

Evaluation of the Electron Density at the Nucleus and the Correlation Energy in Position Space

Hadel A. AL-Jabri , Qassim S. AL – Khafaji
 Department of physics , Kufa University ,Iraq

Abstract: The aim of this work is evaluation of the correlation energy E_{corr} , repulsion energy between electrons $\langle V_{ee} \rangle$, attraction energy between electrons and nucleus $\langle V_{en} \rangle$, electron density at the nucleus $\rho(0)$, one-electron expectation value $\langle r_1^k \rangle$ and inter –electron expectation value $\langle r_{12}^k \rangle$ (where k is an integer takes the value -2,-1,1,2) for some ions $Si^{+11}, P^{+12}, S^{+13}$, All these results in atomic unit .

Keywords : Hartree-Fock , Electron Density , Correlation Energy , Position Space

I. Introduction :

The HF approximation begins with the assumption that the total electronic wave function can be approximated by a product of one-electron wave functions. Furthermore, one must assume that the potential experienced by a given electron is an average of the potentials produced by the remaining electrons [1] . The correlation energy must be taken into account by accurate theories of electronic structure [2] . The correlation energy of any electron system is defined as the difference between the exact non relativistic and Hartree –Fock energies. It is great interesting in studying atoms, ions and molecules taking into consideration the electron correlation energy [3].

II. Theoretical Aspects :

a-Two-particle density Distribuion Function $\Gamma_{HF}(x_i, x_j)$:

The electron pair density $\Gamma(\vec{r}_1, \vec{r}_2)$ is a function that deserves much study because the concept of electron pairs is fundamental to chemistry. The electron pairs density can be obtained from the N-electron wave function Ψ in the usual manner [4].

$$\Gamma(\vec{r}_1, \vec{r}_2) = N(N - 1) / 2 \times \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\sigma_1 d\sigma_2 d\vec{x}_3 \dots d\vec{x}_N \dots (1)$$

In which $\vec{x}_i = (\vec{r}_i, \sigma_i)$ is the combined space-spin coordinate of electron j.

b- Radial distribution functions $D(r_l)$ and expectation values of $\langle r_1^k \rangle$:

To determine the radial distribution function $D_{nl}(r_1) dr_1$ regardless of direction ,we integrate over angle θ and $d\theta$ to get [3].

$$D_{nl}(r_1) = r_1^2 [R_{nl}(r_1)]^2 dr_1 \int_0^\pi \int_0^{2\pi} |Y_{nl}(\theta, \varphi)|^2 \sin\theta d\theta d\varphi = [R_{nl}(r_1)]^2 dr_1 \dots (2)$$

The radial part of the function $R_{nl}(r_1)$ is defined as :

$$R_{nl}(r_1) = N_{nlml} S_{nl}(r_1) \dots (3)$$

Where N_{nlml} is the normalization constant and $S_{nl}(r_1)$ is the Slater- Type Orbital (STOs).

This mean the radial part of STO's become [5]:

$$R_{nl}(\xi, r_1) = (2\xi)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r_1^{n-1} \exp(-\xi r_1) \dots (4)$$

The function $D_{nl}(r_1) dr_1$ used to calculated many properties such as average distance of electron from nucleus .

It should be noted that $D_{nl}(r_1) dr_1$ is the probability that r_l has magnitude between r_l and $r_l + dr_1$ and its integral is unity [6].

$$\int_0^\infty D(r_1) dr_1 = 1 \dots (5)$$

Where $D(r_l)$ is of extreme importance in the study of atom and ions because it measures the probability of finding an electron in each shell [7] .The equation of the one – particle radial density function for each shell is [8] :

$$D(r_1)_{K(1s)} = R_{1s}^2(r_1) r_1^2 \dots (6)$$

$$D(r_1)_{KL(1s)} = D(r_1)_{KL(3s)} = \frac{1}{2} \cdot r_1^2 [R_{1s}^2(r_1) + R_{2s}^2(r_1)] \dots (7)$$

