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Hartree-Fock Computation of Subshell Properties in Carbon and Its Singly Charged Ion

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Abstract: **A comparative analysis of the carbon atom (C) and its singly charged ion (C^+) is conducted within the framework of the Hartree-Fock approximation. Focusing on the ground-state properties of the 1s and 2s subshells. The study includes one- and two-particle radial distributions, inter-electronic distribution functions, expectation values of radial and inter-electronic distances, and energy components. The results show substantial contraction and stabilization in the ionized 2s shell while there are negligible effects on the 1s shell. These results provide insight into the response of the different orbital shells to ionization in a light atomic species and are in good agreement with earlier results published. All computations were performed using a numerical implementation of the Hartree-Fock method in Mathcad 15.**

Keywords: **Hartree-Fock, cation of the carbon atom, radial density function, inter-electronic distribution, subshell energy analysis.**

1. INTRODUCTION

Finding a valid theoretical formulation for multi-electron atoms is still a significant open issue in quantum mechanics due to the presence of electron-electron interactions [1]. Many different approximations have been developed to bypass the complicated quantum mechanics of this problem, one of the most powerful and established methods is the Hartree-Fock (HF) method. Each electron is thought to move in an average field generated by all the other electrons, This makes it a self-consistent approach to predicting how atomic electron structure behaves [2].

The HF wavefunction is a Slater determinant of the spin-orbitals that ensures antisymmetry and satisfies the Pauli exclusion principle, each spatial part of the orbital is represented by Slater-type functions (STFs) optimized using a self-consistent field (SCF) procedure [3]. Even though electron correlation is considered averaged, accurate values for ground-state properties can be achieved [4].

Although numerous studies have employed the Hartree-Fock (HF) method to investigate atomic systems in various states particularly to compute key properties such as radial density distributions, inter-electronic interactions, and internal and external energy components [5, 6], very few have focused on direct comparisons between a neutral atom and its corresponding singly charged ion.

This paper presents a detailed HF analysis of the carbon (C) atom and its singly charged ion (C^+) in an analysis of radial densities in the 1s and 2s shells. The investigation will incorporate radial density functions and inter-electronic distributions; expectation values and their standard deviations; as well as total contributions of kinetic, potential, and overall energy from HF methods. All quantities will be in atomic units using numerical routines implemented in Mathcad 15.

This narrowly focused analysis illustrates the differences in energy structure and electron localization relevant to ionization, in particular, light atomic systems; as well as the distinct responses of inner and outer shells to electronic perturbation.

2. THEORETICAL FRAMEWORK

2.1 Hartree-Fock Approximation

The HF method describes the many-body wavefunction as a Slater determinant of spin-orbitals [7]:

$$\psi_{n\ell m s}(r,\omega) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)\chi_s(\omega)$$ 0.1)

The radial components $R_{n\ell}(r) = N_{n\ell}r^{n-1}e^{-\zeta r}$ exhibit exponential decay. The overall Hartree-Fock energy is determined by minimizing the energy expectation subject to orthonormality constraints.

2.2 One-Particle Radial Density Function [8]

$$D(r_1) = \int \mid \psi(r_1,\theta,\phi) \mid^2 r_1^2 d\Omega$$ (0.2)

Describes the probability of finding an electron at a distance r1 from the nucleus.

2.3 Two-Particle Radial Density Function [9]

$$D(r_1,r_2) = \iint \Gamma(r_1,r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2$$ (0.3)

Describes the probability of finding two electrons at distances r_1 and r_2.

2.4 Inter-Electron Distribution Function [10]

$$f(r_{12}) = \iint \mid \Psi(r_1,r_2) \mid^2 \delta(\mid r_1 - r_2 \mid - r_{12}) dr_1 dr_2$$ (0.4)

Describes the probability of a pair of electrons being separated at a distance r_{12}.

2.5 Expectation Values [11]

$$\langle r_1^n \rangle = \int_0^\infty r_1^n D(r_1) dr_1 \quad , \quad \langle r_{12}^n \rangle = \int_0^\infty r_{12}^n f(r_{12}) dr_{12}$$ (0.5)

Evaluated for $n = -2, -1, 0, 1, 2$ to that explores distributions and spacing of electrons.

2.6 Standard Deviations [12]

$$\Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \quad , \quad \Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2}$$ (0.6)

Provide measures of spatial spread and of probability of inter-electronic spatial uncertainty.

