Estimation Hartree - Fock's energy for the carbon atom and the ions are similar

Saleem H Trier¹, Shaymaa A Kadhim², Zahra Mousa Hamza³ and Qassim Shamkhi AL-Khafaji⁴

¹Department of Environment, College of Science, University of Al-Qadisiyah, Diwaniyah, Iraq
²Department of physics, College of science, University of kufa
³AL furat al awssat Technical University 31003 / Kufa Technical Institute
⁴Department of physics, College of science, University of kufa

E-mail: Salemhamza79@yahoo.com

Abstract. In this paper, was used the technique of fragmentation to analyze the systems studied based on the energy of repulsion between electronic pairs. The energy of Hartree-Fock was calculated for the carbon atom (C) and the similar ions (N⁺¹) and (O⁺²). When the results of the energies compared with the global publications we found a large agreement also studied the atomic properties by using atomic units.

Keywords: Roothaan–Hartree -Fock, density function, radial expectation values, Hamiltonian operator.

1. Introduction

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 and 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). The wave function for the one–particle is defined as[1].

\[
D_{ij}(r_1) = \int_0^\infty D_{ij}(r_1, r_2)dr_2
\] (1)

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 (angular momentum quantum number) while the angular factor(spherical harmonic) \( Y_{lm}(\theta, \phi) \) supplies an angle dependence and deepen \( \Psi ds \) on the \( l \) and \( m_l \) (magnetic quantum number) [2].

2. The Theory:

For multi electrons system ,the Hartree - Fock wave function is given by:
\[ \Psi_{\text{HF}}(1,2,3 \ldots N) = A \prod (1,2,3,\ldots,N) \]  
(2)

Where A is the ant symmetrized operator given by[3]:

\[ A = \frac{1}{\sqrt{N!}} \sum_{P} (-1)^{P} P \]  
(3)

\((-1)^{P}\) takes the values +1 and −1 for even and odd permutation, P is any permutation of the electron, and the factor \( \frac{1}{\sqrt{N!}} \) introduced to ensure that the wave function is normalized.

The product \( \prod (1,2,3,\ldots,N) \) in equation (2) can be defined as [4]:

\[ \Pi (1,2,3,\ldots,N) = |\phi_1(1)\phi_2(2)\phi_3(3)\ldots\phi_N(N)| \]  
(4)

The Hartree - Fock spin-orbital \( \phi \) are designated by the numerals (1,2,3…N) starting with the lowest orbital with spin. Consequently all odd integers for \( \alpha \) spin and all even ones for \( \beta \) spin.

Equation(3) can be expressed in terms of Slater determinant as follows:

\[ \Psi_{\text{HF}}(1,2,3,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\phi_1(2)\ldots\phi_1(N) \\ \phi_2(1)\phi_2(2)\ldots\phi_2(N) \\ \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \\ \phi_N(1)\phi_N(2)\ldots\phi_N(N) \end{vmatrix} \]  
(5)

The HF or analytic self-consistent field atomic wave function provides the un-correlated description of each atom. For any atom or ion, the Hartree - Fock spatial orbital may be written as :

\[ \phi = \sum_{i=1}^{j} c_i \chi_i \]  
(6)

Where \( c_i \) represents the constant coefficient yield from the SCF method. And is the \( \chi_i \) basis function as a standard normalized Slater-type orbital (STO’s), which is given by[5]:

Where \( R_{nl}(r) \) represented the radial part of the wave function and it given as [5]:

\[ R_{nl}(r) = N_{nlm} S_{nl}(r) \]  
(7)

\( N_{nlm} \) is the normalization constant given by:

\[ N_{nlm} = \frac{(2\phi^{n+\frac{1}{2}})}{[(2n)!]^2} \]  
(8)

and

\[ S_{nl}(r) = r^{n-1}e^{-(\xi r)} \]  
(9)

Where \( S_{nl}(r) \) is called Slater type orbital (STO’s), \( \xi \) represents the orbital exponent and \( Y_{lm}(\theta,\phi) \) represents the angular part of the wave function. The one-particle expectation value \( < r_{n1}^{n} > \) can be calculated from [5].
In the case \((n=0)\) one can calculate the Normalization condition as a result of. The radial density distribution function \(D_{ij}(r_1)\) is a measure of the probability of finding an electron in each shell and it is defined as \([5]\).

