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# Evaluation of the energy of subshells for Al-atom and some like electronic series

Qassim Shamkhi AL-Khafaji

Department of Physics, Faculty of Science, University of Kufa, Iraq

**Abstract :** The total energy of subshells(1s,2s,2p,3s and 3p) and some important atomic properties were calculated in this research for systems which have atomic number Z=13-15(Alatom, Si<sup>+</sup> and P<sup>+2</sup>ions) using HF wave function, where the effect of increasing the nuclear charge on the studied properties was observed. The resulted data were obtained numerically using computer program (Mathcad) and these results are evaluated in atomic units. **Keywords :** multi-particles system, Slater determinates, Hartree-Fock approximation, atomic units.

### **1. Introduction**

The Hartree-Fock approximation (HF) is a good approximation for many-particle systems. The base of HFapproximation is to replace the complicated many-particle problem by a one-particleproblem in which particle-particle repulsion can be treated in an average way<sup>1</sup>. The one-particlewave functionsis $\psi_{(n_i,\vartheta_i)}$ , where  $n_i$  represents the four quantum numbers  $n, l, m_l, m_s$  and  $\vartheta_i$  that symbolize the four coordinates. The wave function $\psi_{(x_i)}$  is called the spin orbitals where  $x_i = n_i, \vartheta_i$ . The HF approximation does not take into account electron correlation and that gives some error in calculations. However, the wave function used in HF approximation called uncorrelated wave function which obeys anti-symmetric when replaces the electron's positions<sup>2</sup>. The total N-electron wave function built up as an anti-symmetrized product of spin orbital written as slater determinant.

## 2. Theory

In 1930 Slater created a basis set of functions known as the slater-type orbitals (STOs), used in HF approximation as one-electron wave function which written  $as^3$ .

 $\gamma_{nlm}(r,\theta,\phi) = Nr^{n-1} \exp(-\xi r) Y_{l,ml}(\theta,\phi) \qquad \dots \dots (1)$ 

Where N is normalized factor and equal

$$N = \frac{(2\xi)^{n+\frac{1}{2}}}{((2n)!)^{\frac{1}{2}}} \qquad \dots \dots \dots (2)$$

Where n principle quantum number, r is the distance of the electron from the atomic nucleus,  $Y_{l,ml}$  is spherical harmonic and ( $\xi$ ) the orbital exponent.

Roothaan suggested in the 1951 treated the atomic and molecular orbitals as linear combination of slater orbitals from function called basis functions<sup>4</sup>.

 $\varphi_{HF} = \sum_{i=1}^{k} c_i \gamma_i \dots \dots (3)$ 

Where  $c_i$  represent the constant factor and  $\gamma_i$  is the slater orbitals. The linear combination of normalized slatertype orbital is written as

$$\varphi_{nlm}(r,\theta,\phi) = \sum_{i=0}^{k} c_i \frac{(2\xi)^{n+\frac{1}{2}}}{((2n)!)^{\frac{1}{2}}} r^{n-1} \exp(-\xi r) Y_{l,ml}(\theta,\phi)....(4)$$

The function which contains all of the information necessary to calculate the energy and many properties of the atom is the two-particle density function  $\Gamma(x_m, x_n)$ , which written as<sup>5</sup>.

Where  $x_n$  represent the combined space and spin coordinate of electron n and  $dx_p \dots dx_q$  indicates integration summation over all N-electron except m and n.  $\frac{N(N-1)}{N}$  represent the number of electron pairs, which can be obtained by integration the second-order reduced density function.

The two-particle radial density function  $D(r_1, r_2)$  written as<sup>6</sup>.

$$D(r_1, r_2) = \iint \Gamma(r_1, r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 \dots (6)$$

Can get the One-particle radial density function  $D(r_1)$  by integration  $D(r_1, r_2)$  respect to  $r_2$ , sowritten as<sup>1</sup>.

$$D(r_1) = \int_0^\infty D(r_1, r_2) dr_2....(7)$$

The Inter-particle distribution function  $f(r_{12})$  written as<sup>7</sup>

$$f(r_{12}) = \int \Gamma(r_1, r_2) \, dr_1 dr_2 \qquad \dots \qquad (8)$$

From equation (7) the one-particle expectation value  $\langle r_1^n \rangle$  written as<sup>8</sup>.

$$\langle r_1^n \rangle = \int_0^\infty r_1^n D(r_1) dr_1 \quad \dots \quad (9)$$

In addition, from equation (8) the inter-particle expectation value  $\langle r_{12}^n \rangle$  written as<sup>2</sup>.

$$\langle r_{12}^n \rangle = \int_0^\infty r_{12}^n f_{(r_{12})} dr_{12}$$
 .....(10)

From viral theorem, the expectation value of total energy for the system are related to expectation valueof potential energy<sup>2</sup>.

the expectation value of potential energy can be written as

Where  $\langle V_{en} \rangle$  is the electron-nuclear attraction energy and  $\langle V_{ee} \rangle$  is the electron-electron energy written as<sup>3</sup>.

$$\langle V \rangle = -Z \langle r_1^{-1} \rangle + \langle r_{12}^{-1} \rangle \dots \dots \quad (13)$$

#### 3. Results and Discussion

Figure(1)show that the relation between one – particle radial density distribution function  $D(r_1)$  with the distance between the nucleus and the electrons of each subshell for all studied systems (Al-atom ,Si<sup>+</sup>-ion and P<sup>+2</sup>-ion).