The one-electron expectation value $\langle r_1^k \rangle$ is determined by the expression as[9]:

$$\langle r_1^k \rangle = \int_0^\infty D(r_1) r_1^k dr_1 \dots (8)$$

c- Inter-particle distance function $f(r_{12})$ and the expectation value of $\langle r_{12}^k \rangle$

Inter –particle distribution function can be defined as the measure of the probability distance between two electrons [3]. inter –electron distribution function $f(r_{12})$ is given by equation [10]:

$$f(r_{12}) = 0.5 * r_{12} \left[\int_0^{r_{12}} r_1 dr_1 \int_{|r_1-r_{12}|}^{|r_1+r_{12}|} \Gamma(r_1, r_2) r_2 dr_2 + \int_{r_{12}}^\infty r_1 dr_1 \int_{|r_{12}-r_1|}^{|r_{12}+r_1|} \Gamma(r_1, r_2) r_2 dr_2 \right] \dots\dots\dots(9)$$

The expectation value of two –electron separation is given by equation [11]:

$$\langle r_{12}^k \rangle = \int_0^\infty f(r_{12}) r_{12}^k dr_{12} \dots\dots\dots(10)$$

d- The electron density at the nucleus (0) :

The electron density at the nucleus can be evaluated using the following form[12]:

$$\rho(0) = \left[\frac{D(r_1)}{4\pi r_1^2} \right]_{r_1 \rightarrow 0} \dots\dots\dots(11)$$

e- The Expectation Value Of Energy $\langle E \rangle$:

According to the laws of quantum mechanics state that the electronic and structural properties of a given material, with nuclei and electrons, can, in principle, be calculated by solving Schrödinger’s equation. The time independent Schrödinger’s equation has the form[13]:

$$\hat{H}\Psi = E\Psi \dots\dots\dots(12)$$

where \hat{H} is the Hamiltonian, a differential operator representing the total energy of the system, E is the energy of the state, and Ψ is the wavefunction. the Hamiltonian electronic operator is (in atomic units) [14].

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{r_{ij}} \dots(13)$$

We can write expectation value of energy as [15]:

$$\langle E \rangle = \langle T \rangle + \langle V_{en} \rangle + \langle V_{ee} \rangle \dots(14)$$

Where $\langle T \rangle$ is the expectation value of kinetic energy , $\langle V_{ee} \rangle$ is the Coulomb repulsion between electron-electron, and $\langle V_{en} \rangle$ is an attraction energy between electron-nucleus.

The energy expectation value is related to the potential energy[8].

$$\langle E \rangle = \frac{1}{2} \langle V \rangle \dots\dots\dots(15)$$

The expectation value of the potential energy $\langle V \rangle$ evaluate from equation (15).

$$\langle V \rangle = -Z \langle r_1^{-1} \rangle + \langle r_{12}^{-1} \rangle \dots\dots\dots(16)$$

where Z the atomic number and $\langle r_1^{-1} \rangle, \langle r_{12}^{-1} \rangle$ were related to the density distribution $D(r_1)$ and distribution function $f(r_{12})$ which defined previously.

The correlation energy is defined as the difference between the exact energy and the mean-field (HF) energy is given by equation [16]:

$$E_{corr} = E_{exact} - E_{HF} \dots\dots\dots(17)$$

III. Results and discussion:

- 1- From table (1),The researchers noted the maximum value of $D(r_j)$ increases when atomic number increases for three shells , because the increasing in atomic number ,that means increasing in attraction force between the nucleus and the electrons which lead increasing in the probability of finding the electron ,this behavior shown in fig .(1) and fig.(2) for all shell.
- 2- the maximum probability of pair distribution function $f(r_{12})$ increases as atomic number increases this lead to increases in repulsion force and the distance between electrons r_{12} decrease ,This behavior shows in three –shell as shown in fig .(3),(4)and(5).
- 3- In table (3) for all studied system, the expected values $\langle r_1^k \rangle$ are increased when $k=-I,-2$ are due to the electron probability increases and probability decreases when $k=I, 2$.
- 4- From table (4), when Z increases the values of $\langle r_{12}^k \rangle$ increases for n negative values and reverse for n positive values in addition to the values of $\langle r_{12}^k \rangle$ increases
- 5- From table (5),we noted the electron density at the nucleus increases when atomic number increases .The electron density at the nucleus in K- shell is larger because K- shell is closed to the nucleus .

