Calculation the energy of four electron system have (Z=10-12)

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Abstract : The aim from this research calculate the total energy and correlation energy of some ions have four as (Ne^{+6} , Na^{+7} and Mg^{+8}) which have (Z=10-12) using Hartree - Fock approximation.

Keywords : Hartree-Fock wave function – Hamiltonianoperator correlation energy – four electron system.

I. Introduction

In Hartree-Fock approximation method disregard some correlation between electron (coulomb correlation) however gives nearly 99% of the total electronic energy by using uncorrelated wave function.[1]

Each electron has wave function, this function depending on four quantum number and four coordinate where bi symbolize for the four number n , l , m_1, m_s and   its mean the four coordinate. In Hartree-Fock approximation we can written wave function, output of function spatial coordinates and spin function with quantum number.[2]

$$\psi_{n,l,m\ell,m_s}(r, \theta, \phi, s) = \phi_{n,\ell,m\ell}(r, \theta, \phi)\sigma_{ms}$$

symbolize the spherical coordinate and n, principle quantum number it locate the essential energy level of the atom. Orbital quantum number it located the magnitude of angular momentum.

symbolize magnetic quantum number and locate the direction of angular momentum, m_s refers to spin quantum number it locate the direction of spin quantum number it locate direction of spin angular momentum.

Theory

Many of the properties of an element depend on the energies of its electrons, that mean in each moment, we can specify the energy of the an electron precisely, but not its location at a given instant. So in quantum mechanics when we want determined the location we talk about the probability of finding an electron in specific region from the space at given instant.[3]

Two- particle density   the mean to the probability of finding in same time two electrons at position x_m and x_n in each individual intra shell this function can be written for multi electronic system.[4][5]

$$\Gamma_{HF}(x_n, x_m) = \left(\frac{N}{2}\right) \int \Psi(x_n, x_m, x_d ..., x_N)\Psi^*(x_n, x_m, x_d ..., x_N)$$

$$d_{Xd} ... d_{XN} ... ... (1)$$

Where $\left(\frac{N}{2}\right)$ represents the multitude coefficient, x_i is symbolize the space and spins coordinates for ith electron is denoted to the combination is insures all terms except nth and mth electron.[6]

One particle radial density function this properties one particle radial density distribution function symbolize probability density function of getting nth electron at distance r from the nucleus. This function applied in calculated the expectation value of one particle given by[7]:-

$$D(r_n) = \int_0^\infty D(r_n, r_m)dr_m \ldots\ldots\ldots\ldots (2)$$

One-particle expectation value $\langle r_n^x \rangle$ this properties mean the distance between an electron and the nucleus when m=1 and given by[8]:-

$$\langle r_n^x \rangle = \int_0^\infty D(r_n)r_n^x dr_n \ldots\ldots\ldots\ldots(3)$$

Inter particle distribution function $f(r_{nm})$ this properties suggest first by Coulson and Nelson to study of electron correlation for He in the ground state. As well use to describe the probability of finding two electron detached by distance   from any other this function given by[9]:-

$$f(r_{nm}) = 8\pi^2 r_{nm} \int_0^{r_{nm}} \int_{r_{nm}}^{r_{nm}+r_n} r_n^2 r_m^2 \Gamma(r_n, r_m)dr_m dr_n +$$

$$\int_{r_{nm}}^\infty \int_{r_n-r_{nm}}^{r_{nm}+r_n} r_n^2 r_m^2 \Gamma(r_n, r_m)dr_m dr_n \ldots\ldots\ldots\ldots\ldots(4)$$

Where r_{12} symbolize the distance between the electron given by

Inter-particle expectation value $\langle r_{nm}^x \rangle$ the inter-particle expectation considered as very important property of the electron and by use this property we can calculate the distance between any pair of electron in any individual intra shell, this function given by[10]:-

$$\langle r_{nm}^x \rangle = \int_0^\infty f(r_{nm}) r_{nm}^x dr_{nm} \ldots\ldots\ldots\ldots\ldots (5)$$

The expectation value symbolize distance between pair of electron and when K=-1 observed to the repulsion potential energy between two-electron also when K=2 to calculate the standard deviation, and K=0 be useful to chick the normalization condition.