2.7 Energy Components [13]

- **Kinetic Energy**:

$$\langle T \rangle = -\frac{1}{2}\sum_i \langle \psi_i \mid \nabla^2 \mid \psi_i \rangle$$ (0.7)

- **Electron-Nucleus Attraction**:

$$\langle V_{\text{en}} \rangle = -\sum_i \left\langle \psi_i \mid \frac{Z}{r} \mid \psi_i \right\rangle$$ (0.8)

- **Electron-Electron Repulsion**:
$$\langle V_{\text{ee}}\rangle = \frac{1}{2}\sum_{i\neq j}\iint \frac{|\,\psi_i(r_1)\,|^2|\,\psi_j(r_2)\,|^2}{|\,r_1 - r_2\,|}\,dr_1 dr_2 \qquad (0.9)$$

- **Total Energy**:
$$\langle E\rangle = \langle T\rangle + \langle V_{\text{en}}\rangle + \langle V_{\text{ee}}\rangle \qquad (0.10)$$

Evaluated for the 1s and 2s shells in both carbon and C^+.

3. RESULTS AND DISCUSSION

Table 1: Values for the one particle density function $D(r_1)$ at the maximum and at radial positions for C and C^+.

Ion		**1s shell**		**2s shell**			
		r₁	**Dmax(r1)**	**First peak**		**Second peak**	
				r₁	**Dmax(r1)**	**r₁**	**Dmax(r1)**
C	P.W	0.1752	3.0149	0.1397	0.11069	1.2224	0.6636
	Ref.[5]	0.1743	3.0149	0.1392	0.11069	1.2194	0.66359
C^{+1}		0.1752	3.0182	0.1393	0.12738	1.1805	0.72947

Table 2: Expectation values and standard deviations for $\langle r_1^n\rangle$ for the 1s and 2s subshells

Ion	**shell**	**$< r_1^{-2} >$**	**$< r_1^{-1} >$**	**$<r_1^0>$**	**$< r_1^1 >$**	**$< r_1^2 >$**	**Δr_1**
C	1s	65.23869	5.66438	1	0.26844	0.0972	0.15854
	Ref.[14]	65.23817	5.66471	1	0.26845	0.0972	-
	2s	3.25583	0.89678	1	1.58934	3.05171	0.72505
	Ref.[14]	3.25653	0.89675	1	1.58951	3.05387	-
C^{+1}	1s	65.30764	5.66855	1	0.26811	0.09688	0.15811
	Ref.[15]	65.30838	5.66861	-	0.26811	0.09688	0.15810
	2s	3.71795	0.96118	1	1.47556	2.58984	0.64230
	Ref.[6]	3.717948	0.961175	1.000009	1.475565	2.589839	-

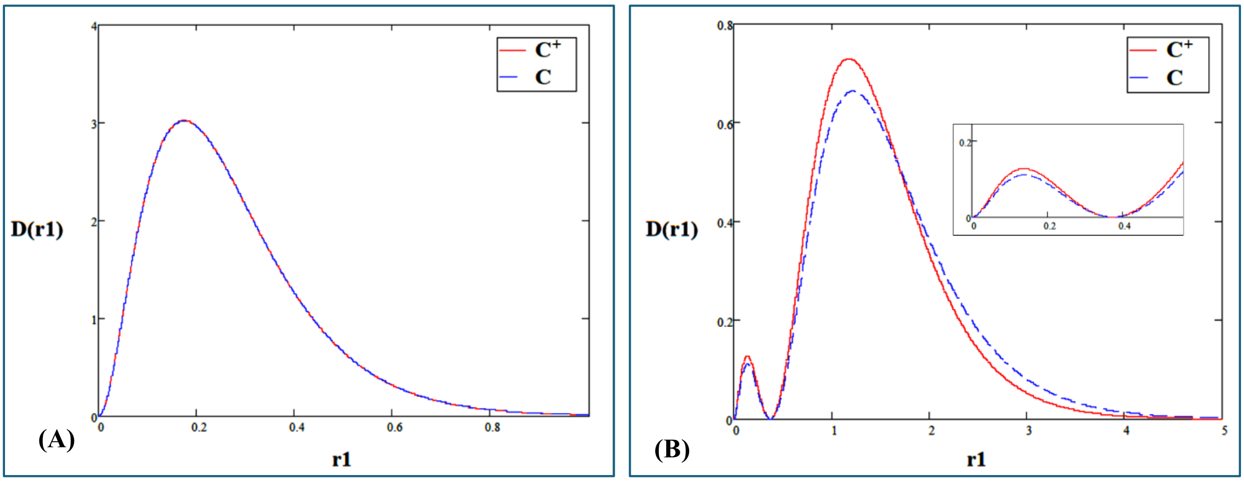

Figure 1: The radial distribution D(r_1) and distance r1 for C and C^+ in the (A) 1s, and (B) 2s, subshells.

