CALCULATION OF THE ENERGIES OF NEGATIVE ION OF (B⁻¹,C⁺¹ AND N⁻¹) FOR GROUND AND EXCITED STATES

Abstract: It this research calculate atomic properties are very important to describe the dynamics in atomic systems energies for 1s,2s shells all like negative ions for ground state (B⁻¹, C⁺¹ and N⁻¹) and excited state (B⁻¹, C⁺¹ and N⁻¹).

In the research division is used technique for the analysis of the three-electron system, also all the examining atomic properties are normalized and the atomic units are used in the calculations and the results is obtained by using Mathcad 14 program.

Key words: Hartree- Fock, atomic units, atomic properties, Hamiltonian operator.

Language: English

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Introduction
The Schrödinger equation for atoms with more than one electron has not been solved analytically Approximate methods must be applied in order to obtain the wave functions or another physical attributes from quantum mechanical calculation[1].

The Hartree-Fock(HF) equations were first proposed by Fock in 1930.Since then, the Hartree-Fock method has taken a central role in studies of atomic and molecular electronic structure. The Hartree-Fock method(HF) is known to be successful in calculating properties of electron systems, in particular, the ground state properties of atoms. Based on a variational principle numerical and algebraic [2]. Numerical computational methods for atomic HF equations have been developed by Froese Fischer. The one-particle Green’s function approach and related many-body methods have been extensively used to calculate ionization and electron attachment spectra of atoms and molecules [3].

2. Theory
The wave function
\[ \Psi(r_1, r_2, r_3, \ldots, r_n) \]  

of any system is a mathematical expression which describes the system properties as position, momentum, energy, etc. In the uncorrelated wave function approximation, each particle is assumed to move in only the average field of all the other particles of the system. This kind uses approximation that called Hartree-Fock approximation (HF). In the correlated wave function approximation one can takes into account the correlation between all the particles of the system by using the configuration interaction approximation (CI). The wave function for the one-particle is defined as:

\[ \Psi_n \propto m_r, m_s(\ell, \sigma) = R_m(r)Y_{lm}(\theta, \varphi)\sigma(s) \]  

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the radial factor $R_{nl}(r)$ is related to the distance of electron from the nucleus and depends on the $n$ (principal quantum number) and $\ell$ (angular momentum quantum number) while the angular factor (spherical harmonic) $Y_{lm,0}(\theta,\phi)$ supplies an angle dependence and depends on the $\ell$ and $m_{\ell}$ (magnetic quantum number) [2].

The Hartree-Fock (HF) atomic wave functions are independent particle-model approximations to non-relativistic Schrödinger equation for stationary states. The single determinant can be written as the antisymmetrized product of all occupied HF spin-orbital for atoms [4]:

Can be expressed of Slater determinant as follows:

$$\Psi_{HF}(123\cdots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) \phi_2(2) & \ldots & \phi_1(N) \\ \phi_2(1) \phi_2(2) & \ldots & \phi_2(N) \\ \vdots & \ddots & \vdots \\ \phi_N(1) \phi_N(2) & \ldots & \phi_N(N) \end{vmatrix}$$

(3)

For any atom or ion, the Hartree-Fock spatial orbital may be written as:

$$\phi = \sum_{i=1}^{j} c_i \chi_i$$

(4)

where $c_i$ represents the constant coefficient yields from the SCF method and $\chi_i$ is the basis function as a standard normalized Slater-type orbital (STO’s).

Many of the properties of an element depend on the energies of its electrons, that means in each moment, one can specify the energy of the an electron precisely, but not its location at a given instant. So in quantum mechanics when one wants determine the location one should talk about the probability of finding an electron in specific region from the space at given instant [5].

The one-electron radial density function $D(r_1)$ represents the probability density function of finding an electron at a distance between $r_1$ and $r_1 + dr_1$ from the coordinate origin defined as [6]:

$$D(r_1) = \int_0^\infty D(r_1, r_2) dr_2$$

(5)

The radial electron-electron distribution function $f(r_{12})$, which describes the probability of locating two electrons separated by distance $r_{12}$ from each other, was first introduced by Coulson and Neilson in their study of electron correlation for He ($^1S$) in the ground state [7,8].