- 6- From table (6), the expectation value of attraction energy $\langle V_{en} \rangle$ negative and expectation value of repulsion energy $\langle V_{ee} \rangle$ increases when atomic number Z increase, because increasing in Z lead to decreasing in the distance between electrons with nucleus and the distance between two electrons, this lead to increasing in attraction energy and repulsion energy according to coulomb law. The expectation value for total potential energy $\langle V \rangle$ increasing in each system when increasing in atomic number, because the increase of $\langle V_{en} \rangle$ are large than that of $\langle V_{ee} \rangle$ and It is noted the expectation value of Kinetic energy $\langle T \rangle$ increasing when Z increasing, because Z would lead to increasing in attraction energy between the electron and nucleus this lead to increasing the velocity of the electron around the nucleus and from table (7) The correlation energy to the total energy for total system decreasing when there is increasing in atomic number
- 7- Fig. (6)A- shows the percentage contribution for each shell in the total energy, Where K- shell has greater share then $K\alpha L\alpha$ -shell and $K\beta L\alpha$ - shell, we can also when increasing in Z the contribution of K- shell energy increasing. While contribution in $K\alpha L\alpha$ -shell and $K\beta L\alpha$ - shell decreasing because K-shell closer to the nucleus from other shells, and B-represent The percentage of correlation energy to the total energy for total system decreasing when there is increasing in atomic number, because Hartree-Fock approximation assumes that each electron moves in the average potential of the other electrons.

Table(1) : value of position and maximum values of the $D(r_1)$ for studied systems for three shells.

ion	K-shell		KaLa-Shell \equiv KβLa-Shell			
	r_1	$D_{max}(r_1)$	First peak		Second peak	
			r_1	$D_{max}(r_1)$	r_2	$D_{max}(r_2)$
Si^{+11}	0.073	7.3540	0.071	3.9454	0.398	1.2241
P^{+12}	0.068	7.8952	0.066	4.2393	0.370	1.3218
S^{+13}	0.060	8.4096	0.060	4.5302	0.340	1.4180

Table(2) :The maximum values of the $f(r_{12})$ and the corresponding values of positions for studied systems for three shells.

ion	K-shell		KaLa-Shell		KβLa-Shell			
	r_{12}	$f_{max}(r_{12})$	r_{12}	$f_{max}(r_{12})$	First peak		Second peak	
					r_{12}	$f_{max}(r_{12})$	r_{12}	$f_{max}(r_{12})$
Si^{+11}	0.122	5.4039	0.42	2.2531	0.127	0.3483	0.429	2.2401
P^{+12}	0.110	5.8019	0.388	2.4312	0.118	0.37894	0.398	2.4160
S^{+13}	0.107	6.2000	0.362	2.608	0.103	0.4089	0.371	2.5907

Table (3): Expectation values of r_1 for each individual shell and for total studied systems.

ion	shell	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$
Si^{+11}	K	376.4491	13.6752	0.11024	0.01627
	$K\alpha L\alpha \equiv K\beta L\alpha$	207.9243	8.4008	0.2907	0.1375
	Average	264.0993	10.1590	0.2305	0.0971
P^{+12}	K	433.3134	14.6750	0.1027	0.0141
	$K\alpha L\alpha \equiv K\beta L\alpha$	239.6289	9.0261	0.2697	0.1183
	Average	304.1904	10.9092	0.2140	0.0835
S^{+13}	K	494.1944	15.6751	0.0961	0.0123
	$K\alpha L\alpha \equiv K\beta L\alpha$	273.5961	9.6511	0.2516	0.1028
	Average	347.1288	11.6591	0.1997	0.0726