The expectation value of energy $\langle E \rangle$ this property given when the Hamiltonian operator prosperity given when function

The Hamiltonian operator is given by equation $V_{ee} = \sum_{j>i} \sum_{i=1}^N \frac{1}{r_{ij}} \frac{e^2}{4\pi e^o} \ldots\ldots\ldots (7)$

By substituting the Hamiltonian operator in atomic unit in equation (6) we get:-

$$\langle E \rangle = \langle \Psi | -\sum_{i=1}^N \frac{1}{2}\widehat{\nabla}_i^2 + \sum_{i=1}^N \frac{z}{r_i^\wedge} + \sum_{j>i}$$

The first term represented the kinetic energy operator the second term symbolized the attraction potential energy operator, the last term is the repulsion potential energy operator, can be written as[11][12]

$$\langle T \rangle = \sum_{i=1}^N \frac{1}{2}\widehat{\nabla}_i^2 \ldots\ldots\ldots\ldots (9)$$

$$\langle V_{en} \rangle = \sum_{i=1}^{N} \frac{1}{2}\frac{Z}{\hat{r}_i} \ldots\ldots\ldots\ldots. (10)$$

$$\langle V_{ee} \rangle = \sum_{j>i} \; \sum_{i=1}^{N} \frac{1}{r_{ij}^{\wedge}} \ldots\ldots. (11)$$

Results and discussion

Table (1) The results of the maximum value of the redail density function $D(r1)_{max}$ with coresponding positions of studied system.

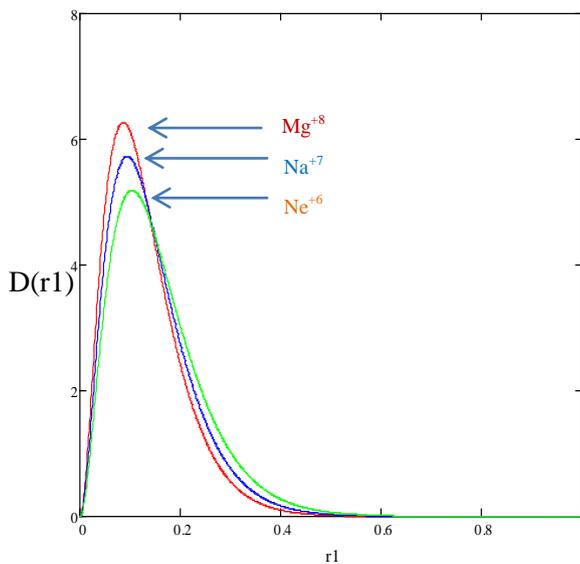| ion		k-shell		L-shell				KL(^{3}s)		KL(^{1}s)	
				Peak 1		Peak 2		Peak 1		Peak 2	
		r1	$D(r1)_{max}$	r1	$D(r1)_{max}$	r1	$D(r1)_{max}$	r1	$D(r1)_{max}$	r1	$D(r1)_{max}$
Ne^{+6}	Present work	0.1	5.183	0.08	0.35033	0.6	1.580	0.1	2.753	0.59	0.79735
	Ref[13]	0.1	5.1835	0.08	0.3503	0.60	1.5802	0.1	2.7539	0.59	0.7973
Na^{+7}	Present work	0.09	5.7214	0.07	0.40101	0.53	1.773	0.09	3.0474	0.53	0.89535
Mg^{+8}	Present work	0.085	6.269	0.065	0.4511	0.49	1.9656	0.083	3.3414	0.481	0.99317

