Pauli shielding and break-down of spin statistics in multi-electron, multi-open-shell dynamical atomic systems

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Supplemental Material

3eAOCC : He, C^{4+} AND C^{3+} DESCRIPTION

Our approach is based on a semiclassical atomic orbital close-coupling treatment, with asymptotic (atomic) descriptions of the neutral and charged collision partners [1, 2]. The approach and our corresponding computer codes are versatile so that we include three active electrons in the calculations to describe accurately C^{4+}, C^{3+} and He, the latter being described by a single electron attached to He^+ through a model potential expressed as:

$$V(r) = \sum_{i=1}^{13} -\frac{c_i}{r} \ e^{-\alpha_i r^2} \qquad (1)$$

where the coefficients and exponents are optimized to get ground state with binding energy close to the first ionization energy (24.6 eV), the first excitation energies and correct Coulombic limits at $r \to 0$ and $+\infty$. They are listed in Table I.

The atomic states centred on He (modelled by the potential of Eq. 1), C^{4+} and C^{3+} are expressed on sets of optimized Gaussian-Type orbitals (GTOs)

$$\mathcal{G}(r) = \mathcal{N}r^\ell e^{-\alpha r^2} \qquad (2)$$

($\mathcal{N}$ is a normalization factor) and antisymmetrized products of these GTOs, in order to obtain ground and excited states of the considered neutral and ionized species, with special emphasis on the levels of interest in our investigation, i.e. $C^{3+}(1s2s2p \ ^4P, \ ^2P_{\pm})$. The GTOs used in our calculations are listed in Table II. The

energies obtained for the C^{4+} and C^{3+} excited states under consideration in the present work are shown in Table III.

The close-coupling calculations presented in this Letter were performed using, for doublet total spin symmetry, 1794 (1807) states and pseudo states for C^{4+}+ He (C^{4+}+ H) collisions, and, for quartet spin symmetry, respectively 802 (812). The convergence of the results were further checked by comparing the present energies and cross sections to the respective values obtained from (i) smaller GTO basis sets and (ii) using a different model potential for He: the level of convergence for the cross sections of importance in our investigation was found to be 15% or better, and induces minimal deviations ($\approx 5\%$) in the ratio R.

SIMPLIFIED STATIC AND DYNAMIC MODELS

To gain further insight into the dynamics of our collision system, we have developed a simplified model, assuming the minimal description of the atomic states under consideration, as well as 2-state OBK-type approach for the dynamics. The $C^{3+}(1s2s2p) \ ^4P$, $^2P_-$ and $^2P_+$ states are described by the simplest expressions using the three orthonormalized atomic orbitals $1s$, $2s$ and $2p$ (written respectively as 1, 2 and 3 for simplicity in the following): they are then expressed by linear combinations of Slater determinants in order to be eigenfunctions of the total spin $\mathbf{S}^2$ operator, as follows,

TABLE I. Coefficients and exponents used to represent the system $He^+ + e^-$ by the model potential defined in Eq. 1.

i	1	2	3	4	5	6	7	8	9	10	11	12	13
c_i	1.0	0.02122	0.23856	0.24184	0.18409	0.12201	0.13192	0.01928	0.10648	0.10665	-0.04115	-0.07789	-0.07425
α_i	0.0	0.73506	4.59598	13.37885	47.82184	260.82361	1.78475	0.50641	1.07305	2.38839	12.09488	30.87964	153.60719

TABLE II. Angular momenta, ℓ, and exponents, α ($7.25^{-3} \equiv 7.25 \times 10^{-3}$), of the GTOs (Eq. 2) used for the calculations reported in this Letter to span He, C^{4+} and C^{3+} species.

He		C^{4+}, C^{3+}			
ℓ	α	ℓ	α	ℓ	α
0	7.25^{-3}	0	5.50^{-2}	0	2.24^{+1}
0	2.90^{-2}	0	1.30^{-1}	0	5.30^{+1}
0	1.16^{-1}	0	3.06^{-1}	0	1.25^{+2}
0	4.66^{-1}	0	7.23^{-1}	1	2.60^{-1}
0	1.86^{00}	0	1.71^{00}	1	7.50^{-1}
0	7.47^{00}	0	4.03^{00}	1	2.45^{00}
0	2.99^{+1}	0	9.51^{00}	1	8.00^{00}

TABLE III. Energies (in a.u.) of some of the important C^{4+} and C^{3+} states included in our basis set used in the close-coupled calculations. The values are relative to the corresponding ground states. For comparison, the last line shows the values from other sources as marked.

C^{4+}		C^{3+}			
$1s2s$		$1s2s2p$		$1s2s3s$	$1s2s3p$
^3S	^4P	$^2P_-$	$^2P_+$	^4S	^4P
10.90	10.73	10.95	11.11	12.17	12.55
10.99[a]	10.77[b]	10.99[b]	11.15[b]	12.22[c]	12.31[b]

[a] NIST (https://www.nist.gov/pml/atomic-spectra-database)
[b] Chen [3]
[c] Dumont *et al.* [4]

$$|^4P > \equiv |123| \tag{3a}$$

$$|^2P_- > \equiv \frac{1}{\sqrt{2}}(|1\bar{2}3| - |\bar{1}23|) \tag{3b}$$

$$|^2P_+ > \equiv \frac{1}{\sqrt{6}}(|\bar{1}23| + |1\bar{2}3| - 2 \times |12\bar{3}|) \tag{3c}$$

for the components of largest M_S value ($+3/2$ for ^4P and $+1/2$ for $^2P_\pm$). In Eqs. 3, for example $|\bar{1}23|$ represents a Slater determinant and the spin-orbital $\bar{1}$ stands for $1s \times \beta$ and 3 for $2p \times \alpha$ (α and β correspond to spin-up and spin-down, respectively). These equations are schematically shown in Eqs. 3 of the Letter. Using the C^{3+} hamiltonian operators H, where all Coulomb interactions, nucleus-electron attraction and electron-electron repulsion, are taken into account, the energy associated with these three states can be expressed as:

