Evaluation the correlation Energies and interelectronic distances $<r_i^d>$and $<r_{ij}^d>$ for some positive Ions.

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Abstract

The aim of this work is evaluation the expectation values of Correlation $<E_{corr}>$, repulsion between electrons $<V_{ee}>$,attraction between electrons and nucleus $<V_{en}>$energies and various one ,two electrons distances $<r_i^d>$and $<r_{ij}^d>$ (where d is an integer takes the values -2,-1,+1,+2) for some positive ions C^{+3},N^{+4},O^{+5}.By employing the partitioning technique, four Hartree-Fock wave functions are analyzed of K , L shells and for Singlet ^1S and Triplet ^3S states.

Introduction

The correlation energy $<E_{corr}>$ of any electron system is defined as the difference between the exact non relativistic and Hartee –Fock energies. It is of great interesting in studying atoms, ions and molecules taking into consideration the electron correlation energy, a good agreement can be obtained between theoretical and experimental results that dealing with energy levels transition probability and polarization. For this purpose several methods are used such as two- particle approximation , 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 discssed by Sinanglu that is the solution of two- particle problem and another method is the Brenigs approximation in which the electron correlation evaluted without perturbation theory used (Kamel et al,1984; Sinanoglu & Brenig, 1957). In this work, Correlation energies are calculated at the Hartee –Fock (Clementi & Roetti, 1974). Level of three electron systems that usually called Fermi correlation which arises from Pauli principle and studied using the Computer program MATHCAD 2001i. All these results are normalized to unity. Atomic Units are employed throughout.

Theoretical Aspects

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

The Hartree-Fock approximation wave function φ is well documented

(Bunge et al., 1993; Robert et al., 1985 and Levine, 2005). Details will be skipped and gives only the key relations .Two-particle density Γ_{HF} (x_i,x_j) for N electron system is given by(Lowe & Peterson,2005).

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

Where $\binom{N}{2}$ is the Binomial factor defined as(Banyard & Mobbs,1977)

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

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 employed the partitioning to pair-wise components (p,q) (Mobbs & Banyard,1983).

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

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 orbitals,the symbol (p,q) represent the spin orbital labels and (x_i,x_j) indicates the electron labels.

b- Radial functions and their expectation values:

The probability of finding electron in any shell lies between r and r+dr with angle θ between θ+d θ and φ between φ and φ+d φ is given by (Al-Bayati ,2004).

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

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

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

The radial part of the function $G_{nl}(r)$ 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(Clementi&Roetti,1974) since 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 distance of electron from nucleus, potential energy. One–particle expectation value is given by the following equation

$$< r_i^{d} >= \int_{0}^{\infty} r^{d} D_{nl}(r)dr \qquad \ldots(8)$$

Where d=-2,-1, +1,+2. But when d=0, the eq.(7)will produce the normalization condition

$$< r_i^{0} >= \int_{0}^{\infty} r^{0} D_{nl}(r)dr = 1 \qquad \ldots(9)$$

The root mean square of this value defined (Donald Fitts ,1999).

$$\Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \qquad \ldots(10)$$

c- 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 (Coulson & Neilson,1960).

$$f(r_{ij}) = \frac{\int \psi^2(r_i, r_j) dr_i dr_j}{dr_{ij}} \qquad \ldots(11)$$

If Ψ involves three distances r_i, r_j, r_{ij} ,then this function takes the form (Al-Bayati ,2004).

$$f(r_{ij})_{K(^1s)} = 8\pi^2 r_{ij} \begin{bmatrix} \int_{r_{ij}}^{\infty} r_i \int_{r_i - r_{ij}}^{r_i + rij} \psi_{1s}^2(i)\psi_{1s}^2(j) r_j dr_j dr_i + \\ \int_{0}^{r_{12}} r_1 \int_{r_{ij} - r_1}^{rij + r_1} \psi_{1s}^2(i)\psi_{1s}^2(j) r_j dr_j dr_i \end{bmatrix} \qquad \ldots(12)$$

And the inter-particle expectation values obtained by (Brown &Larsson ,1977).

$$\langle r_{ij}^{d} \rangle = \int_{0}^{\infty} f(r_{ij})\, r_{ij}^{d}\, dr_{ij} \qquad \ldots(13)$$

d- the energy expectation values <E>

The energy expectation values <E> associates with the Hamiltonian operator is (Al-Tamimei Neema,2005).

