Pauli Shielding and Breakdown of Spin Statistics in Multielectron Multi-Open-Shell Dynamical Atomic Systems

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We report on state-resolved cross sections of electron capture in collisions of swift $C^{4+}(1s2s\ ^3S)$ ions with helium and hydrogen. The study focuses on the formation of doubly-excited triply-open-shell $C^{3+}(1s2s2p)\ ^4P$ and $^2P_\pm$ states with emphasis on the ratio R of their cross sections as a measure of spin statistics. Using zero-degree Auger projectile spectroscopy and a three-electron close-coupling semiclassical approach, we resolve a long-standing puzzle and controversy on the value of R and on the effect of cascades, to clarify the underlying physics. The present results invalidate the frozen core approximation generally used in the past when considering electron capture in multi-electron, multi-open-shell quantum systems. A distinctive screening effect due to the Pauli exclusion principle (Pauli shielding) is proposed to account for the value of R, consistent with our findings.

The dynamics of excited atomic or molecular structures with several unpaired electrons is complex to understand and theoretically model due to the interplay of several fundamental aspects of atomic physics: rich spectral signatures involving multiple spin symmetries, electronic correlation and intricate reactivity sketched by numerous open channels, all under the constraints of the Pauli exclusion principle. High energy few-electron ions in collision with atomic targets provide one of the simplest benchmark quantum systems to probe the underlying physics at the most fundamental level. Their atomic line spectra excited in collisions with electrons, ions or atoms provide important information about the atomic structure of the observed states, as well as their basic production mechanisms [1, 2]. In particular, state-resolved X-ray [3] and Auger electron [4] measurements provide the most stringent tests of this understanding, finding important practical applications in various fields of astrophysical [2, 5] and laboratory [5, 6] plasmas.

Here, we revisit the long-standing problem of how multi-unpaired-electron ion cores behave while undergoing electron processes during fast atomic collisions, and how best to accurately describe them theoretically. Previous work on ionization [7, 8], excitation [9, 10] and electron loss [11] have shown that important dynamic electron correlations involving higher-order processes such as time-ordering and Pauli blocking need to be considered, once one goes beyond the independent electron and frozen core approximations. However, for single electron capture (SEC) involving multi-open-shell excited ions, the situation is much less clear [12]: (i) Are similarly configured final states corresponding to different spins populated according to spin statistics? (ii) How legitimate is the frozen core approximation or, equivalently, does the initial electronic configuration undergo changes during the collision process?

A viable way to explore these issues is to consider the following $2p$ SEC channel in MeV collisions:

$$C^{4+}(1s2s\ ^3S) + \mathrm{He} \rightarrow C^{3+}(1s2s2p\ ^4P,\ ^2P_\pm) + \mathrm{He}^+ \quad (1)$$

which can be readily investigated experimentally since the initial, $1s2s\ ^3S$, ionic core is metastable and therefore naturally found mixed-in with the ground state ions as provided by accelerators [13–15]. Then, the ratio R of the $1s2s2p\ ^4P/^2P_\pm$ SEC cross sections

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

could bare the corresponding population spin statistics signature. Indeed, this ratio results in $R = 1$, when considering only spin multiplicity [16], while $R = 2$, in the frozen core approximation where only the ^4P and a single ^2P can be produced from the $1s2s\ ^3S$ initial state [17, 18]. Such statistical arguments and approximations are often used to simplify difficult problems of computing relative populations in high energy plasmas [2] and can therefore be of important practical use.

It was therefore particularly intriguing when Tanis *et al.* [19] reported a larger value $R \simeq 2.9$, in 20.9 MeV collisions between mixed-state $F^{7+}(1s^2\ {}^1S, 1s2s\ {}^3S)$ ions and He. This led these authors to propose a new mechanism, the dynamic *Pauli exchange interaction*, to explain the preponderance of $1s2s2p\ {}^4P$ state over the $1s2s2p\ {}^2P_{\pm}$ states populations. Alternatively, Zouros *et al.* [20], showed that a similar enhancement of R could also be qualitatively explained by a *selective* cascade feeding mechanism favouring the ${}^4P$ production. As a consequence, in both schemes, the measured ratio R does *not* directly reflect simple final state spin statistics.