The pair distribution function can be written as [9]:

$$f(r_{12}) = 8\pi^2 r_{12} \left[ \int_0^{r_{12}} r_1 d r_1 \int_0^{r_1} \Gamma(r_1, r_2) r_2 d r_2 + \int_0^{r_{12}} r_1 d r_1 \int_{r_1}^{r_{12}} \Gamma(r_1, r_2) r_2 d r_2 \right]$$

(6)

The one-electron expectation value $\langle r_{1n} \rangle$ is determined by the expression [10]:

$$\langle r_{1n}^n \rangle = \int_0^{r_{12}} DR(r_1) r_1^n d r_1$$

(7)

The inter-electron expectation values $\langle r_{12}^n \rangle$ is given by the relation [9]:

$$\langle r_{12}^n \rangle = \int_0^{r_{12}} f(r_{12}) r_{12}^n d r_{12}$$

(8)

The virial theorem is a necessary condition for any stationary state. From the theorem, one is led to [11]:

$$\langle E \rangle = \langle T \rangle + \langle V \rangle$$

(9)

$$\langle E \rangle = -\langle T \rangle = \langle V \rangle / 2$$

(10)

The expectation value of potential energy is proportional to the expectation values of $\langle r_{1}^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$ respectively, where [12]:

$$\langle V_{en} \rangle = -Z \langle r_{1}^{-1} \rangle$$

(11)

$$\langle V_{ee} \rangle = \langle r_{12}^{-1} \rangle$$

(12)
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**Fig(1): Relation between D(r1) with the position( r1) for (1s) shell of ground state for studied systems**

**Fig(2): Relation between D(r1) with the position( r1) for (2s) shell of ground state for studied systems**

**Fig(3): Relation between D(r1) with the position( r1) for (1s) shell of first excited state for studied systems**

**Fig(4): Relation between D(r1) with the position( r1) for (2s) shell of first excited state for studied systems**

**Fig(5): Relation between D(r1) with the position( r1) for (1s) shell of second excited state for studied systems**

**Fig(6): Relation between D(r1) with the position( r1) for (2s) shell of second excited state for studied systems**
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**Fig(7):** The relation between $f(r_{12})$ with corresponding position $r_{13}$ for (1s) shell of ground state for studied systems.

**Fig(8):** The relation between $f(r_{12})$ with corresponding position $r_{13}$ for (2s) shell of ground state for studied systems.

**Fig(9):** The relation between $f(r_{12})$ with corresponding position $r_{12}$ for (1s) shell of first excited state for studied systems.

**Fig(10):** The relation between $f(r_{12})$ with corresponding position $r_{12}$ for (2s) shell of first excited state for studied systems.

**Fig(11):** The relation between $f(r_{12})$ with corresponding position $r_{12}$ for (1s) shell of second excited state for studied systems.

**Fig(12):** The relation between $f(r_{12})$ with corresponding position $r_{12}$ for (2s) shell of second excited state for studied systems.
### Table 1: The one-particle expectation values $\langle r_n^2 \rangle$ where ($n = -2.2$) and standard deviation for studied systems of ground state.

| Ion | State | $\langle r_1^{-2} \rangle$ | $\langle r_1^{-1} \rangle$ | $\langle r_1^{0} \rangle$ | $\langle r_1^{1} \rangle$ | $\langle r_1^{2} \rangle$ | $\Delta r_1$ |
|-----|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-------|
| B$^{-1}$ | $^3P$ | 44.5388 | 4.67400 | 1 | 0.32593 | 0.14344 | **0.1929** |
| C$^{-1}$ | $^4S$ | 65.2223 | 5.66396 | 1 | 0.26851 | 0.09727 | **0.15866** |
| N$^{-1}$ | $^3P$ | 89.8484 | 6.65343 | 1 | 0.22827 | 0.07025 | **0.1347** |

### Table 2: The one-particle expectation values $\langle r_n^2 \rangle$ where ($n = -2.2$) and standard deviation of studied systems for first excited state.

| Ion | State | $\langle r_1^{-2} \rangle$ | $\langle r_1^{-1} \rangle$ | $\langle r_1^{0} \rangle$ | $\langle r_1^{1} \rangle$ | $\langle r_1^{2} \rangle$ | $\Delta r_1$ |
|-----|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-------|
| B$^{-1}$ | $^3D$ | 44.54565 | 4.6744 | 1 | 0.32585 | 0.14336 | **0.19281** |
| C$^{-1}$ | $^2D$ | 65.23456 | 5.66451 | 1 | 0.26845 | 0.09727 | **0.15866** |
| N$^{-1}$ | $^3D$ | 89.86221 | 6.65385 | 1 | 0.22827 | 0.07025 | **0.13468** |