\[
D_{ij}(r_1) = \iiint \Gamma(r_2), r_1 r_2^2 d\Omega_1 d\Omega_2 \tag{11}
\]

In each individual electronic shell, the two-particle radial density distribution function \(D(r_1, r_2)\) is defined by \([5]\).

\[
D(r_1, r_2) = \iiint \Gamma(r_2, r_1) r_1^2 r_2^2 d\Omega_1 d\Omega_2 \tag{12}
\]

Where \(d\Omega_i\) denotes integration over all angular coordinates of the position vector \(r_i\) and it is defined as:

\[
d\Omega_i = \sin\theta_i d\theta_i d\phi_i \tag{13}
\]

The inter-particle expectation values \(<r_{12}^n>\) can be calculated from \([6]\).

\[
<r_{12}^n> = \int f_{ij}(r_{12}) r_{12}^n dr_{12} \tag{14}
\]

The inter-particle distribution function associated with the spin-orbital pair \((i, j)\) is given by:

\[
f_{ij}(r_{12}) dr_{12} = \int \Gamma_{ij}(r_2, r_1) dr_1 dr_2 \tag{15}
\]

where \((r_{12})\) is the inter-particle distance. For an \(N\)-electrons system, the two-particle density can be written as \([7]\).

\[
\Gamma(x_m, x_n) = \binom{N}{2} \int \Psi^*(x_1, x_2, ..., x_n) \Psi(x_1, x_2, ..., x_n) dx_p ... dx_n \tag{16}
\]

Where \(dx_p, ..., dx_n\) indicate integrations of all \(N\)-electrons except \(m\) and \(n\).

The binomial factor \(\binom{N}{2}\) ensures that the second-order density matrix \(\Gamma(x_m, x_n)\) is normalized to the number of electron pairs within the system. The energy expectation value associated with the Hamiltonian operator can be written as follows \([8]\):

\[
E = \langle \hat{H} \rangle = \int \Psi^* \hat{H} \Psi d\tau \tag{17}
\]

and \(\hat{H}\) for the \(N\)-electron system is given by:
\[ \hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}} \]  

(18)

Since \( E = T + V_{en} + V_{ee} \), equation (19) is used to find the expectation values of the kinetic and potential energies, and is given by [9]:

\[ <T> = -\frac{1}{2} \int \Psi^* \left[ \sum_i^N \nabla_i^2 \right] \Psi \ d\tau \]  

(19)

\[ <V> = \int \Psi^* \left[ \sum_i^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}} \right] \Psi \ d\tau \]  

(20)

For an \( N \)-electron atomic wave function that satisfies the virial theorem the energy expectation value is related to the potential energy by [10].

\[ <E> = \frac{1}{2} <V> \]  

(21)

The potential energy simplifies the sum of the electron-nuclear attraction energy and the interelectronic repulsion energy, which are proportional to the expectation values of \( 1/r_1 \) and \( 1/r_{12} \) respectively. Therefore, eq (21) can be written as [11].

\[ <V> = -Z <r_i^{-1}> + <r_{12}^{-1}> \]  

(22)

3. Results and Discussions:

In this research was used the partition technique that depending on electronic repulsion between two electrons, where the studied systems have six electrons, therefore found fifteen pairs of electron represented intra and inter shells which are:

\[
\begin{bmatrix}
K_aK_\beta, K_aL_a, K_\alpha L_\beta, K_\beta L_\alpha, L_aL_\beta, K_\alpha L_2Px\alpha, K_\beta L_2Px\alpha, K_\alpha L_2Py\beta, K_\beta L_2Py\alpha, L_\alpha L_2Px\beta, L_\beta L_2Px\alpha, L_\alpha L_2Py\beta, \\
L_\beta L_2Py\alpha, L_2Px\alpha L_2Py\beta
\end{bmatrix}
\]

The figures(1,2 and 3) represented the relation between one particle density function with the position for the shells 1s,2s and 2p respectively, from this figures we noted the maximum values of one particle radial density function increased as atomic number increased and corresponding position of these peaks contract toward the nucleus because increasing in nucleus charge. Also we noted the maximum values of one particle radial density function for K-shell are the largest while for 2P-shell are smallest.

