Hartree wave function for the atoms (ions) is not antisymmetric in the electron coordinates because it uses the simple product wave function.

The generalization of the Hartree method which takes into account this antisymmetry requirement imposed by the Pauli Exclusion Principle was carried out in 1930 by Fock and Slater [4]. This generalization of Hartree theory is known as the Hartree-Fock method. In the Hartree-Fock approach, it is assumed, in accordance with the independent particle approximation and the Pauli exclusion principle, that the N-electron wave function is a Slater determinant, or in other words an antisymmetric product of individual electron spin-orbitals. The optimum Slater determinant is then obtained by using the variational method to determine the best individual electron spin-orbital [5].

2.1. Singlet and Triplet States

A complete description of the state of the atom requires that we take the spin of electrons into account. Each electron has a spin of \( \frac{1}{2} \). The spin of an electron may be oriented either parallel or antiparallel to the spin of another electron, giving a total spin of one \( S = 1 \) or zero \( S = 0 \). Spin states with \( S = 0 \) are called singlets because they can be obtained in only one way. However, when \( S = 1 \) the resultant spin vector may have three orientations in space, corresponding to \( m_s = +1, 0, \) and \(-1 \). Therefore, spin states with \( S = 1 \) have three spin wave functions and are called triplet.

\[ \chi_A = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right] \quad M_s = 0 \quad \ldots (1) \]
\[ \chi_s = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) + \alpha(2) \beta(1) \right] \]
\[ \begin{bmatrix} \alpha(1) \alpha(2) \\ \beta(1) \beta(2) \end{bmatrix} \quad M_s = +1 \]
\[ M_s = 0 \]
\[ M_s = -1 \]

where \( \chi_A \) is an anti-symmetric spin wave function, \( \chi_s \) is a symmetric spin wave function, and \( \frac{1}{\sqrt{2}} \) is the normalization factor.

We obtain the total wave function of the atom by combining the orbital wave function given by \( \psi_s \) and \( \psi_A \) and the spin wave function given by \( \chi_s \) and \( \chi_A \).

\[ \psi_{total} = (\text{Orbital wave function}) \times (\text{Spin wave function}) \]
According to Pauli Exclusion Principle \( \psi_{\text{total}} \) must be anti symmetric [6].

We can use any one of the three symmetric two-electron spin functions, so instead of the non degenerate level previously found, we have a triply degenerate level with the three zeroth-order wave functions:

\[
\psi_T = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \alpha(1) \alpha(2) \quad \ldots (3)
\]

\[
\psi_T = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \beta(1) \beta(2) \quad \ldots (4)
\]

\[
\psi_T = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) + \alpha(2) \beta(1)] \quad \ldots (5)
\]

The requirement of antisymmetry of the overall wave function leads to the zeroth-order wave function.[7]

\[
\psi_S = \frac{1}{\sqrt{2}} [1s(1)2s(2) + 2s(1)1s(2)] \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \quad \ldots (6)
\]

2.2. Some Atomic Properties

we demonstrate here some of the atomic properties such as the one-particle radial density distribution function \( D(r_1) \), the one particle expectation value \( \langle r_1^a \rangle \) Root Mean Square (Standard Deviation) \( \Delta r_1 \) and the energy expectation value \( \langle E \rangle \).

2.2.1. Two Particles Radial Density Distribution Function \( D(r_1, r_2) \):

In each individual electronic shell, the two-particle radial density distribution function \( D(r_1, r_2) \) is defined by [8].

\[
D(r_1, r_2) = \int \int \Gamma(r_1, r_2) r_1^2 r_2^2 \, d\Omega_1 \, d\Omega_2 \quad \ldots (7)
\]

where \( \Gamma(r_1, r_2) \) tow-particles density \( d\Omega_i \) denotes integration over all angular coordinates of the position vector \( r_i \).