Table(4): Expectation value of r_{12} for each individual shell for total studied systems.

ion	shell	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^1 \rangle$	$\langle r_{12}^2 \rangle$
Si^{+11}	K	124.2080	8.5183	0.1609	0.0325
	KaLa	7.1480	2.4129	0.4889	0.2751
	KβLa	14.5144	2.6692	0.4860	0.2752
	Average	48.6234	4.5334	0.3786	0.1942
P^{+12}	K	143.0693	9.1431	0.1498	0.2823
	KaLa	8.3087	2.6019	0.4535	0.2366
	KβLa	16.8973	2.8800	0.4507	0.2366
	Average	56.0917	4.8750	0.3513	0.1671
S^{+13}	K	163.2671	9.7682	0.1402	0.0247
	KaLa	9.5499	2.7895	0.4228	0.2056
	KβLa	19.4630	3.0898	0.4201	0.2056
	Average	64.0933	5.2158	0.3277	0.1453

Table (5): electron density at the nucleus for studied systems

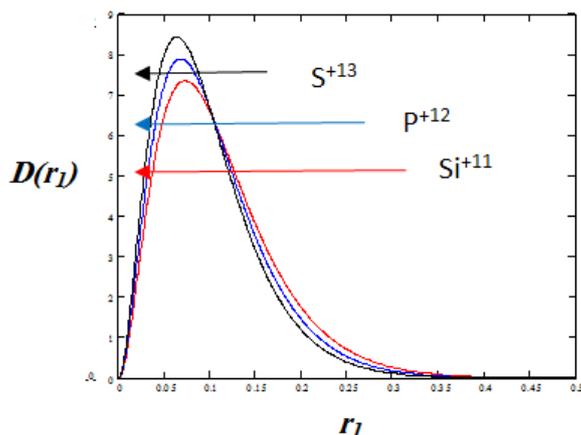
ion	K-shell		KaLa-Shell ≡ KβLa-Shell	Total
Si^{+11}	present work	931.7825	458.5497	1848.8819
	Ref. [9]	1747.475
P^{+12}	present work	1026.3632	566.5876	2159.5384
	Ref. [9]	2159.967
S^{+13}	present work	1249.2696	690.4657	2630.2010
	Ref. [9]	2628.246

Table(6) :The expectation values for all attraction ,repulsion,kinetic , Hartree-Fock energies and correlation energy for total systems.

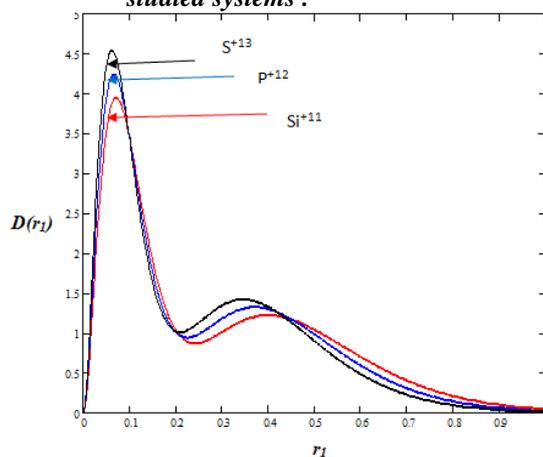
ion	Shell	$-\langle V_{en} \rangle$	$-\langle V_{ee} \rangle$	$-\langle V \rangle$	$\langle T \rangle$	$-\langle E_{HF} \rangle$
Si^{+11}	K	191.4539	8.5183	182.9356	91.4678	91.4678
	KaLa	117.6121	2.4129	115.1992	57.9963	57.9963
	KβLa	117.6121	2.6692	114.9429	57.4714	57.4714
	Total	426.6781	3.6004	413.0777	206.5389	206.5389
P^{+12}	K	220.1251	9.1431	210.9820	105.4910	105.4910
	KaLa	135.3925	2.6019	132.7906	66.3953	66.3953
	KβLa	135.3925	2.8800	132.5125	66.2562	66.2562
	total	490.9101	14.6250	476.2851	238.1425	238.1425
S^{+13}	K	250.8021	9.7682	241.0338	120.5169	120.5169
	KaLa	154.4187	2.7895	151.6291	75.8145	75.8145
	KβLa	154.4187	3.0898	151.3288	75.6644	75.6644
	total	559.6395	15.6475	543.9917	271.9959	271.9959