In a more detailed follow up investigation of the process in Eq. 1, even *larger* experimental ratios $R \simeq 6-9$ were reported [18]. In addition, calculations based on a frozen core single-active electron treatment were included using the non perturbative basis generator method (TC-BGM) [21, 22], with a detailed radiative cascade analysis [18], and additional Auger corrections [23]. These authors clearly demonstrated a selective cascade enhancement of the ${}^4P$ state, resulting in $R \simeq 4.9-5.8$ [18, 23]. Yet, for just $2p$ capture (no cascades), the computed values were found to give $R = 2$ [23], the spin statistics prediction within the frozen core approximation, resulting in a rather puzzling paradoxical situation.

In this Letter, we treat this problem both theoretically and experimentally for the electron capture processes of Eq. 1 induced in 2-18 MeV collisions of $C^{4+}(1s2s\ {}^3S)$ ions with helium and hydrogen targets. We perform intensive close-coupling calculations involving the dynamics of *three active* electrons [24]. The ratio R, stemming from this treatment and the inclusion of cascade effects, is compared to our measurements using the recent two-spectra technique [25, 26] to directly extract the contributions from *just* the metastable component. For the first time, agreement between theory and experiment is found. This resolves the long-standing paradox, while bringing to light the existence of novel strong electron correlation effects, not included in previous treatments, primarily due to their intrinsic *one*-active-electron limitations.

The measurements were performed with the zero-degree Auger projectile spectroscopy (ZAPS) [27] setup [28] currently located at the NCSR "Demokritos" 5.5 MV Tandem accelerator facility, which delivered the He-like C^{4+} ion beams. The electron spectrometer consists of an electrostatic single stage hemispherical deflector analyzer equipped with a four-element injection lens and a 2-D position sensitive detector (PSD) [29]. High statistics spectra were recorded with sufficient resolution to clearly separate the C^{3+} *KLL* Auger lines by pre-retarding the measured electrons by a factor of four, while also exploiting the high efficiency afforded by our multi-channel PSD. Beam intensities on target ranged from $0.1-20$ nA depending on incident energy and stripping conditions, while target gas pressures ranging from $5-40$ mTorr were chosen to ensure single collision conditions. Using different electron stripper combinations [15, 28], beams of $C^{4+}(1s^2, 1s2s\ {}^3S)$ mixed-state ions were prepared with *different* amounts of metastable $1s2s$ component so that the ratio R could be accurately determined by applying our two-spectra technique [25].

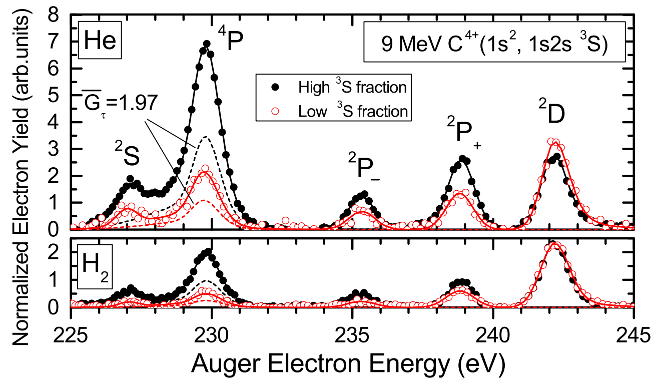

FIG. 1. Typical ZAPS C^{3+} *KLL* Auger spectra after background subtraction and transformation to the projectile rest frame for 9 MeV mixed-state $C^{4+}(1s^2, 1s2s\ {}^3S)$ ion beam collisions with He (top) and H_2 (bottom). The states $1s2s^2\ {}^2S$, $1s2s2p\ {}^4P$, $1s2s2p\ {}^2P_-$, $1s2s2p\ {}^2P_+$ and $1s2p^2\ {}^2D$ are indicated. High (filled black circles) and low (open red circles) $1s2s\ {}^3S$ metastable fraction spectra are shown (see text). The *true* intensity of the ${}^4P$ line is also shown (dashed lines) after division by the indicated factor $\overline{G}_\tau$ [30, 31].

