Evidence for Pauli Exchange Leading to Excited-State Enhancement in Electron Transfer

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Single- and double-electron transfer to autoionizing $1s2l2l'$ configurations in fluorine ions have been investigated for 1.1 MeV/u collisions of F^{7+} and F^{8+} with He and Ne. The resulting Auger electron emission spectra show anomolously large intensities for the formation of the metastable $1s(2s2p\,^3P)\,^4P$ state compared to the similarly configured $1s(2s2p\,^3P)\,^2P_-$ and $1s(2s2p\,^1P)\,^2P_+$ states. The large ^4P intensity, which cannot be explained on the basis of spin statistics, is attributed instead to the Pauli exchange of similarly aligned electrons.

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The dynamics of nonadiabatic collisions between charged particles is governed primarily by the Coulomb interaction of the incident projectile with the target nucleus and the interactions of these nuclei with the active electrons. On the other hand, atomic structure is determined by electron correlation (i.e., the electron-electron interaction) in conjunction with the Pauli exclusion principle, and, of course, the electron-nucleus interaction. Because electrons are fermions, Pauli exclusion should play a significant role not only in the structure of atoms, but also in the population of states during collisional interactions between atoms or ions. However, this latter point has been only sparsely investigated.

Some 30 years ago enhanced K-shell vacancy production yields in relatively slow collisions (less than $\sim$0.1 MeV/u) were attributed to a "Pauli excitation" mechanism [1,2]. More recently, Pauli "blocking" was discussed in connection with K-shell excitation processes in fast ($\sim$10 MeV/u) highly charged projectiles [3], and was also suggested to play a role in giving rise to double-K-shell-vacancy states in lithium following bombardment by relativistic ions ($\sim$100 MeV/u) [4]. In other work for electron capture to and electron loss from hydrogenlike ions in collisions with neutral targets (He^+ + Ne), measured cross sections were found to be consistent with theoretical calculations that included the antisymmetry of the many-electron wave function, while they differed by about a factor of 2 from results obtained from a naive calculation based on multinomial statistics [5], a result that was also attributed to Pauli blocking.

In the present Letter, the effect of the Pauli principle on collision dynamics is isolated by investigating electron transfer leading to the formation of autoionizing $1s2s2p$ configurations in highly charged fluorine ions. An anomolously large intensity, attributed to an electron exchange interaction between projectile and target electrons of the same spin alignment during the transfer process, is observed for formation of the metastable $1s(2s2p^3P)\ ^4P$ state compared to other $1s2s2p$ configured states. Such an enhancement may be useful for controlling the production of certain long-lived ionic excited states with radiative decay rates comparable to nonradiative (Auger) decay rates [6], for example, in the development of high-energy x-ray lasers [7,8].

The measurements were conducted at Western Michigan University using the tandem Van de Graaff accelerator. Fluorine ions with charge states 7^+ or 8^+ were accelerated to 1.1 MeV/u and directed into the scattering chamber where they interacted with a He or Ne gas target contained inside a differentially pumped cell. After exiting the interaction region, Auger electrons emitted from the moving projectile and along the direction of the beam (i.e., at 0°) were detected, while the beam was collected in a Faraday cup. The pressure dependence of the electron yield was measured to ensure that single-collision conditions prevailed in the gas target.

Intermediate-excited states associated with electron capture events were identified from high-resolution measurements of the subsequent Auger emission using a two-stage parallel-plate electron spectrometer, in which electrons emerging from the first stage were retarded to a pass energy of 100 eV prior to entering the second stage. Absolute differential cross sections were determined from auxiliary measurements for elastically scattered (binary encounter) electrons by comparing the measured yields with calculated cross sections as done previously [9,10].

Results for single capture to F^{7+} and double capture to F^{8+} in collisions with He and Ne are shown in Fig. 1, in which the energy spectra of forward ejected electrons from the fast moving projectiles have been transformed to the projectile frame of reference. Identical intermediate excited states with similar intensities are formed for both single and double capture, except for double transfer in F^{8+} + He collisions [Fig. 1(c)].