Fig. The relation of one-particle radial distribution function with the distance between the nucleous and electrons of subshell for studied systems.

From this figure we noted when  $r_1 \oplus r \infty$  the values of  $D(r_1) \rightarrow 0$ , this clearly confirms a physical fact which clarifies that the electrons cannot be existed inside the nucleus. In addition to , it is not possible that these electrons to be existed outside the atomic subshells , also observed the values of  $D(r_1)$  close toward the nucleus as nuclear charge increase.

For s-shell it was noted one peak in 1s-shell ,two peak in 2s -shell and three peaks in 3s-shell while for p-shell there are one peak in 2p-shell and two peaks in 3p-shell , the appearance of the small peaks in 2s,3s and 3p subshells return to the penetration phenomenon which can be defined as the ability of electrons in a given subshell to penetrate another previous subshell for short period of time.

Table(1) indicates the maximum values of  $D(r_1)$  and corresponding positions values of the subshells for studied systems.

As nuclear charge increases, the maximum values of  $D(r_1)$  of all subshells increases and these places become closer toward the nucleus.

Table(2)represents the expectation values of different powers of the distance between the nucleus and electrons ,for all subshells in studied systems .

Table(3)indicated that expectation values of inter-particles of each subshell for studied systems, from the tables(2,3)it was observed when the power of expectation values was negative value(-2,-1), the expectation values of one particle and inter particle increase as nuclear charge increase for all subshells and viceversa when the power takes positive value because the increase in atomic number leads to increase in the attraction force between the nucleus with the electrons,.This consequently decreases the distance between the electrons.

For one system the largest value of  $\langle r_1^n \rangle$  and  $\langle r_{12}^n \rangle$  for negative power of 1s and the smallest value for 3p-shell and viceversa for positive powers ,also from these results it is noted that for 2p-shell the values of  $\langle r_1^n \rangle$  and  $\langle r_{12}^n \rangle$  larger than 3s-shell for negative values and smaller for positive values because the 2p-shell has six

electron while 3s has two only, therefore the attraction force between the nucleus with 2p-shell is larger than 3s-shell.

Table 1. The maximum values of	f one-particle radial	distribution function	withcorresponding locations
for studied systems.			

Shell	Ato	m	$r_1$	<b>D</b> ( <b>r</b> <sub>1</sub> )
	Al		0.08	6.7415
1s	Si <sup>+</sup>		0.07	7.2706
	$\mathbf{P}^{+2}$		0.06	7.813
	Al	Al 1 <sup>st</sup> peak		0.3615
		2 <sup>nd</sup> peak	0.5	1.7401
2s	Si <sup>+</sup>	1 <sup>st</sup> peak	0.05	0.4080
28		2 <sup>nd</sup> peak	0.46	1.8281
	$\mathbf{P}^{+2}$	1 <sup>st</sup> peak	0.04	0.4551
		2 <sup>nd</sup> peak	0.42	2.1173
	Al	1 <sup>st</sup> peak	0.06	0.0190
		2 <sup>nd</sup> peak	0.42	0.0728
		3 <sup>rd</sup> peak	2.1	0.4461
	Si <sup>+</sup>	1 <sup>st</sup> peak	0.05	0.0291
3s		2 <sup>nd</sup> peak	0.38	0.1099
		3 <sup>rd</sup> peak	1.76	0.5751
	$\mathbf{P}^{+2}$	1 <sup>st</sup> peak	0.04	0.04119
		2 <sup>nd</sup> peak	0.35	0.1486
		3 <sup>rd</sup> peak	1.53	0.698
	Al		0.43	1.5314
2p	Si <sup>+</sup>		0.39	1.7278
	$\mathbf{P}^{+2}$		0.36	1.923
	Al	1 <sup>st</sup> peak	0.36	0.0380
		2 <sup>nd</sup> peak	2.68	0.3142
3n	Si <sup>+</sup>	1 <sup>st</sup> peak	0.32	0.0752
3p		2 <sup>nd</sup> peak	2.05	0.4625
	$\mathbf{P}^{+2}$	1 <sup>st</sup> peak	0.29	0.1157
		2 <sup>nd</sup> peak	1.69	0.5915

