

# A Theoretical Study of the Atomic Properties for Subshells of $N^+$ and $O^{+2}$ Using Hartree-Fock Approximation

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**Abstract** In this research, we calculated the atomic properties of systems have been studied ( $N^+$  and  $O^{+2}$ ) for intra-shells (1s, 2s and 2p) using Hartree-Fock wave function. These properties included, one-particle radial density function, one-particle and inter-particle expectation values, inter-particle density function and expectation values of energies. All these atomic properties increase with atomic number, have highest values in 1s shell and lowest values in 2p shell. All results are obtained numerically by using the computer program (MathCad 14) because it able to calculation and plot functions. All atomic properties are calculated in atomic units.

**Keywords:** Hamiltonian operator  $\hat{H}$ , wave function  $\psi$ , Approximation methods, multi-electron systems and Hund's rules

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## 1. Introduction

The Hartree-Fock Self-Consistent Field approximation (HF-SCF), it is a good approximation to many-electron systems, which is described by wave function. The essence of HF-SCF approximation is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way [1]. The approximation is based on two grounds, first, each electron moves in the potential field of the nucleus plus the  $N-1$  other electrons (central field approximation) that mean the electrons move independently [2]. The second must on initial wave function consistent with final it when inter in the calculation. The wave functions  $\psi(x_i)$  where  $x_i$  spin orbitals included four quantum number ( $n, l, m_l, m_s$ ), using in the calculation obey on Pauli exclusion principle, so consequently the wave function antisymmetric when two electrons exchange their locations.

## 2. Theory

In order to wave function satisfy the antisymmetric principle have to have written as slater determinant which named after John C. Slater [3].

$$\Psi_{HF}(x_1, x_2, \dots, x_N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \varphi_1(x_1) & \dots & \varphi_j(x_1) \\ \vdots & \ddots & \vdots \\ \varphi_1(x_N) & \dots & \varphi_j(x_N) \end{vmatrix} \quad (1)$$

Slater created such a basis set of functions known as the slater-type orbitals (STO's), which written [4].

$$\gamma_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{l,m}(\theta, \varphi) \quad (2)$$

Where  $R_{nl}(r)$  represented radial part of the wave function and its given as [5].

$$R_{nl}(r) = N_{nlm} S_{nl}(r) \quad (3)$$

$N_{nlm}$  Normalized constant and written as

$$N = \frac{(2\xi)^{n+\frac{1}{2}}}{((2n)!)^{\frac{1}{2}}} \quad (4)$$

$$S_{nl}(r) = r^{n-1} \exp(-\xi r) \quad (5)$$

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

The Hartree-Fock spin orbitals can be described as a linear combination of slater orbitals from the function called basis functions written as [6].

$$\varphi_{HF} = \sum_{i=0}^k c_i \gamma_i \quad (6)$$

Where  $c_i$  represent the constant coefficient and  $\gamma_i$  is the slater orbitals.

The two-particle density  $\Gamma(x_m, x_n)$  contains all of the information necessary to calculate the energy and many properties of the atom or ion [7]. Written as

$$\begin{aligned} \varphi_{HF} &= \sum_{i=0}^k c_i \gamma_i \\ \Gamma_{HF}(x_m, x_n) &= \frac{N(N-1)}{N} \iint |\psi_{(x_m, x_n, x_p, \dots, x_q)}|^2 dx_p \dots dx_q \end{aligned} \quad (7)$$

Where  $x_n$  represents 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  $n$ .