Because of the relatively long lifetimes of the ^4P state ($\sim 10^{-8}$ s) [6,11], instrumental corrections must be made to the measured intensity of this state for two competing effects (all other observed states have sufficiently short lifetimes so that corrections are not needed). First, ions

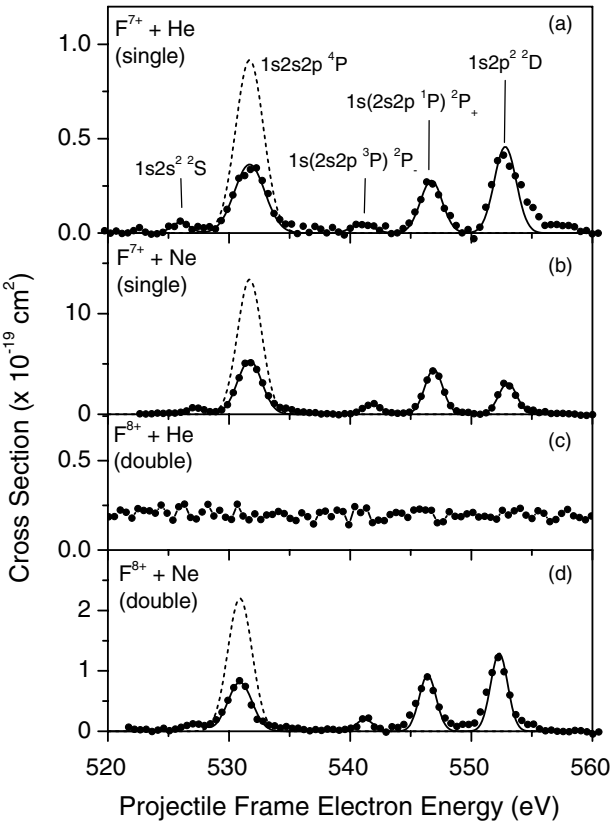

FIG. 1. Measured spectra for single electron transfer to F^{7+} and double electron transfer to F^{8+} for 1.1 MeV/u collisions of these ions with He and Ne. The observed $1s2l2l'$ intermediate states are indicated (for F^{8+} + He no measurable intensity was observed for these states). The dashed curves represent the true intensity of the $1s2s2p\ ^4P$ state after correction for instrumental effects due to the long lifetime of this state (see text).

that decay in flight after exiting the gas cell but prior to entering the spectrometer have an increasing solid angle for detection as they approach the spectrometer entrance, thereby increasing the observed intensity. On the other hand, ions that pass through the spectrometer before decaying are "lost" from detection and consequently decrease the measured intensity. Corrections for these competing effects were made by numerical integration [12] over the flight path using relevant lifetimes from Ref. [6]. The corrected intensities for the ^4P state (dashed curves in Fig. 1) are significantly larger than the measured intensities due to the dominance of the correction for ions that pass through the spectrometer prior to decay.

The most striking feature of the spectra of Fig. 1 is the large intensity (as indicated by the dashed curves) of the metastable $1s(2s2p\,^3P)\ ^4P$ state as contrasted with the considerably smaller intensities observed for the similarly configured $1s(2s2p\,^3P)\ ^2P_-$ and $1s(2s2p\,^1P)\ ^2P_+$ states. For F^{8+} + He [Fig. 1(c)] there is no measurable intensity for double capture to any of the $1s2l2l'$ states. It is noted that the F^{7+} beam contained a mixture of $1s^2$ ground state (~80%) and $1s2s\ ^3S$ metastable state (~20%) ions [10]. However, formation of the $1s2s2p\ ^4P$ state is attributed almost entirely to single capture by $F^{7+}(1s2s\,^3S)$ because single capture to the $F^{7+}(1s^2)$ ground state is unlikely to be accompanied by $1s \rightarrow 2p$ excitation such that a ^4P state is formed (see below).

In order to understand the large intensity for the $1s(2s2p\,^3P)\,^4P$ line in single capture to $F^{7+}(1s2s\,^3S)$ and in double capture to F^{8+} $(1s)$, we first consider its expected intensity compared to the similarly configured $1s(2s2p\,^3P)\ ^2P_-$ and $1s(2s2p\,^1P)\ ^2P_+$ states based on spin statistics. Since each of these states has the same total orbital angular momentum, it is necessary to consider only the total spin of the three states to determine their multiplicities. The ^4P line with a total spin $S = 3/2$ has a multiplicity of four, while the $^2P_-$ and $^2P_+$ states with total spin $S = 1/2$ have a multiplicity of two each. Thus, the statistical multiplicity of the ^4P state is expected to be just twice that of either the $^2P_-$ and $^2P_+$ states.

