

Calculation the Energy of the intra-shells for the Ground and minimum Excited States of Carbon Atom.

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Abstract

In the present study, the atomic properties of carbon atom for ground state ³P as well as the minimum excited states (¹D and ¹S) for intra-shells (1s, 2s and 2p) have been calculated through the use of Hartree-Fock wave functions. These include radial density function, one-particle of one-particle and expectation values with inter-particle, density functions with inter-particle, expectation values of energies, the electronic density at nucleus and the nuclear magnetic shielding constant. Each plot in the present study has been normalized to unity. The results have been collected statistically through the use of 'MathCad 14' and the atomic properties have been measured in atomic units.

1 Introduction

The actual beginning of quantum mechanics with Erwin Schrodinger in 1926 which produced wave mechanics and Schrodinger equation to give a good explanation for atomic and subatomic particle's motion. Schrodinger regarded the electron as having wave properties and the equation governs the electron is Schrodinger equation. Wave mechanics and Schrodinger equation give a large motivation to know the atomic structure. The one-particle problem (i.e. hydrogen atom) can get the exact energy and wave function but when the electrons become ≥ 2 the problem becomes difficult and when electrons increase, the problem becomes impossible to be solved (assumption the nucleus is a point charge with infinite mass). Because the electrons are indistinguishable particle (negates the existence of trajectories) [1]. The total wave function depends on all coordinate of electrons, so there will be a huge number of variables 10^{3N} where N number of electrons such as for iron N=26, the total wave function contains 10^{78} variables, so Schrodinger equation should be solved by a good method that uses approximation [2]. One of the best approximation methods used for this purpose is Hartree-Fock Self-Consistent Field (HF-SCF), the fundamental point of the (HF-SCF) is through having a guess initially at the orbitals of spin, the average fields shown through every electron could be calculated and get the Schrodinger equation solved for a new group of orbitals of spin. Having such new orbitals, a new field could be obtained and conduct the procedures again till self-consistency is achieved till the fields have no longer changes [3].

2 Methods

In multi-electrons system to solve Schrodinger equation, one has to find the Hamiltonian operator which depends on wave function as Schrodinger equation

$$\hat{H}\psi_i = E_i \psi_i \quad (1)$$

As \hat{H} represents Hamiltonian operator, E refers to eigenvalue while ψ_i remarks the wave function. In the same time, the wave function depends on Hamiltonian operator "problem". Hartree in 1927 produced approximation method to solve this "problem" by following the procedure: every electron has movement in the possible field of the nucleus plus the N-1 of the rest of electrons. This indicates that the he electrons are moving independently. The total wave function is set as [4].

$$\Psi_{(r_1, r_2, \dots, r_N)} = \varphi_1(r_1) \varphi_2(r_2) \dots \varphi_N(r_N) = \prod_{i=1}^N \varphi_i(r_i) \quad (2)$$

Where r_i represents spatial coordinate to electrons. Equation (2) does not obey the Pauli exclusion and it does not take into account the antisymmetric wavefunctions. Fock does this.

$$\Psi_{HF(x_1, x_2, \dots, x_N)} = \hat{A} \prod_{i=1}^N \varphi_i(x_i) \quad (3)$$

Where x_i are spin orbitals contain four quantum number (n, l, m_l, m_s) and four coordinate (r, θ, ϕ, s) for single electron, s is spin of electrons. \hat{A} is antisymmetric operator or antisymmetrizer, written as [5].

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_p (-1)^p \hat{P} \quad (4)$$

Where \hat{P} is an exchange operator or permutations operator in relation to interchange of the electron coordinates i as well as j. The anti-symmetry of eigenfunction can be written [6].

$\hat{P}\psi = (-1)^p \psi$ (5) Where $(-1)^p = \pm 1$ for even or odd permutations.

