Calculation of the energy of subshells for six electron systems

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Abstract

In the present study, the atomic properties have been calculated for each electron in (1s), (2s), and (2p) for the six-electron system for (Ne^{+4}, Na^{+5}, Mg^{+6}, Al^{+7}, Si^{+8}, and P^{+9}-ions) with an atomic number (Z=10 to 15). The calculated atomic properties include the one particle radial distribution function $D(r_1)$, the expectation values $\langle r_1^n \rangle$ and $\langle r_{12}^n \rangle$, the standard deviation Δr_1 and Δr_{12}, the inter-electronic distribution function f (r_{12}), the energy expectation value $\langle E_{HF} \rangle$, $\langle V_T \rangle$, $\langle V_{en} \rangle$, $\langle V_{ee} \rangle$ and $\langle T \rangle$ and other properties. Hartree-Fock approximation has been used to determine each of these attributes. The software package Mathcad14 was used to acquire the results numerically. All results were derived using the atomic unit.

Keywords: *Hartree-Fock; atomic properties; Hamiltonian operator; Hartree-Fock Energies; six electron system.*

Introduction

The motion of planets, electrons, and subatomic particles are all described by quantum mechanics; hence, classical mechanics is a subset of quantum mechanics. Even though they have the beginning condition, events in the quantum theory are probabilistic and not deterministic, with one significant exception. The theory of probability is quantum theory, which is a statistical theory, even for a single particle. The possibilities don't just lie in the state's nature that serves as a representation of the approach; they also lie in the number of states that must be normalized in the system [1].

Schrodinger introduced wave mechanics into the collection of ideas, equations, interpretations, and theories that were common to explain the growing body of observations of the wave equation that it obeys. The basis for our current understanding of quantum phenomena and the mathematical techniques we use to test them is Schrodinger's wave mechanics. The Schrodinger equation with time independence [2]

$$\hat{H}\Psi = E\Psi \qquad (1)$$

Where the electron's behavior is dictated by the wave function, represented by the symbol Ψ.

It was observed that the Schrödinger equation is an Eigenvalue equation when written as in equation (1), hence the equation becomes[3]

$$(operator).(function)$$
$$= constant\ factor$$
$$\times same\ function$$

E is called the eigenvalue of the operator $\hat{H}$. The factor $\hat{H}$ in equation (1) represents the Hamiltonian operator, which is defined as

follows for a single electron of an atom with a charge of Ze [4]

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \qquad (2)$$

Where $\hbar = \frac{h}{2\pi}$, h : is Planck's constant, m_e: is the mass of an electron and ∇^2: Laplacian operator, which can be written in spherical coordinate (r, θ, ϕ) as follows [5]

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 \sin\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \qquad (3)$$

the Hamiltonian of an atom with N electrons is as follows:[6]

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla^2{}_i + \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{r_{ij}} \qquad (4)$$

the first term is the kinetic energy operator for the N-electrons while the second term for the attraction of the electrons to the charged nucleus is the potential energy Ze., r_i is the distance between the electron and the nucleus, and the final term is the electron's potential energy[7]. This term equals zero when located an infinite distance from the nucleus center. Because the energy of an electron in an atom is smaller than when the nucleus and electron are separated by an infinite distance, the constraint j > i prevents counting the same inter-electronic repulsion twice and avoids terms like $\frac{e^2}{r_i}$ [8]. Because of the inter-electronic repulsion factors $\frac{e^2}{r_{ij}}$, the Schrödinger equation for the atom cannot be separated [9].

The Hatree-Fock approximation suggests that the body wave function $\Psi(r_1, r_2, …, r_N)$, is approximated by a single Slater determinant. The wave function can be expressed as [10]:

$$\Psi_{HF} = \det(\Phi_1(x_1)\Phi_2(x_2).….\Phi_N(x_N)) \qquad (5)$$

$$\Psi_{HF} = \begin{bmatrix} \Phi_1(x_1) & \Phi_1(x_2) & \cdots & \Phi_1(x_N) \\ \Phi_2(x_1) & \Phi_2(x_2) & \cdots & \Phi_2(x_N) \\ \vdots & \vdots & & \vdots \\ \Phi_N(x_1) & \Phi_N(x_2) & \cdots & \Phi_N(x_N) \end{bmatrix} \qquad (6)$$

Calculations

We will discuss some important atomic properties of the ions under study, including:

1. One particle radial density distribution function $D(r_1)$:
   The one-particle radial density distribution function $D(r_1)$,which shows the potential for having electrons in each electron shell and is known as the following, is important for the study of electrons in an atom or ion [11].