However, configuration mixing of the $^2P_-$ and $^2P_+$ states must also be considered because these states have the same total orbital and spin angular momenta. This mixing has the effect of reducing the intensity of the $^2P_-$ state and increasing the intensity of the $^2P_+$ state. Hence, a more appropriate comparison of intensities based on spin statistics is the ratio $^4P/(^2P_- + {}^2P_+)$, which should give a value of unity. Table I lists the measured values of this ratio for the spectra of Fig. 1, showing the ^4P line to be enhanced by at least a factor of 2 over this expected value.

Another consideration that can alter the relative intensities is the contribution of resonant-transfer-excitation (RTE) [13,14] to the formation of some of the $1s2l2l'$ states. In this process, electron transfer to the ground state of $F^{7+}(1s^2)$ is accompanied by simultaneous electronic excitation $(1s \rightarrow 2p)$ of the ion. The intensities of the $1s(2s2p\,^1P)\ ^2P_+$ and $1s2p^2\ ^2D$ states are most strongly increased by RTE (more than a factor of 2 for the present collision velocity), while the $1s(2s2p\,^3P)\ ^4P$ state is not affected at all by RTE [15]. Since the ^2D state does not involve the $1s2s2p$ electronic configuration, it will not be considered further here. Consequently, any RTE contribution to $^2P_+$ (or $^2P_-$) would decrease the expected value of unity for the ratio $^4P/(^2P_- + {}^2P_+)$ based on spin statistics alone.

To understand the enhancement of the ^4P state, we consider the pathways by which electrons can be transferred from the target (He or Ne) to the projectile to form

TABLE I. Measured $^4P/(^2P_- + {}^2P_+)$ ratios for the spectra shown in Figs. 1(a), 1(b), and 1(d). The uncertainties in the listed ratios are estimated to be less than ±10%.

Collision system	$^4P/(^2P_- + {}^2P_+)$
$F^{7+}(1s2s\,^3S)$ + He	2.9
$F^{7+}(1s2s\,^3S)$ + Ne	2.5
$F^{8+}(1s)$ + Ne	2.0

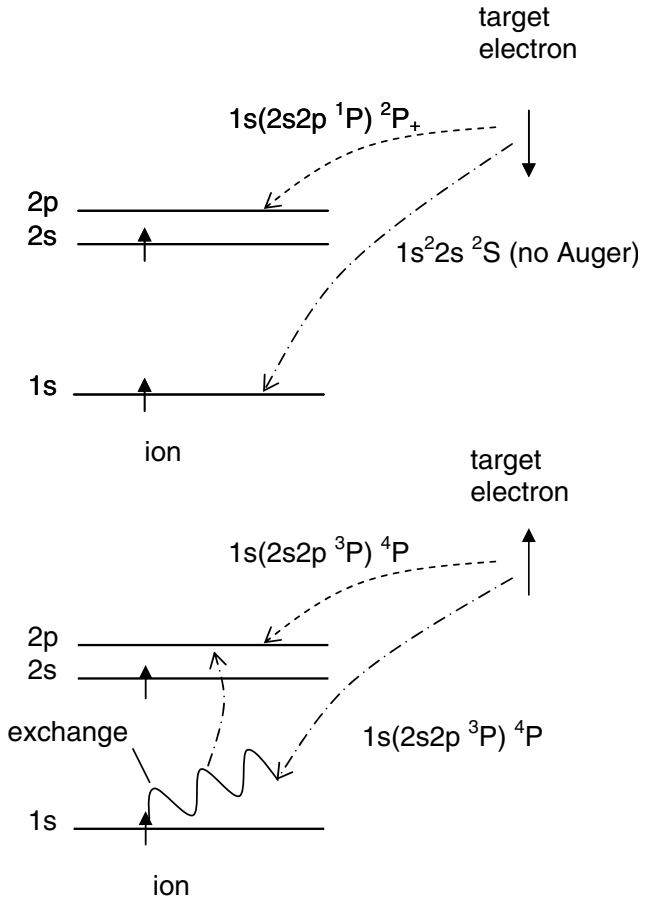

FIG. 2. Pathways for formation of the $1s(2s2p\,^1P)\ ^2P_+$ and $1s(2s2p\,^3P)\ ^4P$ states by transfer of a target electron antialigned (upper part) and aligned (lower part), respectively, with the $F^{7+}(1s2s\,^3S)$ projectile electrons. The Pauli exchange interaction contributing to formation of the $1s2s2p\ ^4P$ state is indicated by the wavy line connecting the $1s$ electron and the incoming target electron.