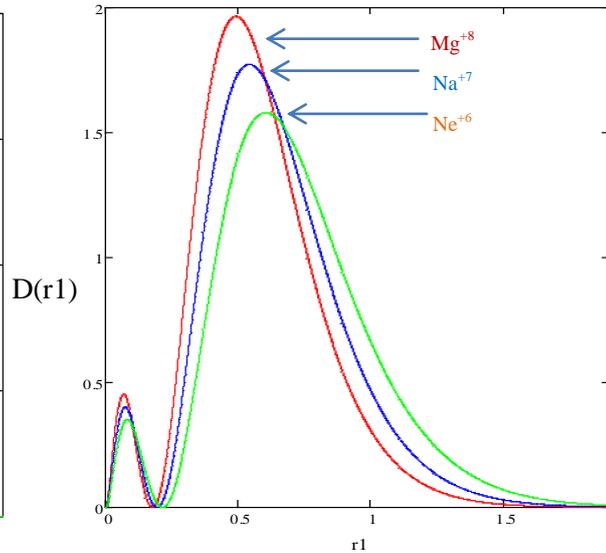Fig (1) the relationship between one electron radial density function D(r1) with the position r1 for K-shell in a.u.

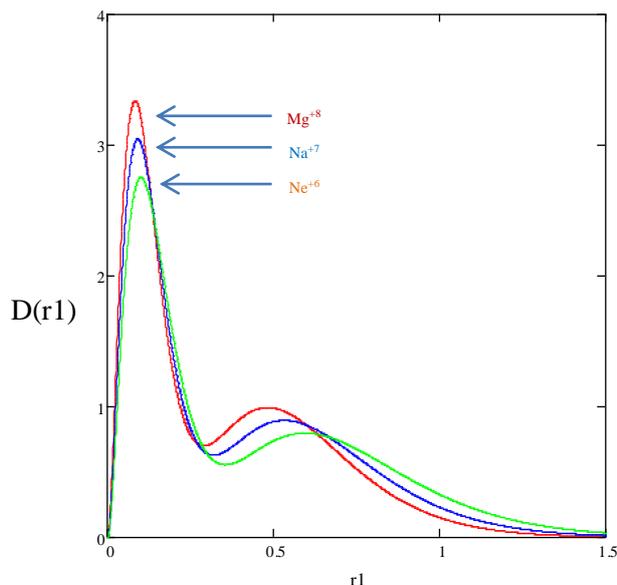Fig (2) the relationship between one electron radial density function D(r1) with the position r1 for L-shell in a.u.

Fig (3) the relationship one electron radial density function D(r1)
with the position r1 for KL(s)^1 -shell and KL(s)^3 -shell in a.u.

Table (2) expectation values of $\langle r_1 \rangle^n$ and standard deviation of dividual shell for studied system in a.u.

ion	shell		$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^{0} \rangle$	$\langle r_1^{1} \rangle$	$\langle r_1^{2} \rangle$	Δr_1
Ne^{+6}	k	Present work	188.58172	9.67307	1	0.15618	0.0327	0.091
		Ref[13]	188.8538	9.6732	1	0.1562	0.0327	0.091
	L	Present work	16.79054	2.04059	1	0.71179	0.59261	0.2932
		Ref[13]	16.79054	2.04061	1	0.71180	0.59262	0.2932
	KL(^{3}s)	Present work	102.82113	5.85683	1	0.43398	0.31266	0.35259
		Ref[13]	102.8210	5.85682	1	0.4340	0.3127	0.3526
	KL(^{1}s)	Present work	102.821	5.857	1	0.434	0.313	0.353
		Ref[13]	102.8214	5.8568	1	0.4340	0.3127	0.3526
	Average	Present work	102.77610	5.85685	1	0.433985	0.31215	0.2991616
		Ref[13]	102.8214	5.8568	1	0.4340	0.3127	0.2991
Na^{+7}	k	Present work	229.70305	10.67258	1	0.14146	0.02682	0.08249
	L	Present work	21.16772	2.29133	1	0.63587	0.4727	0.26149
	KL(^{3}s)	Present work	125.43539	6.48195	1	0.38866	0.24976	0.31417
	KL(^{1}s)	Present work	125.43539	6.48195	1	0.38866	0.24976	0.31417
	Average	Present work	125.43538	6.481952	1	0.3886616	0.249765	0.2667766
Mg^{+8}	k	Present	274.55087	11.67197	1	0.12927	0.02239	0.075

	work					
L	Present work	26.05119	2.54205	1	0.57467	0.38598	0.23607
KL(^{3}s)	Present work	150.30103	7.10701	1	0.35197	0.20418	0.28337
KL(^{1}s)	Present work	150.30103	7.10701	1	0.35197	0.20418	0.28337
Average	Present work	150.30103	7.10701	1	0.35136	0.2041825	0.21945

Table (3) the maximum values of the f(r12) and corresponding values for in dividual shell for total studied system in a.u.