$$E[^4P] = \sum_{i=1}^{3}(I_i + \sum_{j>i}^{3} J_{ij}) - (K_{23} + K_{13} + K_{12}) \tag{4a}$$

$$E[^2P_-] = \sum_{i=1}^{3}(I_i + \sum_{j>i}^{3} J_{ij}) - \frac{1}{2}(K_{23} + K_{13} - 2K_{12}) \tag{4b}$$

$$E[^2P_+] = \sum_{i=1}^{3}(I_i + \sum_{j>i}^{3} J_{ij}) + \frac{1}{2}(K_{23} + K_{13} - 2K_{12}) \tag{4c}$$

Here, I_i are the monoelectronic integrals:

$$I_i = <i| - \frac{1}{2}\Delta_\mu - \frac{Z_p}{r_\mu}|i> \equiv T_{ii} + V_{ii}^P \tag{5}$$

($Z_p=6$) and J_{ij} and K_{ij} are, respectively, the direct and exchange bielectronic integrals:

$$J_{ij} = <ij|\frac{1}{r_{\mu\nu}}|ij> \equiv <ij||ij> \tag{6a}$$

$$K_{ij} = <ij|\frac{1}{r_{\mu\nu}}|ji> \equiv <ij||ji> \tag{6b}$$

where μ (ν) represents any electron among the three active ones. Knowing that K_{23} between $2s$ and $2p$ is the largest exchange integral, the three states in Eqs. 3 show the correct energy ordering, $E[^4P] < E[^2P_-] < E[^2P_+]$, in agreement with experiment, as seen in Fig. 1 of the Letter.

The relative strength of electron capture to these three states can be estimated using the Oppenheimer-Brinkman-Kramers (OBK) [5] approximation in its *prior* form for the evaluation of transition probability $i \rightarrow f$ given by:

$$\left|c_{fi}^{OBK}(b)\right|^2 = \left|-i \int_{-\infty}^{+\infty} dt <\Psi_f|W^P|\Psi_i> e^{-i\Delta E_{if}t}\right|^2, \tag{7}$$

where W^P is the interaction between the electron initially (say λ) on the target and the projectile nucleus and the two other electrons (μ, ν)

$$W^P \equiv -\frac{Z_p}{r_\lambda} + \frac{1}{r_{\lambda\mu}} + \frac{1}{r_{\lambda\nu}} \tag{8}$$

Here, the final state Ψ_f is one of the three states of Eqs. 3, while the initial state $\Psi_i = |12\underline{3}|$ or $|12\bar{\underline{3}}|$,

corresponds to $C^{3+}(1s2s\ ^3S)$ and one electron in the He $1s$ orbital (labelled as $\underline{3}$). $\Delta E_{if} = E_i - E_f - v^2/2$ is the energy difference between the initial state and final states, augmented by the kinetic part of the electron translation factor [5]. Neglecting the rather small energy differences between the three final P states under consideration compared to the overall energy difference ΔE_{if}, the probability to populate these states becomes proportional to the square of the coupling matrix element $M_f^P \equiv\ <\Psi_f|W^P|\Psi_i>$ in Eq. 7. This can be evaluated for the final states ^4P, $^2P_-$ and $^2P_+$ as:

$$M_{^4P}^P = V_{3\underline{3}}^P + <13||1\underline{3}> + <23||2\underline{3}>$$
$$- <13||\underline{3}1> - <23||\underline{3}2> \tag{9a}$$

$$M_{^2P_-}^P = \frac{1}{\sqrt{2}}\left(<13||\underline{3}1> - <23||\underline{3}2>\right) \tag{9b}$$

$$M_{^2P_+}^P = -\sqrt{\frac{2}{3}}V_{3\underline{3}}^P - \sqrt{\frac{2}{3}}(<13||1\underline{3}> + <23||2\underline{3}>$$
$$+ \frac{1}{2}<13||\underline{3}1> + \frac{1}{2}<23||\underline{3}2>) \tag{9c}$$

where the orthonormalisation relations of the spin functions have already been used. Here, all matrix elements include the electron translation factor and orthogonality is assumed between the four atomic orbitals under consideration. The monoelectronic matrix element

$$V_{3\underline{3}}^P = <3| - \frac{Z_p}{r_\mu}|\underline{3}> \tag{10}$$

(referred to as I^P in the Letter) couples the $1s$ AO ($\underline{3}$) centred on He to the $2p$ AO (3) centred on carbon. It is proportional to the charge of the projectile nucleus, $Z_p = 6$, and is therefore the dominant term in Eqs. 9. The

probabilities for capture to the ^4P and $^2P_+$ are therefore proportional to $|I^P|^2$ and $(2/3)|I^P|^2$ respectively, and larger than the one for $^2P_-$, expressed only in terms of bielectronic matrix elements.

Then, neglecting the bielectronic, direct and exchange, matrix elements, the ratio R of the $1s2s2p$ capture cross sections for the quartet state, $\sigma(^4P)$, to the doublet states, $\sigma(^2P_\pm)$

$$R = \frac{\sigma(^4P)}{\sigma(^2P_+) + \sigma(^2P_-)} \tag{11}$$

becomes equal to $3/2$. Within this model and approximation, this value represents an upper limit to the ratio R, which can only fortuitously (depending on the actual magnitude and sign of the bielectronic integrals) equal to 1 or 2, corresponding, respectively, to the limits of "pure spin statistics" and "frozen $1s2s\ ^3S$ spin statistics" in the Letter.

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