$$< E >= \frac{< \psi^{*} \left| \hat{H} \right| \psi >}{< \psi^{*} \left| \psi \right. >} \qquad \ldots(14)$$

Where H Hamiltonian operator given by (Benesch &Vedene Smith, 1971)
Where Z nuclear charge of spices and the first term:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i}^{n}\frac{Z}{r_i} + \sum_{i=1}^{n-1}\sum_{j=1+1}^{n}\frac{1}{r_{ij}} \qquad \ldots(15)$$

$\frac{1}{2}\sum_{i=1}^{n}\nabla_i^{\,2}$ represent the kinetic energy operator <T> which given by (Gader & Narasimhan ,1977).

$$\langle T \rangle = -\frac{1}{2}\int \psi^{*}\left[\sum_{i}^{N}\nabla_i^2\right]\psi \; d\tau \qquad \ldots(16)$$

And the repulsion energy is

$$\langle V \rangle = \int \psi^{*}\left[\sum_{i}^{N} -\frac{Z}{r_i} + \sum_{J=i+1}^{N}\frac{1}{r_{ij}}\right]\psi \; d\tau \qquad \ldots(17)$$

Hence total energy expectation value is

$$< E >= \langle T \rangle + \langle V_{en} \rangle + \langle V_{ee} \rangle \qquad \ldots(18)$$

From the viral theorem, the total energy <E>is given by (Levine, 2005).

$$<E>=1/2<V> \qquad \ldots(19)$$

Where

$$<v_{en}>=-Z[N^{*}<r^{-1}>] \qquad \ldots(20)$$

Where N* number of the electrons within system and

$$<v_{ee}>=<r_{ij}^{-1} \qquad \ldots(21)$$

The correlation energy is

$$<E_{corr}> =E_{exact} - E_{HF} \qquad \ldots(22)$$

Results and discussion

Table (1) contains One –particle expectation values $<r_i^d>$ of K and L shells as shown in Figs.(1 & 2) which obtained by eq.(7)from these results we conclude:

1. For K and L shells the expectation values $<r_i^d>$ in regions close to nucleus (d= -1,-2) increases as Z increase .This due to increasing attraction force between electrons and nucleus .But for remote regions (d=1,2) the expectation values decrease as Z increases and seems to be coincided (as shown in Figs.(1 & 2)) approximately due that each shell has the same

electrons on the other hand, due to reduction of attraction force as a result of increase the separation distances between electrons and nucleus.

2. The uncertainty in the radial locations Δr_i decrease as Z increases due to the weakness of the interaction as electrons become far from nucleus. The similar behavior of these ions are due to the fact they have Z=3.

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

Table (2) contains one –particle expectation values $<r_{ij}^{d}>$ of K Singlet ^1S and Triplet ^3S shells as shown in Figs.(3,4and 5) which obtained by eq.(11)from these results we conclude:

a. For K and L shells the expectation values $<r_{ij}^{d}>$ in regions close to nucleus (d= -1,-2) increases as Z increase .But for remote regions (d=1,2) the expectation values are decrease due to reduction of attraction force as a result of increase the separation distances between electrons and nucleus.

b. For regions (d= -1,-2) the expectation values $<r_{ij}^{d}>$ of singlet state ^1S exceeds that of triplet state ^3S.In other words ,the probability density parallel spin electrons will be very small within i.e., when they are close together since their is little chance of finding them close together due to their repulsion in the triplet state ^3S electrons.

Table (3) contains expectation values of attraction energy between Nucleus and orbital electrons $<V_{en}>$,the repulsion energy between electrons$<V_{ee}>$ and total energy $<V>$ for both K , L shells and Singlet ^1S and Triplet ^3S states which obtained by equations(19,20 and 21)from the present results we conclude:

1. For K and L shells the expectation values $<V_{en}>$ increases as atomic number Z increase .This behavior can be understood from the fact that each shell contract toward nucleus as result of increasing the nuclear charges influence on the orbital electrons hence the separation distances are reduced thus reduction of attraction and repulsion forces according to Coulomb law.
2. The expectation values attraction energy $<V_{en}>$ for K shell exceeds that of L shell because of closeness of K electrons rather than L which lies in greater distances.
3. The expectation values repulsion energy $<V_{ee}>$ for ^1S electrons exceeds that of ^3S state because of average distance between two electrons is greater in^3S state where the spin are "parallel" rather than in ^1S state where the spin

are "antiparallel". Consequently the Coulomb repulsion energy acting between electrons is smaller in ^3S state for which the spin magnitude equals to S'=√1(1+1)h, than in ^1S state which equals to S'=0.