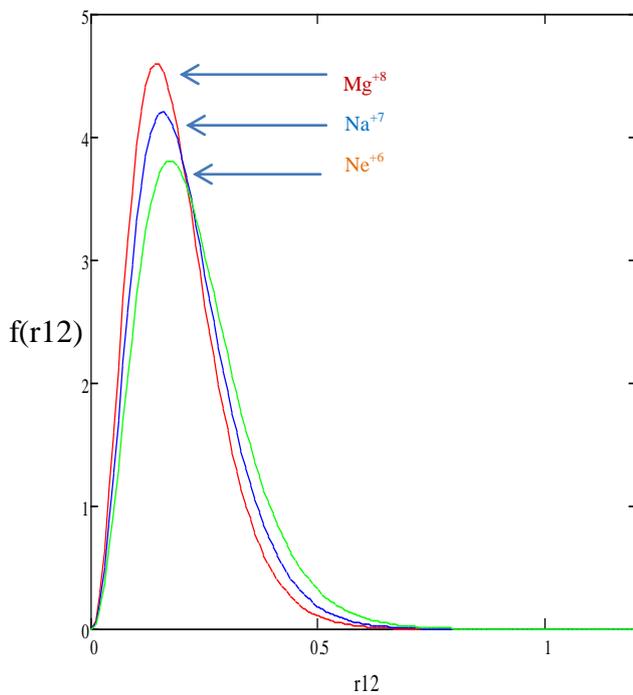| ion		k-shell		L-shell		KL(^{3}s)		KL(^{1}s)			
								Peak 1		Peak 2	
		r12	f (r12)$_{max}$	r12	f (r12)$_{max}$	r12	f (r12)$_{max}$	r12	f (r12)$_{max}$	r12	f (r12)$_{max}$
Ne^{+6}	Present work	0.17	3.8089	0.91	0.9485	0.62	1.4828	0.64	1.4823	0.14	0.3700
	Ref[3]	0.17	3.8089	0.91	0.9485	0.61	1.48283	0.64	1.4824	0.140	0.3701
Na^{+7}	Present work	0.16	4.2053	0.81	1.0615	0.54	1.6613	0.55	1.6587	0.12	0.4222
Mg^{+8}	Present work	0.14	4.6031	0.74	1.1744	0.51	1.839	0.52	1.8337	0.11	0.476

Fig (4) the relationship between inter-particle distribution function with r12 for K-shell of four electron system in a.u.
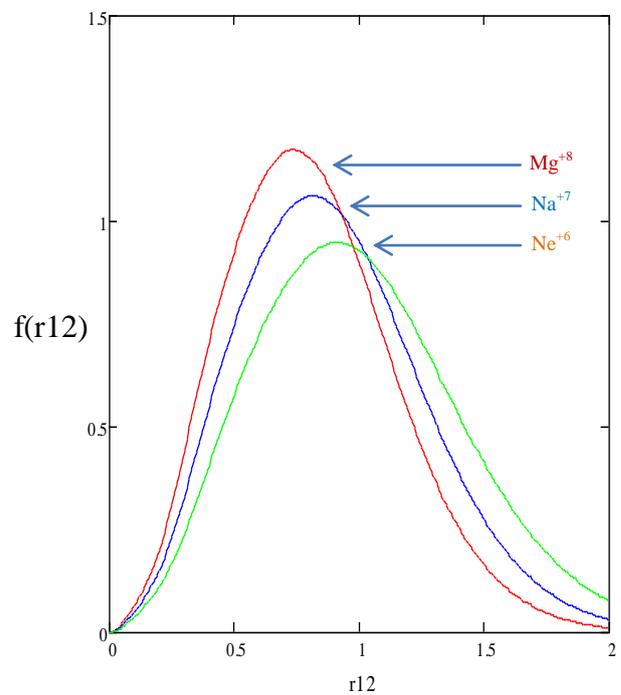

