AL-Qadisiya Journal For Science Vol .15 No.3 Year2010

Calculation of The Diamagnetic Susceptibility χ, Nuclear magnetic shielding constants σd and Fermi Hole $\Delta f(r_{ij})$ For the Ions Al^{+10} , $Mg^{+9}$and Si^{+11} By Employing Hartree- Fock Wave Function.

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Abstract

In this research many physical properties evaluated like Fermi holes $\Delta f(r_{ij})$, inter-particle distribution function $f(r_{ij})$. The Diamagnetic Susceptibility χ, Nuclear magnetic shielding constants σ_d one particle radial distribution function $D(r_i)$ and various one ,two electrons distances $<r_i^d>$and $<r_{ij}^d>$ (where d is an integer -2,-1,+1,+2) for some positive ions like Al^{+10},$Mg^{+9}$and ,Si^{+11}By employing the partitioning technique, to four Hartree-Fock wave functions are analyzed of K , L shells and for Singlet ^1S and Triplet ^3S states.

حساب معاملات التأثيرية الدايامغناطيسية χ وثابت الحجب المغناطيسي -النووي وσ_d فجوة فيرمي $\Delta f(r_{ij})$ لايونات Al^{+10}, Mg^{+9}, Si^{+11} باستخدام دالة هارتري – فوك الموجية

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الخلاصة :-

في هذا العمل البحثي تم حساب عدة خواص فيزيائية مثل فجوة فيرمي $\Delta f(r_{ij})$،دالة المسافة البينية الالكترونية $f(r_{ij})$ و معاملات التأثيرية الدايامغنطيسية χ وثابت الحجب المغناطيسي النووي σd دالة التوزيع القطرية لجسيم واحد $D(r_i)$ والقيم المتوقعة للمسافات البينية إلكترونية بين إلكترون أو إلكترونين مثل $<r_i^d>$و$<r_{ij}^d>$ (حيث ان d عدد صحيح -2 -1+1+2) لعدة ايونات موجبة شبيه بذرة البريليوم Al^{+10},Mg^{+9},Si^{+11} باستخدام تقنية التجزئة تم تحليل أربعة دوال هارتري –فوك الموجية للغلافين L , K وكذلك الحالة الأحادية 1S والحالة الثلاثية3S.

1-Introduction:-

The electron correlation is a general term describing how the individual electrons interact with each other which is constitutes one of the biggest difficulties in modern electron structure theory. The simplest form of electron correlation (taken into account at Hartee –Fock level) usually called the Fermi correlation or Fermi hole was coined by Wigner and Seitz when they studying the effect of Pauli exclusion principle on electrons of parallel spin in metallic sodium .In their words " there is a hole in the uniform electron fluid around every electron because the probability of two electron fluid having parallel spin being nearly is very small we shall call this Fermi hole"[1]. It is of great interesting in studying the electronic properties and different types energies within atoms, ions and molecules by taking into consideration the electron correlation effects. For this purpose two- particle approximation used, this method is generalization of one electron Hartree-Fock approximation in which every two electron moves in the effective potential of the other (N-2) electron in the system .This method was first discussed by Sinanglu which is the solution of two- particle problem and another method is the Brenigs approximation in which the electron correlation evaluated without application perturbation theory [1, 2, 3]. In this work, Correlation energies are calculated at the Hartee–Fock[4].Level of three electron systems using soft ware MATHCAD 2001i. All these results are normalized to unity. Atomic Units are employed throughout.

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

The Hartree-Fock approximation wave function ϕ is well documented [5, 6, 7].Details will be skipped and gives only the key relations .Two-particle density $\Gamma_{HF}(x_i,x_j)$ for N electron system is given by[8].

$$\Gamma_{HF}(x_i,x_j) = \binom{N}{2} \int \phi(x_1,x_2.......x_N)\phi^*(x_1,x_2........x_N)dx_P....dx_N \quad ....(1)$$

Where $\binom{N}{2}$ is the Binomial factor defined as [8]

$$\binom{N}{2} = \left[\frac{N!}{2!(N-2)!}.\right] \quad .... (2)$$

Where N is the number of electrons within system and $dx_P.....dx_N$ indicates that the integration is over N electrons except i and j .Since the partitioning technique enable correlation to be examined in depth for various intra and inter shells electron pairs thus we had employed this technique to pair-wise components (p,q) [9].

$$\Gamma_{HF}(x_i,x_j)=\sum_{p\langle q}^{N}\Gamma_{pq}(x_i,x_j) \quad ....(3)$$

Hence

$$\Gamma_{pq}(x_i,x_j)=\frac{1}{2}\sum_{p<q}^{N}\left[\,\left[\psi_p(x_i)\psi_q(x_j)-\psi_q(x_i)\psi_p(x_j)\,\right]^2\right. \quad .... (4)$$

Where Ψ is the occupied normalized Hartree –Fock spin orbital, the symbol (p,q) represent the spin orbital labels and (x_i,x_j) indicates the electron labels.