The $D(r_1)$ function represents the spatial probability density of the electron in terms of the electron's distance from the nucleus [16]. As shown in **Table 1**, the position of the peak for the 1s shell is equivalent following the ionization process indicating that the inner shell electron remains localized. The 2s shell exhibits more obvious changes. Following ionization both the inner and outer peaks of the 2s density function shift inward and increase in height, as shown in **Error! Reference source not found.B** demonstrating contraction and increased density of the 2s orbital due to ionization and due to the altered electrostatic environment resulting from the removed valence electron. This contraction observed in the 2s shell is absent in the 1s shell **Error! Reference source not found.A**, thus demonstrating that the inner shell electron density is relatively insensitive to perturbation. The expectation values in **Table 2** further support the above findings. The $\langle r_1^{-1}\rangle$ and $\langle r_1\rangle$ values were all lower in C^+ in the 2s shell, meaning the electron is better bound, and the radial distance is smaller. The lower standard deviation further confirms increased localization of the 2s electron cloud in C^+ than in the neutral state, $\Delta r1$ is lower. These results are consistent with Al-Khafaji [15], and Al-Sharaa et al. [6] therefore validating that this study is numerically accurate and conceptually consistent with the literature.

Table 3: Peak values and positions for the inter-electron distribution function, $f(r_{12})$, for C and C^+.

Ion	1s shell		2s shell	
	r12	f_{max}(r12)	r12	f_{max}(r12)
C	0.295	2.2089	1.943	0.41774
C^{+1}	0.296	2.2129	1.836	0.45427

Table 4: Expectation values and standard deviations for $\langle r_{12}^n\rangle$ in 1s and 2s subshells.

Ion	shell	$< r_{12}^{-2} >$	$< r_{12}^{-1} >$	$< r_{12}^{0} >$	$< r_{12}^{1} >$	$< r_{12}^{2} >$	Δr_{12}
C	1s	21.18490	3.50904	1	0.39244	0.19440	0.20097
	Ref.[14]	21.18682	3.50928	1	0.39245	0.19439	-
	2s	0.53609	0.57288	1	2.25673	6.10347	1.00531
C^{+1}	1s	21.22107	3.51265	1	0.39190	0.19376	0.20043
	Ref.[15]	21.22107	3.51266	….	0.39190	0.19376	0.20043
	2s	0.61516	0.61462	1	2.08769	5.17972	0.90625
	Ref.[15]	0.61516	0.61462	…	2.08769	5.17972	0.90623

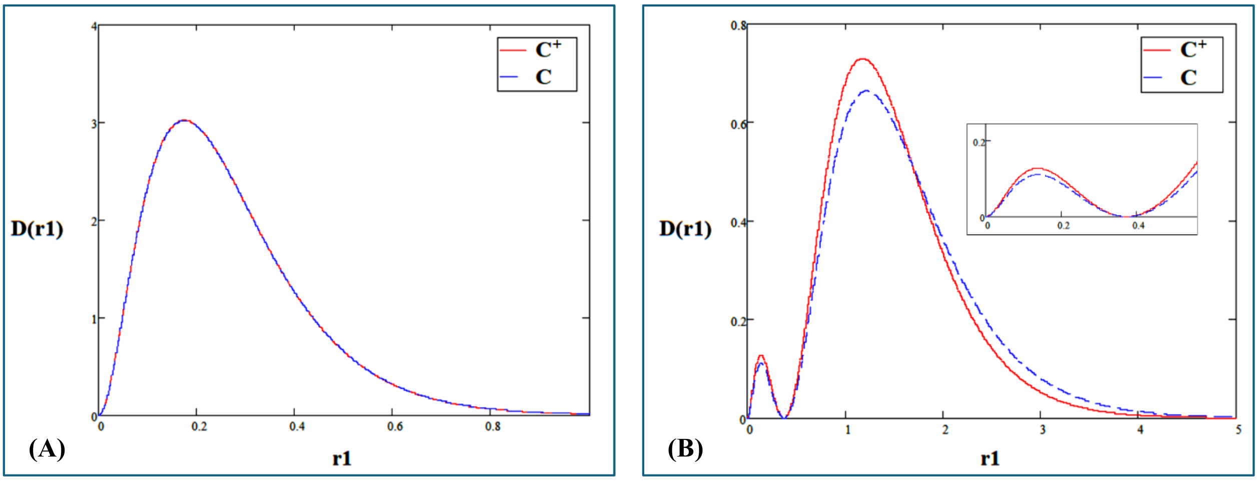

Figure 2: Distance r1 and the inter-particle distribution function f(r12) for: (A) 1s shell, (B) 2s shell.

The probability density function f(r12) represents the probability density of finding two electrons separated by a distance r12 [17]. As illustrated in **Table 3** both systems exhibit nearly identical distributions in the 1s shell, the positions and height of the peaks barely change. This provides additional evidence as mentioned earlier, that the inner electrons are indeed very well bound spatially, and following the removal of an electron from the outer shell, its binding state, remained high, and they did not appreciably change.