Table(7) :The values of Hartree-Fock energy ,Exact value and correlation energy for total systems.

ion	$-E_{HF}$	Exact value Ref.[18]	$-E_{corr}$
Si^{+11}	206.5389	207.0665	0.5276
	206.5384 Ref. [17]		
P^{+12}	238.1425	238.8294	0.6869
	238.1404 Ref. [17]		
S^{+13}	271.9959	272.8805	0.8846
	271.9924 Ref. [17]		



Fig(1): The relation between one electron radial density function $D(r_1)$ and the position (r_1) for K-shell for studied systems .



Fig(2): The relation between one electron radial density function $D(r_1)$ and the position (r_1) $K\alpha L\alpha$ and $K\beta L\alpha$ shells ($K\alpha L\alpha \equiv K\beta L\alpha$) for studied systems.

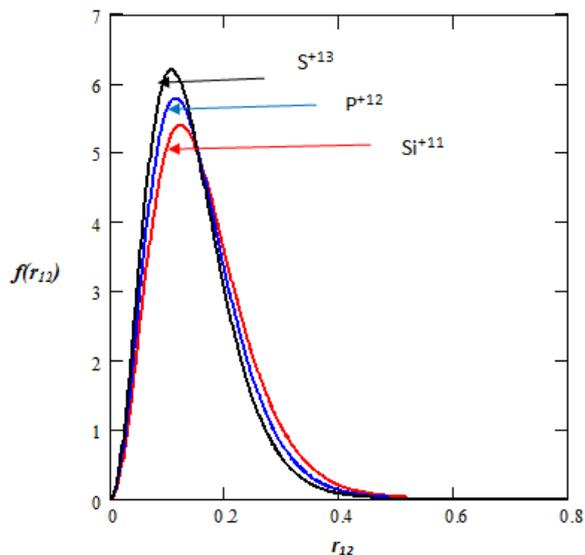


Fig (3) : The relation between the inter – electron distribution $f(r_{12})$ and the position r_{12} for K-shell of three electron systems

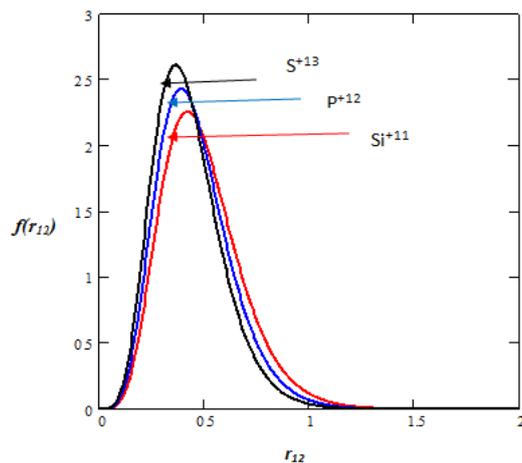


Fig (4) : The relation between the inter – electron distribution $f(r_{12})$ and the position r_{12} for $K\alpha L\alpha$ -shell of three electron systems.

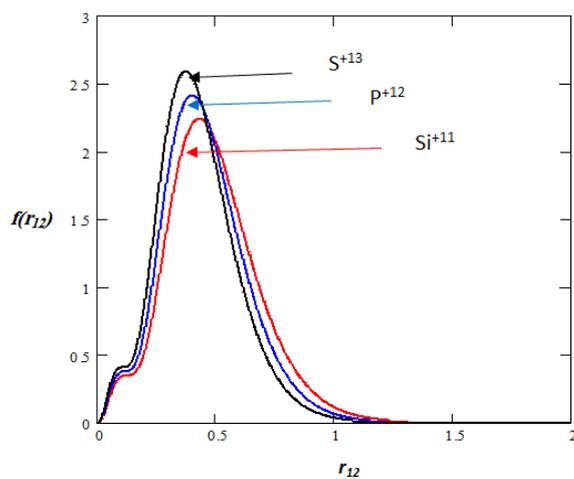


Fig (5) : The relation between the inter – electron distribution $f(r_{12})$ and the position r_{12} for $K\beta L\alpha$ -shell of three electron systems