2.2.2. One-particle Radial distribution function \( D(r_1) \):

The one particle radial density distribution \( D(r_1) \) is very important in the study of the electrons in atom, which means the probability of finding electron in each shell and it represents the density distribution of one electron in each shell, and is defined as [9,10].

\[
D(r_1) = \int_0^\infty D(r_1, r_2) \, dr_2 \quad \ldots (8)
\]
2.2.3. *One particle expectation value* $\langle r_1^n \rangle$:

The one particle expectation value $\langle r_1^n \rangle$ is given by using HF approximations [11]:

$$\langle r_1^n \rangle = \int_0^\infty r_1^n D(r_1)dr_1$$

...(9)

As $n = 0$, the expectation value satisfies the normalization condition

Thus $\langle r_1^0 \rangle = 1$

2.2.4. *Mean Square (Standard Deviation) $\Delta r 1$* :

The standard deviation is a useful quantity characterizing certain distribution. It measures the spread of value about the average value which defined as [12]

$$\Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2}$$

.....(10)

stands for the uncertainty of particle radial position $\Delta r_1$.

2.2.5 *Energy expectation value* $< E >$ :

The potential energy is simply the sum of the electron-nuclear attraction energy and inter electronic repulsion energy, which are proportional to the expectation values $\langle r_i^{-1} \rangle$ and $\langle r_{ij}^{-1} \rangle$ respectively. Therefore we may write: [13] :

$$\langle V \rangle = -Z \sum_i^N \langle r_i^{-1} \rangle + \sum_{i<j}^N \langle r_{ij}^{-1} \rangle$$

...(11)

The energy expectation value related to the potential energy by [14] :

$$\langle E \rangle = \frac{1}{2} \langle V \rangle$$

Therefore:

$$\langle E \rangle = \frac{1}{2} \left[-Z \sum_i^N \langle r_i^{-1} \rangle + \sum_{i<j}^N \langle r_{ij}^{-1} \rangle \right]$$

...(12)

where $Z$ is the atomic number and energy is in atomic units (a.u.).

3. **Result and Discussion.**

for the shells (k, L), r1 and r2 are decreased by increased the atomic number $Z$, as shown the tables (1) and (2), and the function D (r1, r2) is increased by Z. This is obvious because increasing the atomic number leads to an increase in the effect of the effective charge on the envelopes so approaching the nucleus.
Table (3) show that the results of the one-electron radial density distribution function $D(r_1)$, we can note the maximum values of $D(r_1)$ increase as Z increases and decrease their positions towards the nucleus as Z increases according to Coulomb law.

The maximum values for L shell, mean there are two peaks observed, the small peak represented for the probability of finding an electron close to nucleus while the second big peak represented a remote electron from nucleus existing in L shell as shown in fig (1). It was also observed when $r_1 = 0$, then $D(r_1) = 0$. This implies the electron is cannot found in the nucleus, and when $r_1 = \infty$, then $D(r_1)=0$. That implies the electron within the atom it is not found outside its. Note from Table (7) $\langle V_{en} \rangle$ and $\langle V_{ee} \rangle$ increases by increases the atomic number (Z). This behavior can be understood by the fact that each casing shrinks toward the nucleus because of the increased attraction of its nucleus. The distance between the electrons and the nucleus is decreased, and the distance between the two electrons is less, so the potential energy of attraction and contrast increases (the energy between two charges is directly proportional to the amount of the charge and vice versa with the distance between those two charges).

The attraction energy expectation values $\langle V_{en} \rangle$ are larger than the repulsion energy expectation value $\langle V_{ee} \rangle$. This causes the distance between the electrons and the nucleus to be smaller than the distance between the electrons. This difference increases by increasing the atomic number.