Table(2): results of one –particle expectation values for different powers of studied systems.

shell	Atom or ion	$\langle r_1^{-2}  angle$	$\langle r_1^{-1}  angle$	$\langle r_1^1  angle$	$\langle r_1^2  angle$
1s	Al	320.1189	12.5891	0.1202	0.0194
	Si <sup>+</sup>	372.4072	13.5814	0.1114	0.0167
	$P^{+2}$	428.6512	14.5739	0.1037	0.0149
2s	Al	22.7931	2.3490	0.6200	0.4589
	Si <sup>+</sup>	27.7167	2.5919	0.5625	0.3766
	$P^{+2}$	33.1503	2.8363	0.5147	0.3146
3s	Al	1.3585	0.567	2.6003	7.8989
	Si <sup>+</sup>	2.8277	0.6345	2.0923	5.0426
	$P^{+2}$	3.2704	0.7580	1.7688	3.5811
2p	Al	6.9160	2.2051	0.6005	0.4553
	Si <sup>+</sup>	8.5239	2.4570	0.5352	0.3594
	$P^{+2}$	10.2977	2.7082	0.4829	0.2911
3р	Al	0.3105	0.3793	3.4308	13.9623
	Si <sup>+</sup>	0.6167	0.5294	2.4721	7.1199
	$P^{+2}$	0 9776	0.6652	1 9834	4 5429

Shell	Atom or ion	$\langle r_{12}^{-2}  angle$	$\langle r_{12}^{-1}  angle$	$\langle r_{12}^1  angle$	$\langle r_{12}^2  angle$
1s	Al	105.0454	7.8239	0.1756	0.0389
	Si <sup>+</sup>	122.2890	8.4427	0.1627	0.0334
	$P^{+2}$	140.8574	9.0619	0.1516	0.0289
2s	Al	3.5285	1.4632	0.8784	0.9178
	Si <sup>+</sup>	4.2833	1.6116	0.7964	0.7533
	$\mathbf{P}^{+2}$	5.1143	1.7603	0.7283	0.6291
	Al	0.1932	0.3482	3.6575	15.7979
3s	Si <sup>+</sup>	0.2961	0.4314	2.9336	10.0853
	$P^{+2}$	0.4188	0.5095	2.4767	7.1623
2p	Al	3.8293	1.5333	0.8623	0.9107
	Si <sup>+</sup>	4.7852	1.7169	0.7974	0.7189
	$P^{+2}$	5.8452	1.9000	0.6915	0.5823
	Al	0.1117	0.2645	4.8466	27.9246
3р	Si <sup>+</sup>	0.2134	0.3656	3.4769	14.1398
	$\mathbf{P}^{+2}$	0.3307	0.4546	2.7848	9.0859

Table(3):results of inter-particle expectation values for different powers of studied system

Table.4 :the energies of each subshell for studied systems

shell	Atom or ion	$\langle V_{ee} \rangle$	$-\langle V_{en} \rangle$	$-\langle V \rangle$	$-\langle E \rangle$
1s	Al	7.8239	327.3167	319.4929	159.7464
	Si <sup>+</sup>	8.4427	380.2792	371.8364	185.9182
	$P^{+2}$	9.06119	437.2188	428.1568	214.0784
2s	Al	1.4632	61.0745	59.6112	29.8056
	Si <sup>+</sup>	1.6116	72.5734	70.9118	35.4809
	$\mathbf{P}^{+2}$	1.7603	85.0914	83.3310	41.6655
3s	Al	0.3482	13.1744	12.8261	6.4130
	Si <sup>+</sup>	0.4314	17.7671	17.3357	8.6678
	$\mathbf{P}^{+2}$	0.5095	22.7412	22.2316	11.1158
2p	Al	22.9996	172.0024	142.0028	74.5014
	Si <sup>+</sup>	25.7985	206.3888	180.5903	90.2951
	$P^{+2}$	28.5	243.7416	215.2416	107.6208
3р	Al	-	4.9320	4.9320	2.4660
	Si <sup>+</sup>	-	7.4124	7.4124	3.7062
	$\mathbf{P}^{+2}$	-	9.9893	9.9893	4.9896

Table(4) shows the energies of each subshell in studied system as electron-electron repulsion energy, electron-nucleus attraction energy, total potential energy and the total energy of each subshell.

From this table, all energies increase for each subshell as nuclear charge increase, also it was noted that 2p-shell has largest energies when compared with other shells except 1s-shell because it has six electrons that mean it has six term of attraction force between the nucleus with each electron, it also has fifteen repulsion terms resulted from the interaction between the electrons.

## 4-Conclusions

It can be concluded that the main influential factor on the atomic properties of the system is the resulted from increase in nuclear charge. Finally it was observed that the number of subshells increase the time of penetration phenomenon takeplace increases.

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