The whole function of N-electron wave made up as the product that characterized as being anti-symmetrized to spin orbital written as Slater determinant [7].

$$\Psi_{HF}(x_1, x_2, \dots, x_N) = (N!)^{-\frac{1}{2}} \begin{vmatrix} \varphi_1(x_1) & \dots & \varphi_j(x_1) \\ \vdots & \ddots & \vdots \\ \varphi_1(x_N) & \dots & \varphi_j(x_N) \end{vmatrix} \quad (6)$$

Slater has set the basis that is composed of a group of functions so called "slater-type orbitals" (STO's), that are as follow [8].

$$\gamma_{nlm}(r, \theta, \phi) = N r^{n-1} \exp(-\xi r) Y_{l,ml}(\theta, \phi) \quad (7)$$

Where N is normalized factor and equal

$$N = \frac{(2\xi)^{n+\frac{1}{2}}}{((2n)!)^{\frac{1}{2}}} \quad (8) \quad \text{As } n \text{ refers to principle quantum}$$

number, r refers to the space between the electron and atomic nucleus, $Y_{l,ml}$ indicates the spherical harmonic, while (ξ) represents the orbital exponent. One could describe the Hartree-Fock spin orbitals as it indicates the linear combinations of slater orbitals from function known as basis-functions set as [9]

$$\varphi_{HF} = \sum_{i=0}^k c_i \gamma_i \quad (9)$$

Where c_i indicates the constant coefficient and γ_i refers to the slater orbitals. From equation (9) the linear combination of slater orbitals become

$$\varphi_{HF} = \sum_{i=0}^k c_i \frac{(2\xi_i)^{n+\frac{1}{2}}}{((2n_i)!)^{\frac{1}{2}}} r^{n_i-1} \exp(-\xi_i r) Y_{l,ml}(\theta, \phi) \quad (10)$$

1. The atomic properties

3.1: The density of two-particles $\Gamma(x_m, x_n)$

It has every important information that is required to conduct calculation to the energy as well as several properties of the atom [10]. Written as

$$\Gamma_{HF}(x_m, x_n) = \frac{N(N-1)}{N} \iint |\psi(x_m, x_n, x_p, \dots, x_q)|^2 dx_p \dots dx_q \quad (11)$$

Where x_n indicates the combined space as well as the spin coordinate of electron n and $dx_p \dots dx_q$ refers to the integration summation over every N -electron but m while n . $\frac{N(N-1)}{N}$ represents the electron pairs' number, which can be obtained by the integration of the second-order reduced density function.

3.2: Radial Density function $D(r_1, r_2)$ of Two-Particle

The probability density that is related to find the electron 1 at r_1 as well as electron 2 at r_2 from simultaneous nucleus is set as [11]

$$D(r_1, r_2) = \iint \Gamma(r_1, r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 d\sigma_1 d\sigma_2 \quad (12)$$

3.3 Radial density Function $D(r_1)$ of One-Particle Radial Density

The probability density functions that are related with having certain electron at a distance r_1 as well as $r_1 + dr_1$ from the coordinated origins (nucleus) formulated in [12]

$$D(r_1) = \int_0^\infty D(r_1, r_2) dr_2 \quad (13)$$

3.4: expectation value $\langle r_1^n \rangle$

of One-particle

One could calculate it by having the below formula [13]

$$\langle r_1^n \rangle = \int_0^\infty r_1^n D(r_1) dr_1 \quad (14)$$

3.5: Standard deviation Δr_1

It is differentiated from the expectation value and set as [14]

$$\Delta r_1 = [\langle r_1^2 \rangle - \langle r_1 \rangle^2]^{1/2} \quad (15)$$

3.6: inter-particle distribution functions $f(r_{12})$

This refers to the probable density functions of having the electron 1 and electron 2 at the distance from r_{12} to $r_{12} + dr_{12}$ formulated as [15]

$$f(r_{12}) = \int \Gamma(r_1, r_2) dr_2 dr_1 \quad (16)$$

3.7: inter-particle expectation value $\langle r_{12}^n \rangle$

This is set through [16]

$$\langle r_{12}^n \rangle = \int_0^\infty r_{12}^n f(r_{12}) dr_{12} \quad (17)$$

3.8: Standard deviation Δr_{12}

It is defined as [17].

$$\Delta r_{12} = [\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2]^{1/2} \quad (18)$$

3.9: The expectation value of energies

From virial theorem, its expectation values for whole energy of its system are associated with the expectation value of potentially given energy [18].

$$\langle E_T \rangle = \frac{1}{2} \langle V_T \rangle = -\langle T \rangle \quad (19)$$

Where E_T is the intra-shells total energy. The intra-shells expectation value potential energy can be written as

$$\langle V_T \rangle = -\langle V_{en} \rangle + \langle V_{ee} \rangle \quad (20)$$

Where $\langle V_{en} \rangle$ and $\langle V_{ee} \rangle$ both indicate energies in which the former represent the nuclear attraction energy of the electron while the latter refers to inter-electronic repulsion one which is written as [19].

