

Energy and expectation values of excited states for Helium atom using Hartree–Fock approximation

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Abstract- Some radial atomic properties and excited states energies are obtained using two electron density function $D(r_1, r_2)$ to solve Hartree-Fock equations using Slater type orbitals for Helium atom (He-atom) in different excited states (1S2S, 1S3S, 1S4S, 1S5S). Radial expectation values for one electron $\langle r^{-1} \rangle$ and two electrons $\langle r_1^{-1} r_2^{-1} \rangle$, repulsion $\langle V_{ee} \rangle$, attraction $\langle V_{en} \rangle$, potential $\langle V \rangle$, kinetic $\langle T \rangle$, and Hartree-Fock energies are calculated using partitioning technique.

Keywords – Hartree-Fock-Roothaan method, Slater type orbitals, two electron density function, radial expectation values, Helium atom

I. INTRODUCTION

Roothaan Hartree Fock (RHF) method is one of the simplest approximations for calculations of various properties of multi electron of atomic and molecules systems not only for ground state but also for excited states [1]. Many literature reviews are addressed this subject [2-4]. In this study, one electron basis whose radial part is expanded in terms of Slater type orbitals for examined some atomic properties of He-atom in the excited states using Hartree Fock equations. In the Roothaan Hartree Fock or basis set expansion method, the Slater type orbitals (STO) defined as [5]

$$\chi_{nlm}(\xi, r) = \sum_{n} \frac{2\xi}{(2n+1)!} r^n \exp(-\xi r) Y_{lm}(\theta, \phi) \quad (1)$$

where, $Y_{lm}(\theta, \phi)$ = a spherical harmonics, $\xi > 0$ = the orbital exponent, n = a positive principal quantum number of (STO). The determination of nonlinear parameters n and ξ is very important for describing the atomic orbitals.

II. THEORY

Most of the physically properties of a multi electron system can be calculated from the two-particle reduced density matrix $\Gamma(r_1, r_2)$, without reference to the wavefunction Ψ . It contains all the necessary information to compute the energy and many properties of the atoms. It can be gained by integrating the spin and spatial coordinates of all electrons except two electrons (r_1, r_2) from the N -particle density matrix, so the two-electron reduced density matrix $\Gamma(r_1, r_2)$ given by [6, 7].

$$\Gamma(r_1, r_2) = \frac{1}{2} \int \Psi^2(r_1, r_2, \dots) dr_3 \dots dr_N \quad (2)$$

where (r, s) is combined space and spin variable with $s = \alpha, \beta$ and $n = 1, 2, \dots, N$

III. EXPECTATION VALUES

Expectation value for one-electron $\langle r^{-m} \rangle$ is determined by the following expression [8]

$$\langle r^{-m} \rangle = \int_0^\infty D(r) r^{-m} dr \quad (3)$$

where $m =$ integer number ($-2 \leq m \leq 2$), $D(r) =$ the one-electron radial density function which represents the probability density function to finding an electron at a distance between r_1 and $r_1 + dr_1$ from the coordinate origin (i.e nucleus). The single-electron radial density $D(r_1)$ is obtained from integration over two-electron radial density function $D(r_1, r_2)$ and defined as [9, 10].

$$D(r_1) = \int D(r_1, r_2) dr_2 \quad (4)$$

where $\Gamma(r_1, r_2)$ is the two-electron radial density function and represents the probability density that one electron is located at a radius r_1 and the other electron at a radius r_2 simultaneously. The two-electron radial density function is given by [11].

$$D(r_1, r_2) = \iint \Gamma(r_1, r_2) r_1^2 r_2^2 ds_1 ds_2 d\Omega_1 d\Omega_2 \tag{5}$$

$$d\Omega = \sin \theta d\theta d\phi$$

where Ω = the solid angle. Inter particle expectation value $\langle r_{12}^m \rangle$ is shown in Eq. 6 [12]

$$\langle r_{12}^m \rangle = \int_0^\infty f(r_{12}) r_{12}^m dr_{12} \tag{6}$$

where r_{12} represents the distance between two-electrons. $f(r_{12})$ = radial electron-electron distribution function, which describes the probability of finding two electrons separated by distance r_{12} from each other. Pair distribution function can be written as [13].

$$f(r_{12}) = \frac{1}{8\pi^2 r_{12}^2} \int_0^\infty \int_0^\infty \Gamma(r_1, r_2) r_1^2 r_2^2 dr_1 dr_2 \tag{7}$$

