# calculation the Hartree -Fock energy of 1s shell for some ions

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# Abstract:

In this research we calculated the important atomic properties such as Hartree- Fock energy of 1S shell for the ions  $Si^{+12}$ ,  $P^{+13}$ ,  $S^{+14}$ ,  $Cl^{+15}$ ,  $Ar^{+16}$  and  $K^{+17}$ , Also we found the values the energies in hartree unit (-187.358095,-215.73959,-246.114628,-278.482499,-312.858707,-349.23) hartree respectively. All the studied atomic properties were normalized and we used the atomic units in our calculations.

Keywords: Hartree-Fock, atomic properties, atomic units

الخلاصة:

Si<sup>+12</sup>, ) في هذا البحث تم حساب بعض الخواص الذرية المهمة مثل طاقة هارتري فوك للغلاف 1s للايونات (Si<sup>+12</sup>, ) فوجدنا ان قيم الطاقات بوحدة الهارتري كانت (P<sup>+13</sup>,S<sup>+14</sup>,Cl<sup>+15</sup>,Ar<sup>+16</sup> and K<sup>+17</sup>) فوجدنا ان قيم الطاقات بوحدة الهارتري كانت (215.73959- 215.73959- 215.73959- 312.858707) مارتري على التوالي. جميع الخواص الذرية المدروسة كانت عياريه واستخدمنا الوحدات الذرية في حساباتنا.

كلمات مفتاحية: هارترى فوك ، الخصائص الذرية ، الوحدات الذرية

### Introduction:

In 1926 Erwin Schrödinger developed an equation, called a wave equation, to describe the behavior of matter waves. An acceptable solution to Schrödinger's wave equation had called a wave function. By using Schrödinger's equation scientists can find the wave function, which solves a particular problem in quantum mechanics. Unfortunately, it is usually impossible to find an exact solution to this equation, so certain assumptions have been used in order to obtain an approximate answer for the particular problem. Both Erwin Schrödinger and Werner Heisenberg (1927) independently formulated general quantum theory. At first sight, the two methods appeared to be different because Heisenberg's method has formulated in terms of matrices whereas Schrödinger's method has formulated in terms of partial differential equations. Just a year later, however, Schrödinger was able to show that the two formulations are mathematically equivalent[1].

## **Theory:**

The wave function  $\psi(r_1, r_2, r_3, \dots, r_N)$  of many particles system is a mathematical expression that carries the information about the system properties such as position, momentum, energy and etc. There are two main kinds of the wave function approximation methods [2]

- 1- The uncorrelated wave function approximation.
- 2- The correlated wave function approximation.

In the uncorrelated wave function approximation, each particle is assumed to move in only the average field of all other particles in the system. This procedure uses an approximation method called the Hartree-Fock approximation (HF).

In the correlated wave function approximation, one 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 in the atomic system is defined as [2]

 $\Psi_{nlm_lm_s}(r) = R_{nl}(r)Y_l^m(\theta,\phi)\sigma(s) \dots (1)$ 

The radial function  $R_{nl}(r)$  is related to the distance of electron from the nucleus and it depends on the ( the principal quantum number) and  $Y_l^m(\Theta, \phi)$  represents function of spherical harmonic [4].

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 vibrational method is accurate enough, for atoms of higher atomic number, the best approach to find a good wave in first calculation function lies 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. [5]

 $\sum_{i < j} \frac{1}{r_{ij}}$ 

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 equation (1).

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[2] .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  $\phi$ , or in other words an antisymmetric product of individual electron spin-orbitals. The optimum Slater determinant is then obtained by using the vibrational method to determine the best individual electron spin-orbital.

The Hartree-Fock method is therefore a particular case of the vibrational method, in which the trial function for the N-electron atom is a Slater determinant whose individual spin-orbitals are optimized.

It should be noted that the N-electron atom wave function  $\psi(1,2,3,...N)$  solution of the Schrödinger equation stated below

$$\sum_{i=1}^{N} (-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}) + \sum_{i < j} \sum_{i=1}^{N} (\frac{1}{r_i}) \psi(1, 2, \dots, N) = E \psi(1, 2, \dots, N) \dots$$
(2)

can only be represented by an infinite sum of Slater determinants.