The two-particle radial density function  $D(r_1, r_2)$  it is probability density of finding the electron 1 at  $r_1$  and electron 2 at  $r_2$  from nucleus simultaneously written as [8]

$$D(r_1, r_2) = \iint \Gamma(r_1, r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 d\sigma_1 d\sigma_2 \quad (8)$$

The one-particle radial density function  $D(r_1)$  it is the probability density function of finding an electron at a distance  $r_1$  and  $r_1 + dr_1$  from the coordinate origin (i.e. nucleus) written as [9].

$$D(r_1) = \int_0^{\infty} D(r_1, r_2) dr_2. \quad (9)$$

The one-particle expectation value  $\langle r_1^n \rangle$  can be calculated from the following equation [10].

$$r_1^n = \int_0^{\infty} r_1^n D(r_1) dr_1. \quad (10)$$

Standard deviation  $\Delta r_1$  it is spread out or difference in the expectation value written as [11]

$$\Delta r_1 = \left[ \langle r_1^2 \rangle - \langle r_1 \rangle^2 \right]^{1/2}. \quad (11)$$

The inter-particle distribution function  $f(r_{12})$  it is the probability density function of finding the electron 1 and electron 2 at the distance between  $r_{12}$  and  $r_{12} + dr_{12}$  written as [12]

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

The inter-particle expectation value  $\langle r_{12}^n \rangle$  It is given by [13]

$$\langle r_{12}^n \rangle = \int_0^{\infty} r_{12}^n f(r_{12}) dr_{12} \quad (13)$$

Standard deviation  $\Delta r_{12}$  it is defined as [14].

$$\Delta r_{12} = \left[ r_{12}^2 - r_{12} \right]^{1/2} \quad (14)$$

The expectation value of total energy for the system written by equation

$$E = \langle \hat{H} \rangle = -\langle T \rangle + -\langle V_{en} \rangle + \langle V_{ee} \rangle \quad (15)$$

Where  $T$  kinetic energy,  $V_{en}$  electron-nucleus attraction energy and  $V_{ee}$  electron-electron repulsion energy.

$$\langle V_{en} \rangle = -Z \langle r_1^{-1} \rangle \quad (16)$$

$$\langle V_{ee} \rangle = \langle r_{12}^{-1} \rangle \quad (17)$$

From condition of the virial theorem [15]. The energy expectation value of total energy is related to expectation value of potential energy.

$$\langle E_T \rangle = \frac{1}{2} \langle V_T \rangle = -\langle T \rangle. \quad (18)$$

### 3. Results and Discussion

Table 1 and Table 2 have contained the results of one-particle distribution function  $D(r_1)$  and the inter-particle distribution function  $f(r_{12})$  respectively.  $D(r_1)$  and  $f(r_{12})$  increases when atomic number  $Z$  increase because the distance between electrons and nucleus in 1s shell is smallest as well as the distance between electrons as a Figure 1, Figure 2. The greatest value of  $D(r_1)$  in 1s shell and smallest value in 2p shell. From Figure 1 when  $r_1=0$  or  $\infty$ ,  $D(r_1)=0$ , that means the probability of finding the electron inside the nucleus or far away from it equal zero. We noted two peaks of  $D(r_1)$  for 2s shell, the first peak represented the probability of finding the electron in 1s shell due to penetration phenomenon and the second peak represented the probability of finding the electron in 2s shell. The largest value of  $f(r_{12})$  in 1s shell for each system as a Figure 2. From Figure 2 when  $r_{12}=0$  or  $\infty$ ,  $f(r_{12})=0$  that means the probability of finding two electrons in the same position or too far away from each other equal zero.