3- Radial functions and their expectation values:

The probability of finding electron in any shell lies between r & r+dr with angle θ between $\theta+d\,\theta$ and ϕ between ϕ and $\phi+d\phi$ is given by [10].

$$|\psi_{nlm}|^2=[G_{nl}(r)]^2\, Y_{lm}(\theta,\phi)^2 r^2 \sin\theta dr\, d\theta d\phi \quad .... (5)$$

To determine the radial distribution function $D_{nl}(r)dr$ regardless of direction ,we integrate over angle θ and dθ to Get

$$D_{nl}(r)=r^2[G_{nl}(r)]^2 dr\int_0^{\pi}\int_0^{2\pi}|\mathrm{Y}_{lm}(\theta,\phi)|^2 \sin\theta\, d\theta\, d\phi = r^2[G_{nl}(r)]^2 dr \quad ... (6)$$

The radial part of the function Gnl(r) is defined as

$$G_{nl}(r)=N_{nlml}\,S_{nl}(r) \quad ....(7)$$

Where N_{nlml} is the normalization constant and $S_{nl}(r)$ is the Slater-Type Orbital(STOs)taken from Clementi and Roetti tables[4]since the spherical harmonics are normalized, the value of the double integration is unity. The function $D_{nl}(r)dr$ used to calculate many properties such as average

$$<r_i^{\,d}>=\int_0^{\infty} r^d D_{nl}(r)dr$$

distance of electron from nucleus, potential energy. One–particle expectation value is given by the following equation

………………..…. (8)

Where d=-2,-1, +1, +2. But when d=0, the eq. (8) will produce the normalization condition

$$< r_i^{\,0} >= \int_0^{\infty} r^0 D_{nl}(r)\,dr = 1 \quad \text{………….. (9)}$$

The root mean square (standard deviation) of this value is defined [11].

$$\Delta r_i = \sqrt{\langle r_i^2 \rangle - \langle r_j \rangle^2} \quad \text{……………. (10)}$$

4-Inter-particle distance function f(r$_{ij}$)and the expectation value of <r$_{ij}^{d}$>:-

Distribution function can be defined as the measure of the probability distance between two electrons i and j respectively. This function for first time used by Coulson and Neilson as follow [12].

$$f(r_{ij}) = \frac{\int \psi^2(r_i, r_j)\,dr\,dr_j}{dr_{ij}} \quad \text{……………. (11)}$$

If Ψ involves three distances r_1, r2, r12, then this function takes the form [12].

$$f(r_{ij})_{K(^1s)} = 8\pi^2 r_{ij} \left[\int_{r_{ij}}^{\infty} r_1 \int_{ri-r_{ij}}^{r_i+r_{ij}} \psi_{1s}^2(1)\psi_{1s}^2(2)\, rjdr_j dr_1 + \int_0^{r_{ij}} r_1 \int_{r_{ij}-r_i}^{r_{ij}+r_i} \psi_{1s}^2(1)\psi_{1s}^2(2)\, r_j dr_j dr_i \right] \quad \text{……….(12)}$$

And the inter-particle expectation values obtained by [14, 15].

$$\langle r_{ij}^d \rangle = \int_0^{\infty} f(r)\, r_{ij}^d\, dr_{ij} \quad \text{…………………….. (13)}$$

and the Fermi – hole can be defined as the following:-

$$\Delta f(r_{ij}) = f\,^3S\,(r_{ij}) - f\,^1S\,(r_{ij}) \quad \text{………………………….(14)}$$

Where $f\,^3S\,(r_{ij})$ and $f\,^1S\,(r_{ij})$ are the inter-particle distribution function of Triplet and singlet states respectively.

5- Diamagnetic Susceptibility(χ)

Diamagnetism is the phenomena of magnetic moments of all electrons in each atom or ion are cancelled ,leaving the atom or ion with zero magnetic moment The diamagnetic susceptibility (χ) is defined as [20]:

$$\chi = -\frac{1}{6}\alpha^2 < \psi I \sum_{i=1}^{n} (r_1^{\,2}) I \psi > \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Where (α) is the Fine structure constant which is equal to 7.297353×10^{-3} a.u and (r_1^2) is the mean square distance of an arbitrary electron in any shell from the nucleus ,Equation (15) indicates that χ is negative and the outer electrons of an atom make the largest contribution to the diamagnetic susceptibility since χ proportional to r_1^2 value .