So that the Hartree-Fock method may be considered as a first step in the determination of atomic wave function and energies. We also remark that the Hartree-Fock method is also applied to other systems such as molecules or a solids.[3] In the Hartree-Fock method, the trial wave function is a Slater determinant.

Let us denote the ground state energy of the system by  $E_0$ : According to the vibrational method

$$E_0 = \langle \psi | H | \psi \rangle \dots (3)$$

where  $\Psi$  is a trial wave function which is assumed to be normalized to unity  $\langle \psi | \psi \rangle = 1$ 

We can write the HF wave function for two electron atom as

$$\psi(r_1, r_2) = \phi_{1s}(1)\phi_{1s}(2)$$
 ... (4)

**Results and discussion:** 

✤ One particle radial density distribution

function **D**(**r**<sub>1</sub>) :

One –Electron radial density distribution function is the

For 2-electron systems .[6]

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \dots \dots (5)$$

The standard method for determining the optimal form of the spatial part of the spin orbital in a determinant wave function such as equation (5).

$$D(r_1)1s=R^{2}_{1S}(r_1)r_1^{2}$$
......(6)

probability of finding the electron in a spherical shell at distance  $r_1$ from the nucleus , we calculated from the equation(6).[8]

Table(1):-values of positions and maximum values of the  $D(r_1)$  for studied system for 1s shell.

Ions	Si <sup>+12</sup> P <sup>+13</sup>		S+14	<b>Cl</b> +15	Ar <sup>+16</sup>	K <sup>+17</sup>	
<i>r</i> <sub>1</sub>	0.07	0.0698	0.0601	0.06	0.0599	0.05	
D <sub>max</sub> (r <sub>1</sub> )	7.351	7.896	8.419	8.986	9.49	10.028	



From table (1)we noted, That the maximum values for  $D(r_1)$  increases when the atomic number increase, that means the probability of finding an electron increase and the locations of these peaks are contracted toward the nucleus .From fig.(1) we observed that:

the distance equal to zero from the systems , 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.

# • One-particle expectation value $< r_1^m > :$

The one-particle expectation value and the standard deviation  $\Delta_{r_1}$  were calculated by using equations .[8]

$$\langle \mathbf{r}_{1}^{m} \rangle = \int_{0}^{\infty} D(r) \boldsymbol{r}_{1}^{m} dr_{1} \dots \dots (7)$$
$$\Delta r_{1} = \left[ \langle r_{1}^{2} \rangle - \langle r_{1} \rangle^{2} \right]^{\frac{1}{2}} \dots \dots (8)$$

Consecutively for different values for m where m is integer number and takes the values  $2 \ge m \ge -2$ , the results of the radial expectation values of  $< r_1^m >$  and standard deviation are tabulated in fig. (2) .

Table(2): Values of one-particle expectation values for different values of (m) and stander deviation.

Ions	$\left\langle r_{1}^{-2}\right\rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^0 \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$	$\Delta r_1$
Si <sup>+12</sup>	376.9701	13.68727	1	0.110099	0.016219	0.06401
P <sup>+13</sup>	433.9028	14.68774	1	0.102572	0.014073	0.0596
s <sup>+14</sup>	494.8187	15.68772	1	0.096006	0.012327	0.05576
C1 <sup>+15</sup>	559.7133	16.68728	1	0.090229	0.010886	0.05239
Ar <sup>+16</sup>	628.6313	17.68736	1	0.08511	0.00968412	0.0494
к <sup>+17</sup>	701.5424	18.68727	1	0.080539	0.008670737	0.04674

from table(2) we noted :

1- In all studied systems we found the oneparticle expectation value  $< r_1^m >$  increase when the atomic number increase when m take negative value -2,-1 where the  $\langle r_1^{-1} \rangle$ related to the attraction energy expectation value  $< V_{en} > = -Z[N, \langle r_1^{-1} \rangle]$ , N represent the number of electron in the shell and  $\langle r_1^{-2} \rangle$ indicates how the density distribution in near regions of the nucleus. 2- We observed when Z increase the oneexpectation value  $\langle r_1^m \rangle$  begins decrease form positive values +1, +2. Where  $\langle r_1^2 \rangle$  is related to the stander deviation and  $\langle r_1^1 \rangle$ represented the distance between the nucleus and the electron.