the observed $1s2l2l'$ states. Figure 2 shows possibilities for single transfer to $F^{7+}(1s2s\,^3S)$ of an electron that is antialigned (upper part) or aligned (lower part) with the projectile electrons, respectively. The upper part shows transfer of an antialigned target electron to the $2p$ subshell to produce the $1s(2s2p\,^1P)\ ^2P_+$ state, while the lower part indicates an aligned target electron also going directly to $2p$ to produce the $1s(2s2p\,^3P)\ ^4P$ metastable state. For antialignment the transferred electron could also go to $2s$ giving the $1s2s^2\ ^2S$ state, but this pathway occurs with relatively small probability, in accordance with the multiplicity of this state (Fig. 1).

For transfer to the $1s$ subshell, an antialigned target electron (upper part of Fig. 2) gives the $1s^22s\ ^2S$ ground state from which there can be no Auger emission. On the other hand, for an aligned target electron (lower part) both electrons cannot occupy 1s due to the Pauli exclusion principle. It is proposed that the incoming aligned target electron interacts with the projectile $1s$ electron via a *Pauli exchange interaction* such that one of them is transferred to $2p$ to form the $1s(2s2p\,^3P)\ ^4P$ state, as illustrated schematically in Fig. 2. Hence, by means of this exchange, the ^4P state is enhanced beyond the intensity expected for direct transfer of an aligned target electron to the $2p$ orbital, and the ratio $^4P/(^2P_- + {}^2P_+)$ provides a measure of the magnitude of this effect.

It is noted that the transferred electron is also aligned with the projectile $2s$ electron, so a similar exchange could occur in the $2s$ orbital resulting in formation of the ^4P state. This latter pathway is likely to be less significant, however, in view of the small intensity observed for formation of the $1s2s^2\ ^2S$ state (Fig. 1).

The actual situation is, of course, a bit more involved than depicted in Fig. 2. In order to ensure that the three-electron states under discussion are eigenfunctions of total angular momentum L and spin S they must be constructed as linear combinations of Slater determinants formed from the indicated one-electron states. Nevertheless, only the ^4P state has a contribution for which the spins of all three electrons are aligned as indicated in the lower part of Fig. 2.

Within the time-dependent Hartree-Fock (TDHF) picture of the collision, the dynamical Pauli exchange corresponds to a time-dependent potential between similarly aligned electrons. Although it is impossible to predict its effect on the electron dynamics accurately without a full TDHF calculation some qualitative statements can be made: Before the collision, the exchange potential between target and projectile electrons does not contribute due to the spatial separation of these electronic orbitals. However, this potential becomes nonzero during the collision as the time-propagated electronic wave packets extend over similar regions in space. This situation is met in the present experiments, in which (at least) one target electron is transferred while the initial projectile electrons have a large probability to remain bound. In the case of antialigned electrons the exchange potential is zero at all times. Thus, the Pauli exchange translates directly into a term in the collisional interaction potential that has the possibility to lead to an alteration of the expected line intensities in accordance with the observations of Fig. 1.

For double transfer to $F^{8+}(1s)$ in collisions with Ne [Fig. 1(d)] the measured ratio for $^4P/(^2P_- + {}^2P_+)$ is also considerably larger than the expected value of unity based on spin statistics (Table I), suggesting a similar mechanism for enhancing the ^4P state. Figure 3 shows some pathways for the transfer of two electrons to $F^{8+}(1s)$ in collisions with the Ne target. Two different initial target electron spin configurations are considered: (1) one spin aligned and one spin antialigned with the projectile $1s$ electron (upper part), and (2) both spins aligned with the projectile $1s$ electron (lower part). It is noted that both target spins could also be antialigned with the projectile electron but this case will not be considered separately here. For oppositely aligned target spins (upper part), it is seen that if one-electron is transferred to $2p$