6- Nuclear Magnetic Shielding Constant σ_d

The nuclear magnetic shielding constant is obtained by[20] :

$$\sigma_d = \frac{1}{3}\alpha^2 < \psi I \sum_{i=1}^{n} (r^{-1}_{\;i}) I \psi^* > \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

α^2 is the fine structure constant ; shielding constants are different for K or L shells because σ_d dependence inversely upon the expected radial distributions ,for example (s) electrons is most likely to be found close to the nucleus than the (p) electrons shell hence (s) electrons experience less shielding and they are more tightly bound than (p) electrons

7-Results and discussion:

Table (1) represents the max. value of the one particle radial distribution function D (r_{ij}) and its locations r_{ij} in the position space for both K and L shell by employing Eq.(6) we concluding the following :

1- The one particle radial distribution function D (r_{ij}) increases with atomic number Z this effect explained the fact that the attraction force of nucleus for near electrons is greater for electrons within K shell, on the other hand the repulsion of K electrons with that of L shell this is in accordance with Coulomb law [18] as shown in Fig. 1&2.

2- The values of Max. D(r_{ij}) of L shell as shown in fig .2 two peak are observed the small one stands for the probability of finding an electrons close to nucleus while the second big peak represent a remote electron from nucleus existing in L shell .

Table (2) represent the expectation values of one particle $\langle r_i^d \rangle$ for K and L shell obtained by Eq.(8 and 9) as shown in Figs (3 ,4) we found the following :-

1-For all ions the expectation values of $\langle r_i^d \rangle$ for electron shell in regions where d= -1,-2 respectively increases with in other words, the probability of determination an electrons increasing as they approaching the atomic nucleus and vice versa for the regions where d= +1,+2.

2- For K and L shells in d= -1,-2 the expectation values of $\langle r_i^d \rangle$ increases with Z but in d= +1, +2 the situation is inverse due to the weakness of attraction forces exchanged between nucleus and electrons in these regions. For the same reason the uncertainty in the radial locations Δr_i decrease as Z.

4-As d=0, the result is unity for all ions due to the application of normalization condition eq. (9).

Table (3) contains the max. positions and max. values of the inter–particle distance f(r_{ij}) expectation values for K shell ,Singlet ^{1}S and Triplet ^{3}S states obtained by Eq.(12) .we conclude the following :-

1- For k shell the max. values of f (r_{ij}) increases with Z due their position with respect to the nucleus Figs.(5,6,7)

2- For the singlet state at small distance of r_{ij} the distribution function f(r_{ij}) influenced mainly with the behavior of electron pairs within state which represented by the small peaks Fig .(8) this due to the penetration of outer electron of K shell electrons.

3- In Fig. (8) there are flat regions at small distance of r_{ij} of triplet which is results from Fermi effect[19].

4- The max. values of $\langle r_{ij}^d \rangle$in triplet state Fig. (8) table is less than the values of singlet state the same Figure in regions near nucleus this results from the attraction force of nucleus to electron of parallel spin much greater than that of electrons of antiparallel spin because the repulsion energy of Triplet state less than of singlet accordance to Pauli principle [19] .

Finally the table (5) shows the expectation values of Diamagnetic Susceptibility(χ) and nuclear magnetic shielding constants which obtained by employing equations (15 and 16) respectively .

Table (1) the expectation values of One-Particle radial distribution function D (r_i) for K and L shells (Atomic Units).

	Z	Ion	r_i	Max.D(r_i)
K	12	Mg^{+9}	0.0844	6.270642
	13	Al^{+10}	0.0840	6.777244
	14	Si^{+11}	0.0695	7.04830

L	12	Mg^{+9}	0.040/0.055	2.417322/0.5888
	13	Al^{+10}	0.06/0.45	0.537247/2.2218
	14	Si^{+11}	0.065/0.477	0.48540/2.03359

Table (2) the expectation values of One-Particle $<r_i^d>$ for K and L shells (Atomic Units).

Shell	Z	Ion	d=-2	D=-1	D=0	d=1	d=2	Δr_1
K	12	Mg^{+9}	274.7108	11.6759	1	0.129234	0.022376	
	13	Al^{+10}	323.5758	12.6755	1	0.11698	0.01896	
	14	Si^{+11}	353.93916	13.08777	1	0.107834	0.0160	
L	12	Mg^{+9}	27.804042	2.625344	1	0.559233	0.36471	
	13	Al^{+10}	33.3522	2.875942	1	0.511442	0.3050	
	14	Si^{+11}	39.3994	3.12645	1	0.471777	0.2589	

Table (3) The expectation values of inter –Particle distance function $f(r_{ij})$ for K , L shells ,singlet and triplet states (Atomic Units) .