3- When m equal to zero , the one-particle expectation value  $< r_1^m >$  equal to unity for all studied systems ,this represents the normalization condition because the One-

particle radial density distribution function

D(r<sub>1</sub>) is normalized 
$$\int_{0}^{\infty} D(r_1) \boldsymbol{\gamma}_1^m dr_1 = 1$$

**4-** The standard deviation for all studied systems  $\Delta r_1$  decrease with increasing atomic number, because the distance between electron-nucleus become small.

# \* Inter-particle Distribution Function

 $f(r_{12})$ :

The pair distribution function

evaluated from equation below[5]:

$$f(r_{12})_{(1S)} = 0.5r_{12} \begin{bmatrix} \int_{r_{12}}^{\infty} r_1 \int_{r_{12}-r_{12}}^{r_1+r_{12}} R_{1S}^2(r_1) R_{1S}^2(r_2) r_2 dr_2 dr_1 + \\ \int_{r_{12}}^{r_{12}-r_{12}+r_1} R_{1S}^2(r_1) R_{1S}^2(r_2) r_2 dr_2 dr_1 \end{bmatrix} - -(9)$$

It represents coulomb repulsion between a pair of electron with .The results are tabulated for all systems in the table(3).And fig.(2) indicates the relation between  $f(r_{12})$  and inter electronic distance  $r_{12}$ .

Table(3): The location and maximum values of the inter-particle

Ions	Si+12	P+13	S+14	Cl+15	Ar <sup>+16</sup>	K+17
r <sub>12</sub>	0.12	0.11	0.103	0.1	0.0989	0.090
f(r <sub>12</sub> )	5.409	5.801	6.198	6.606	6.982	7.402

distribution function  $f(r_{12})$  for studied systems.



From fig(2),as atomic number increase , the distance  $r_{12}$  between two electron decreases , this behavior from the fact that ,electrons shrinkage toward the nucleus.

From the table(3) we noted the maximum value  $f(r_{12})$  of increases as Z increases and the inter-particle distance decreases because

increasing the atomic number which lead to increases the attraction force between the nucleus and the electron then the distance between electrons decreases.

# ✤ Inter-particle Expectation

Value  $\langle r_{12}^m \rangle$ 

We evaluated the inter-particle expectation value  $\langle r_{12}^m \rangle$  and standard deviation by using equations below[8]

$$< r_{12}^{m} > = \int_{0}^{\infty} f(r_{12}) r_{12}^{m} dr_{12} \dots (10)$$

$$\Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2} \dots (11)$$

Respectively and tabulated of the results in table (4), which show the relationship between  $\langle r_{12}^m \rangle$  with m.

$\left\langle r_{12}^{-2}\right\rangle$	$\left\langle r_{12}^{-1}\right\rangle$	$\langle r_{12}^0 \rangle$	$\langle r_{12}^1 \rangle$		$\langle r_{12}^2 \rangle$	$\Delta r_{12}$ Standard deviation
+12 Si	124.44829	8.52751	1	0.16069	0.03244	0.08135
P <sup>+13</sup>	143.34102	9.15305	1	0.1497	0.02815	0.07575
S+14	163.55861	9.77804	1	0.14011	0.02465	0.07088
c1 <sup>+15</sup>	185.10032	10.40259	1	0.13167	0.02177	0.0666
+16 Ar	207.98606	11.02769	1	0.12419	0.01937	0.0628
к <sup>+17</sup>	232.20111	11.65259	1	0.11752	0.01734	0.05942

Table(4): expectation values  $\langle r_{12}^m \rangle$  where  $-2 \ge m \ge 2$  and standard deviation.

from analyzed the inter-particle expectation value  $\langle r_{12}^{m} \rangle$  and standard deviation  $\Delta r_{12}$ presented in table (4) we noted :

1- The inter-particle expectation value  $\langle r_{12}^m \rangle$  increase when Z increase and when m takes values -2,-1, where  $\langle r_{12}^{-1} \rangle$  represented repulsion energy between two-electrons.

