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## Excited states of $S^{+14}$ ion (1S nS) in singlet and triplet states ( $^1S$ , $^3S$ ) by Hartree–Fock method

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**Abstract:** The excited states of  $S^{+14}$  ion in (1SnS) states of n (2, 3, 4 and 5) are studied in singlet and triplet states ( $^1S$ ,  $^3S$ ). This study focuses on studying expectation values of energies (potential ( $V$ ), kinetic ( $T$ ), attraction ( $V_{en}$ ), repulsion ( $V_{ee}$ ) and total energy ( $E$ )) for  $S^{+14}$  ion in the states (1s 2s, 1s 3s, 1s 4s, 1s 5s). The study also examines some radial atomic properties as expectation values for one electron  $r^m$ , inter particle expectation value  $r^m_{12}$  and analyses one-particle radial density functions  $D(r_1)$  using Hartree–Fock wave function for these systems. This system consists of two electrons, one electron is in (1S) state (K-shell) and the second electron is in shells (L, M, N, O) (nS) states. In this paper the atomic units are used and all the atomic properties are normalised to unity. All the results were calculated by the software (MATHCAD 2001i).

**Keywords:** Hartree–Fock; orbitals; excited states; slater determinant.

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## 1 Introduction

Hartree–Fock (HF) technique is an approximation method to solve Schrodinger's equation and determine wave function and the properties of more electron systems. This method is the simplest approximation theory to solve the solution of ground state and excited states for these systems.

Many literature reviews have included this subject (Chang et al., 2010). Within the HF approximation, the wave function is approximated by a Slater determinant, and anti-symmetrised product of one-electron wave functions. This method indicates that inter-electron Coulomb repulsion accounts for an average integration of the repulsion term, i.e. the interactions of the electron with the other electrons are accounted for as the interaction of this electron with an average field induced by others.

The one-electron orbitals  $\phi_i$  contain a radial function  $R_{nl}(r)$ , a spherical harmonic  $Y_{lm}(\theta, \phi)$  and a spin function  $\sigma_{m_s}(s)$  as (Hudson et al., 2009)

$$\phi = R_{nl}(r)Y_{lm}(\theta, \phi)\sigma_{m_s}(s) \quad (1)$$

The frequently used basis functions for atomic calculations are Slater Type Orbitals (STO) which are defined as (Dosh and AL-Khafaji, 2013),

$$\chi_{nlm_i}(\xi, r) = R_{nl}(\xi, r)Y_{lm_i}(\theta, \phi) \quad (2)$$

$$\chi_{nlm_i}(\xi, r) = \sum_i \frac{(2\xi_i)^{n_i + \frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} r^{n_i-1} \exp(-\xi_i r) Y_{lm_i}(\theta, \phi) \quad (3)$$

The radial part is:

$$R_{nl}(\xi, r) = (2\xi)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} \exp(-\xi r) \quad (4)$$

Here,  $\xi_i > 0$  is the (orbital exponent). The quantity  $n$  is a principal quantum number of (STO).

## 2 Theory

By using 'two-particle density matrix'  $\Gamma(x_m, x_n)$ , we can estimate the properties of electronic structure of more electron systems in a state using wave function  $\psi(x_1, x_2, \dots, x_N)$  because the (two-particle density matrix)  $\Gamma(x_m, x_n)$  has all the essential information to estimate the properties and energy of more electron systems, and is written as (Oyamada et al., 2010)

$$\Gamma(x_1, x_2) = \frac{N(N-1)}{2} \int \dots \int |\psi(x_1, x_2, \dots, x_N)|^2 dx_3, \dots, dx_N \quad (5)$$

where  $N$  is the number of electrons and  $x_i = (r_i, s_i)$  are space and spin variables  $s = \alpha$  (spin up) and  $\beta$  = (spin down).  $\Gamma(x_1, x_2)$  provides the probability that one

electron will be found at  $(x_1)$  and another electron will be found at  $(x_2)$  of  $N$  electrons.  $\frac{N(N-1)}{2}$  denotes the number of electron pairs.