Fig (5) the relationship between inter-particle distribution function with r12 for L-shell of four electron system in a.u.
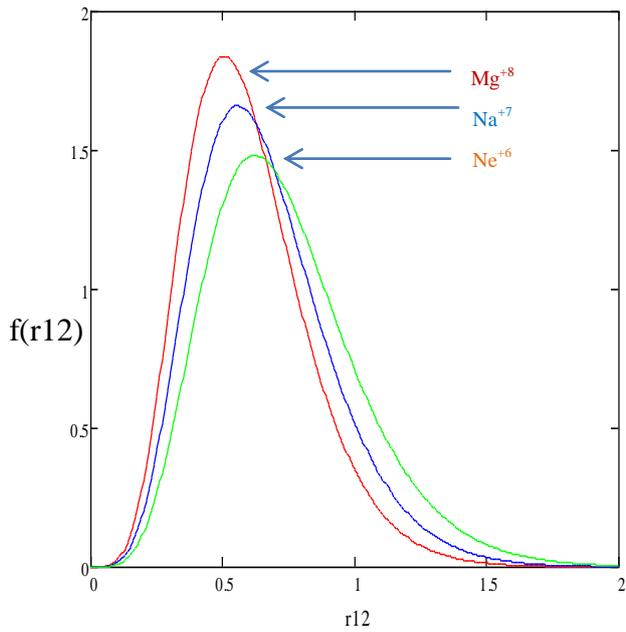
Fig (6) the relationship between inter-particle distribution function with r12 for KL(^{3}s)-shell of four electron system in a.u.
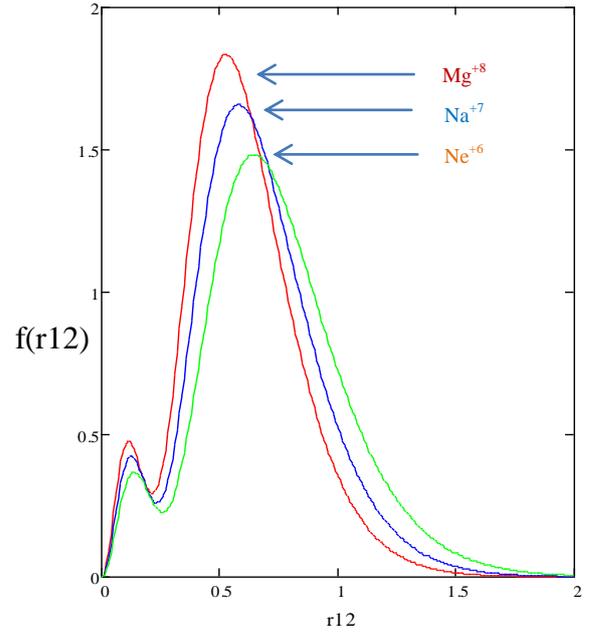

Fig (7) the relationship between inter-particle distribution function with r12 for KL(^{1}s)-shell of four electron system in a.u.

Table (4) Expectation values of $<r_{12}^n>$ and for each in dividual shell and for total studied system in a.u.

ion	shell		$<r_{12}^{-2}>$	$<r_{12}^{-1}>$	$<r_{12}^0>$	$<r_{12}^1>$	$<r_{12}^2>$	Δr_{12}
Ne^{+6}	k	Present work	62.04716	6.01709	1	0.22804	0.06541	0.11578
		Ref[13]	62.0472	6.0171	1	0.22801	0.0654	0.1158
	L	Present work	2.65422	1.26876	1	1.00375	1.18523	0.42156
		Ref[13]	2.65421	1.2688	1	1.00373	1.18522	0.4216
	KL(^{3}s)	Present work	3.21386	1.61364	1	0.73519	0.62532	0.30915
		Ref[13]	3.21390	1.61363	1	0.7352	0.62533	0.3092
	KL(^{1}s)	Present work	9.45642	1.9234	1	0.72784	0.62532	0.30915
		Ref[13]	9.45641	1.9234	1	0.72785	0.62533	0.3092
	Average	Present work	13.96656	2.34169	1	0.69420	0.62532	0.28670
		Ref[13]	13.9665	2.3416	1	0.6941	0.6253	0.2866
Na^{+7}	k	Present work	75.56904	6.6418	1	0.20653	0.05363	0.10478
	L	Present work	3.33108	1.42006	1	0.89666	0.94541	0.37604
	KL(^{3}s)	Present work	4.00777	1.80282	1	0.65741	0.49953	0.25951
	KL(^{1}s)	Present work	11.88756	2.1564	1	0.65056	0.49953	0.27622