Table(1) represented the expectation values of one particles position between the electron and nucleus < \( r_i^> \), table (2) represented expectation values of inter – particle position between two electrons < \( r_{12}^> \) where \( n \) is integer number and takes the values (-2 ≤ \( n \) ≤ 2), where noted from these tables as the atomic number increases the expectation value < \( r_i^> \) and < \( r_{12}^> \) are increased for (\( n \)) negative values for all shells and vice versa for positive values, but when (\( n = 0 \)) the expectation value of position equal one, this represented normalization condition. Also from these table we noted identical properties for some shells which is resulted from the Hartree-Fock approximation that neglected electronic correlation, also we observed the K-shell has the
maximum values of expectation values of position when (n) takes negative values while the L₂P shell has the minimum values and vice versa for positive values because the K-shell is nearest for nucleus. Table (3) represented the values of energies for the studied systems such as attractive potential $\langle V_{en} \rangle$, repulsion potential $\langle V_{ee} \rangle$, total potential energy $\langle V \rangle$, kinetic energy $\langle T \rangle$ and finally the Hartree - Fock energy $\langle E \rangle$ of the system or the total. From this table we noted the results of total energy of studied systems are agreement with the global publications [12], which is refer to successful using for this approximation. Also we observed the K-shell has most contribution in energy system.

Table (1): Expectation values of one particle position for the studied system

| shell       | Atom or Ion | $\langle r^{-2} \rangle$ | $\langle r^{-1} \rangle$ | $\langle r^0 \rangle$ | $\langle r^1 \rangle$ | $\langle r^2 \rangle$ |
|-------------|-------------|--------------------------|--------------------------|----------------------|----------------------|----------------------|
| $K_{\alpha}$ $K_{\beta}$ | C           | 65.23817                 | 5.66471                  | 1                    | 0.26845              | 0.0972               |
| N$^{+1}$    | 89.90649    | 6.65643                  | 1                        | 0.22807              | 0.07009              |
| O$^{+2}$    | 118.57589   | 7.65045                  | 1                        | 0.19821              | 0.05289              |
| $L_{\alpha}$ $L_{\beta}$ | N$^{+1}$    | 47.59842                 | 3.89869                  | 1                    | 0.74045              | 0.9723               |
| O$^{+2}$    | 63.21103    | 4.51946                  | 1                        | 0.61596              | 0.66041              |
| C           | 34.24658    | 3.28067                  | 1                        | 0.929               | 1.57557              |
| $K_{\beta}$ $L_{\alpha}$ | N$^{+1}$    | 47.59839                 | 3.89868                  | 1                    | 0.74045              | 0.9723               |
| O$^{+2}$    | 63.21084    | 4.51945                  | 1                        | 0.61596              | 0.66041              |
| C           | 3.25653     | 0.89675                  | 1                        | 1.58951              | 3.05387              |
| $L_{\alpha}$ $L_{\beta}$ | N$^{+1}$    | 5.28874                  | 1.14084                  | 1                    | 1.25284              | 1.87455              |
| O$^{+2}$    | 7.84746     | 1.38853                  | 1                        | 1.03369              | 1.26792              |
Table (2): Expectation values of inter particle position for the studied system