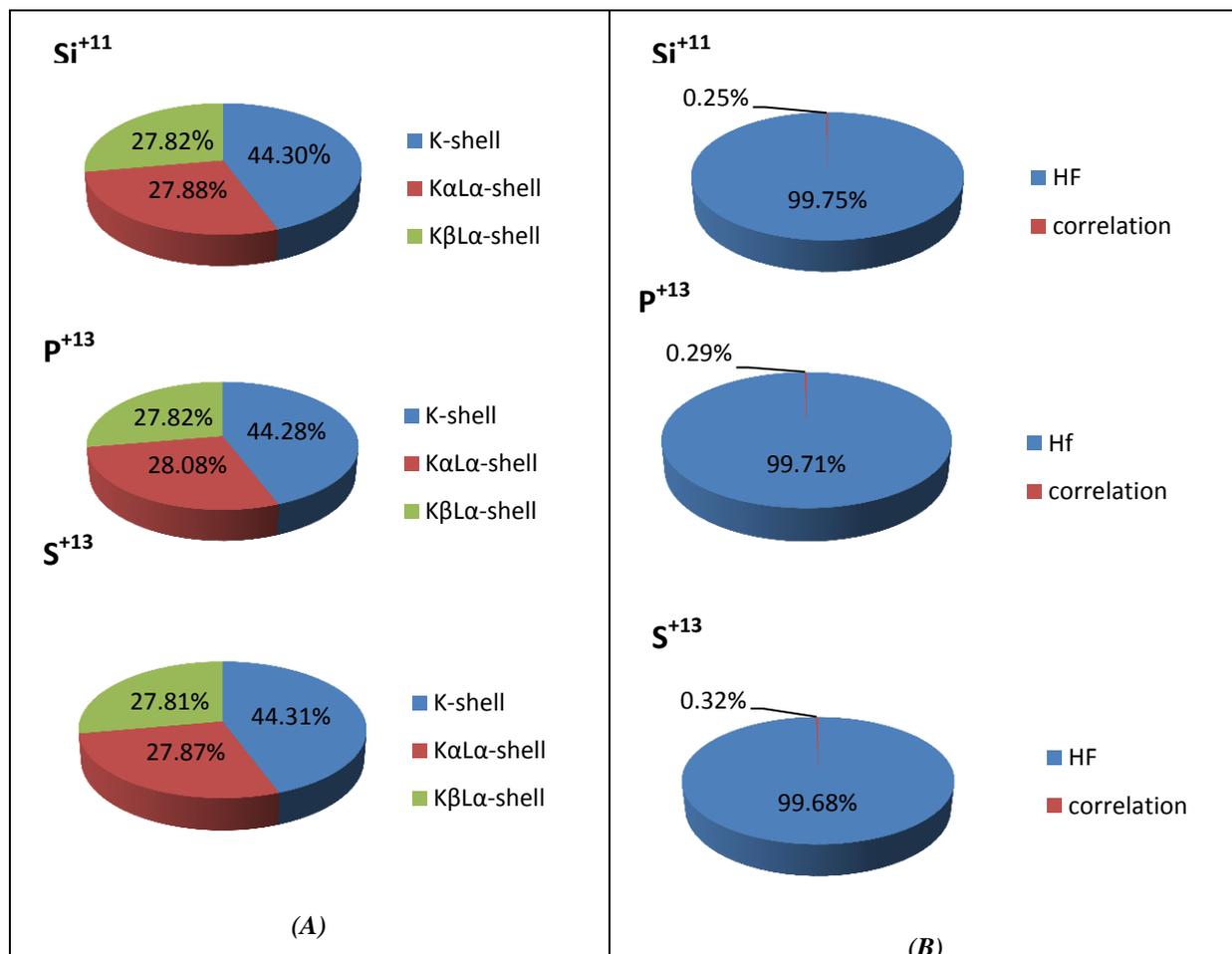


Fig (6) : (A) The percentage of Hartree-Fock for each shell relative to the total energy Hartree-Fock of the systems .

