

## Calculation of The Energies of k-shell for Atoms (Z=8 to 10) by using Hartree- Fock Method

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### Abstract:

The atomic properties are important to describe of the dynamics in atoms for the two-electron atomic systems studied in this work include the neutral atom O, F and Ne ,Hartree-Fock wave functions are used to determine the atomic properties like one electron radial density function  $D(r_1)$  and its expectation value  $\langle r_1^n \rangle$ , inter electron distribution function  $f(r_{12})$  and its expectation value  $\langle r_{12}^n \rangle$ , two electron radial density function  $D(r_1, r_2)$ , standard deviation for one and two electrons  $\Delta r_1 \Delta r_{12}$ , expectation values for all energies  $\langle V_{en} \rangle, \langle V_{ee} \rangle, \langle V \rangle, \langle T \rangle, \langle E_{HF} \rangle$

**Key words:** Hartree- Fock Method, two electron radial density function, inter electron distribution function and its expectation values

حساب طاقة الغلاف k لعدد من الذرات (z=8 to10) باستخدام طريقة هاتري\_فوك

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### الخلاصة :

الخواص الذرية المدروسة مهمة لوصف ديناميكية الذرة لإلكترونين درسنا بهذا البحث الذرات الطبيعية هي الأوكسجين والفلور والنيون التي تم حسابها باستخدام الدالة الموجية لهاتري فوك مع تحليل دالة الكثافة القطرية لإلكترون واحد والقيمة المتوقعة لإلكترون واحد ودالة المسافة البينية والقيمة المتوقعة لها ودالة الكثافة القطرية لإلكترونين والانحراف المعياري  $\langle V_{en} \rangle, \langle V_{ee} \rangle, \langle V \rangle, \langle T \rangle, \langle E_{HF} \rangle$ ، لإلكترون واحد وإلكترونين والقيم المتوقعة لجميع الطاقات

الكلمات المفتاحية: هاتري فوك، دالة الكثافة القطرية لإلكترونين، دالة توزيع المسافة البينية، والقيم المتوقعة للنظام.

### 1-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 other 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. Detailed accounts of the diverse techniques developed in this field and an overview of applications can be found in recent review articles [3,4].

### 2.theory

The Hartree-Fock (HF) approximation ignores the correlation between electrons but gives roughly 99% of the total electronic energy. We start from the standard N-electron Hamiltonian (in Hartree atomic units  $e = \hbar = m_e = 1$  used throughout)

$$\hat{\mathcal{H}} = \hat{T}_{electron} + \hat{V}_{en} + \hat{V}_{ee} \quad (1)$$

Where ( $\hat{T}_{electron}$ ) is the kinetic energy

$$\hat{T}_{electron} = - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 \quad (2)$$

Where  $\nabla_i^2$  is the Laplacian operator

$$\hat{V}_{en} = \frac{Ze^2}{r_i} \quad (3)$$

$\hat{V}_{en}$  attractive electron-nucleus potential operator

$$\hat{V}_{ee} = \left\langle \sum_{i \neq j}^N \frac{e^2}{r_{ij}} \right\rangle \quad (4)$$

$\hat{V}_{ee}$  is the two-electron Coulomb repulsion operator

$r_i$  are the electron-nucleus distances for the electron(1) and electron(2)

$r_{ij}$  is the interelectronic distances

$$\hat{\mathcal{H}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \frac{Z}{r_i} + V_{HF} \quad (5)$$

The introduction of this effective potential means that each electron is subjected to a field that models the effect of the other electrons in the system.

In The Hartree-Fock approximation, the many body wavefunction  $\psi(x_1, x_2 \dots x_N)$  is approximated by a single Slater determinant .

We can write wavefunction as

$$\Psi_{HF} = \det(\phi_1(x_1) \phi_2(x_2) \dots \phi_N(x_N))$$

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & & \vdots \\ \phi_3(x_1) & \phi_3(x_2) & \dots & \phi_3(x_N) \end{vmatrix} \quad (6)$$

The factor  $\frac{1}{\sqrt{N!}}$  ensures the normalization condition on the wavefunction . Here the variables  $x_i$  include the coordinates of spin and space ,  $\phi_i(x_j)$  terms are called spin orbitals and these spin orbitals are orthonormal functions, which are spatial orbitals times a spin functions. The wavefunction  $\Psi_{HF}$  in equation (6) is clearly antisymmetric because interchanging any pair of particles is equivalent to

interchanging two columns and hence changes the sign of the determinant. Moreover, if any pair of particles are in the same single-particle state, then two rows of the Slater determinant are identical and the determinant vanishes, in agreement with the Pauli exclusion principle.