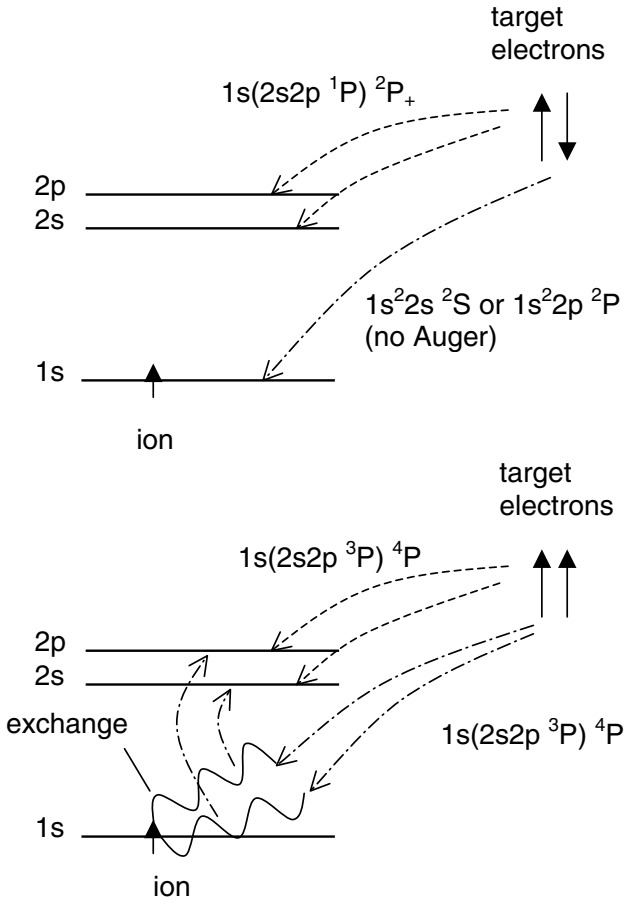

FIG. 3. Pathways for formation of the $1s(2s2p\,^1P)\ ^2P_+$ and $1s(2s2p\,^3P)\ ^4P$ states by transfer of target electrons with one spin aligned and one spin antialigned (upper part) and both spins aligned (lower part), respectively, with the $F^{8+}(1s)$ projectile electron. The double Pauli exchange interaction contributing to formation of the $1s2s2p\,^4P$ state is indicated by the wavy lines connecting the $1s$ electron with the incoming target electrons.

and one to $2s$ the $1s(2s2p\,^1P)^2P_+$ state is formed (both electrons could also go to $2p$ to form the $1s2p^2\ ^2D$ state, but this possibility is not considered here). Similarly, for both target spins aligned (lower part) the $1s(2s2p\,^3P)\ ^4P$ is formed when one-electron is transferred to $2p$ and one to $2s$.

For transfer to the $1s$ level (upper part of Fig. 3) the antialigned electron can go to the K shell to form the $1s^22s\ ^2S$ ground state or the $1s^22p\ ^2P$ excited state. In either case, no Auger emission will result. On the other hand, for both target spins aligned (lower part) two electrons cannot occupy the $1s$ level due to the Pauli exclusion principle, a situation similar to that for single capture pictured in the lower part of Fig. 2, but with an important difference. While an incoming spin aligned target electron can again exchange with the projectile $1s$ electron promoting one of them to $2s$ or $2p$, there must be a *double exchange* to form the $1s(2s2p^3P)\ ^4P$ state, as illustrated schematically in Fig. 3. Then, by means of this double Pauli exchange, the ^4P state can be enhanced beyond the intensity expected for direct transfer of aligned target electrons to $2s$ and $2p$, with the ratio $^4P/(^2P_- + {}^2P_+)$ providing a measure of this effect.

In summary, anomalously large probabilities have been observed for forming the $1s(2s2p^3P)\ ^4P$ state in single and double-electron transfer to $F^{7+}(1s2s^3S)$ and $F^{8+}(1s)$, respectively. The enhancement of the ^4P state is at least a factor of 2 larger than expected based on independent-particle dynamics and spin statistics, and is attributed to a dynamical exchange potential between similarly aligned target and projectile electrons that results from the Pauli exclusion principle, which prevents electrons with like spins from simultaneously occupying the $1s$ (or $2s$) orbital. A major challenge posed by the present observations is the calculation of the effect of the Pauli exchange potential for the collision systems studied here. Such a TDHF-type calculation would determine whether exchange can quantitatively explain the observed enhancement of the ^4P state, or whether dynamical correlation effects must also be considered.

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