### 3 Expectation values of energy

Expectation value of energy  $E$  is given by the equation (Dosh et al., 2018)

$$E = T + V \quad (6)$$

where  $T$  is kinetic energy and  $V$  is the potential energy given by

$$V = V_{en} + V_{ee} \quad (7)$$

$V_{en}$  is the attraction energy between an electron and nucleus given by the equation (Dosh and Abojassim, 2019).

$$V_{en} = -Zr_1^{-1} \quad (8)$$

$$V_{ee} = r_{12}^{-1} \quad (9)$$

$r_1^{-1}$  represents 'one electron expectation value' and it is determined by Trier et al. (2019)

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

$m$  is integer number,  $r_1$  is the distance between an electron and nucleus,  $D(r_1)$  represents (one-electron radial density function) which is given by the equation (Dosh, 2015)

$$D(r_1) = \int_0^{\infty} D(r_1, r_2) dr_2 \quad (11)$$

$D(r_1, r_2)$  denotes (two electron radial density function) that describes the probability density in which one electron is found in the radius  $r_1$  and the other electron is found in the radius  $r_2$  instantaneously, and is defined by

$$D(r_1, r_2) = \int \int \Gamma(r_1, r_2) r_1^2 r_2^2 ds_1 ds_2 d\Omega_1 d\Omega_2 \quad (12)$$

$$d\Omega_i = \sin \theta_i d\theta_i d\phi_i$$

$\Omega_i$  is (the solid angle),  $\langle V_{ee} \rangle$  is (repulsion energy) between electron-electron

$\langle r_{12}^{-1} \rangle$  is an (inter particle expectation value) given by the relation

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

$f(r_{12})$  represents radial electron-electron distribution function and  $r_{12}$  represents the distance between two-electrons.

'Nuclear magnetic shielding constant'  $\sigma_d$  :

'Nuclear magnetic shielding constant' is evaluated by the equation (Ruqaya et al., 2016).

$$\sigma_d = \frac{1}{3} \alpha' \psi \left| \sum_{i=1}^n (r_i)^{-1} \right| \psi \quad (14)$$

( $\alpha'$ ) is the fine structure constant  $\alpha' = \frac{1}{c}$  where  $c$  is speed of light in atomic unit.

The diamagnetic susceptibility  $\chi_d$  :

The diamagnetic susceptibility is determined by the equation (King and Dressel, 1989)

$$\chi_d = -\frac{r^2}{6c^2} \quad (15)$$

Correlation coefficients  $\tau_r$  :

The correlation coefficients  $\tau_r$  are like those used in classical statistics. They are determined by the relation (Gálvez et al., 2003).

$$\tau_r = \frac{r_1^1 r_2^1 - r_1^{12}}{r_1^2 - r_1^{12}} \quad (16)$$

## 4 Results

By using Hartree–Fock wave function and Slater type orbitals, the excited states of  $S^{+14}$  ion were studied in the state (1SnS) where  $n = 2, 3, 4$  and  $5$  in singlet state ( $^1S$ ) and triplet state ( $^3S$ ). This ion consists of two electrons, one electron is in ( $^1S$ ) state (K-shell) and the second electron is in (L, M, N, O) shells (nS) state. The results between the singlet state ( $^1S$ ) and triplet state ( $^3S$ ) of this system were compared. Table 1 shows the expectation values for the electron in ( $^1S$ ) state (K-shell)  $\langle r_1^m \rangle$ , where  $m$  takes the values  $(-2, -1, 1, 2)$  for the excited states. It is noted that the results of the singlet state ( $^1S$ ) are higher than triplet state ( $^3S$ ) and when  $m$  takes negative values ( $m = -1, -2$ ) the expectation values decrease when ( $n$ ) increases. When  $m = 2$  the expectation values increase when ( $n$ ) increases in the singlet state ( $^1S$ ) while in the triplet state ( $^3S$ ) the same is seen for all the excited states. When  $m = 1$  the results of the triplet state ( $^3S$ ) are steady for all the excited states.