The one-electron orbitals used to construct the  $\phi_i$  each consist of a radial function  $R_{nl}(r)$ , a spherical harmonic  $Y_{lm}(\theta, \phi)$  and a spin function  $\sigma_{m_s}(s)$  as [12],

$$\phi = R_{nl}(r)Y_{lm_l}(\theta, \phi)\sigma_{m_s}(s)$$

The spatial part of one-electron spin orbital may be expressed as linear combination of Slater type orbital called basis functions,

$$\Phi_{nlm}(r, \theta, \phi) = \sum_i c_i \chi_i \quad (7)$$

Where  $c_i$  the expansion coefficient determined by minimizing the energy using one of several procedures and this process is continued until  $\hat{H}_{HF}$  and  $\Psi_{HF}$  converge, at which point a self-consistent field (SCF) has been achieved. This usually yields the lowest-energy single

determinant within the basis .  $\chi_i$  is a Slater type orbital.

$$\chi_{nlm_l}(\xi, r) = R_{nl}(\xi, r)Y_{lm_l}(\theta, \phi) \quad (8)$$

The radial part is:

$$R_{nl}(\xi, r) = (2\xi)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} \exp(-\xi r) \quad (9)$$

Here,  $\xi_i > 0$  is the orbital exponent. The quantity n occurring in eq. (9) is a positive principal quantum number of (STO). The determination of nonlinear parameters n and  $\xi$  is very important for describing the atomic orbitals.

### 2-1-Two-electron radial density distribution D (r<sub>1</sub>, r<sub>2</sub>)

The two-particle radial density distribution D (r<sub>1</sub>, r<sub>2</sub>) in each individual electronic shell is defined by :[6]

$$D(r_1, r_2) = \int_0^\pi \int_0^{2\pi} \Gamma(r_1, r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 \quad (10)$$

$$d\Omega_i = \sin \vartheta_i d\vartheta_i d\phi_i \quad (11)$$

Such that:

$$\int_0^\infty \int_0^\infty D(r_1, r_2) r_1^2 r_2^2 dr_1 dr_2 = 1 \quad (12)$$

This density function is a measure of the probability of

finding the two-electrons such that, simultaneously, their radial coordinates are r<sub>1</sub> and r<sub>2</sub> respectively

### 2-2-One-particle radial density distribution function D(r<sub>1</sub>):

The radial density distribution function D (r<sub>1</sub>) is a measure of the probability of finding an electron in each shell and it is defined as [7]:

$$D(r_1) = \int_0^\infty D(r_1, r_2) dr_2 \quad (13)$$

### 2-3-One-particle expectation value <r<sub>1</sub><sup>n</sup>>:

The one-particle expectation value <r<sub>1</sub><sup>n</sup>> can be calculated from [8]:

$$\langle r_1^n \rangle = \int D_{ij}(r_1) r_1^n dr_1 \quad (14)$$

In the case (n=0) one can calculate the <r<sub>1</sub><sup>n</sup>> Normalization condition as a result of <r<sub>1</sub><sup>n</sup>>

### 2-4-Standard Deviation $\Delta r_1$

The standard deviation of the distance of the test electron  $r_1$  from the nucleus, is defined as [9]:

$$\Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \quad (15)$$

### 2-5-inter-particle distribution function $f(r_{12})$

The radial electron-electron distribution function, which describes the probability of locating two electrons separated by distance  $r_{12}$  from each other  $f(r_{12}) = \int \Gamma(r_1, r_2) dr_1 dr_2 / dr_{12}$  (16)  $f(r_{12})$  representing a function of the distribution of the distance between electron 1 and electron 2

### 2-6-The inter-particle

expectation values  $\langle r_{12}^n \rangle$ :The

inter-particle expectation values

$\langle r_{12}^n \rangle$  can be calculated from

[10]:

$$\langle r_{12}^n \rangle = \int f_{ij}(r_{12}) r_{12}^n dr_{12} \quad (17)$$

### 2-7-Standard Deviation $\Delta r_{12}$ :

The standard deviation of the inter electronic distance of the two electrons, is defined as

[10]:

$$\Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2} \quad (18)$$

## 10-Results and Discussion

Table (1) : The locations and maximum values of the  $D(r_1, r_2)$  for studied systems.

Atom	$r_1$	Max $D(r_1, r_2)$ Where $r_1$ fixed
O	0.13	16.644
F	0.11	21.23
Ne	0.10	26.394

Table (2): values of positions and maximum values of  $D(r_1)$  by using Hartree-Fock wave function

Atom	$r_1$	Max $D(r_1)$
O	0.13	4.08
F	0.11	4.608
Ne	0.10	5.137

Table (3): Expectation values  $\langle r_1^n \rangle$  for atoms  $-2 \geq n \geq 2$  and standard deviation .