Finally Table (4) contains expectation values of $<V_{en}>$, $<V_{ee}>$,$<E>$ and and E_{exact} obtained from Weiss table(19)who used the superposition of configuration with expansion lengths ranging from 35 for Helium to 55 for Berylium correlation energy $<E_{corr}>$ by using eq.(20) for both K , L shells and Singlet ^1S and Triplet ^3S states from these results we conclude

1. For all ions , the expectation values of $<V_{en}>$ and $<V_{ee}>$ are increased as Z increases due to that the Coulomb interaction became stronger as Z increased .

2. The percentage of repulsion and attraction energies $<V_{ee}>/<V_{en}>*100\%$ were as following: (C^{+3}:7.214%) , (N^{+4}: 6.236%) and (O^{+5}: 5.491%) respectively.

3. Because the Hartree-Fock method take into consideration only "Static correlation" and neglect "Dynamic correlation" this gives an over estimated electron-electron repulsion energy that is represented by $<E_{corr}>$ which increased with Z as in Fig(6) .

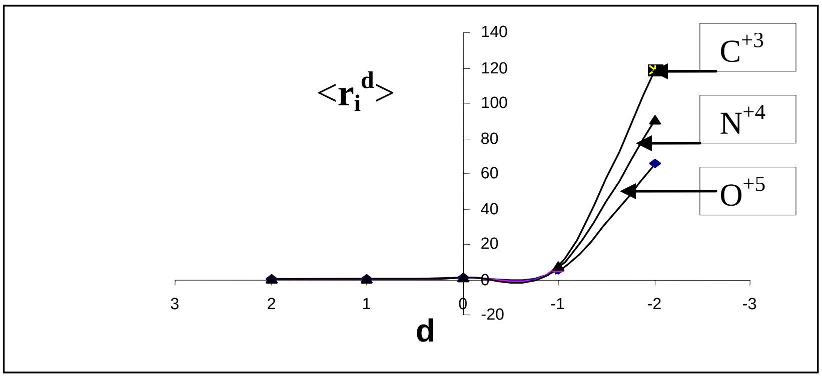

Fig (1): One Particle expectation values $<r_i^d>$ of K shells for some positive ions.

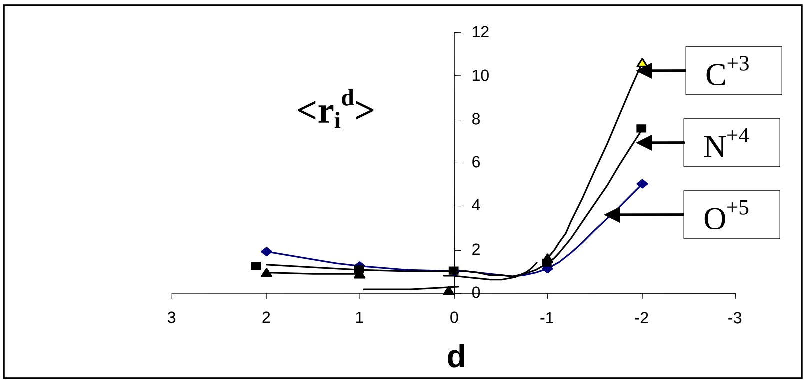

Fig (2): One Particle expectation values $<r_i^d>$ of L shells for some positive ions.