IV. EXPECTATION ENERGY VALUE $\langle E \rangle$

Hartree-Fock method satisfied the virial theorem. The virial theorem is necessary condition for the stationary state, the condition of the virial theorem is [14],

$$\langle E \rangle = 2\langle T \rangle \tag{8}$$

where $\langle E \rangle$ = the total expectation value of potential energy and $\langle T \rangle$ is the expectation value of kinetic energy. From the virial theorem find:

$$\langle E \rangle = \langle T \rangle + \langle V \rangle \tag{9}$$

$$\langle E \rangle = -\langle V \rangle = \frac{1}{2} \langle V \rangle \tag{10}$$

Expectation value of potential energy is proportion with the expectation values of $\langle r^{-1} \rangle$ and $\langle r^{-2} \rangle$, respectively [16].

$$\langle E \rangle = -\langle r^{-1} \rangle = \frac{1}{2} \langle r^{-2} \rangle \tag{11}$$

V. RESULTS AND DISCUSSION

In the present study, different excited states of He-atom are analyzed. The configurations (1S2S, 1S3S, 1S4S, 1S5S) states are examined using Hartree-Fock wave function. Table 1 shows the expectation values of one electron $\langle r^{-m} \rangle$, where m takes integer values (-2, -1, 1, 2) for K-shell to different excited states. Table 2 represents the expectation values for another electron in 2S, 3S, 4S, and 5S states. Table 3 summarizes the expectation values for inter electrons $\langle r_{12}^{-m} \rangle$.

Table 1: One particle expectation value r^m in K-shell of 1S state in different excited states for He-atom

states	r^2	r	r	r^2
1S2S	8.13006	2.02080	0.74772	0.81469
1S3S	8.05643	2.00882	0.75852	0.95634
1S4S	8.02208	2.00346	0.75816	1.02022
1S5S	8.01082	2.00170	0.75705	1.07832

Table 2: One particle expectation value r^m in different excited states for He-atom.

States	r^2	r	r	r^2
1S2S	0.08628	0.24583	04.78795	26.44061
1S3S	0.02967	0.11546	11.26221	144.09095
1S4S	0.01214	0.06430	21.04786	498.519449
1S5S	0.00608	0.04092	33.82797	1282.05952

Table 3: Inter particle expectation values r^m_2 for He-atom for different excited states.

states	r^2_2	r_2	r_2	r^2_2
1S2S	0.08061	0.24524	4.85022	27.25531
1S3S	0.02598	0.11533	11.533	145.04641
1S4S	0.01045	0.06425	21.06211	499.50842
1S5S	0.0052	0.04089	33.82096	1282.34489
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Fig.1 shows the one electron radial density function $D(r)$ as a function of r_1 for He-atom in 1S2S, 1S3S, 1S4S, and 1S5S states, which represents the probability density of finding the one electron in the 1S state for these states, these probabilities are close to each other. Fig. 2 illustrates the one electron radial density function $D(r)$ for other electron in 2S, 3S, 4S, and 5S states separated by distance r_1 from the nucleus. There is one peak (the most probability of finding the electron) for 2S state, while there are two peaks in excited 3S state. The 1st peak represents the most probability of finding an electron in the 2S state with the small probability. Whereas, the 2nd peak represents the most probability of finding an electron in the 3S state with the larger probability. 4S state shows 3 peaks (1st, 2nd, and 3rd peaks). These peaks represent the small probability of finding an electron in the 2S, 3S, and 4S, respectively. The 2nd peak larger than the 1st peak and the 3rd peak larger than 1st and 2nd peaks. The similar conclusion is obtained when examined the 5S state, which it has 4 peaks.