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

2. One-particle expectation value $\langle r_1^n \rangle$:
   To determine the high probability of an electron being present at a specific position in the nucleus and its density of radial probability [11, 12], use the equation shown below.

$$\langle r_1^n \rangle = \int_0^\infty D(r_1)r_1^n dr_1 \qquad (8)$$

3. The electron-electron distribution function f(r₁₂):
   The pair distribution function is calculated from the following equation [13]

$$f_{ij}(r_{12}) = \int \Gamma_{ij}(r_1, r_2)dr_1 dr_2 \qquad (9)$$

4. electron-electron expectation values $\langle r_{12}^n \rangle$:

   The following equation represents the expected value of the separation between two electrons [14]:

   $$\langle r_{12}^n \rangle = \int_0^\infty f(r_{12}) r_{12}^n \, dr_{12} \qquad (10)$$

5. The expectation value for energy $\langle E \rangle$:

Equations (11 and 12) were used to calculate both the total energy and the potential energy [15-17]:

$$\langle E \rangle = -\langle T \rangle = \frac{\langle V \rangle}{2} \qquad (11)$$

$$\langle V \rangle = Z \left\langle \frac{1}{r_1} \right\rangle + \left\langle \frac{1}{r_{12}} \right\rangle \qquad (12)$$

Results and Discussions:

The results were tabulated and represented using the Mathcad 14 application using the above equations:

Table 1 The maximum value of the radial density distribution function of a one-particle Dmax(r1) with the positions corresponding to r1 for six electronic systems.

ions	Atomic Number(Z)	1s shell		2s shell			2p shell	
		r_1	$D_{max}(r_1)$	peak	r_1	$D_{max}(r_1)$	r_1	$D_{max}(r_1)$
Ne^{+4}	10	0.1036	5.1630	Peak1	0.0806	0.30093	0.5420	1.3470
				Peak2	0.6381	1.4360		
Na^{+5}	11	0.0932	5.7019	Peak1	0.073	0.35103	0.4730	1.5459
				Peak2	0.565	1.629		
Mg^{+6}	12	0.0854	6.2411	Peak1	0.0668	0.40158	0.4223	1.7437
				Peak2	0.51	1.8217		
Al^{+7}	13	0.0789	6.7807	Peak1	0.0612	0.4524	0.3778	1.9410
				Peak2	0.4637	2.0147		
Si^{+8}	14	0.0730	7.3203	Peak1	0.0568	0.5034	0.3479	2.1387
				Peak2	0.4260	2.2066		
P^{+9}	15	0.0680	7.8603	Peak1	0.0529	0.55461	0.3229	2.3350
				Peak2	0.3930	2.3989		