Shell	12	Ion	r_{ij}	Max.$f(r_{ij})$
K	12	Mg^{+9}	0.15	4.5926
	13	Al^{+10}	0.132	5.00684
	14	Si^{+11}	0.122	5.040297
Singlet	12	Mg^{+9}	0.49	1.881442
	13	Al^{+10}	0.46	2.06383
	14	Si^{+11}	0.43	2.168857
Triplet	12	Mg^{+9}	0.5	1.89764
	13	Al^{+10}	0.45	2.0754
	14	Si^{+11}	0.43	2.180291

Table (4) the expectation values of Inter-Particle distance $<r_{ij}^d>$ for K shell, Single 1S and Triplet 3S states (Atomic Units)

Shell	Z	Ion	d= -2	d= -1	D=0	d=1	d=2
K	12	Mg^{+9}	90.48671	7.26876	1	0.18866	0.044752
	13	Al^{+10}	106.68824	7.893537	1	0.17369	0.037923
	14	Si^{+11}	114.0959	7.92191	1	0.152473	0.031056
^1S	12	Mg^{+9}	10.2873	2.24826	1	0.576414	0.38768
	13	Al^{+10}	12.3106	2.4588	1	0.52737	0.3240
	14	Si^{+11}	13.95521	2.58391	1	0. 47131	0.266969

^3S	12	Mg^{+9}	5.0920	2.0360	1	0.57981	0.387086
	13	Al^{+10}	6.0769	2.22453	1	0.53054	0.3240
	14	Si^{+11}	6.94457	2.3399	1	0.474037	0.266868

Table (5) the expectation values of Diamagnetic susceptibility and Nuclear magnetic shielding constants .(Atomic units)

Shell	Z	Ion	$X \times 10^{-6}$	$\sigma_d \times 10^{-5}$
K	12	Mg^{+9}	-0.1985	20.7
	13	Al^{+10}	-0.1682	22.499
	14	Si^{+11}	-0.1420	23.23
L	12	Mg^{+9}	-3.2369	4.66
	13	Al^{+10}	-2.70	5.104
	14	Si^{+11}	-2.2977	5.549

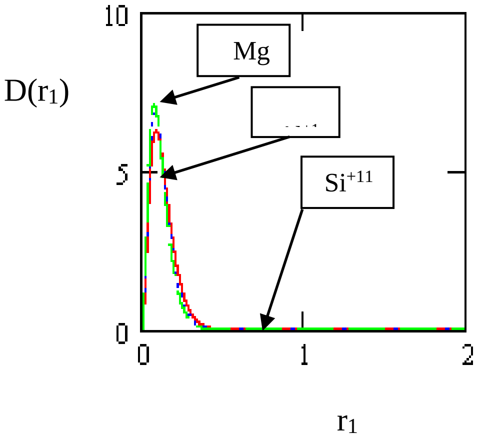

Fig.(1): Represent a comparison of the one particle radial distribution function $D(r_i)$ for K shell of some ions

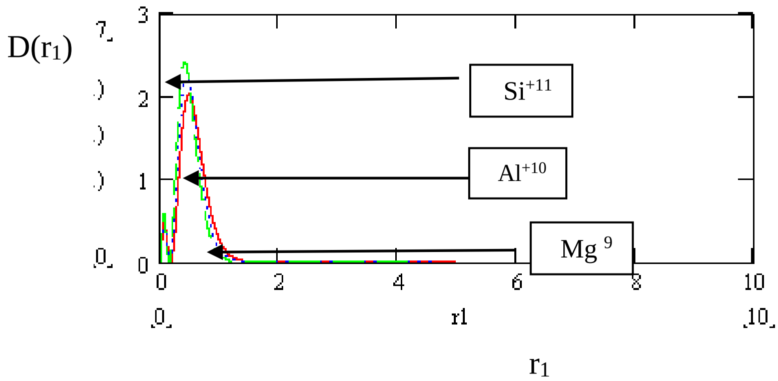

Fig.(2): Represent a comparison of the one particle radial distribution function $D(r_i)$ for L shell of some ions