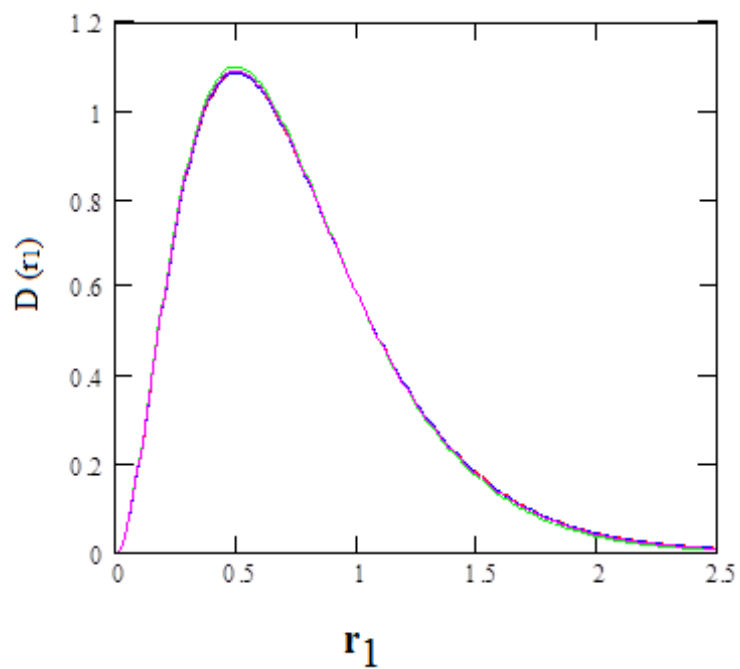


Figure 1. One-particle radial density function for one electron in the 1S state for excited He-atom.

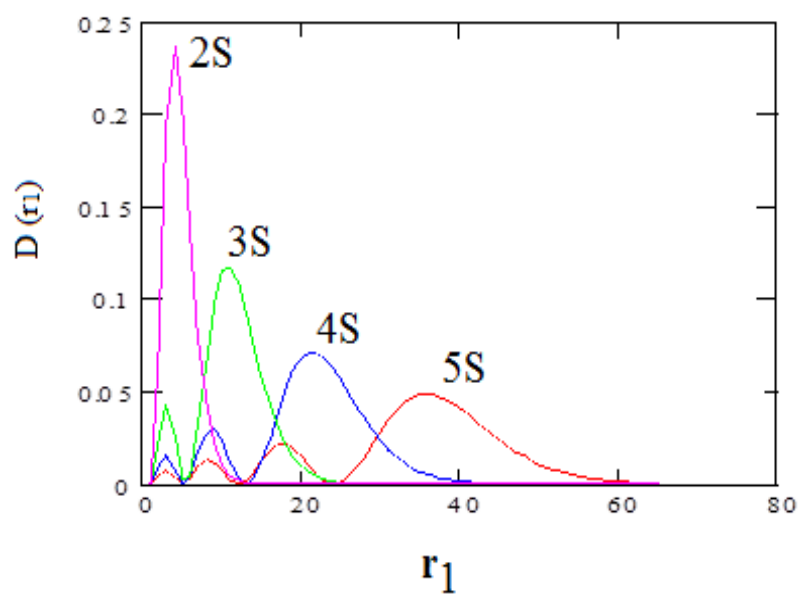


Figure 2. One-particle radial density function for the second electron in the (2S, 3S, 4S, 5S) states for excited He-atom.

Table 3 showed the results of expectation values of attraction $\langle V_{ee} \rangle$, repulsion $\langle V_{ee} \rangle$, expectation values of potential $\langle V \rangle$, kinetic $\langle T \rangle$, and Hartree-Fock E energies of He-atom for different excited states.

Table 3: Repulsion $\langle V_{ee} \rangle$, attraction $\langle V_{ee} \rangle$, potential $\langle V \rangle$, kinetic $\langle T \rangle$, and Hartree-Fock E energies of He-atom for different excited states

States	$\langle V_{ee} \rangle$	$\langle V_{ee} \rangle$	$\langle V \rangle$	$\langle T \rangle$	E
1S2S	4.53328	0.24524	4.28804	2.14402	2.14402
1S3S	4.24860	0.11533	4.13327	2.066635	2.066635
1S4S	4.13544	0.06425	4.07119	2.035595	2.035595
1S5S	4.08404	0.04089	4.04315	2.021575	2.021575

VI. CONCLUSION

This study shows that the radial expectation values for one electron and two electrons effect on different excited states for He-atom in the Hartree-Fock method. There is one peak for 2S state, while there are two peaks in excited 3S state. The first peak represents the most probability of finding an electron in the 2S state with the small probability. Whereas, the second peak is represents the most probability of finding an electron in the 3S state with the larger probability. The 4S state shows 3 peaks (1st, 2nd, and 3rd peaks) and these peaks represent the small probability of finding an electron in the 2S, 3S, and 4S, respectively, the 2nd peak larger than 1st peak and the third peak larger than those two peaks. It concluded that the 5S state also has 4 peaks.

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