### Table 3: The one-particle expectation values $\langle r_n^2 \rangle$ where ($n = -2.2$) and standard deviation for studied systems of second excited state.

| Ion | State | $\langle r_1^{-2} \rangle$ | $\langle r_1^{-1} \rangle$ | $\langle r_1^{0} \rangle$ | $\langle r_1^{1} \rangle$ | $\langle r_1^{2} \rangle$ | $\Delta r_1$ |
|-----|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-------|
| B$^{-1}$ | $^1S$ | 44.54733 | 4.67381 | 1 | 0.32583 | 0.14333 | **0.19278** |
| C$^{-1}$ | $^2P$ | 65.24335 | 5.66407 | 1 | 0.26841 | 0.09717 | **0.15852** |
| N$^{-1}$ | $^1S$ | 89.87177 | 6.65441 | 1 | 0.22824 | 0.07022 | **0.13464** |
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Table (4): The inter-particle expectation values $\langle r_{12}^n \rangle$ where $n = -2.2$ and standard deviation for studied systems for ground state.

| Ion | state | shell | $< r_{12}^{-2} >$ | $< r_{12}^{-1} >$ | $< r_{12}^{0} >$ | $< r_{12}^{1} >$ | $< r_{12}^{2} >$ | $\Delta r_{12}$ |
|-----|-------|-------|-------------------|-------------------|-----------------|-----------------|-----------------|----------------|
| B$^{-1}$ | 3P | 1s | 14.4021 | 2.89169 | 1 | 0.47662 | 0.28689 | 0.244 |
| | | 2s | 0.3067 | 0.43249 | 1 | 3.02106 | 11.07267 | 1.39495 |
| C$^{-1}$ | 4S | 1s | 21.18226 | 3.50868 | 1 | 0.39256 | 0.19454 | 0.20109 |
| | | 2s | 0.48219 | 0.54144 | 1 | 2.41214 | 7.05184 | 1.11059 |
| N$^{-1}$ | 3P | 1s | 29.25978 | 4.12508 | 1 | 0.33365 | 0.14045 | 0.17081 |
| | | 2s | 0.7143 | 0.65844 | 1 | 1.98112 | 4.75041 | 0.90862 |

Table (5): The inter-particle expectation values $\langle r_{12}^n \rangle$ where $n = -2.2$ and standard deviation of first excited state for studied systems.

| Ion | State | shell | $< r_{12}^{-2} >$ | $< r_{12}^{-1} >$ | $< r_{12}^{0} >$ | $< r_{12}^{1} >$ | $< r_{12}^{2} >$ | $\Delta r_{12}$ |
|-----|-------|-------|-------------------|-------------------|-----------------|-----------------|-----------------|----------------|
| B$^{-1}$ | 1D | 1s | 14.40501 | 2.89199 | 1 | 0.47648 | 0.28671 | 0.24428 |
| | | 2s | 0.31787 | 0.44063 | 1 | 2.9584 | 10.59318 | 1.35685 |
| C$^{-1}$ | 2D | 1s | 21.18648 | 3.50911 | 1 | 0.39246 | 0.19442 | 0.20099 |
| | | 2s | 0.49346 | 0.54793 | 1 | 2.38025 | 6.85692 | 1.09147 |
| N$^{-1}$ | 1D | 1s | 29.26267 | 4.12553 | 1 | 0.33366 | 0.14049 | 0.17077 |
| | | 2s | 0.72091 | 0.66154 | 1 | 1.97108 | 4.70046 | 0.90295 |

Table (6): The inter-particle expectation values $\langle r_{12}^n \rangle$ where $n = -2.2$ and standard deviation of second excited state for studied systems.