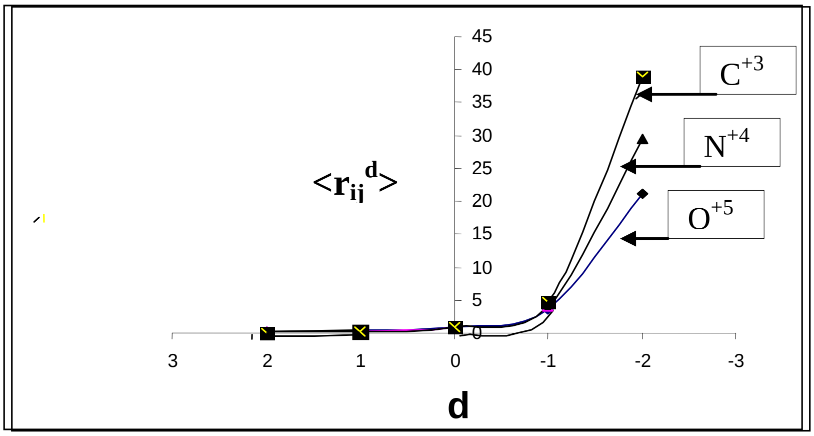

Fig (3): Inter-particle distance expectation values $<r_{ij}^d>$ of K shells for some positive ions.

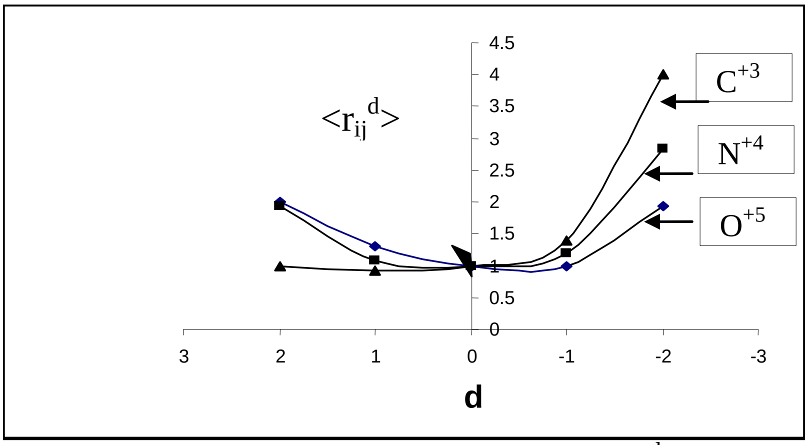

Fig.(4) Inter -particle distance expectation values $<r_{ij}^d>$ of Singlet states for some positive ions .

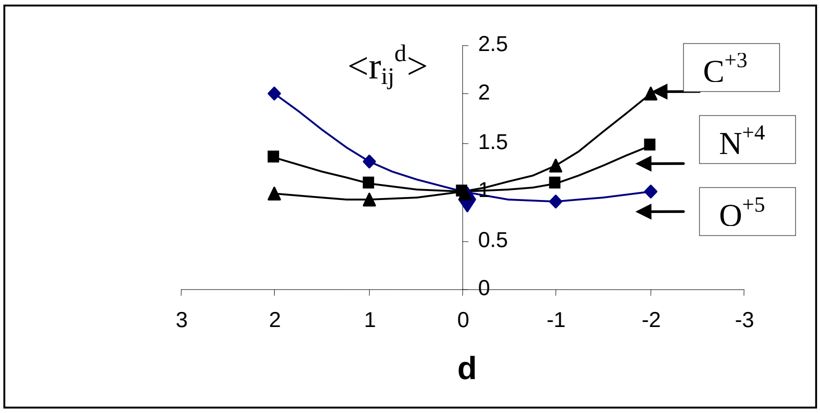

Fig (5): Inter-particle distance expectation values $\langle r_{ij}^{d} \rangle$ of Triplet states for some positive ions.

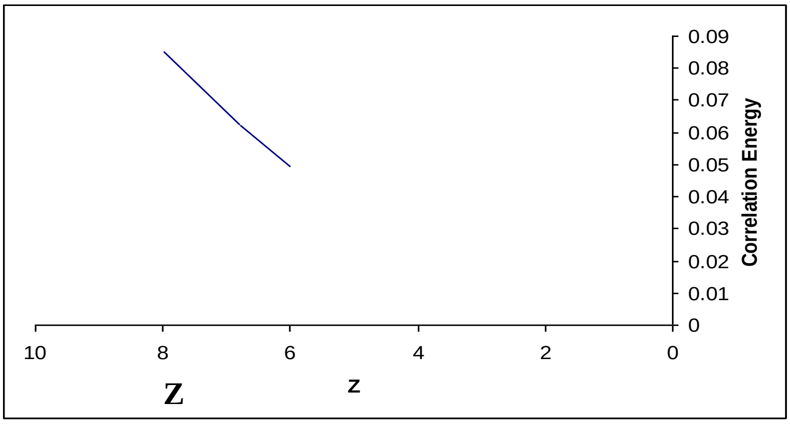

Fig (6): Correlation Energy expectation values $\langle E_{corr} \rangle$ vs. atomic number Z for some positive ions.