(B) The ratio between Hartree-Fock energy and correlation energy relative to the exact energy for each system.

IV. Conclusions

- 1- The maximum value of $D(r_1)$ increases when atomic number increases for three shells .
- 2- The maximum probability of pair distribution function $f(r_{12})$ increases as atomic number increases this lead to increases in repulsion force and the distance between electrons r_{12} decrease.
- 3- When atomic number increases the expected values $\langle r_1^k \rangle$ are increased when $k=-1, -2$ and decreases when $k=1, 2$.
- 4- The electron density at the nucleus increases when atomic number increases for three shells
- 5- Values of energies $\langle V_{en} \rangle, \langle V_{ee} \rangle, \langle V \rangle, \langle T \rangle$ and $\langle E_{HF} \rangle$ increases when the atomic number increases which is interpreted as the influence of nuclear charge for all shells and for total system.
- 6- The correlation energy increases with increases in atomic number .

Reference:

- [1] B.J.Killan,Ph.D.Thesis,"On Electronic representation In Molecular Reaction Dynamics",Uni-versity Florida of USA,(2005).
- [2] S.P. McCarthy and A.J. Thakkar, J.chemical physics,Vol.134,044102(2011).
- [3] S.M.Aman Allah , Journal of Kirkuk University Scientific studied, Vol.3,No.1, 101-112 (2008).
- [4] A.J.Thakkar,Chemical physics letters ,Vol.381, 80-85 (2003).
- [6] R. Yassen and M. Algarni, Int. J. Contemp. Math. Sciences, Vol. 7, No. 27, 1325 – 1335, (2012).
- [6] A.H.Al-Hayani ,Tikrit journal of pure science ,Vol.11,No.1(2006).
- [7] T. Koga , Theor.Chem. Acc, Vol. 117, 575-578, (2007).
- [8] E.M.Al-Robayi ,M.Sc.Thesis "Study of electronic density distributions function of the electronic shells for the positive boron ion ($1s^2 2s^2$) using Hartree-Fock approximation " College of Education (Ibn Al-Haithem),Baghdad University (2002).
- [9] C.Chen , J. The European Physical D,Vol.56 (2010) 303-309.
- [10] E.M.Al-Robayi, Ph.D. Thesis "A study of coulomb hole in momentum space for closed and open shells" College of Education (Ibn Al-Haithem) ,Baghdad University (2006).
- [11] E. F. S. Al-Kunani, Ms. D. Thesis" Theoretical Study of Radial Correlation and Other Atomic Properties for He Atom and He- like ions" AL-Nahrain University,(2007),
- [12] K.H.Al-Bayati,A.K.Taki and M.N.Murshed , Vol.4,No.2, 301-304 (2007).
- [13] N. A. Barrios, Ph. D. Thesis " A Computational Investigation of the Interaction of the Collagen Molecule with Hydroxyapatite", University College London, (2010).
- [14] H. Safouhi, J. Math Chem ,Vol.48 ,(2010) 601–616.
- [15] A.F.Riveros and A.Contreras , J.Physics Letters A,Vol.372 (2008) 6175-6182.
- [16] J. W. Hollett and P. W. Gill , J. Chemical Physics, Vol. 134, No. 114111 (2011) 114111-1 to 1141115.
- [17] E.Clement and C. Roetti , J. Atomic Data and Nuclear Data Table Vol.14,No.3, 177-478 (1974).
- [18] K. Rashid , B. Fricke , D. Heinemann , and Z.A. Saadi , J. Phys. D - Atoms, Molecules and Clusters , Vol. 7, 139 – 146 (1987).