Figure 1 Relationship between one-particle radial density distribution function and location r1 for 1s,2s and 2p respectively, in a six_electron system.
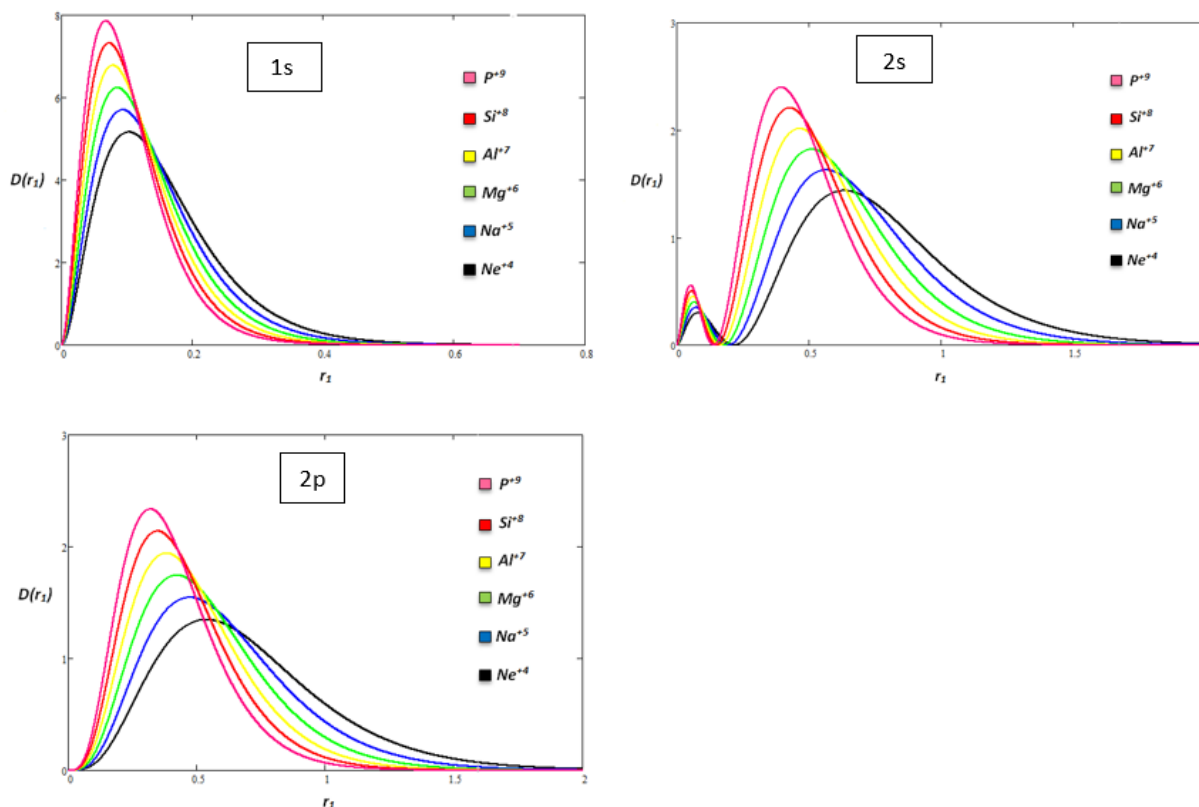

Table 1 and Figure 1 shows that the maximum values for D(r_1)increase with decreasesd position r_1, which means that the probability of finding an electron increases as the distance between the nucleus and the electron decreases. The locations of these peaks are contracted toward the nucleus .The probability of finding an electron is zero when r_1=0, which means that the electron is not found in the nucleus. Similarly, when the distance from the nucleus is great, the probability of finding an electron is zero when r_1= ∞ ,which means that the electron is not found in the atom.

Figure 1 for 2s shell shows that for each of the systems under discussion, the first peak corresponds to an electron that can temporarily settle in the 1s shell due to the penetration effect, and the second peak corresponds to the probability that the electron will be found in the 2s shell .Additionally, Since the 1s shell is closest to the nucleus, it receives all of the nucleus' charge, whereas the 2s shell receives less since the 1s shell blocks some of the nucleus's charge, the probability of finding an electron in the 1s shell is greater than that in the 2s shell.

Table 2 Expectation values $\langle r_1^n \rangle$ where $-2 \leq n \leq 2$ and standard deviation for 1s_shell for six electron systems.

ions	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^{+1} \rangle$	$\langle r_1^{+2} \rangle$	Δr_1
Ne^{+4}	187.89200	9.64100	0.15700	0.03300	0.09208
Na^{+5}	228.53958	10.63787	0.14218	0.02715	0.08329
Mg^{+6}	273.18904	11.63492	0.12992	0.02266	0.07603
Al^{+7}	321.83538	12.63256	0.11960	0.01919	0.06992
Si^{+8}	374.48034	13.63023	0.11078	0.01646	0.06472
P^{+9}	431.13020	14.62849	0.10319	0.01428	0.06023

Table 3 Expectation values $\langle r\_1^n \rangle$ where -2≤n≤2 and standard deviation for 2s_shell for six electron systems.

ions	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^{+1} \rangle$	$\langle r_1^{+2} \rangle$	Δr_1
Ne+4	*14.49900*	*1.88700*	*0.76700*	*0.69300*	*0.32425*
Na+5	*18.58478*	*2.13675*	*0.67920*	*0.54285*	*0.28554*
Mg+6	*23.17089*	*2.38662*	*0.60970*	*0.43683*	*0.25512*
Al+7	*28.26141*	*2.63660*	*0.55325*	*0.35940*	*0.23090*
Si+8	*33.85291*	*2.88662*	*0.50634*	*0.30076*	*0.21066*
P+9	*39.94348*	*3.13667*	*0.46678*	*0.25544*	*0.19379*

Table 4 Expectation values $\langle r_1^n \rangle$ where $-2 \leq n \leq 2$ and standard deviation for 2p_shell for six electron systems.