In Fig. 1, we present typical Auger spectra from collisions of 9 MeV mixed-state $C^{4+}(1s^2\ {}^1S, 1s2s\ {}^3S)$ with He and H_2. Similar spectra were also recorded at 6, 12 and 15 MeV for He, and also at 6 and 12 MeV for H_2 targets. At each collision energy, as shown in Fig. 1 for 9 MeV, *two* spectra were recorded, each with a *different* $1s2s\ {}^3S$ metastable fraction, as evidenced by the distinct intensities of the $1s2s2p\ {}^4P$ peaks [25]. Indeed, the ${}^4P$ state is populated almost exclusively by SEC to the $1s2s\ {}^3S$ state due to spin considerations [32], while the $1s2p^2\ {}^2D$ state is mainly produced by transfer excitation (TE) [33] from the $1s^2$ ground state [20, 25, 34], in this range of impact energies. The rest of the observed *KLL* states can be populated from both the ground state $1s^2$ by TE and the metastable state by SEC [20, 25, 32, 34]. This dual spectrum measurement is the cornerstone of our recently reported technique [25] for separating out from the measured yields the contribution of *just* the metastable $1s2s\ {}^3S$ beam component. Also shown in Fig. 1, is the value of the computed $\overline{G}_\tau$ intensity correction factor [27, 28, 30, 31] applied to the detection of the *delayed* Auger electrons emitted at 0° to the beam direction from the long-lived $C^{3+}(1s2s2p\ {}^4P_J)$ J-states [35]. This important correction accounts for two competing effects: the *increase* in solid angle for electrons emitted from ions approaching the spectrometer, and the *loss* of electrons emitted from ions inside and beyond the spectrometer. In our setup, it reduces the observed intensity by about 2, depending on projectile velocity [31].

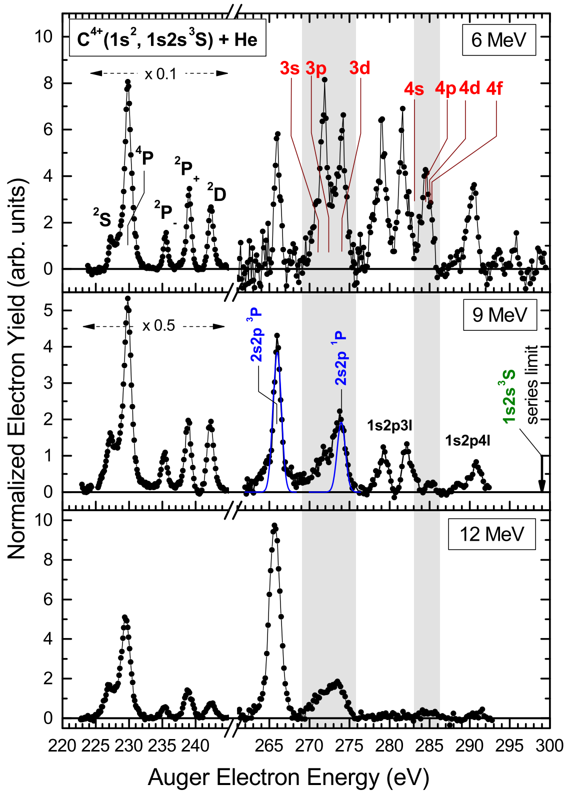

FIG. 2. ZAPS C^{3+} and C^{4+} K-Auger spectra for 6, 9 and 12 MeV collisions of mixed-state $C^{4+}(1s^2, 1s2s\ ^3S)$ with He. Within the grey bands, some of the observed higher-lying $1s2sn\ell\ ^2L$ states are identified in red by their $n\ell$ values. Other lines labeled in black (middle panel) are the $1s2pn\ell$ doublets and do not contribute to the cascades. Indicated in blue, for completeness, are the strong $C^{4+}(2s2p)$ excitation lines. Note that the lines in the 220-245 eV domain are scaled.