Table 2 displays the expectation values for the second electron in (ns) states for different excited states. It is noticed in this table that when  $m$  takes negative values ( $m = -1, -2$ ) the results of triplet state ( $^3S$ ) are higher than the singlet state ( $^1S$ ) and when  $m=1$ , the results of singlet state ( $^1S$ ) are higher than the triplet state ( $^3S$ ). When  $m = 2$ , the results of the singlet state ( $^1S$ ) are higher than the triplet state ( $^3S$ ) except in (1s2s). It is also found that when  $m = -1, -2$ , the expectation values decrease when ( $n$ ) increases. When  $m = 1$  (which represents the distance between the electron and the nucleus) the expectation values increase when ( $n$ ) increases, because the electron pulls away from the nucleus. When  $m = 2$  the expectation values increase when ( $n$ ) increases.

**Table 1** One electron expectation values  $\langle r_1^m \rangle$  in K-shell (1s) state for  $S^{+14}$  ion

Excited state	State	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$
1s 2s	$^1S$	554.46784	16.77628	0.09245	0.01397
	$^3S$	512.43056	16.00716	0.09375	0.011719
1s 3s	$^1S$	522.28586	16.18003	0.09652	0.01685
	$^3S$	512.09296	16.001417	0.09375	0.011719
1s 4s	$^1S$	515.97948	16.06902	0.096165	0.0177
	$^3S$	512.0348	16.00051	0.09375	0.011719
1s 5s	$^1S$	513.95264	16.03374	0.095756	0.01859
	$^3S$	512.01669	16.00024	0.09375	0.011719

**Table 2** One electron expectation values  $\langle r_1^m \rangle$  in (ns) states for  $S^{+14}$  ion

Excited state	State	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$
1s 2s	$^1S$	15.37178	3.02982	0.39041	0.17416
	$^3S$	57.55775	3.80489	0.38854	0.17598
1s 3s	$^1S$	6.639845	1.500071	0.883216	0.886093
	$^3S$	16.84219	1.68263	0.8827	0.88471
1s 4s	$^1S$	3.126251	0.873755	1.579982	2.810537
	$^3S$	7.06088	0.94419	1.57689	2.79711
1s 5s	$^1S$	1.67542	0.56887	2.47661	6.87327
	$^3S$	3.60136	0.60341	2.47108	6.83856

Table 3 explains the expectation values of inter-particle  $\langle r_{12}^m \rangle$  for  $S^{+14}$  ion for different excited states. It is observed that when ( $m$ ) takes negative values ( $m = -1, -2$ ) the results of expectation values in the triplet state ( $^3S$ ) are higher than singlet state ( $^1S$ ) where  $\langle r_{12}^{-1} \rangle$  value represents the repulsion energy between two electrons. It means that the repulsion energy in the triplet state ( $^3S$ ) is higher than the singlet state ( $^1S$ ). When ( $m$ ) takes positive values ( $m = 1, 2$ ) the expectation values in the singlet state ( $^1S$ ) are higher than triplet state ( $^3S$ ). Also, it is noted that  $\langle r_{12}^1 \rangle$  (which represents the distance between two electrons) in singlet state ( $^1S$ ) is higher than triplet state ( $^3S$ ). When ( $m = -1, -2$ ), the expectation values decrease when ( $n$ ) increases and when ( $m = 1, 2$ ) the expectation values increase as ( $n$ ) increases. The distance  $\langle r_{12}^1 \rangle$  increases when ( $n$ ) increases, because the distance between two electrons becomes larger.