| Ion | State | shell | $< r_{12}^{-2} >$ | $< r_{12}^{-1} >$ | $< r_{12}^{0} >$ | $< r_{12}^{1} >$ | $< r_{12}^{2} >$ | $\Delta r_{12}$ |
|-----|-------|-------|-------------------|-------------------|-----------------|-----------------|-----------------|----------------|
| B$^{-1}$ | 1S | 1s | 14.4083 | 2.8924 | 1 | 0.47646 | 0.28666 | 0.24423 |
| | | 2s | 0.32202 | 0.44324 | 1 | 2.94372 | 10.50036 | 1.35458 |
| C$^{-1}$ | 2P | 1s | 21.18934 | 3.5094 | 1 | 0.39239 | 0.19434 | 0.20093 |
| | | 2s | 0.5012 | 0.55231 | 1 | 2.36114 | 4.74941 | 1.08371 |
| N$^{-1}$ | 1S | 1s | 29.26835 | 4.12603 | 1 | 0.33362 | 0.14045 | 0.17073 |
| | | 2s | 0.7307 | 0.66608 | 1 | 1.95648 | 4.62876 | 0.89496 |
Table (7): The expectation values for all attraction, repulsion, and Hartree-Fock energies of the ground state of 1s and 2s shells for studied ions.

| Ion | state | shell | $\langle V_{ee} \rangle$ | $\langle V_{en} \rangle$ | $\langle V \rangle$ | $\langle T \rangle$ | $-\langle E_{HF} \rangle$ |
|-----|-------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B$^+$ | $^3P$ | 1s    | 2.89169 | 46.7400 | 43.84831 | 21.92416 | 21.92416 |
|      |       | 2s    | 0.43249 | 6.74350 | 6.31101  | 3.29036  | 3.29036  |
| C$^+$ | $^4S$ | 1s    | 3.50868 | 67.96752 | 64.45884 | 32.22942 | 32.22942 |
|      |       | 2s    | 0.54144 | 10.22748 | 9.6867   | 4.91359  | 4.91359  |
| N$^+$ | $^3P$ | 1s    | 4.12508 | 93.14802 | 89.0231  | 44.5147  | 44.5147  |
|      |       | 2s    | 0.65844 | 14.6006  | .13.9431 | 6.97157  | 6.97157  |

Table (8): The expectation values for all attraction, repulsion, kinetic and Hartree-Fock energies of the first excited state of 1s and 2s shells for studied ions.

| Ion | State | shell | $\langle V_{ee} \rangle$ | $\langle V_{en} \rangle$ | $\langle V \rangle$ | $\langle T \rangle$ | $-\langle E_{HF} \rangle$ |
|-----|-------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B$^+$ | $^1D$ | 1s    | 2.89199 | 46.7441  | 43.852  | 21.926  | 21.926  |
|      |       | 2s    | 0.44063 | 6.8626   | 6.42197 | 3.21098 | 3.21098 |
| C$^+$ | $^2D$ | 1s    | 3.50911 | 67.9741  | 64.465  | 32.2325 | 32.2325 |
|      |       | 2s    | 0.54793 | 10.348   | 9.79967 | 4.89983 | 4.89983 |
| N$^+$ | $^1D$ | 1s    | 4.12553 | 93.154   | 89.028  | 44.514  | 44.514  |
|      |       | 2s    | 0.66154 | 14.670   | 14.008  | 7.0044  | 7.0044  |

Table (9): The expectation values for all attraction, repulsion, kinetic and Hartree-Fock energies of the second excited state of 1s and 2s shells for studied ions.

| Ion | State | shell | $\langle V_{ee} \rangle$ | $\langle V_{en} \rangle$ | $\langle V \rangle$ | $\langle T \rangle$ | $-\langle E_{HF} \rangle$ |
|-----|-------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B$^+$ | $^1S$ | 1s    | 2.8924  | 46.748   | 43.856  | 21.928  | 21.928  |
|      |       | 2s    | 0.44324 | 6.9137   | 6.47046 | 3.23523 | 3.23523 |
| C$^+$ | $^2P$ | 1s    | 3.5094  | 67.978   | 64.469  | 32.235  | 32.235  |
|      |       | 2s    | 0.55231 | 10.427   | 10.979  | 5.4895  | 5.4895  |
| N$^+$ | $^1S$ | 1s    | 4.12603 | 93.162   | 89.036  | 44.518  | 44.518  |
|      |       | 2s    | 0.66608 | 14.7696  | 14.104  | 7.0518  | 7.0518  |
Noted from the above figures (1), (3) and (5) for 1s of the ground and excited states respectively, figures (2), (4) and (6) for 2s of the ground and excited states respectively. Represents the relation between one-particle radial density distribution function $D(r_1)$ versus position $(r_1)$ for studied system. From these figures it is observed that the maximum values of $D(r_1)$ increases as $Z$ increases, while the locations of these peaks are contracted toward the nucleus where it is noted that the maximum probability density distribution function $D(r)$ for $N^1$ is closer to the nucleus from $D(r_1)$ for $N^1$. This difference occurs because the $N^1$ ion $Z=7$ exerts a much stronger attractive force on electrons than does the $B^1$ ion ($Z=5$), it is also observed from these figures when the distance is equal to zero the probability of finding an electron equal to zero (when $r = 0$, $D(r_1) = 0$). This means that the electron cannot be existed inside the nucleus and when the distance is far away the probability of finding an electron equal to zero also (when $r = \infty$, $D(r_1) = 0$), this means that it is not possible of the electron to be existed outside the atom.