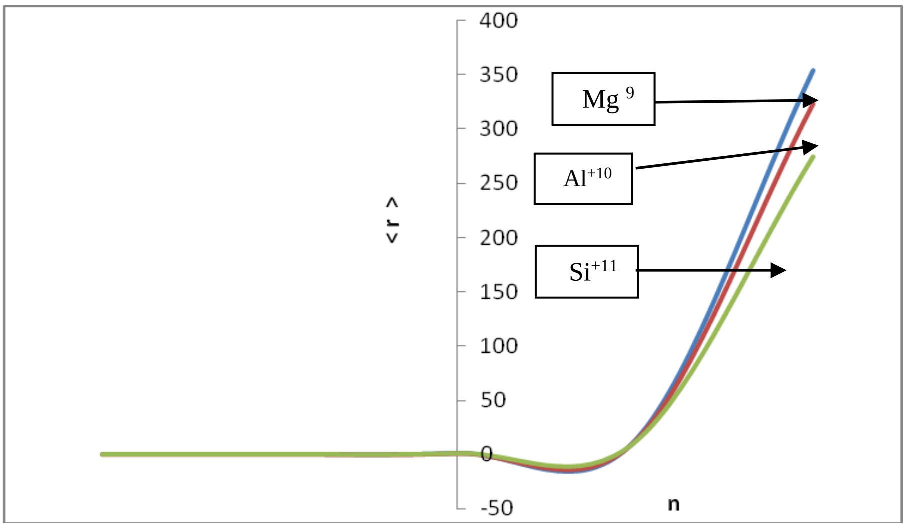

Fig.(3): Represent a comparison of the inter- particle radial distance $<r_i^2>$ for K shell of some ions.

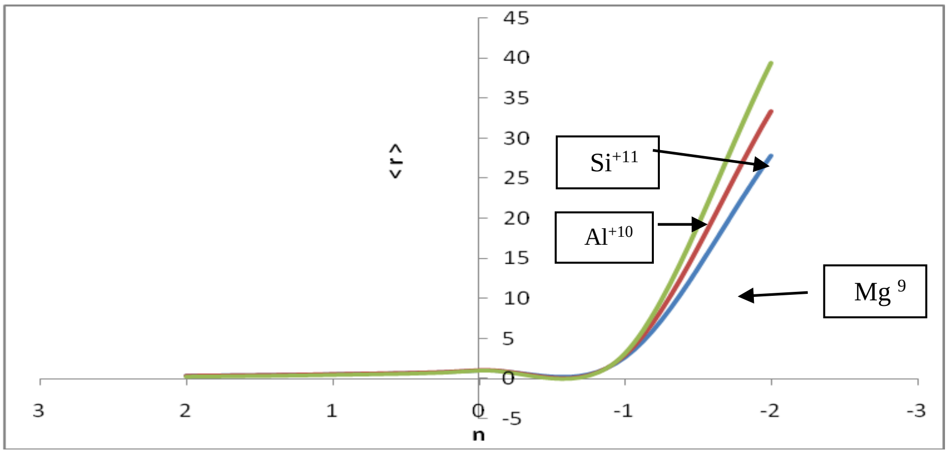

Fig.(4): Represent a comparison of the inter- particle radial distance $<r_i^2>$ for L shell of some ions.

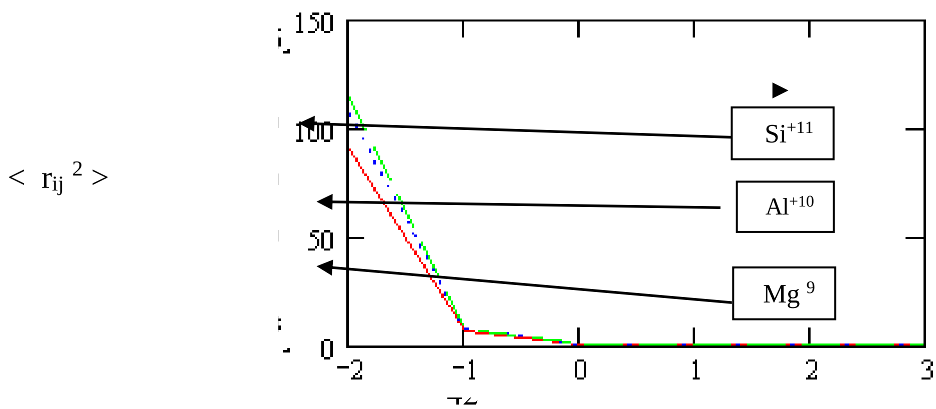

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Fig.(5): Represent a comparison of the inter- particle radial distance $<r_{ij}^2>$ for K shell of some ions.

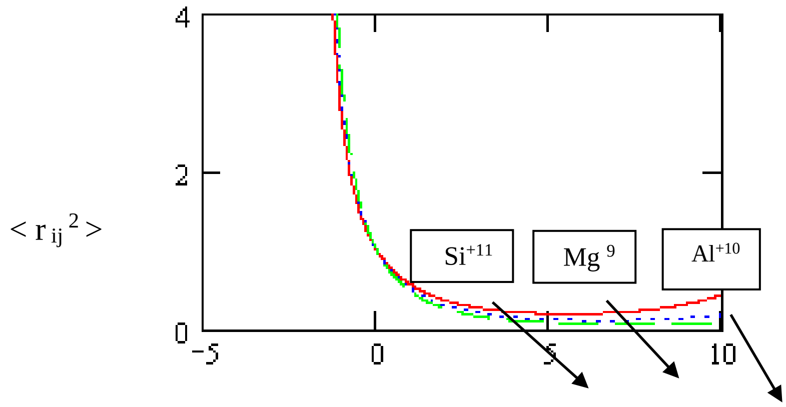

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Fig.(6): Represent a comparison of the inter- particle radial distance $<r_{ij}^2>$ for L shell of some ions.