However, there is more change in the 2s shell after ionization. Once the ionization occurs we see the f(r12) function shift the peak towards lower r12, and also provides evidence of a greater height for the peak. As can be seen in **Error! Reference source not found.**B, the electron distributions for C^+ become steeper and narrower compared to that of the neutral atom. The behavior implies that there was some greater attraction of the respective electrons since the ionization would likely be due to orbital contraction, resulting in a less diffuse spatial distribution.

The statistical expectation values and standard deviations associated with the r12 function for the two systems provided in **Table 4** again add to this trend, in that when we compare C^+ to the neutral atom once again in the 2s shell, both $\langle r_{12}^{-1} \rangle$ and $\langle r_{12} \rangle$ decrease in value between the C^+ and neutral atom. The decrease corresponds to an increase in Coulombic interaction between electrons. Since there was an overall decrease in the average distance (spatial separation) of the electrons overall. The decrease in standard deviation Δr_{12} further indicates enhanced spatial confinement of the other relative to the interaction distance with the other electron. These effects are a direct consequence of loss of shielding and a net increase in nuclear charge is the driving force related to the more compact distribution. Interestingly, again for the 1s shell, the expectation values do not change from either system after ionization. So there was no change in the amount of electron separation, nor in the strength of correlation as a result of removing a 2s electron. This work highlights that inter-electronic interactions of outer shell electrons specifically in the 2s subshell are more affected by ionization, while inner-shell pairs remain largely unaffected.

Table 5: Values of energy components for C and C^+ in the 1s and 2s subshells.

Ion	shell	$\langle Vee \rangle$	$-\langle V_{en} \rangle$	$-\langle V \rangle$	$\langle T \rangle$	$-\langle E_H \rangle$
C	1s	3.50904	67.97254	64.46350	32.23175	32.23175
	Ref.[14]	3.50928	67.97652	64.46724	32.23336	32.23336
	2s	0.57288	10.76140	10.18852	5.09426	5.09426
	Ref.[14]	0.57289	10.761	10.188	5.09406	5.09406
C^{+1}	1s	3.51265	68.02260	64.50995	32.25497	32.25497
	Ref.[15]	3.51265	68.02332	64.51067	32.25533	32.25533
	2s	0.61462	11.53410	10.91948	5.45974	5.45974
	Ref.[15]	0.61462	11.53416	10.91954	5.45977	5.45977

The expectation values of energy values for the 1s and 2s subshells provide insight into how atomic energy is distributed among repulsion, attraction and stability overall. As shown in ***Table 5***, these values, calculated using the Hartree-Fock method, reveal how ionization influences energy distribution

In the 1s shell, there is minimal change in kinetic energy ⟨T⟩, electron-nucleus attraction $\langle V_{en} \rangle$, and electron-electron repulsion $\langle V_{ee} \rangle$ between C and C^+, demonstrating the stability of this inner shell. The $\langle V_{en} \rangle$ was slightly higher in C^+ compared to C, and therefore, total energy $\langle E_H \rangle$ was also slightly higher, due to the generally more attractive interaction of those electrons with the nucleus consistent with previous studies [15].

In contrast, the 2s shell shows a more pronounced energetic response to ionization. All energy components increase in magnitude (i.e., become more negative) in C^+, reflecting stronger nuclear attraction and a more tightly bound electronic structure.

Overall, these findings underscore the selective effect of ionization: while the 1s shell remains energetically unaffected, the 2s shell undergoes significant energetic stabilization, consistent with the spatial and inter-electronic distribution results.

4. CONCLUSIONS

In this study, we utilized the Hartree-Fock approximation to analyze the electronic structure of carbon (C) and its singly-charged ion (C^+). The analysis provides the following conclusions:

1. The radial densities $D(r_1)$ of both the carbon atom (C) and its singly charged ion (C^+) showed little difference in the 1s shell; however, the 2s shell of C^+ exhibited clear spatial contraction and peak enhancement due to diminished electron shielding.
2. The inter-electronic distributions $f(r_{12})$ was stable in the 1s shell, but became more localized in the 2s shell of C^+, indicating enhanced electron correlation.

3. The expectation values and standard deviations both confirmed the contracted spatial distribution for the 2s shell after ionization, while the values for the 1s shells remained nearly unchanged.
4. The energy components for the 2s shell in C^+ were more negative, indicating stronger binding, whereas the corresponding energy terms in the 1s shell remained nearly identical in both systems.

In general, the conclusions drawn when comparing C and C^+ indicate that ionization of ionization primarily affects the outer-shell (2s) electrons, leading to greater electron confinement and deeper binding energy, with the core electronic structure remaining mostly stable. This method confirms the shell-specific nature of only the valence electrons to increase nuclear charge as expected for light atomic systems based on theory.

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