$$\langle V_T \rangle = -Z \langle r_1^{-1} \rangle + \langle r_{12}^{-1} \rangle \quad (21)$$

3.10: Electronic Density at Nucleus $\rho(0)$

It is written as [20]

$$\rho(0) = \left[\frac{D(r_1)}{4\pi r_1^2} \right]_{r_1 \rightarrow 0} \quad (22)$$

3.11: Nuclear Magnetic Shielding Constant σ_d

It is determined by the equation [21].

$$\sigma_d = \frac{1}{3} \alpha^2 \langle \psi | \sum_{i=1}^N \langle r_i \rangle^{-1} | \psi \rangle \quad (23)$$

Where α is the fine structure constant and r_i represents the distance from the nucleus to the electron (i).

3 Results and Discussion

Tables I and II contain the results of maximum values of $D(r_1)$ and the maximum values of $f(r_{12})$ respectively. The maximum values of $D(r_1)$ and $f(r_{12})$ in 1s shell and minimum values in 2p shell for three states as in figure (1), (2) because the probability of finding the electrons increases when the shell close to nucleus. Also, the maximum values of $D(r_1)$ and $f(r_{12})$ for 1s and 2s shells in 1S state and minimum value in 3P state, while for 2p shell vice versa that is due to Hund's first and second rules. As in figure (1) there are two peaks in 2s shell, the first one indicates the possibility to find the electron in 1s shell for small period of time because of penetration phenomenon while the other one refers to the possibility to find an electron in 2s shell. In addition, when $r_1=0$ or ∞ , $D(r_1)=0$, that means that the possibility to find the electron in 1s shell for small period of time is because of penetration phenomenon while the other one refers to the possibility to find the electron in 2s shell. In addition, when $r_1=0$ or ∞ , $D(r_1)=0$, that means that the possibility to find the electron within the nucleus or away equals zero. in figure (2) when $r_{12}=0$ or ∞ , $f(r_{12})=0$ which indicates that the possibility to find two electrons in one location or separately equals zero. Tables III and IV contain the results of $\langle r_1^n \rangle$ and $\langle r_{12}^n \rangle$ standard deviation and expectation values for three states. If $n = -1$ indicates the maximum value of expectation values in 1s shell and minimum value in 2p shell, while for $n = 1, 2$ vice versa because the expectation value $\langle r_1^n \rangle$ represents the distance between electrons and nucleus and the expectation value $\langle r_{12}^n \rangle$ represents the distance between electrons. The standard deviation Δr_1 and Δr_{12} have the maximum values in 2p shell and minimum values in 1s shell due to large distance from nucleus give maximum deviation. The maximum values of $\langle r_1^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$ for 1s, 2s in 1S state and the minimum values of $\langle r_1^{-1} \rangle$ in 3P state, for 2p shell and vice versa. When $n = 1, 2$ the maximum values for 1s, 2s shells in 3P state, for 2p shell vice versa that are compatible with the interpretation of Hund's rules. From Table V that contains the results of expectation values of energies, the maximum values of expectation values of energies in 1s shell and minimum values in 2p shell. If one compares among three states, we find the maximum values of energies for 1s, 2s shells in 1S state and minimum values in 3P state, for 2p shell vice versa that are due to Hund's first and second rules. The 3P state has the largest total energy more than other states. In addition, 1D state is larger than 1S state as illustrated in figure (3). Therefore, 3P state is considered as ground state and 1D , 1S as excited states. From Table VI which contains the results of the electronic density

at nucleus $\rho(0)$ and the nuclear magnetic shielding constant σ_d . Both $\rho(0)$ and σ_d are having maximum values in 1s shell and the minimum values in 2p shell because $\rho(0)$ depend on $D(r_1)$, σ_d depend on $\langle r_1^{-1} \rangle$, for this reason the maximum values of $\rho(0)$ and σ_d for 1s, 2s shell in 1S state and minimum values in 3P state, for 2p shell vice versa.