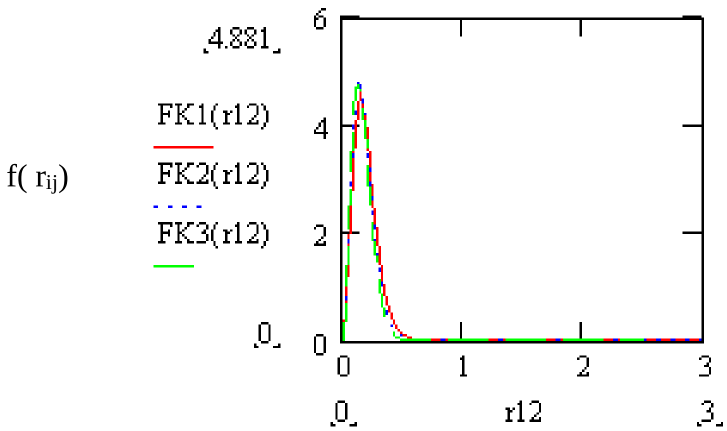
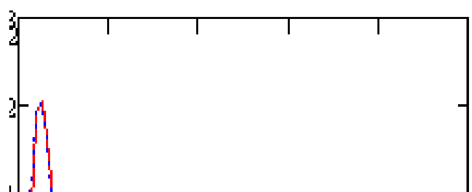


Fig.(7): Represent a comparison of the inter- particle radial distance function $f(r_{ij})$ for K shell of some ions.

$f(r_{12})$

$f(r_{12})$



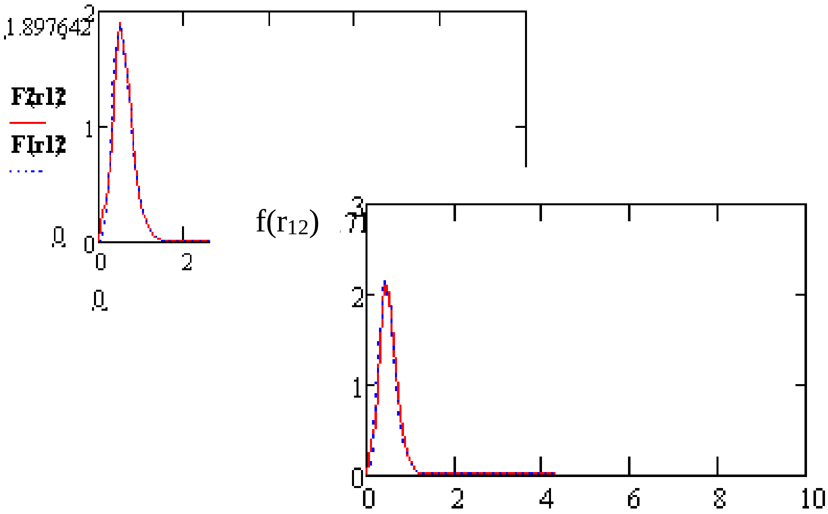


Fig.(8): Represent a comparison of the inter- particle radial distribution function $f(r_{ij})$ for singlet(red) and triplet states (blue dotted) of some ions.