Moreover, our measurements (and calculations) highlighted the fact that higher-lying C^{3+} states are also significantly populated in the collision. This can be seen in Fig. 2, where KLn Auger lines, extending to the carbon $1s2s\ ^3S$ series limit ($\simeq$ 299 eV), are presented. Among others, lines from $1s2sn\ell\ ^2L$ states with $n = 3$ and 4 (marked $n\ell$ in the figure) are clearly observed. Indeed, these doublets are emptied very rapidly due to their strong Auger rates. This results in much reduced $E1$ radiative branching ratios [23], so that their populations *never* cascade to the lowest lying $1s2s2p\ ^2P_{\pm}$. In contrast, the corresponding $1s2sn\ell\ ^4L$ ($n = 3, 4$) states are *not* observed in Fig. 2, even though they lie in the same energy range as their doublet counterparts and should be similarly populated by SEC. This absence is in fact due to their very weak Auger decay to $C^{4+}(1s^2)$ [36], forbidden due to spin conservation. Consequently, these quartets have very large $E1$ radiative branching ratios to lower lying quartets [36–38] and therefore their populations are efficiently transferred by cascades to the lowest quartet, the $1s2s2p\ ^4P$ state. This demonstrates that our measured ^4P cross sections and related R ratios arise not only from direct, genuine collision induced transfer, but also from cascades, as pointed out in the introduction.

In parallel with the experimental investigations, we have performed *ab initio* dynamical calculations involving *three* active electrons within a full configuration interaction approach. Our treatment is based on a semiclassical atomic orbital close-coupling approach (referred to as 3eAOCC in the following), with asymptotic descriptions of the atomic collision partners [24, 39, 40]: the time-dependent Schrödinger equation is solved non perturbatively, with inclusion of all couplings related to the static and dynamic interelectronic repulsions and effects stemming from the Pauli exclusion principle. This allows for an accurate modelling of the C^{4+} and C^{3+} electronic structures, including spin and spatial components, and of their dynamics inducing, among others, excitation and capture to doubly excited states on the carbon center [41]. It therefore goes much beyond frozen core models advocated in the past [18, 23], where only *one* active electron is considered in the dynamics. Both atomic center electronic structures are represented in terms of sets of Gaussian-type orbitals (GTO) and selected products of these GTOs, in order to obtain fully antisymmetrised, electron indistinguishable wavefunctions for states of singlet, doublet, triplet and quartet spin symmetries. The GTO sets were optimised to accurately describe up to three open-shell electronic configurations with special emphasis on $C^{3+}(1s2\ell n\ell')$ for $n = 2, 3$ and $\ell, \ell' = 0, 1$ (see Supplemental Material for details [42]). Total cross sections (after multiplying by a factor of 2 to account for the two electrons on the real targets) can then be computed for all processes spanned by the basis sets. The ratio R (Eq. 2) is evaluated, using partial (M_L=0) cross sections for the three P states under consideration, in accordance with known ZAPS sensitivity [33] to the component parallel to the impact velocity direction (defining the z-axis in our calculations). Since states lying above the $C^{3+}(1s2s2p\ ^{2,4}P)$ levels are present as well in our basis sets, R was also evaluated including radiative cascade feeding within the quartet symmetry [18, 20, 23], in accordance with the above discussion.