**Table 1.** Maximum values of the two-particle radial density distribution function $D(r_1, r_2)$ and the location in the Hartree-Fock (HF) wave function for (K,L)Shell, all values are in a.u.
Table 2. Maximum values of the two-particle radial density distribution function $D(r_1, r_2)$ and the location in the Hartree-Fock (HF) wave function for KL-shell, all values are in a.u.

| Atom & Ion |  KL(3s)-shell | KL(1s)-shell |
|-----------|---------------|--------------|
|           | $r_1$ | $r_2$ | D($r_1,r_2$) | $r_1$ | $r_2$ | D($r_1,r_2$) |
| Li        | 0.4616 | 0.4616 | 0.093813 | 3.8608 | 0.3809 | 0.189301 |
|           | 0.3809 | 3.8608 | 0.189135 | 0.3809 | 3.8608 | 0.189301 |
| Li$^+$    | 0.5326 | 0.5326 | 0.105908 | 0.3714 | 5.4248 | 0.133468 |
|           | 5.4248 | 0.3714 | 0.133464 | 5.4248 | 0.3714 | 0.133468 |
| Be        | 0.3182 | 0.3182 | 0.412309 | 0.2768 | 2.5142 | 0.398157 |
|           | 2.5142 | 0.2768 | 0.396476 | 2.5142 | 0.2768 | 0.398157 |
| Be$^+$    | 0.2967 | 0.2967 | 0.249182 | 0.2728 | 2.1538 | 0.467058 |
|           | 2.1538 | 0.2728 | 0.463248 | 2.1538 | 0.2728 | 0.467058 |
| B$^{+2}$  | 0.2178 | 0.2178 | 0.455438 | 0.2134 | 1.5228 | 0.851467 |
|           | 1.5228 | 0.2134 | 0.837639 | 1.5228 | 0.2134 | 0.851467 |

Table 3. Maximum values of the one-particle radial density distribution function $D(r_1)$ and position by using Hartree-Fock wave function for (K,L)Shell, all values are in a.u.

| Shell | Atom or ion | Z | $r_1$ | Max.D($r_1$) |
|-------|-------------|---|-------|--------------|
| K(1s) | Li          | 3 | 0.3637 | 1.405855    |
|       | Li$^+$      | 3 | 0.3636 | 1.406211    |
|       | Be          | 4 | 0.2671 | 1.945026    |
|       | Be$^{+1}$   | 4 | 0.2670 | 1.945326    |
|       | B$^{+2}$    | 5 | 0.2208 | 2.455357    |
|       | Li          | 3 | 0.2979 | 0.028822    |
|       | Li$^+$      | 3 | 0.2989 | 0.013844    |
| L(1s) | Be          | 4 | 0.2151 | 0.053143    |
|       | Be$^{+1}$   | 4 | 0.2142 | 0.075202    |
|       | B$^{+2}$    | 5 | 0.21854| 0.14167     |
Table 4. values of positions and maximum values of D(r₁) by using Hartree -Fock wave function for KL-Shell, all values are in a.u.

| Shell  | Atom or ion  | Z  | r₁   | Max.D(r₁) |
|--------|--------------|----|------|-----------|
| KL(1s) | Li           | 3  | 0.3615 | 0.71659   |
|        | Li⁺         | 3  | 0.3625 | 0.709700  |
|        | Be          | 4  | 0.2647 | 0.997413  |
|        | Be⁺⁺       | 4  | 0.2637 | 1.007845  |
|        | B⁺²        | 5  | 0.22951| 1.3312    |

Table 5. The one particle expectation value ⟨r₁ⁿ⟩ and standard deviation Hartree -Fock wave function for (K-L) Shell , all values are in a.u.

| Shell   | Atom or Ion | Results and comparisons | n=-2  | n=-1  | n=+1  | n=+2  | Δ r₁  |
|---------|-------------|-------------------------|-------|-------|-------|-------|-------|
| K(1s)   | Li          | Present work Ref.[14]   | 14.8883 | 2.6850 | 0.5731 | 0.4468 | 0.3440 |
|         | Li⁺         | Present work Ref.[14]   | 14.8923 | 2.6855 | 0.5729 | 0.4464 | 0.3437 |
|         | Be          | Present work Ref.[14]   | 27.7534 | 3.6819 | 0.4150 | 0.2330 | 0.2464 |
|         | Be⁺⁺       | Present work Ref.[14]   | 44.63224| 4.68068| 0.32521| 0.14267| 0.1921 |
| L(1s)   | Li          | Present work Ref.[14]   | 0.4354  | 0.3454 | 3.8737 | 17.7384| 1.6532 |
|         | Li⁺         | Present work Ref.[14]   | 0.2255  | 0.2496 | 5.7503 | 43.5989| 3.2454 |
|         | Be          | Present work Ref.[14]   | 1.0556  | 0.5225 | 2.6494 | 8.4262 | 1.1861 |
|         | Be⁺⁺       | Present work Ref.[14]   | 1.4496  | 0.6074 | 2.2800 | 6.0885 | 0.9434 |
|         | B⁺²        | Present work Ref.[14]   | 2.98160 | 0.86320| 1.6366 | 3.1303 | 0.6720 |
Table 6. The one particle expectation value \(\langle r^2 \rangle \) and standard deviation, in Hartree-Fock wave function for (KL) Shell, all values are in a.u.