Atom	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$	$\Delta r_1$
O	118.23011	7.63785	0.19875	0.05328	<b>0.117</b>
Ref.[11]	-----	7.637847	-----	-----	-----
F	150.76068	8.62941	0.17579	0.04166	<b>0.104</b>
Ref.[2]	150.83417	8.630362	0.175747	0.041612	-----
Ne	187.27378	9.61756	0.1577	0.03351	<b>0.093</b>
Ref.[11]	-----	9.617559	-----	-----	-----

Table(4) : The location and maximum values of the inter-particle distribution function  $f(r_{12})$  for studied systems

Atom	$r_{12}$	Max $f(r_{12})$
O	0.22	2.989
F	0.19	3.379
Ne	0.17	3.768

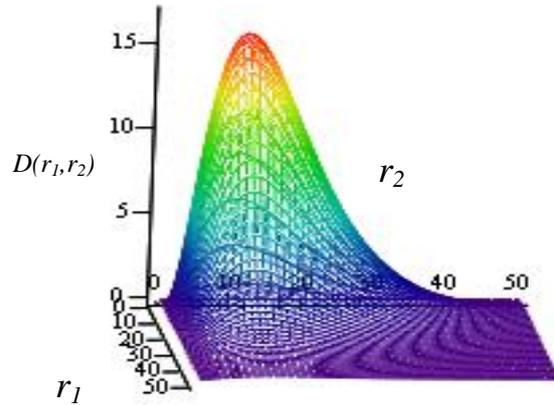
Table (5): Expectation values  $\langle r_{12}^n \rangle$  where  $-2 \leq n \leq 2$  and standard deviation for studied systems

Atom	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^1 \rangle$	$\langle r_{12}^2 \rangle$	$\Delta r_{12}$
O	38.59036	4.73843	0.29051	0.10655	0.149
F	49.29188	5.35635	0.25692	0.08332	0.132
Ne	61.22332	5.97008	0.23046	0.06702	0.118

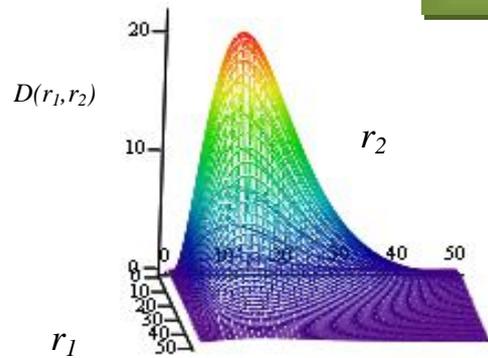
Table(4-7):The expectation values for all attraction, repulsion, kinetic and Hartree-Fock energies for studied systems.

Atom	$-\langle V_{en} \rangle$	$\langle V_{ee} \rangle$	$-\langle V \rangle$	$\langle T \rangle$	$-\langle E_{HF} \rangle$
O	122.2056	4.73843	117.46717	58.73359	58.73359
F	155.32938	5.35635	149.97303	74.98652	74.98652
Ne	192.3512	5.97008	186.38112	93.19056	93.19056