**Table 3** Inter particle expectation values  $\langle r_{12}^m \rangle$  for  $S^{+14}$  ion for different excited states. Atomic units are used

Excited state	State	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$
1s 2s	$^1S$	12.9642	2.99421	0.40253	0.18813
	$^3S$	31.96505	3.55034	0.39888	0.18764
1s 3s	$^1S$	4.77603	1.48317	0.8892	0.90294
	$^3S$	9.21407	1.60187	0.88813	0.89643
1s 4s	$^1S$	2.14591	0.86514	1.5832	2.82823
	$^3S$	3.84568	0.90959	1.58013	2.80883
1s 5s	$^1S$	1.12796	0.56409	2.47857	6.89185
	$^3S$	1.95768	0.5856	2.47321	6.85027

Table 4 lists the expectation values of potential energy  $\langle V \rangle$ , expectation values of attraction energy  $\langle V_{en} \rangle$ , expectation values of repulsion energy  $\langle V_{ee} \rangle$ , expectation values of kinetic energy  $\langle T \rangle$  and expectation values of Hartree–Fock energy  $\langle E \rangle$ . The table indicates that the potential energy expectation values  $\langle V \rangle$ , kinetic energy expectation values  $\langle T \rangle$ , and expectation values of Hartree–Fock energy  $\langle E \rangle$  in singlet state ( $^1S$ ) are higher than in triplet state ( $^3S$ ). This means that the triplet state ( $^3S$ ) is more stable than the singlet state ( $^1S$ ). Also, it is noticed these energies decrease as ( $n$ ) increases. The expectation values of repulsion energy  $\langle V_{ee} \rangle$  between two electrons for the triplet state ( $^3S$ ) are higher than the singlet the state ( $^1S$ ) which means that the electrons with parallel spin ( $^3S$ ) (of the same spin) has repulsion energy greater than the electrons with anti-parallel spin ( $^1S$ ). Also, it is observed that  $\langle V_{ee} \rangle$  decreases by increasing ( $n$ ), because the distance between two electrons becomes longer. The expectation value of attraction energy  $V_{en}$  for 1s between the electron in k-shell and the nucleus of different configurations states in the singlet state is higher than the triplet state. Furthermore, when ( $n$ ) increases, the  $V_{en}$  for 1s decreases. The results of attraction energy expectation values  $\langle V_{en} \rangle$  for ( $ns$ ) between the second electron in (L, M, N, O) shells ( $ns$ ) of excited states and the nucleus of ( $^3S$ ) state is greater than ( $^1S$ ) state. It is observed that when ( $n$ ) increases,  $\langle V_{en} \rangle$  for ( $ns$ ) decreases, because the separation distance between electron and the nucleus becomes larger when the electron translates to high excited state leading to decreasing the attraction energy.

**Table 4** The expectation values of (potential energy  $\langle V \rangle$ ), kinetic energy  $\langle T \rangle$ , Hartree–Fock energy  $\langle E \rangle$ , repulsion energy  $\langle V_{ee} \rangle$  and attraction energy  $\langle V_{en} \rangle$  for  $S^{+14}$  ion in its excited state in singlet state ( $^1S$ ) and triplet state ( $^3S$ )

Excited state	State	$-V$	$\langle T \rangle$	$-E_{HF}$	$V_{ee}$	$-V_{en}$ for $1s$	$-V_{en}$ for $ns$
1s 2s	1s	313.90343	156.95171	156.95171	2.99421	268.42048	48.47712
	3s	313.44235	156.721175	156.721175	3.55034	256.11456	56.80544
1s 3s	1s	281.39843	140.699217	140.699217	1.48317	258.88048	24.001136
	3s	281.34298	140.67149	140.67149	1.60187	256.022672	26.92208
1s 4s	1s	270.21999	135.10999	135.10999	0.86514	257.10432	13.98008
	3s	270.205499	135.10275	135.10275	0.90959	256.00816	15.10704
1s 5s	1s	265.07943	132.53971	132.53971	0.56409	256.53984	9.10192
	3s	265.072859	132.536429	132.536429	0.5856	256.00384	9.65456