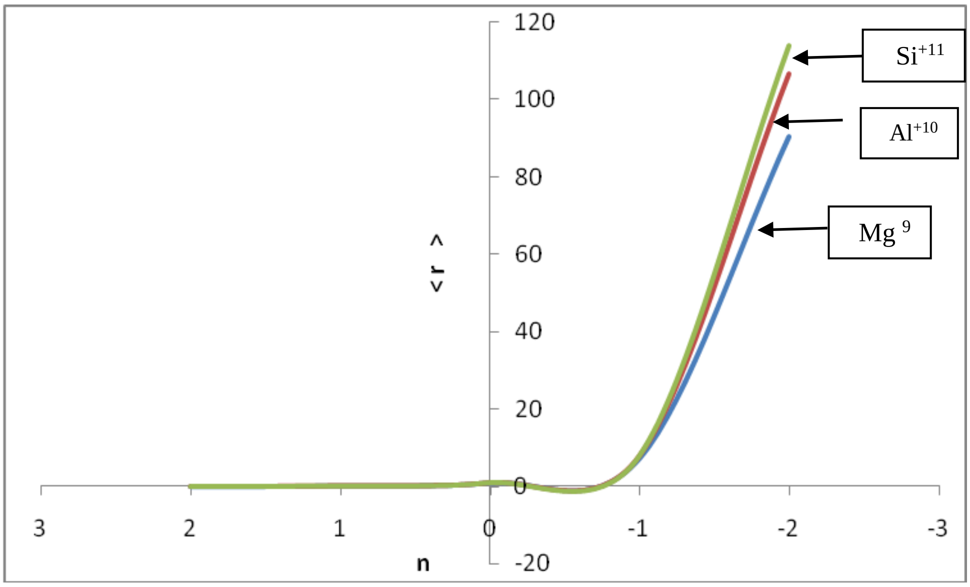


Fig.(9): Represent a comparison of the inter- particle radial distance $<r_{ij}^2>$ for K shell of some ions.

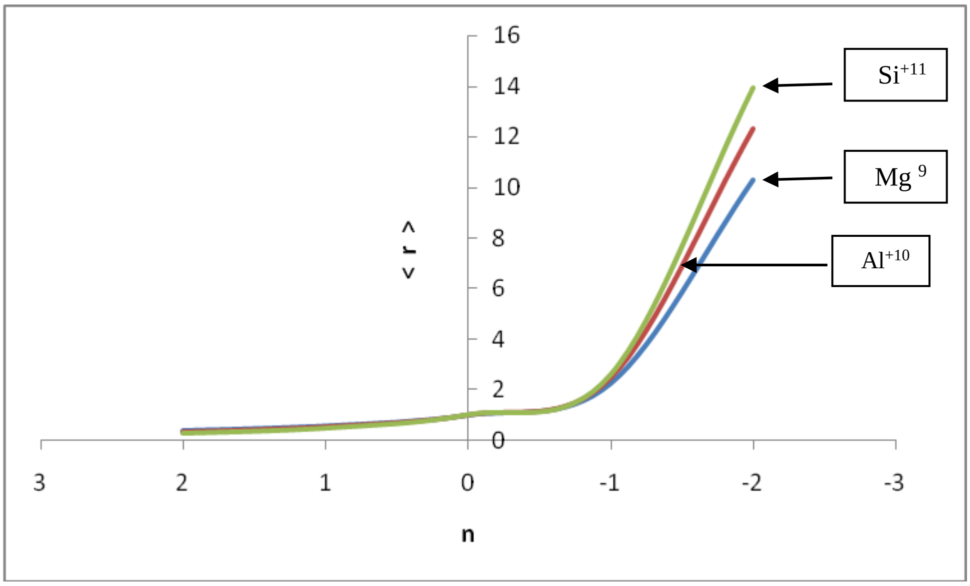


Fig.(9): Represent a comparison of the inter- particle radial distance $<r_{ij}^2>$ for singlet state of some ions.

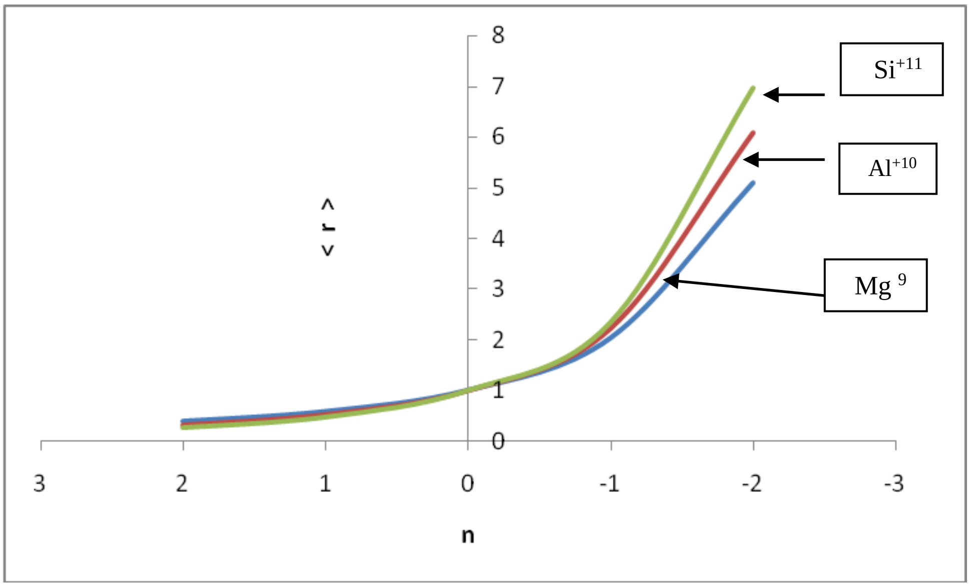


Fig.(10): Represent a comparison of the inter- particle radial distance $<r_{ij}^2>$ for singlet state of some ions.