	Average	Present work	17.13516	2.60445	1	0.62099	0.49952	0.25592
Mg^{+8}	k	Present work	90.42134	7.26629	1	0.18872	0.04477	0.09569
	L	Present work	4.0842	1.57117	1	0.81038	0.77196	0.33948
	KL(^{3}s)	Present work	4.88812	1.99174	1	0.59461	0.40837	0.23411
	KL(^{1}s)	Present work	14.59409	2.38923	1	0.58821	0.40837	0.24975
	Average	Present work	20.62733	2.86698	1	0.56185	0.40836	0.23120

Table (5) Expectation values for all attraction, repulsion, kinetic and Hartree-Fock energies for K, L, KL(^{3}s) and KL(^{1}s) shell system.

ion	shell	-<Ven>	<Vee>	-<V>	<T>	-<EHF>	Theoretical Value
Ne^{+6}	k	-193.4614	+6.01709	-187.4443	+93.7221	-93.7221	110.23203 Ref[15]
	L	-40.8118	+1.26876	-39.54304	+19.77152	-19.77152	
	KL(^{3}s)	…………..	+1.61364	+1.61364	-0.80682	+0.80682	
	KL(^{1}s)	…………..	+1.9234	+1.9234	-0.9617	+0.9617	
	Total	-234.2732	14.05017	-220.2230	110.11146	-110.11100	
	Ref [14]	…………..	…………….	-220.22154	110.11053	-110.11146	
Na^{+7}	k	-234.79676	+6.6418	-228.15496	+114.0775	-114.07748	134.97111 Ref[15]
	L	-50.40926	+1.42006	-48.9892	+24.4946	-24.4946	
	KL(^{3}s)	…………..	+1.80282	+1.80282	-0.90141	+0.90141	
	KL(^{1}s)	…………..	+2.1564	+2.1564	-1.0782	+1.0782	
	Total	-285.20602	15.62672	269.5793	+134.78965	-134.78965	
	Ref [14]	…………..	…………….	269.57594	+134.78755	-134.78839	
Mg^{+8}	k	-280.12719	+7.26629	-272.86099	+136.43049	-136.43049	161.99872 Ref[15]
	L	-61.0092	+1.57117	-59.43803	+29.71902	-29.71902	
	KL(^{3}s)	…………..	+1.99174	+1.99174	-0.99587	+0.99587	
	KL(^{1}s)	…………..	+2.38923	+2.38923	-1.19461	+1.19461	
	Total	-341.13639	+17.20191	-323.9345	+161.96729	-161.96720	
	Ref [14]	…………..	…………….	-323.93152	+161.96545	-161.96607	

From table (1)We observe the maximum values of increase when atomic number increases for all shells because the increasing in atomic number means increasing in attraction force between the nucleus and the electrons which lead to increasing in the probability of finding the electron near from nucleus.

We noticed the distance between the nucleus and the electron r_1 decreases with increasing atomic number because increasing in attraction force lead to decreasing in the position towards the nucleus.

From figure (1) we noticed one peak represented the probability of finding the electron in K-shell. Also in figure (2) there are two peaks for L-shell, where the first peak represented the finding of electron in small distance 1S form nucleus and the second peak represents the probability of finding the electron in larger distance from nucleus 2S, in figure (3) we observe two peak appear for the

$K_{\alpha}L_{\alpha} - shell, K_{\beta}L_{\beta} - shell, K_{\alpha}L_{\alpha} - shell\ and\ K_{\beta}L_{\alpha} - shell$, the first peak represented the probability of finding the electron in K-shell and the second peak represented one electron radial density function.