ions	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^{+1} \rangle$	$\langle r_1^{+2} \rangle$	Δr_1
Ne^{+4}	4.64171	1.83450	0.69971	0.60016	0.33251
Na^{+5}	5.99577	2.08948	0.61219	0.45807	0.28861
Mg^{+6}	7.51662	2.34341	0.54439	0.36142	0.25507
Al^{+7}	9.20426	2.59659	0.49028	0.29265	0.22865
Si^{+8}	11.05885	2.84928	0.44606	0.24193	0.20725
P^{+9}	13.07995	3.10149	0.40919	0.20335	0.18949

According to Tables 2,3and 4, all of the systems under study showed an increase in the one-particle expectation value $\langle r_1^m \rangle$ when the atomic number increased. This was especially true when m took on a negative value (-2, -1), which is related to the attraction energy expectation value $\langle V_{en} \rangle$, which is equal to $\langle V_{en} \rangle = -Z[N \cdot \langle r_1^{-1} \rangle]$. N represents the number of electrons in the shell and shows how the density of electrons distribution is distributed close to the nucleus. Additionally, we saw that when Z increased, the one-particle expectation value, or $\langle r_1^m \rangle$, started to fall for positive values of (m), such as (+1) and (+2), which stands for the distance between the electron and the nucleus.

Since the distance between the electron and the nucleus is smaller for 1s-shell than it is for 2s-shell, the standard deviation Δr_1 is also smaller for each of the six-electron systems as well as for other atomic shells.

Table 5 Maximum f(r12) Values with Corresponding Values of r12 in 1s,2s and 2p_shells for six electron System Under Study in a.u.

ions	Atomic number(z)	1s shell		2s shell		2p shell	
		r_{12}	f_{max}	r_{12}	f_{max}	r_{12}	f_{max}
Ne^{+4}	10	0.173	3.7879	0.970	0.87754	0.835	0.92609
Na^{+5}	11	0.157	4.1840	0.862	0.99112	0.733	1.06100
Mg^{+6}	12	0.144	4.5803	0.777	1.10450	0.653	1.19520
Al^{+7}	13	0.132	4.9771	0.705	1.21740	0.590	1.32900
Si^{+8}	14	0.122	5.3738	0.647	1.33050	0.536	1.46250
P^{+9}	15	0.114	5.7711	0.596	1.44330	0.493	1.59570

Figure 2 The Inter particle Distribution Function and r12 for 1s,2s and 2p shell respectively, for the six-electron system Relationship.
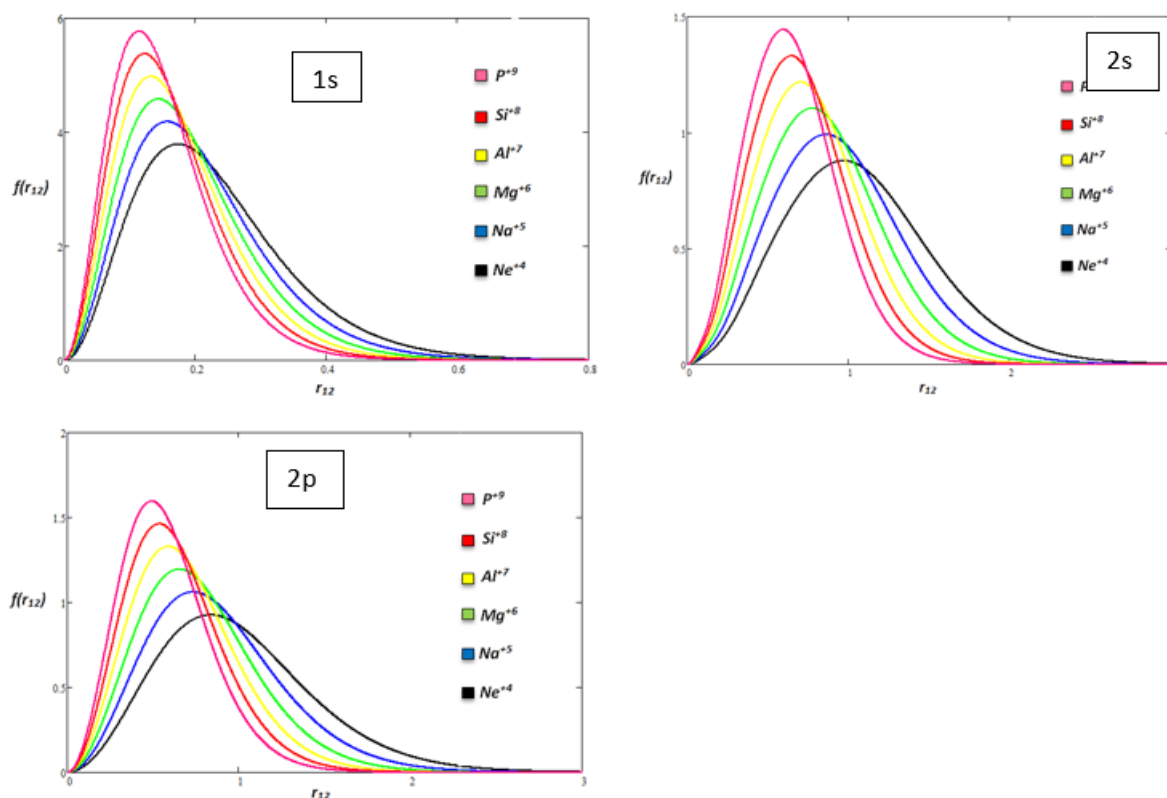
Also from Table 5, the relationship between the inter-particle distance r_{12} and maximum values of the inter-particle distribution function for the systems under study, we noticed that the maximum value increases as Z increases and the inter-particle distance decrease because increasing the atomic number leads to an increase in the nucleus-to-electron attraction