Table I. The highest value of one-particle distribution functions and correspondent position r_1 of carbon atom for three states.

shell	The highest value and positions	3P	1D	1S
1s	$D(r_1)$	3.0149	3.0153	3.0158
	r_1	0.1752	0.1739	0.1737
2s	$D(r_1)$	0.66359	0.66741	0.67336
	r_1	1.2225	1.2204	1.2145
2p	$D(r_1)$	0.52861	0.50846	0.47862
	r_1	1.2064	1.2233	1.2411

Table II. The highest value of inter-particle distribution functions and correspondent position of carbon atom for three states.

shell	The highest value and positions	3P	1D	1S
1s	$f(r_{12})$	2.2098	2.2102	2.2107
	r_{12}	0.2957	0.2949	0.2945
2s	$f(r_{12})$	0.41774	0.4198	0.42301
	r_{12}	1.9333	1.9269	1.9142
2p	$f(r_{12})$	0.36688	0.3523	0.33102
	r_{12}	1.9622	2.0004	2.0729

Table III. The one-particle expectation values $\langle r_1^n \rangle$ where ($n = -1, 1, 2$) and standard deviation of carbon atom for three states.

shell	Expectation values	3P		1D	1S
		P.w.	Ref. [22]		
1s	$\langle r_1^{-1} \rangle$	5.66438	5.664439	5.66491	5.66558
	$\langle r_1^1 \rangle$	0.26844	0.268443	0.26840	0.26834
	$\langle r_1^2 \rangle$	0.09720	0.097199	0.09716	0.09710
	Δr_1	0.15854	-----	0.15849	0.15842
2s	$\langle r_1^{-1} \rangle$	0.89678	0.896798	0.90069	0.90742
	$\langle r_1^1 \rangle$	1.58934	1.589344	1.58225	1.57123
	$\langle r_1^2 \rangle$	3.05171	3.052065	3.02389	2.97942
	Δr_1	0.72505	-----	0.72136	0.71461
2p	$\langle r_1^{-1} \rangle$	0.78351	0.783503	0.76666	0.74078
	$\langle r_1^1 \rangle$	1.71450	1.714494	1.77201	1.87056
	$\langle r_1^2 \rangle$	3.74720	3.746799	4.04421	4.59495
	Δr_1	0.89871	-----	0.95089	1.04687

Table IV. The inter-particle expectation values where ($n = -1, 1, 2$) and standard deviation of carbon atom for three states.

shell	Expectation values	3P	1D	1S
1s	$\langle r_1^{-1} \rangle$	3.50904	3.50948	3.51002
	$\langle r_1^1 \rangle$	0.39244	0.39237	0.39227
	$\langle r_1^2 \rangle$	0.1944	0.19432	0.1942
	Δr_1	0.20097	0.20090	0.20082
2s	$\langle r_1^{-1} \rangle$	0.57288	0.57539	0.57932
	$\langle r_1^1 \rangle$	2.25673	2.24644	2.23036
	$\langle r_1^2 \rangle$	6.10347	6.04774	5.95884
	Δr_1	1.00531	1.00063	0.99213

2p	$\langle r_1^{-1} \rangle$	0.53861	0.52298	0.4988
	$\langle r_1^1 \rangle$	2.46803	2.55694	2.71057
	$\langle r_1^2 \rangle$	7.49442	8.08842	9.18975
	Δr_1	1.18459	1.24519	1.35742

Table V. The expectation values for all attraction, repulsion, kinetic and total energies of intra-shells of carbon atom for three states.

shell	Expectation values of energies	3P	1D	1S
1s	$-\langle V_{en} \rangle$	67.97256	67.97892	67.98696
	$\langle V_{ee} \rangle$	3.50904	3.50948	3.51002
	$-\langle V_T \rangle$	64.46352	64.46944	64.47694
	$\langle T \rangle$	32.23176	32.23472	32.23847
	$-\langle E_T \rangle$	32.23176	32.23472	32.23847
2s	$-\langle V_{en} \rangle$	10.76136	10.81152	10.88904
	$\langle V_{ee} \rangle$	0.57288	0.57539	0.57932
	$-\langle V_T \rangle$	10.18848	10.23613	10.30972
	$\langle T \rangle$	5.09424	5.11806	5.15486
	$-\langle E_T \rangle$	5.09424	5.11806	5.15486
2p	$-\langle V_{en} \rangle$	9.40212	9.19992	8.88936
	$\langle V_{ee} \rangle$	0.53861	0.52298	0.4988
	$-\langle V_T \rangle$	8.86351	8.67694	8.39056
	$\langle T \rangle$	4.43175	4.33847	4.19528
	$-\langle E_T \rangle$	4.43175	4.33847	4.19528