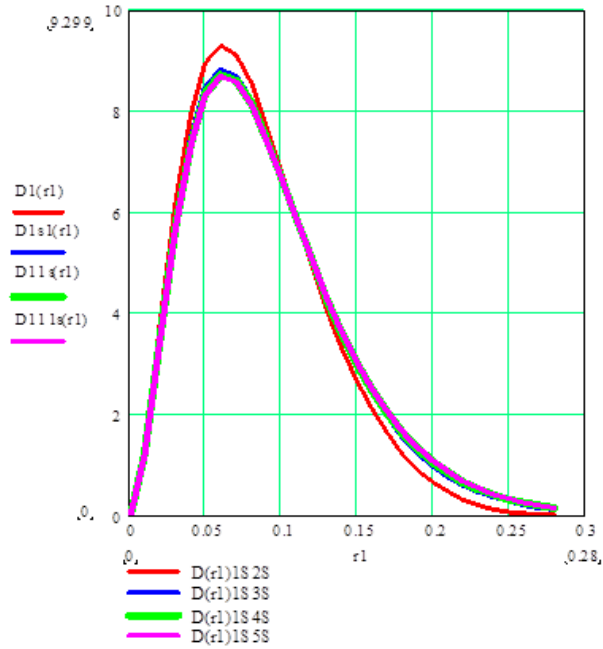
**Table 5** Shows the nuclear magnetic shielding constant  $\sigma_d$ , the diamagnetic susceptibility  $\chi_d$ , and the radial correlation coefficient  $\tau_r$  for  $S^{+14}$  ion in singlet state ( $^1S$ ) and triplet state ( $^3S$ )

Excited state	State	$\sigma_d \times 10^{-5}$	$\chi_d \times 10^{-6}$	$-\tau_r$
1s 2s	1s	5.37807	1.54569	5.31558
	3s	6.75384	1.56141	4.54212
1s 3s	1s	2.66269	7.86427	6.53001
	3s	2.98674	7.85202	6.59509
1s 4s	1s	1.55095	24.9441	7.44978
	3s	1.67598	24.825	7.53144
1s 5s	1s	1.00977	61.0018	7.96538
	3s	1.07109	60.6938	8.02175

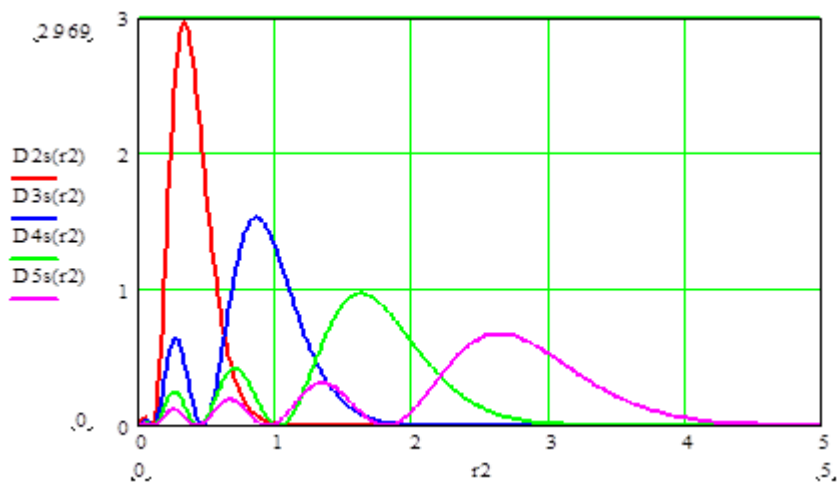
## 5 Discussion

It is indicated in Figures 1 and 3 that  $D(r_1)$  (which symbolises the probability density to detect the first electron in (K-shell) (1S) state) is convergent for all studied excited states. Meanwhile, Figures 2 and 4 show that  $D(r_1)$  (which shows the probability density to detect the second electron in state ( $ns$ )) has one peak in state (2S), two peaks in state (3S), three peaks in state (4S) and four peaks in state (5S). We can also notice in  $r = 0$ ,  $D(r_1)$  equals zero and when  $r = \infty$ ,  $D(r_1)$  equals zero too. This means that the electron cannot be found in the nucleus ( $r = 0, D(r_1) = 0$ ) and the electron cannot be found outside the atom ( $r = \infty, D(r_1) = 0$ ).