Table (1): The expectation values of One-Particle $\langle r_{i}^{d} \rangle$ for K and L shells (Atomic Units)

Shell	Z	Ion	d=-2	d=-1	d=0	d=1	d=2	Δr_i
K	6	C^{+3}	65.508	5.679	1	0.2673	0.0962	0.1573
	7	N^{+4}	90.377	6.678	1	0.2269	0.0692	0.1743
	8	O^{+5}	119.244	7.677	1	0.1971	0.0521	0.1154
L	6	C^{+3}	5.0254	1.116	1	1.2801	1.9133	0.5238
	7	N^{+4}	7.5686	1.3695	1	1.0525	1.2926	0.4298
	8	O^{+5}	10.6123	1.6123	1	0.8942	0.9327	0.3664

Table (2): The expectation values of Inter-Particle distance $<r_{ij}^{d}>$ for K shell, Single ^{1}S and Triplet ^{3}S states(Atomic Units).

Shell	Z	Ion	d=-2	d=-1	d=0	d=1	d=2
K	6	C^{+3}	21.116	3.521	1	0.3906	0.1924
	7	N^{+4}	29.50	4.145	1	0.3315	0.1384
	8	O^{+5}	39.0374	4.770	1	0.2879	0.1044
^{1}S	6	C^{+3}	1.930	0.9798	1	1.3122	2.0095
	7	N^{+4}	2.825	1.1925	1	1.0807	1.945
	8	O^{+5}	3.995	1.404	1	0. 919	0.9849
^{3}S	6	C^{+3}	0.999	0.900	1	1.318	2.006
	7	N^{+4}	1.465	1.090	1	1.0859	1.362
	8	O^{+5}	2.018	1.280	1	0.924	0.985

Table (3): The expectation values of One-Particle $<r_i^{d}>$,the expectation values of attraction energy between electrons and nucleus $<V_{en}>$,the expectation values of repulsion energy between electrons $<V_{ee}>$ and total potential energy $<V>$.

shell	Z	Ion	$<r^{-1}>$	$-<V_{en}>$	$<V_{ee}>=r_{ij}^{-1}$	$<V>$
K	6	C^{+3}	5.679	68.152	3.5211	64.630
	7	N^{+4}	6.678	93.497	4.1455	89.352
	8	O^{+5}	7.677	122.84	4.7700	118.07
L	6	C^{+3}	1.117	6.7023	--------	6.7018
	7	N^{+4}	1.369	9.5863	--------	9.5863
	8	O^{+5}	1.612	12.899	--------	12.899
^{1}S	6	C^{+3}	--------	-------	0.9798	--------
	7	N^{+4}	--------	-------	1.1925	--------
	8	O^{+5}	--------	-------	1.4044	--------
^{3}S	6	C^{+3}	--------	-------	0.900	--------
	7	N^{+4}	--------	-------	1.090	--------
	8	O^{+5}	--------	-------	1.280	--------

Table (4): the expectation values of attraction energy between electrons and nucleus $<V_{en}>$, the expectation values of repulsion energy between electrons $<V_{ee}>$, and total potential energy $<V>$, the expectation energy $<E_{HF}>$ and the expectation value of correlation energy $<E_{corr}>$.