2- when m takes positive values +1,+2, the inter-particle expectation value decrease with Z increase.

3- The inter-particle expectation value  $\langle r_{12}^m \rangle$  equal to unity for all systems when m = 0, this represent the normalization condition because the inter-particle distribution function is normalized

$$\int_{0}^{\infty} f(r_{12}) dr_{12} = 1$$

4- The standard deviation decrease when Z increase for all systems. The standard deviation contains much information concerning the shape of the two-particle

distribution function  $f(r_{12})$ , the  $\Delta r_{12}$  shape results indicate  $f(r_{12})$  become less diffuse.

# The expectation value of energy $\left< E \right>$ :-

The potential energy and total energy were calculate by using equations below[8,9] :

These results are listed in table (5).

Table(5): The expectation values for attraction , repulsion , kinetic and Hartree- Fock energies of the Ions.

Ions		$-\langle V_{_{en}} angle$	$\left< V_{ee} \right>$	$-\langle V \rangle$	$\langle T \rangle$	$-\langle E_{\scriptscriptstyle HF}  angle$
si <sup>+12</sup>	present .work	383.2437	8.52751	374.71619	187.358095	187.358095
	Ref .work[10]			374.7198	187.35874	187.6108
+13	present .work	440.63223	9.15305	431.47918	215.73959	215.73959
Р	Ref .work[10]			431.47008	215.73607	215.73401
s <sup>+14</sup>	present .work	502.00729	9.77804	492.22926	246.114628	246.114628
	Ref .work[10]			492.22024	246.11107	246.10917
Cl <sup>+15</sup>	present .work	567.36758	10.40259	556.965	278.482499	278.482499
	Ref .work[10]			556.97024	278.48606	278.48418
+16 Ar	present .work	636.7451	11.02769	625.71741	312.858707	312.858707
	Ref .work[10]			625.72021	312.86106	312.85915
к <sup>+17</sup>	present .work	710.11633	11.65259	698.46375	349.231873	349.231873
	Ref.work[101]			698.47036	349.23606	349.23430

From the table (5):

1- we observed the results of the expectation values for total potential energy ,kinetic energy and the total energy of Hartraee-Fock are large agreement with published results .

**2-** Both  $\langle V_{en} \rangle$ ,  $\langle V_{ee} \rangle$  for ions increase when atomic number increase . This result can be understood from the fact that all shell shrink toward the nucleus due to the increase attractive force between the proton and the electrons because the distance between nucleus-electron and electron-electron decrease, this result leads to increase in repulsion potential energy and attraction potential energy ,the expectation values for total potential energy $\langle V \rangle$  increase in each system because the increase of  $\langle V_{en} \rangle$ are larger than that of  $\langle V_{ee} \rangle$  .

**3**- The expectation for kinetic energy  $\langle T \rangle$ increases when Z increase. The total energy or Hartree-Fock energy become larger when Z increase also indicates the  $\langle E_{HF} \rangle$  as a function of Z.

### Conclusions

From the present work , we deduce some notes for some atomic properties for some

ions(Si<sup>+12</sup> ,P<sup>+13</sup> ,S<sup>+14</sup> ,Cl<sup>+15</sup> ,Ar<sup>+16</sup> and K<sup>+17</sup>) as follows :

- 1- when Z increase the maximum values for one-particle radial density distribution function  $D(r_1)$  and interparticle distribution function  $f(r_{12})$ increase, and the position of these maximum values decrease with Z increase.
- 2- For both one-particle expectation  $\langle r_1^m \rangle$ , and two-particle expectation  $\langle r_{12}^m \rangle$  increase when Z increases and when m = -2, -1and both decrease for m = +2, +1when  $m = \text{zero} \cdot \langle r_1^0 \rangle$  this value represents the normalization condition.
- **3-** The standard deviation of oneparticle  $\Delta r_1$  and two-particle  $\Delta r_{12}$ decrease for all systems when the ion number increase .

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 increase and these values are given large agreement with the published results .

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