force, which causes the distance between electrons to decrease. Figure 2 also shows that as the atomic number rises, the distance r_{12} between two electrons decreases. This behavior results from the fact that each shell shrinks toward the nucleus, which causes an increase in the inter-particle distribution function. However, this is not the case when $r_{12} = 0$ and when $r_{12} = \infty$, because the coulomb interaction is neglected when the distance between two electrons is very great.

The nuclear attraction of the K.shell is stronger than the other shells, causing a reduction in the distance between the electrons r_{12}, which raises $f(r_{12})$ in the 1s-shell relative to other shells for each state, and the smallest value of $f(r_{12})$ in the 2p-shell.

Table 6 Expectation values $\langle r_{12}^n \rangle$ where $-2 \leq n \leq 2$ and standard deviation for 1s_shell for six electron systems in a.u.

ions	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^{+1} \rangle$	$\langle r_{12}^{+2} \rangle$	Δr_{12}
Ne^{+4}	61.58670	5.99117	0.22933	0.06625	0.11687
Na^{+5}	75.01377	6.61354	0.20767	0.05431	0.10574
Mg^{+6}	89.77282	7.23624	0.18973	0.04532	0.09653
Al^{+7}	105.86836	7.85494	0.17464	0.03838	0.08880
Si^{+8}	123.28993	8.48260	0.16176	0.03292	0.08220
P^{+9}	142.05023	9.10638	0.15065	0.02855	0.07651

Table 7 Expectation values $\langle r_{12}^n \rangle$ where $-2 \leq n \leq 2$ and standard deviation for 2s_shell for six electron systems a.u.

ions	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^{+1} \rangle$	$\langle r_{12}^{+2} \rangle$	Δr_{12}
Ne^{+4}	2.28836	1.17999	1.08294	1.38580	0.46156
Na^{+5}	2.91819	1.33130	0.95908	1.08569	0.40724
Mg^{+6}	3.62449	1.48250	0.86073	0.87364	0.36440
Al^{+7}	4.40698	1.63345	0.78094	0.71880	0.33004
Si^{+8}	5.26580	1.78448	0.71463	0.60152	0.30137
P^{+9}	6.20109	1.93538	0.65873	0.51087	0.27739

Table 8 Expectation values $\langle r_{12}^n \rangle$ where $-2 \leq n \leq 2$ and standard deviation for 2p_shell for six electron systems in a.u.

ions	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^{+1} \rangle$	$\langle r_{12}^{+2} \rangle$	Δr_{12}
Ne^{+4}	2.72934	1.30445	0.99771	1.20032	0.45265
Na^{+5}	3.55501	1.48983	0.87227	0.91615	0.39407
Mg^{+6}	4.48555	1.67442	0.77522	0.72283	0.34909
Al^{+7}	5.52104	1.85843	0.69787	0.58531	0.31351
Si^{+8}	6.66166	2.04210	0.63472	0.48386	0.28458
P^{+9}	7.90681	2.22540	0.58207	0.40669	0.26054

When Z increases and (m) takes values of -2,-1, which reflect the repulsion energy between two electrons $\langle r_{12}^{-1} \rangle$, the inter-particle expectation value $\langle r_{12}^m \rangle$ increases, as shown by an analysis of the inter-particle expectation value $\langle r_{12}^m \rangle$ shown in Tables 6,7 and 8. In other words, as the nucleus's attraction force increases, the distance between electrons contracts, which lowers r12. The value of $\langle r_{12}^{-1} \rangle$ in all Tables for all systems is highest in the 1s-shell while it is lowest in the 2p-shell due to the stronger repulsive force in the 1s-shell than in the other shells and the smaller distance between two electrons in the 1s-shell. However, the inter-particle expectation value decreases with an increase in Z when (m) assumes positive values like +1, and +2.