Z	Ion	$<V_{en}>$	$<V_{ee}>$	$-<V>$	$<E_{HF}>=r_{ij}^{-1}$	$<E_{exact}>$ Weiss	$<E_{corr}>$
6	C^{+3}	74.853	5.400	69.45	34.72642	34.77573	0.04930
7	N^{+4}	103.08	6.428	96.65	48.31453	48.37728	0.06275
8	O^{+5}	135.74	7.454	128.2	64.14380	64.22917	0.08540

References

- Al-Tamimei Neema Ch.,(2005): Calculation of effect of electronic correlation force on the energy of some atoms. M.Sc.Thesis, Baghdad.
- Al-Bayati Khalid M., (2004): Study of Fermi holes and Coulomb Holes for many ayomic systems, Ph.D,thesis College of Education ,Ibn-Al Hitham Baghdad University, Iraq, pp.115-121.
- Banyard K.E and Mobbs R.J., (1977): Coulomb holes and correlation Coefficient for several electronic shells , A comparative analysis of several wavefunctions for Be. Journal Chem. Phys, USA Vol. 67,3433p.
- Benesch R. ,and Vedene Smith H.,(1971): Radial Electron – electron distribution and Coulomb Holes for Be.Journal of chemical physics Vol.155. Issue 2, pp. 482-48.
- Boyd R.J. and Coulson C.A., (1974): The Radius of the Fermi Hole .J.Phys. B: At. Mol. Phys. Vol.7, 1805p.
- Brenig, W., (1957): Electron Correlations Independent of Perturbation Theory. Nuclear Physics. Vol.4, 364p.
- Brown R. and Larsson., (1977): Correlation effects to the expectation values of the Atomic systems. International Journal of quantum chemistry.Vol. XII, 83p.
- Bunge C., Barrientons J. and Bunge A., (1993): Roothaan-Hartree-Fock ground state atomic wave functions: Slater-Type Orbital expansions and expectation Values for Z=2-54).Atomic Data And nuclear Data Tables Vol.53, 1113p.
- Clementi and Roetti., (1974): Basis functions and their Coefficients) Atomic Data and Nuclear Data Tables.Vol.14.
- Coulson C.A.and Neilson A.H.,(1960): Electron Correlation in the ground state of He. Proc. Phys.Socity.Vol.78, 186p.
- Donald Fitts D.,(1999): Principles of Quantum Mechanics as Applied to Chemistry and Physical Chemistry.1st edition University of Cambridge England,pp.181-185.

- Gader S. R. and Narasimhan P. t.,(1977): Electron Momentum Distributions from Valence-Bond Wave Function.International Journal of Quantum Chemistry ,Vol.XII ,pp.105-113.
- Kamel M.A.,Dhahir T.A. and Al-Khtaab W.O.,(1984): Calculation of the Energy of many electron Atoms using Two-particle approximation,Iraqi.J.Sci, Vol.25, 88p. Iraq.
- Levine N. Ira., (2005): physical Chemistry.5th edition MC-Graw-Hill Higher Education USA, 671p.
- Lowe P. John and Peterson A. Kirk., (2005): Quantum Chemistry.3rd Elsevier Academic press USA, 138p.
- Mobbs R.J and Banyard K.E., (1983): Correlation effect in momentum space for the electronic shell in Be. Journal Chem. Phys,USA, Vol.78, 6106p.
- Robert E. and Robert R.,(1985): Quantum Physics of atoms, Moleclues , Solids ,Nuclei and particles.2nd edition John Wiley & Sons USA,pp.319-324.
- Sinanoglu,O.,(1957): Two particle approximation of Hartree-Fock. Advance Chemical Physics.Vol.6, 237p.
- Weiss A.W., (1961): Configuration Interaction in simple Atomic systems Physical review.Vol.122, 1826p.

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حساب طاقات الترابط والمسافات الالكترونية البينية $\langle r_i^d \rangle$ و $\langle r_{ij}^d \rangle$ لعدة ايونات الموجبة

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الخلاصة

الهدف من هذا البحث هو حساب القيم المتوقعة لطاقة الترابط $\langle E_{corr} \rangle$, طاقة التنافر بين الكترونـــات $\langle V_{ee} \rangle$, طاقة التجاذب بين الكترونات و النواة $\langle V_{en} \rangle$ والمسافات البينية إلكترونية مثل $\langle r_i^d \rangle$ و $\langle r_{ij}^d \rangle$ (حيث ان d عدد صحيح يأخذ القيم -٢ -١+١+٢)ولعدة ايونات موجبة C^{+3}, N^{+4}, O^{+5}. باستخدام تقنية التجزئة تـــم تحليـــل اربعة دوال هارتري -فوك الموجية للغلافين K , L وكذلك الحالة الأحادية ^1S والحالة الثلاثية ^3S.