In Fig. 3, we show the present results (in black lines and squares) on the ratio R for He and H_2, together with the previous independent results (in red lines and circles) for the He target [18, 23], pointing out the disagreement existing to date. For R evaluated theoretically, we provide three limiting cases: (i) the genuine R value (dotted lines) calculated using the $2p$ SEC cross sections stemming from the 3eAOCC calculations, and (ii) two R values taking into account radiative cascade contributions within the quartet series, in accordance with the discussion above.

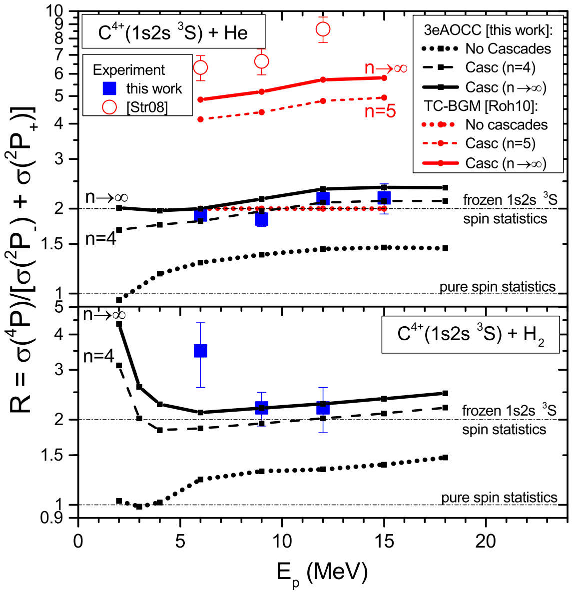

FIG. 3. Ratio R (Eq. 2), for $C^{4+}(1s2s\ ^3S)$ collisions with He (top) and H_2 (bottom) as a function of projectile energy. Experiment (ZAPS): Squares (this work), circles [18]. Theory: Black lines (3eAOCC - this work), red lines [23]. Results *without* (dotted) and *with* radiative cascades from $1s2snl\ ^4L$ states up to the indicated n (dashed) and extrapolated to $n \to \infty$ (solid) are shown. The *frozen* $1s2s\,^3S$ core spin statistics and *pure* spin statistics values are also indicated.

These two latter R values were evaluated using radiative branching ratios calculated with the COWAN code [43] and SEC cross sections to higher-lying $1s2sn\ell\ ^4L$ states provided by our AOCC treatment. We then include cascades from SEC populating only the $n = 3$ and $n = 4$ quartet levels (black dashed lines) and extrapolate to include all higher quartets (black solid lines) based on an n^{-3} population model, also used previously [23]. Excellent agreement with our measured R values is observed for both targets. This unambiguously demonstrates that cascades make an important contribution to the measured ratio R, increasing with decreasing impact energies, while masking the spin statistic considerations advocated in the past. Finally, the difference observed with the TC-BGM calculations [23] (red lines in Fig. 3) can be readily attributed to the present use of a dynamic approach involving *several* active correlated electrons, thus avoiding the constraints of the $1s2s\,^3S$ frozen core approximation required in *one*-electron treatments.

The important new understanding provided by the present 3eAOCC approach is that the value of R computed without cascades (dotted black lines in Fig. 3), i.e. stemming from the genuine scattering $2p$ capture process alone, is found to lie between 0.9 and 1.5 for both targets. These results depart *significantly* from the two limits one can expect from spin statistics arguments, and indicate that all *three* levels are populated, in a *non* statistical way. This also shows that even in our high impact energy domain, i.e. for collision time scales of the order of 10^{-17} s (attosecond regime), the 1s2s projectile core electrons *cannot* be considered frozen, but that channel couplings and electronic correlations play a crucial role in determining the state populations created by the addition of the captured electron. Therefore, one-electron models describing simply the dynamics of the captured electron alone, cannot give a realistic view, though they may provide reasonable cross sections.