O atom



F atom



Ne atom

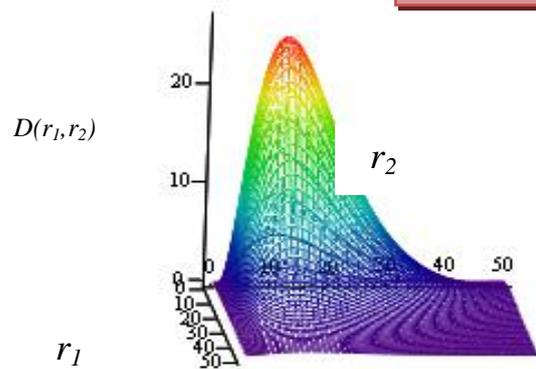
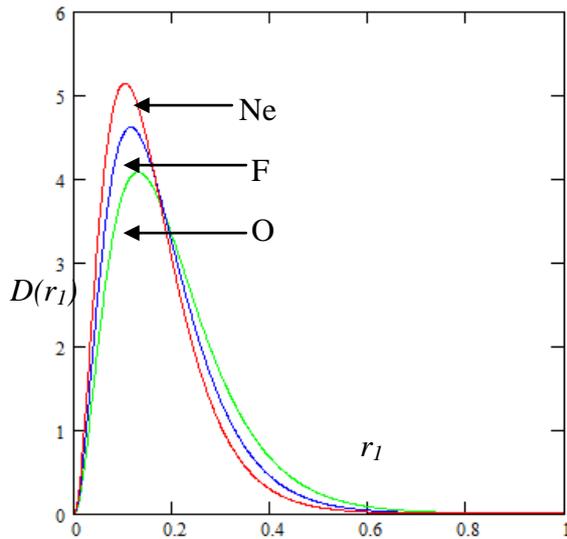
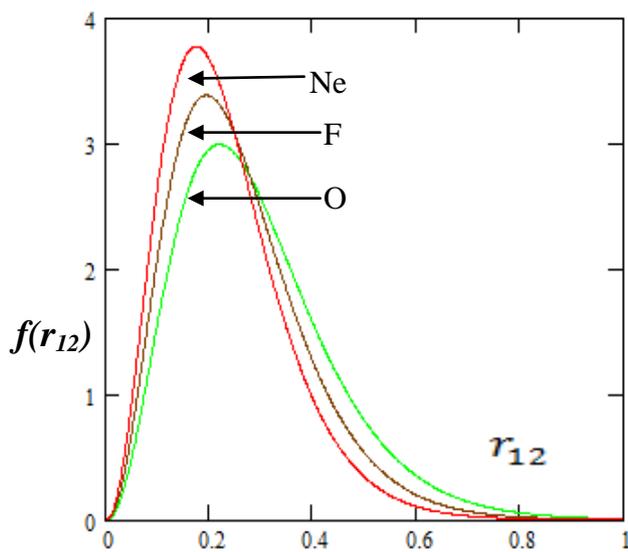


Figure (1): the two-particle radial density function  $D(r_1, r_2)$  for studied systems .



Fig(4-1): Relation between the one-particle radial density distribution function  $D(r_1)$  and the position ( $r_1$ ) for K-shell.



Fig(4-7):Relation between inter-particle distribution and  $r_{12}$  for studied systems

1.The maximum values of  $D(r_1, r_2)$  from table (4-6) increase when atomic number increases and the values of their maximum locations decrease due to increasing in attraction force when  $Z$  increases which attracts the two electrons towards the nucleus and decreasing in their positions according to Coulomb law .

2. It was also observed when the distance equal to zero from the nucleus, the probability of finding an electron equal to Zero { when  $r = 0$   $D(r_1) = 0$  }. This means that the electron is not found in the nucleus and when the distance is far from nucleus, the probability of finding an electron equal to Zero also { when  $r = \infty$   $D(r_1) = 0$  }. That means the electron is not found out the atom.

3. when the positions of maximum values decrease when atomic number increases .these results agree with Coulomb law because increasing in attraction force leads to decreasing in the positions towards the nucleus

4. When  $r_{12} = 0, f(r_{12}) = 0$ , and when  $r_{12} = \infty, f(r_{12}) = 0$ , because the coulomb interaction neglect, when the distance between two-electrons is very large

5. In the framework, we found the one-particle expectation value  $\langle r_1^n \rangle$  increases when the atomic number  $Z$  increases, when  $n$  take negative values  $-2, -1$ , where the  $\langle r_1^{-1} \rangle$  related to the attraction energy expectation value  $\langle V_{en} \rangle = -Z [ N. \langle r_1^{-1} \rangle, N$  represents the number of electrons in the shell (the number of electrons in the Present work = 2 for atom).

6. The attraction energy expectation values  $\langle V_{en} \rangle$  are larger than the repulsion energy expectation value  $\langle V_{ee} \rangle$  because the distances between the electrons and the nucleus are smaller than the distances between the electrons.

### Conclusions

From these results, we Conclude

1. when the atomic number  $Z$  increases, for both approximations the one, two-particle radial density distribution function  $D(r_1)$ ,  $D(r_1, r_2)$ ,

and the inter-particle distribution function  $f(r_{12})$  are increased.

2. When  $Z$  increases the positions of these maximum values for both approximations the one, two-particle radial density distribution function  $D(r_1)$ ,  $D(r_1, r_2)$ , and inter-particle distribution function  $f(r_{12})$  decreases.

3. For both one-particle expectation  $\langle r_1^m \rangle$ , and two-particle expectation  $\langle r_{12}^m \rangle$  increase when  $Z$  increase and when  $m = -2, -1$  and both decrease for  $m = +2, +1$ .

4. The standard deviation of one-particle  $\Delta r_1$  and two-particle  $\Delta r_{12}$  decreases for all systems when the atomic number increases.

5. All the expectation values of the energies  $\langle V_{en} \rangle$ ,  $\langle V_{ee} \rangle$ ,  $\langle V \rangle$ ,  $\langle T \rangle$  and  $\langle E_{HF} \rangle$  increase when the atomic number increases.

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