**Figure 1** One-particle radial density functions  $D(r_1)$  in the K-shell (1S) state excited for  $S^{+14}$  ion in singlet state ( $^1S$ )

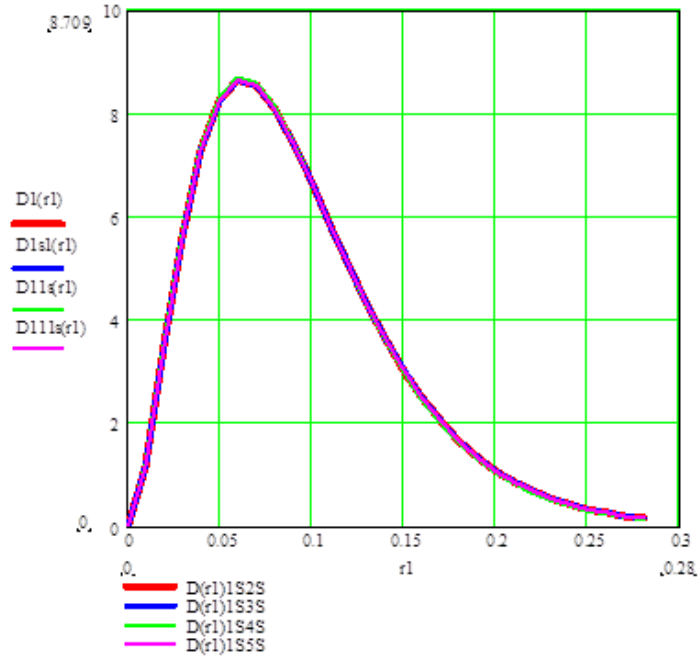


**Figure 2** One-particle radial density functions  $D(r_1)$  in the (2S, 3S, 4S, 5S) states for excited  $S^{+14}$  ion in singlet state ( $^1S$ )

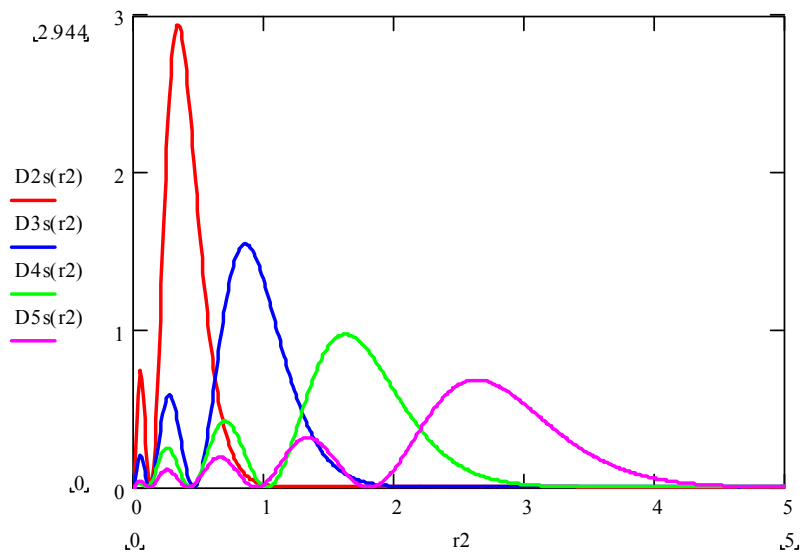




**Figure 3** One-particle radial density functions  $D(r_1)$  in the (2S, 3S, 4S, 5S) states for excited  $S^{+14}$  ion in triplet state ( $^3S$ )



**Figure 4** One-particle radial density functions  $D(r_1)$  in the (2S, 3S, 4S, 5S) states for excited  $S^{+14}$  ion in triplet state ( $^3S$ )