To gain further insight into the SEC dynamics (Eq. 1), we consider the simplest representation of the three $1s2s2p\ ^4P$, $^2P_\pm$ states in terms of the $1s$, $2s$ and $2p$ atomic orbitals, schematically represented only by their spins as:

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

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

$$|^2P_+> \equiv \frac{1}{\sqrt{6}}(|\downarrow\uparrow\uparrow| + |\uparrow\downarrow\uparrow| - 2|\uparrow\uparrow\downarrow|) \tag{3c}$$

(see Supplemental Material [42]). These simple determinantal state wavefunctions are eigenfunctions of $\mathbf{S}^2$, the total spin operator, and correspond for simplicity here, to the *largest* M_S components. They do provide *correct energy ordering* of the states, as driven by the dominant exchange integral between $2s$ and $2p$ orbitals. Starting from the initial $1s2s\ ^3S$ state ($\equiv\uparrow\uparrow$), a spin-up or -down electron from He can be directly transferred to the projectile to create respectively, the ^4P state (Eq. 3a) or the $^2P_+$ state (through the third term in Eq. 3c). However, the creation of the $^2P_-$ state requires, in addition to transfer, a spin exchange between the active target electron and one of the projectile electrons. This involves a second-order process, less likely than the direct capture mechanism populating the ^4P and $^2P_+$ states. To support and further quantify this model, we estimate the relative magnitude of electron capture to these three levels using the Oppenheimer-Brinkman-Kramers (OBK) approximation [42, 44]. Capture to the two favoured levels, ^4P and $^2P_+$, is then described as dominantly driven by the projectile nucleus-electron attraction matrix element I^P between the target $1s$ and the carbon $2p$ orbitals, i.e. I^P for ^4P and $\sqrt{2/3}\ I^P$ for $^2P_+$ (see Supplemental Material [42]). However, capture to the $^2P_-$ level is *exclusively* controlled by *exchange* electron-electron couplings, approximately a factor $Z_p = 6$ *weaker*.

This rather simple explanatory model, based on a correct spin and spatial description of the states, nevertheless gives a reasonable estimate of the ratio R, with an upper limit (neglecting the weak $^2P_-$ capture contribution) equal to 3/2, in agreement with our elaborate *ab initio* 3eAOCC calculations. It clearly exposes the weaknesses of frozen core approximations and pure spin statistics considerations and provides evidence for the existence of a sophisticated, counterintuitive [45] effect. This latter selectively *bars* direct capture to the $^2P_-$, expected to be the only active doublet channel in the frozen core picture, by *shielding* the Coulomb attraction between the projectile nucleus and the active electron (no I^P coupling to promote this channel in OBK). This mechanism is only active when the Pauli exclusion principle can be advocated, i.e. in multi-electron systems and approaches, and we therefore refer to it as *Pauli shielding.* This mechanism is clearly different from other Pauli excitation, exchange and blocking mechanisms advocated in past investigations [7, 19, 46]. This simple explanatory model brings out all the physical features needed to interpret the outcome of the experiment. However, only configuration interaction and close-coupling (included in 3eAOCC) can provide a quantitative description of the C^{3+} doubly excited states populated during the collision.

In conclusion, we provide experimental results for the $1s2s2p\ ^4P/^2P_\pm$ line ratio R for single electron capture in fast collisions of $C^{4+}(1s2s\ ^3S)$ with helium and hydrogen targets. Our measured R values are found to be nearly constant with collision energy and close to 2, in contrast to previous findings. In parallel, the ratio R calculated using a sophisticated multi-electron close-coupling approach is found to be in agreement, for the first time, with experiment, when post-collisional radiative cascades are also taken into account. These results resolve the previously existing disagreement between theory and experiment and draw attention to the limited predictive power of the frozen core approximation as regards to spin statistics in highly correlated dynamical atomic systems. To better understand our findings, we propose an elegant Pauli shielding mechanism related to strong exchange effects which selectively (and counter intuitively) obstructs specific reaction channels. Systematic isoelectronic studies will be of great interest to further validate these conclusions in a more general context.

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