| Shell  | Atom or Ion | Results and comparisons | \( n=-2 \) | \( n=-1 \) | \( n=+1 \) | \( n=+2 \) | \( \Delta r_1 \) |
|--------|-------------|-------------------------|---------|---------|---------|---------|---------|
| KL(\(1s\)) & Li | Present work | 7.6619 | 1.5152 | 2.2234 | 9.0926 | 2.0369 |
| & KL(\(1s\)) & Li\(^+\) | Present work | 7.5589 | 1.4675 | 3.1616 | 22.0226 | 3.4679 |
| KL(\(1s\)) & Be | Present work | 14.4045 | 2.1022 | 1.5322 | 4.3296 | 1.4078 |
| KL(\(1s\)) & Be\(^+\) | Present work | 14.6065 | 2.1449 | 1.3475 | 3.1608 | 1.1598 |
| B\(^{+2}\) & B\(^{+2}\) | Present work | 23.28609 | 2.7719 | 1.02435 | 1.80924 | 0.8211 |

Table 7. The attraction energy expectation values \(\langle V_{en} \rangle\) and The repulsion energy expectation values \(\langle V_{ee} \rangle\) in the HF wave functions and the total energy, all values are in a.u.

| Atom or Ion | \( \langle V \rangle \) | \( -\langle E\rangle = -1/2\langle V \rangle \) | E\(_{corr}\) |
|-------------|-----------------|-----------------|-------|
| Li | 17.14637 | 2.28092 | 14.86545 | 7.43273 | 7.43272 | 0.04534 |
| Li\(^+\) | 17.61005 | 2.75354 | 14.856506 | 7.42826 | 7.42800 | 0.06735 |
| Be | 33.63518 | 4.48915 | 29.146034 | 14.5730 | 14.5730 | 0.0944 |
| Be\(^+\) | 31.88935 | 3.33456 | 28.55479 | 14.2774 | 14.2774 | 0.0474 |
| B\(^{+2}\) | 51.01327 | 4.433070 | 46.5802 | 23.2901 | 23.4787 | ----- |
Figure 1. The relation between one-electron radial density distribution function with the position for (Li, Li$^{+}$, Be, Be$^{+1}$, B): (A) for K shell, (B) for KL shell, (C) for L shell.

4. Conclusion

1. As $Z$ increases not only $D(r_1, r_1)$ becomes more diffuse but it also decreases in magnitude. These results are due to the Coulomb attraction force between nucleus and electrons which will be greater when $Z$ goes from 2 to 4 or when $Z$ goes from 3 to 5.

2. The maximum of one-particle density distribution is shifting to the origin by increasing the atomic number ($Z$), due to the attraction forces between the nucleus and the electron clouds.

3. The maximum probability of the function $D(r)$ is directly proportional to the atomic number ($Z$).

4. For each $Z$, the one-particle expectation values for HF wave functions are increasing when $n$ goes from 1 to 2 and decreasing when $n$ goes from 2 to 1. This means that the expectation values weight different regions of space.

5. As atomic number is $Z$ increase, all the total energies are increases because the increasing nuclear charge effect.

6. The attraction energy expectation values $\langle V_{en} \rangle$ are larger than the repulsion energy expectation value $\langle V_{ee} \rangle$. 


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