Noted from the above figures (7), (9) and (11) for 1s of the ground and excited states respectively, figures (8), (10) and (12) for 2s of the ground and excited states respectively.

The maximum value of the inter particle distribution function increases where $Z$ increases.

The maximum probability of the inter particle distribution function $f(r_{12})$ increases as atomic number increases because the influence of increasing in attraction nuclear force.

It was also observed from the figures when $r_{12} = 0$ the probability of the inter particle distribution function $f(r_{12}) = 0$ [ when $r_{12} = 0$ $f(r_{12}) = 0$]. This means that the electron not be closed on another electron and when the distance is far between two electrons the probability of the inter particle distribution function $f(r_{12})$ equal to zero also [ when $r = \infty$, $f(r_{12}) = 0$], that means the diameter is not found out the atom.

From tables (1), (2) and (3) for ground and excited states respectively, it is noted that the one-particle expectation value ($r^n_1$) when $n$ takes the values (-2,-1) the one-particle expectation value ($r^n_1$) increases where the atomic number $Z$ increases, this is due to the attraction energy between the nucleus and electron increases. While when $n$ takes the values (+1,+2) the one-expectation value ($r^n_1$) decreases by atomic number ($Z$) increases, where the ($r^{-1}_1$) which represents the attraction energy expectation value ($V_{en}$) $= -Z[\langle r^{-1}_1 \rangle]$ and the ($r^{-1}_1$) represents the distance between the nucleus and electron. It is also noted from tables (4), (5) and (6) for ground and excited states respectively, when $Z$ increases the inter-particle expectation value ($r^n_{12}$) increases where ($r^n_{12}$) represents repulsion energy between two-electrons. When $n$ equal to zero the one-particle expectation value ($r^n_1$) and the inter-particle expectation value ($r^n_{12}$) for all the states equal to unity for all studied systems this represented the normalization condition.

From the Tables (7), (8) and (9) for ground state for excited states respectively, we observed that the results of the expectation value of attraction energy ($V_{en}$) and expectation value of repulsion energy ($V_{ee}$) increases when atomic number increases because increasing in $Z$ leads to decreasing in the distance between electrons with nucleus, as well as, the distance between two electrons, this product increasing in attraction energy and repulsion energy according to coulomb law.

From these the tables it arises that the increasing in attraction energy is greater than that in the repulsion energy, so this leads to increase in expectation value of potential energy ($V$) when atomic number increases for each individual shell and for total system.

Above tables, it is noted the expectation values of kinetic energy ($T$) increases as $Z$ increases because of the increase in kinetic energy is the force of attraction of the nucleus of a electron that reduces the distance between the electron and the nucleus, maintain the stability of the atomic system increases the speed of rotation of the electron in orbit to increase the power of centrifugal and the following increase in its kinetic energy ($T$).

Expectation value of HF energy ($E_{HF}$) increases as atomic number increases, which indicates the relation between ($E_{HF}$) and $Z$ because increasing in the potential energy and kinetic energy lead to increasing in the total energy of the system (HF energy).

**Conclusions**

1. When the atomic number $Z$ increases, the one-particle radial density distribution function $D(r_1)$ and the inter-particle distribution function $f(r_{12})$ are increased.

2. For both one-particle expectation ($r^n_1$), and inter-particle expectation ($r^n_{12}$) are increased when $Z$ increases.

3. All the expectation values of the energies ($V_{en}$), ($V_{ee}$), ($V$), ($T$) and ($E_{HF}$) are increased when the atomic number increases.

4. The results of expectation values of all energies for 1s shell is larger than those in the 2s shells.
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