| shell       | Atom or Ion | \( \langle r_{12}^{-2} \rangle \) | \( \langle r_{12}^{-1} \rangle \) | \( \langle r_{12}^0 \rangle \) | \( \langle r_{12}^1 \rangle \) | \( \langle r_{12}^2 \rangle \) |
|-------------|-------------|-----------------------------------|-----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| \( K_\alpha L_{2p_x} \equiv K_\beta L_{2p_x} \) | C           | 21.18682                          | 3.50928                           | 1                                | 0.39245                         | 0.19439                          |
|             | N\(^{+1}\)  | 29.29135                          | 4.12789                           | 1                                | 0.33334                         | 0.14018                          |
|             | O\(^{+2}\)  | 38.72658                          | 4.74821                           | 1                                | 0.28964                         | 0.10577                          |
|             | C           | 0.73581                           | 0.75921                           | 1                                | 1.62005                         | 3.15114                          |
| \( K_\alpha L_{2p_x} \equiv K_\alpha L_{2p_y} \equiv K_\beta L_{2p_y} \) | N\(^{+1}\)  | 1.13703                           | 0.94874                           | 1                                | 1.28085                         | 1.9446                           |
|             | O\(^{+2}\)  | 1.62793                           | 1.13893                           | 1                                | 1.05947                         | 1.32082                          |
|             | C           | 1.91563                           | 0.86192                           | 1                                | 1.61233                         | 3.15112                          |
| \( K_\beta L_{2p_x} \equiv K_\alpha L_{2p_x} \equiv K_\beta L_{2p_y} \) | C           | 3.07238                           | 1.019121                          | 1                                | 1.27323                         | 1.9446                           |
|             | N\(^{+1}\)  | 4.51769                           | 1.32308                           | 1                                | 1.05213                         | 1.32082                          |
|             | O\(^{+2}\)  | 0.53612                           | 0.57289                           | 1                                | 2.25705                         | 6.10774                          |
| \( L_{2p_x} L_{2p_y} \) | C           | 0.85756                           | 0.72448                           | 1                                | 1.7744                          | 3.74909                          |
|             | N\(^{+1}\)  | 1.25764                           | 0.86755                           | 1                                | 1.46203                         | 2.53585                          |
| \( K_\alpha L_{2p_x} \equiv K_\beta L_{2p_x} \equiv K_\beta L_{2p_y} \) | C           | 0.94195                           | 0.77795                           | 1                                | 1.74013                         | 3.84784                          |
|             | N\(^{+1}\)  | 1.67312                           | 1.04295                           | 1                                | 1.26807                         | 2.0026                           |
|             | O\(^{+2}\)  | 2.58007                           | 1.30015                           | 1                                | 1.00747                         | 1.25242                          |
| \( L_{2p_x} L_{2p_y} \equiv L_{2p_y} L_{2p_x} \equiv L_{2p_y} L_{2p_y} \) | C           | 0.49279                           | 0.5542                            | 1                                | 2.36437                         | 6.80418                          |
|             | N\(^{+1}\)  | 0.84165                           | 0.72857                           | 1                                | 1.77844                         | 3.80709                          |
|             | O\(^{+2}\)  | 1.27015                           | 0.89778                           | 1                                | 1.43544                         | 2.46745                          |
| \( L_{2p_y} L_{2p_y} \) | C           | 0.47531                           | 0.53859                           | 1                                | 2.46878                         | 7.50125                          |
|             | N\(^{+1}\)  | 0.88217                           | 0.73785                           | 1                                | 1.78177                         | 3.86509                          |
|             | O\(^{+2}\)  | 1.39291                           | 0.92953                           | 1                                | 1.40714                         | 2.39905                          |

Table (3): Expectation values of energies for the studied system

| shell       | Atom or Ion | \( \langle V_{en} \rangle \) | \( \langle V_{ee} \rangle \) | \( \langle V \rangle \) | \( \langle T \rangle \) | \( \langle E \rangle \) |
|-------------|-------------|-------------------------------|-------------------------------|-------------------------|-------------------------|-------------------------|
| \( K_\alpha K_\beta \) | C           | 6.797652                      | -46.46724                    | 64.46724                | -32.2336                |
|             | N\(^{+1}\)  | 93.19002                      | -49.06213                    | 89.06213                | -44.53106               |
|             | O\(^{+2}\)  | 122.4072                      | -117.65899                   | 117.65899               | -58.890                 |
| \( K_\alpha L_{2p_x} \equiv K_\alpha L_{2p_y} \equiv K_\beta L_{2p_y} \) | C           | -0.75921                      | 0.75921                     | 0.75921                 | 0.379605                |
|             | N\(^{+1}\)  | -0.94874                      | 0.94874                     | 0.94874                 | 0.47343                |
|             | O\(^{+2}\)  | 1.13893                      | 1.13893                     | 1.13893                 | 0.56                   |
| \( K_\beta L_{2p_x} \equiv K_\beta L_{2p_y} \equiv K_\beta L_{2p_y} \) | C           | -0.86192                      | 0.86192                     | 0.86192                 | 0.43096                |
|             | N\(^{+1}\)  | 1.019121                      | 1.019121                    | 1.019121                | 0.5095605              |
As Z increases all the energies of the system are increases.

The maximum values of one particle radial density function increases as Z increases and corresponding position contract toward the nucleus.

The K shell has the most contribution in the total energy of the system.

4. Conclusions:

1- As Z increases all the energies of the system are increases.
2- The maximum values of one particle radial density function increases as Z increases and corresponding position contract toward the nucleus.
3- The K shell has the most contribution in the total energy of the system.

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