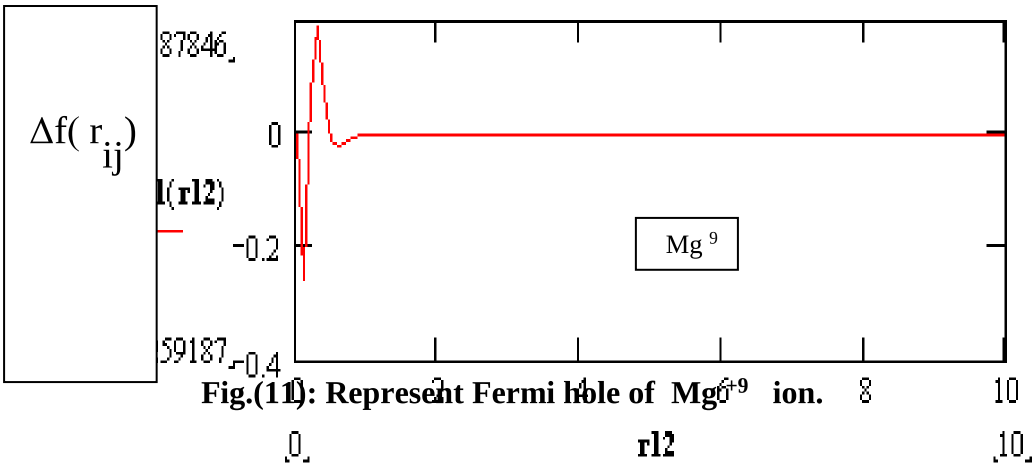


Fig.(11): Represent Fermi hole of Mg^{+9} ion.

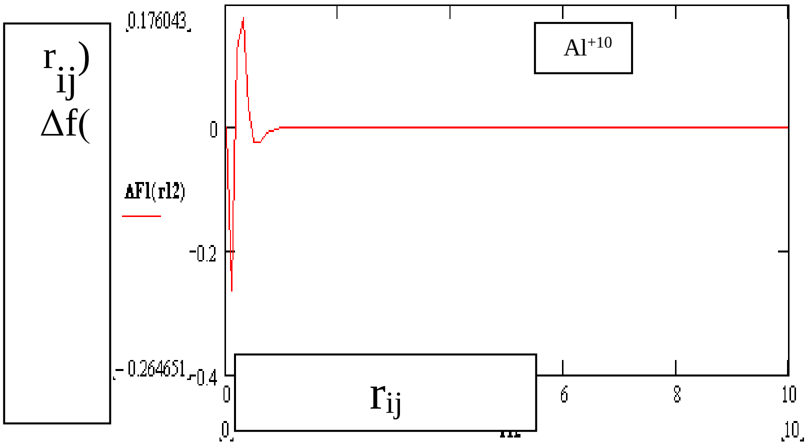


Fig.(12): Represent Fermi hole of Al^{+10} ion

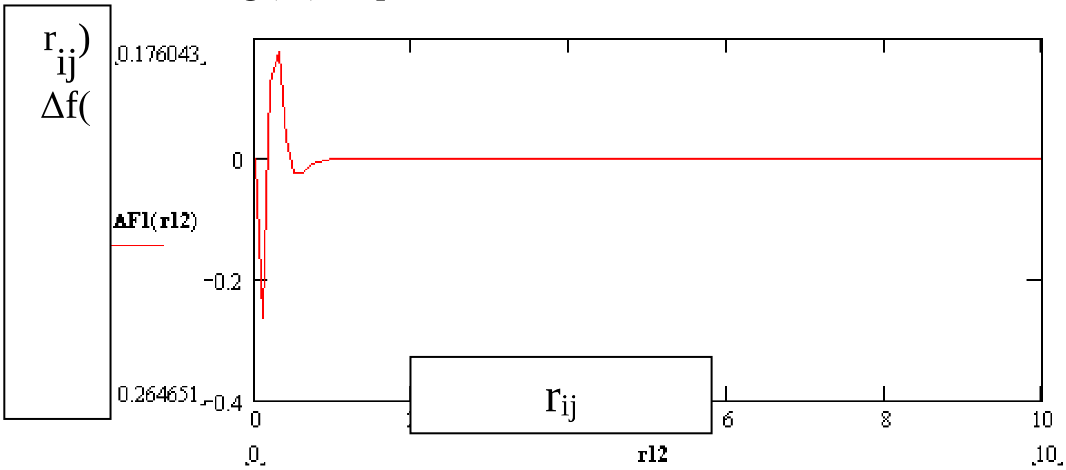


Fig.(13): Represent Fermi hole of Si^{+11} ion

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