Table VI. The electronic density at nucleus $\rho(0)$ and the nuclear magnetic shielding constant σ_d of carbon atom for three states.

shell	The electronic density and the nuclear magnetic shielding	3P	1D	1S
1s	$\rho(0)$	60.99894	61.01047	61.02338
	$\sigma_d \times 10^{-5}$	10.0545	10.0555	10.0567
2s	$\rho(0)$	2.77113	2.80097	2.84785
	$\sigma_d \times 10^{-5}$	1.59182	1.59924	1.61071
2p	$\rho(0) \times 10^{-10}$	2.95387	2.85935	2.60197
	$\sigma_d \times 10^{-5}$	1.39077	1.36086	1.31492

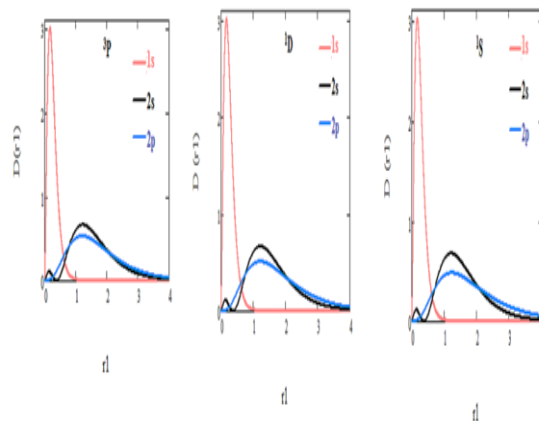


Fig. 1: The relation between one-particle radial density distribution function and location r_1 of carbon atom for three states.

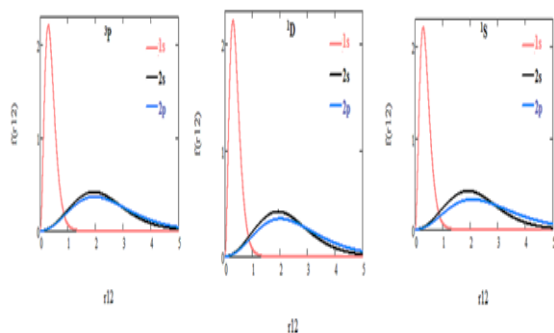


Fig. 2: The relation between inter-particle distribution function and location of carbon atom for three states

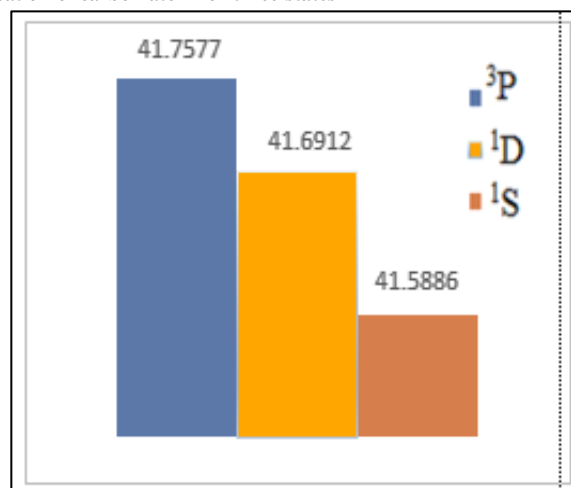


Fig. 3: Comparison between total energies of intra-shells of states 3P , 1D and 1S for carbon atom.

4 Conclusions

The one-particle and inter-particle distribution functions, the expectation values of energies, the nuclear magnetic shielding constant and the electronic density at nucleus are having the maximum values in 1s shell and the minimum values in 2p shell. In addition, these atomic properties have the highest value for 1s, 2s shells in 1S state and minimum values in 3P state, for 2p shell vice versa. For expectation values $\langle r_1^{-1} \rangle$, $\langle r_1^{-2} \rangle$, where $n = -1$ its maximum values in 1s shell and minimum values in 2p shell. Moreover, the highest value for 1s, 2s in 1S state and minimum values in 3P state and vice versa for 2p shell. When $n = 1, 2$ the maximum values in 2p shell and minimum values in 1s shell. In addition, the maximum values for 1s, 2s shells in 3P state and minimum values in 1S state and vice versa for 2p shell. The 3P state has the highest total energy of intra-shells than 1D , 1S states, and 1D state higher total energy of intra-shells than 1S state, so 3P state ground state and 1D , 1S are excited states.

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Conflict of Interest

There was no interest in this study.

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