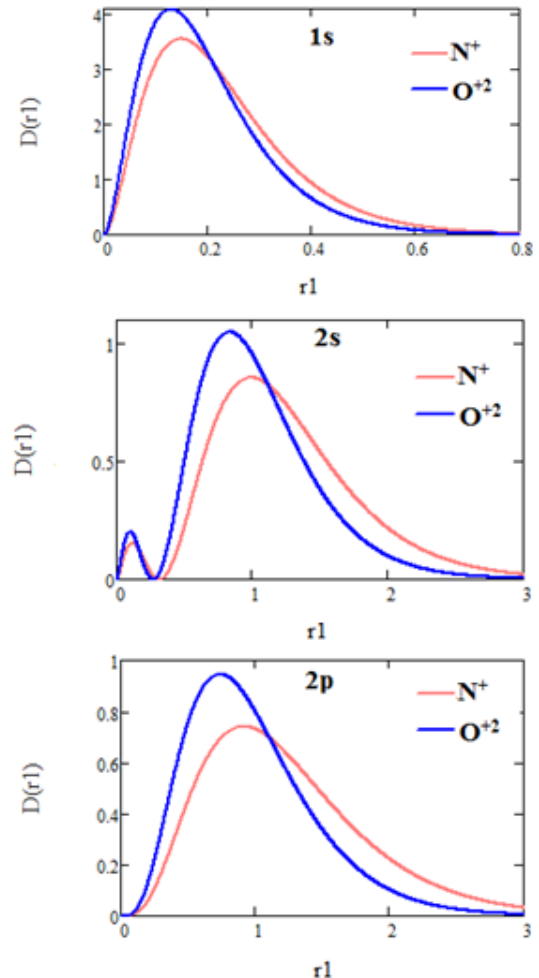


Figure 1. The relation between one-particle radial density distribution function and location for each system

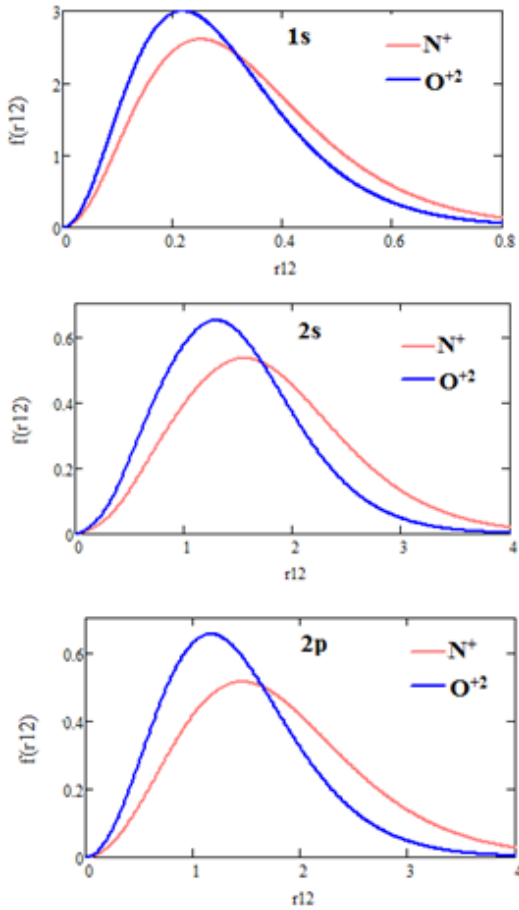


Figure 2. The relation between inter-particle distribution function and location for each system

Table 1. The maximum values of the one-particle distribution function and corresponding location  $r_1$  for each system

Shell	N <sup>+</sup>		O <sup>+2</sup>	
	$r_1$	D( $r_1$ )	$r_1$	D( $r_1$ )
1s	0.149	3.5506	0.1295	4.0873
2s	0.995	0.85549	0.8383	1.0493
2p	0.9184	0.74078	0.7397	0.94572

Table 2. The maximum values of the inter-particle distribution function and corresponding location for each system

Shell	N <sup>+</sup>		O <sup>+2</sup>	
	$r_{12}$	$f(r_{12})$	$r_{12}$	$f(r_{12})$
1s	0.2515	2.6028	0.2179	2.9971
2s	1.5496	0.53358	1.2904	0.64889
2p	1.4508	0.51315	1.1614	0.65307

Table 3. The one-particle expectation values  $\langle r_1^n \rangle$  where (n=-1,1,2) and standard deviation for each system

Shell	N <sup>+</sup>		O <sup>+2</sup>	
	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$
1s	$\langle r_1^{-1} \rangle$	6.65657	7.65037	
	$\langle r_1^1 \rangle$	0.22808	0.19821	
	$\langle r_1^2 \rangle$	0.07009	0.05289	
	$\Delta r_1$	0.13442	0.11661	
2s	$\langle r_1^{-1} \rangle$	1.14084	1.38855	
	$\langle r_1^1 \rangle$	1.25284	1.03371	
	$\langle r_1^2 \rangle$	1.87455	1.26794	
	$\Delta r_1$	0.55221	0.44653	
2p	$\langle r_1^{-1} \rangle$	1.05597	1.31909	
	$\langle r_1^1 \rangle$	1.24366	0.98447	
	$\langle r_1^2 \rangle$	1.93255	1.19954	
	$\Delta r_1$	0.62118	0.47996	