We noted from table (2) when we take n =-1,-2 the one-particle expectation values is largest in K-shell and smallest in L-shell for specific atom for each state because the electron-nucleus attraction potential energy to K-shell is larger than other shell's and the expectation values increasing when decreasing the distance between electron and nucleus. In addition we observe the one particle expectation value increases when atomic number Z increases of all shells for each state, because the one-particle expectation value refers to electron-nucleus attraction potential energy as equation.   .

But when we take n=1,2 noted the one-particle expectation value is smallest in K-shell and largest in L-shell for each state, the one particle expectation value represent the distance between electron and nucleus when atomic number increases, the one particle expectation value decreases for all state because increases lead to decrease the distance between electrons and nucleus.

When n = 0 the one – electron expectation value to unity for all shells of studied system this is a symbolized the normalization condition because the one-electron radial density distribution function is normalized . We noted the standard deviation decrease when atomic number increase to all systems because increase attraction force of nucleus leads to decrease the distance between and the nucleus.

From table (3) we noted the maximum value of inter-particle distribution function increases when the atomic number Z increases while decrease the distance between electrons (4,5,6,7) because increase attraction force of nucleus decreases the lead to increase the probability of finding pair of electrons   .

For each state the highest value of in K-shell and lowest value of in L-shell because the attraction nuclear force of K-shell largest than other shells leading to decrease the distance between electrons that increases in K-shell than other shells. From figures (4,5,6,7) when that mean the probability of finding two electron in the same position equal Zero, while when that mean the probability of finding two electron far away from each other equal Zero.

And from figures we observed one peak in and two peak in the have two electrons in same spin value, according to pauli exclusion principle therefore, there is one probability of finding two electrons simultaneous in , while in the has two peak, the first peak indicates the probability of finding two electron in small distance and the second peak represented the probability of finding two electron in the larger distance between them.

From table (4) when n = -1, -2 we noted the inter-particle expectation value increases when atomic number Z increases to all system, where represents the electron-electron repulsion expectation value , that means when attraction force of nucleus increases, the distance between electron electron decrease lead to increase.

From table (4) for all system, the highest value of in K-shell, but for L-shell the is lowest value, because the repulsion force in K-shell is larger than those another shells.

When n=1,2 where represents the distance between two electrons, when Z increases the inter-particle expectation value decreases for each system because increases of the attraction nuclear force leads to decrease the distance between electrons.

We observed when n=-1,-2 the values of in the is largest than those in because the distance between two electrons is small in because the two electron have different spin value.

When n=1 the value of in the is larger than those in the because the two electrons in have the same spin (parallel), this means the repulse force between two electrons in larger than repulsion force in , this leads to the distance between two electrons to be larger while the distance between two electrons in the is smaller because they have different spine.

We noted from table (4) the standard deviation decreases when Z increase because decreases the distance between electrons that make the deviation on the expectation value is small consequently decrease.

From table (5) we observed the expectation value of attraction energy negatively increases when atomic number increases as a result of increasing in Z leads to decreasing in the distance between electron with nucleus, and expectation value of repulsion energy increasing with atomic number increases because the distance between two electron decreases, this product negatively increasing in attraction energy and increasing in repulsion energy according to coulomb law.

It table (5) we noticed in K-shell the expectation value of all energy's is larger than those other shells because K-shell is near to the nucleus than other shell and we observe in L-shell the expectation value is less than those in other shells because L-shell is far than those in other shells.

Conclusions:-

From this results can be concluded [1]the property one – electron density function increases as atomic number increases for all shell and their position decreasing at the nucleus which means increasing in probability of finding the electron when there is increasing in atomic number[2], inter particle density function increase when atomic number increases, the results of K-shell is larger than those in the other shells for properties and While the results of L-shell is smaller than those in the other shells for and [3].Expectation value of one-electron and expectation value of the two electrons when n =-1,-2 increase as atomic number increases and when n =1,2 these values decrease by increasing in atomic number[4].We conclude the values of energies increase when the atomic number increases[5].The results of expectation value of energies , for K-shell is nearer to the nucleus than other shells andL-shell is smaller than those in the other shells[6].The standard divation of one-particle expectation value decreas as atomic number increase, and have smallest value in K-shell and biggest value in L-shell.

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