## 6 Conclusion

This paper studied  $S^{+14}$  ion in selected excited states (1s2s, 1s3s, 1s4s, 1s5s) in the singlet state ( $^1S$ ) and triplet state ( $^3S$ ) and estimated the expectation values for (potential, repulsion, attraction, kinetic and Hartree–Fock) energies. The results between ( $^1S$ ) and ( $^3S$ ) states were compared and it was found that the total energy for ( $^1S$ ) is greater than that in ( $^3S$ ), which means that the triplet state ( $^3S$ ) is more stable than the singlet state ( $^1S$ ). Also in this study we calculated and examined one electron expectation value  $r_1^m$ , and inter electron expectation values  $\langle r_{12}^m \rangle$  for the studied states using (Mathcad 2001i) program and all the results were in atomic unit.

## References

- Chang, J.L., Huang, S.T., Chen, C.C., Yang, T.T., Hsiao, C.C., Lu, H.Y. and Lee, C.L. (2010) ‘Theoretical calculations of  $C_{2v}$  excited states of  $SO_2^+$ ’, *Chemical Physics Letters*, Vol. 486, Nos. 1–3, pp.12–15.
- Dosh, R.J. (2015) ‘Energy and expectation values of excited states for Helium atom using Hartree–Fock approximation’, *International Journal of Latest Trends in Engineering and Technology*, Vol. 5, No. 1.
- Dosh, R.J. and Abojassim, A.A. (2019) ‘Excited states of  $^+CL$  ion using Hartree-Fock wave function’, *International Journal of Civil Engineering and Technology*, Vol. 10, No. 5, pp.506–511.
- Dosh, R.J. and AL-Khafaji, Q.S. (2013) ‘Study of energy and some atomic properties for electronic shells at ground state of three electron systems by analysis Hartree-Fock-Roothaan wavefunction’, *Journal of Kufa-Physics*, Vol. 5, No. 1.
- Dosh, R.J., Hkadhim, S., Abojassim, A.A. and Munim, R. (2018) ‘Energy and some atomic properties for excited state of AR ion using Hartree-Fock method’, *International Journal of Mechanical and Production Engineering Research and Development*, Vol. 8, No. 6, pp.827–830.
- Gálvez, F.J., Buendia, E. and Sarsa, A. (2003) ‘Excited states of beryllium isoelectronic series from explicitly correlated wave functions’, *The Journal of Chemical Physics*, Vol. 118, No. 15, pp.6858–6867.
- Hudson, C.E., Ramsbottom, C.A., Norrington, P.H. and Scott, M.P. (2009) ‘Breit-Pauli R-matrix calculation of fine-structure effective collision strengths for the electron impact excitation of  $Mg V$ ’, *Astronomy & Astrophysics*, Vol. 494, No. 2, pp.729–737.
- King, F.W. and Dressel, P.R. (1989) ‘Compact expressions for the radial electronic density functions for the 2 S states of three-electron systems’, *The Journal of Chemical Physics*, Vol. 90, No. 11, pp.6449–6462.
- Oyamada, T., Hongo, K., Kawazoe, Y. and Yasuhara, H. (2010) ‘Unified interpretation of Hund’s first and second rules for 2 p and 3 p atoms’, *The Journal of Chemical Physics*, Vol. 133, No. 16, 164113.
- Rugaya, J.H., Abojassim, A.A. and Najam, L. (2016) ‘Radial atomic properties of excited states for beryllium atom (1s 2 2s ns)(s)’, *American Journal of Modern Energy*, Vol. 2, No. 1, pp.1–4.
- Trier, S.H., Kadhim, S.A., Hamza, Z.M. and AL-Khafaji, Q.S. (2019, September) ‘Estimation Hartree-Fock’s energy for the carbon atom and the ions are similar’, *Journal of Physics: Conference Series*, Vol. 1294, No. 2, 022017.