Table 3 and Table 4 have contained the one-particle  $\langle r_1^n \rangle$  and inter-particle  $\langle r_{12}^n \rangle$  expectation values and standard deviation. When  $n = -1$  the expectation values increase when the atomic number increase and the highest value of  $\langle r_1^{-1} \rangle$  in 1s shell and lowest value in 2p shell. When  $n = 1,2$  the expectation values decrease when Z increase. The highest value in 2s shell and lowest value in 1s shell.

Table 4. the inter-particle expectation values  $\langle r_{12}^n \rangle$  where (n=-1,1, 2) and standard deviation for each system

Shell	N <sup>+</sup>		O <sup>+2</sup>	
	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^1 \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^1 \rangle$
1s	$\langle r_{12}^{-1} \rangle$	4.12789	4.74807	
	$\langle r_{12}^1 \rangle$	0.33334	0.28964	
	$\langle r_{12}^2 \rangle$	0.14018	0.10577	
	$\Delta r_{12}$	0.17047	0.14793	
2s	$\langle r_{12}^{-1} \rangle$	0.72448	0.87655	
	$\langle r_{12}^1 \rangle$	1.7744	1.46203	
	$\langle r_{12}^2 \rangle$	3.74909	2.53585	
	$\Delta r_{12}$	0.77499	0.63112	
2p	$\langle r_{12}^{-1} \rangle$	0.73785	0.92953	
	$\langle r_{12}^1 \rangle$	1.78177	1.40714	
	$\langle r_{12}^2 \rangle$	3.86509	2.39905	
	$\Delta r_{12}$	0.83088	0.64731	

The standard deviation  $\Delta r_1$  and  $\Delta r_{12}$  decrease when atomic number increase because decrease the distance between electrons and between electrons and nucleus. in addition, the largest value of  $\Delta r_1$  in 2p shell and smallest value in 1s shell for each system.

Table 5. The expectation values for all attraction, repulsion, kinetic and total energies of intra-shells for each system.

Shell	N <sup>+</sup>		O <sup>+2</sup>	
	$\langle V_{en} \rangle$	$\langle V_{ee} \rangle$	$\langle T \rangle$	$\langle E_T \rangle$
1s	$\langle V_{en} \rangle$	79.87884	91.80444	
	$\langle V_{ee} \rangle$	4.12789	4.74807	
	$\langle T \rangle$	75.75095	87.05637	
	$\langle E_T \rangle$	37.87548	43.52819	
2s	$\langle V_{en} \rangle$	13.69008	16.6626	
	$\langle V_{ee} \rangle$	0.72448	0.87655	
	$\langle T \rangle$	12.9656	15.78605	
	$\langle E_T \rangle$	6.4828	7.89302	
2p	$\langle V_{en} \rangle$	12.67164	15.82908	
	$\langle V_{ee} \rangle$	0.73785	0.92953	
	$\langle T \rangle$	11.93379	14.89955	
	$\langle E_T \rangle$	5.9669	7.44978	

Table 5 contained the results of expectation of energies which increase when atomic number increase. They have highest value in 1s shell and lowest value in 2p shell.

### 4. Conclusions

When to increase the atomic number, the one-particle distribution function, the inter-particle distribution function and the expectation values of energies are increased. These properties have highest values in 1s shell and lowest values in 2p shell. When  $r_1=0$  or  $\infty$  and  $r_{12}=0$  or  $\infty$ ,  $D(r_1)=0$  and  $f(r_{12})=0$  respectively. For expectation values  $\langle r_1^n \rangle$ ,  $\langle r_{12}^n \rangle$ , where  $n = -1$  increase when Z increase and the highest of  $\langle r_1^{-1} \rangle$  in 1s shell. While when

$n = 1,2$  the expectation values decrease when  $Z$  increase and lowest value in 1s shell.

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