The standard deviation Δr_{12} lowers as (Z) increases, as can be shown from all Tables, because decreasing the distance between electrons causes the variation in the expectation value to be small.

Table 9 Expectation Values for All Attraction, Repulsion Potential, Kinetic and Total Energy for 1s,2s and 2p_shells for six_electron system in a.u.

ions	shells	$-\langle V_{en} \rangle$	$\langle V_{ee} \rangle$	$-\langle V_T \rangle$	$\langle T \rangle$	$-\langle E_T \rangle$
Ne^{+4}	1s	192.8200	5.99117	186.82883	93.41441	93.41441
	2s	37.74000	1.17999	36.56001	18.28001	18.28001
	2p	36.69000	1.30445	35.38555	17.69277	17.69277
Na^{+5}	1s	234.03314	6.61354	227.41960	113.70980	113.70980
	2s	47.00850	1.33130	45.67720	22.83860	22.83860
	2p	45.96856	1.48983	44.47873	22.23936	22.23936
Mg^{+6}	1s	279.23808	7.23624	272.00184	136.00092	136.00092
	2s	57.27888	1.48250	55.79638	27.89819	27.89819
	2p	56.24184	1.67442	54.56742	27.28371	27.28371
Al^{+7}	1s	328.44734	7.85949	320.58707	160.29353	160.29353
	2s	68.55160	1.63345	66.91815	33.45908	33.45908
	2p	67.51134	1.85843	65.65291	32.82646	32.82646
Si^{+8}	1s	381.64644	8.48260	373.16384	186.58192	186.58192

	2s	80.82536	1.78448	79.04088	39.52044	39.52044
	2p	79.77984	2.04210	77.73774	38.86887	38.86887
P+9	*1s*	438.85470	9.10638	429.74832	214.87416	214.87416
	2s	94.10010	1.93538	92.16472	46.08236	46.08236
	2p	93.04470	2.22540	90.81930	45.40965	45.40965

The results of the expectation values for attraction potential energy between nucleus-electron and repulsion potential energy between two-electron, as well as the expectation values of the total energy or Hartree-Fock energy, are similar to published data, as shown in Table 9.

Both $\langle V_{en}\rangle$ and $\langle V_{ee}\rangle$ for ions increase as atomic number increases. This result can be explained by the fact that all shells shrink toward the nucleus as a result of the attraction force between the proton and the electrons $\langle V_{en}\rangle$ increasing as the distance between the nucleus-electron and electron-electron decreases. This result causes an increase in repulsion potential energy as well as attraction potential energy. The expectation values for total potential energy $\langle V\rangle$ increase in each system as a result.

To sustain the entity of the atom, we noted that the energy of attraction increases more rapidly than the energy of repulsion when Z increases. We also noticed that the energy of kinetic energy increases when Z increases. When Z increases, the total energy or Hartree-Fock energy similarly increases, indicating the function of Z.

Conclusions:

From the current research, we put some conclusions about some atomic properties of such elements (Ne^{+4}, Na^{+5}, Mg^{+6}, Al^{+7}, Si^{+8} and P^{+9}-ions) , The one-particle radial density distribution function $D(r_1)$ and the inter-particle distribution function $f(r_{12})$ both reach their maximum values with an increase in Z, and the position of these maximum values changes as Z increases. When Z increases, the one-particle expectation $\langle r_1^m\rangle$ and the two-particle expectation $\langle r_{12}^m\rangle$ both increase for (m = -2, -1) and decrease for (m = +2, +1) for (m = 0) $\langle r_1^0\rangle$, this value represents the normalization condition . Additionally, it should be noted that as atomic number increases, so do the expectation values of all energies $\langle V_{en}\rangle, \langle V_{ee}\rangle, \langle V_T\rangle, \langle T\rangle$ including, $\langle E_{HF}\rangle$.

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