Quantifying Relativistic Interactions from Angular Momentum Partitioning Measurements during Photoionization

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We have measured the degree of helicity of fluorescent radiation from $Ar^+\{3p^4[^3P]4p\}\,^2P^o_{1/2}$ formed by circularly polarized synchrotron radiation in the region of double excitations converging to $Ar^+ 3p^4\,nl$ satellite states. Angular momentum coupling allows the partitioning of the one unit of angular momentum brought into the system to be demarcated. We obtain a nonvanishing expectation value of the total spin of the residual ion-photoelectron system indicating significant relativistic interactions during the photoionization process.

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Quantifying the degree and nature of interparticle interactions in dynamic processes is one of the major goals of current atomic and molecular physics research. One particular class of interactions, namely those in many electron systems, results in the correlated or organized motion of the electrons during dynamic processes. One of the most effective methods for studying the measurable consequences of correlated motions of electrons in isolated atoms is the experimental characterization of many-electron processes in photoionization [1]. Since a photon interacts with a single electron, it follows that measurable consequences of *multielectron* phenomena must result from some form of dynamic, interelectron interaction. Historically, most of these studies have used the information from the measurement of the properties of the photoelectron such as the energy dependence of total and/or differential cross sections, angular distributions of the photoelectrons, and their spins [1,2]. This work culminated in the measurements of the emission angle and spins of the photoelectrons from Xe $4d$ line along with the subsequently emitted $N_{4,5}O_{2,3}O_{2,3}$ Auger electrons to extract partial wave probabilities and the phase differences of the photoelectron at an ionizing photon energy of 93.8 eV [3].

In this Letter, we articulate a new paradigm beyond the use of energy, emission angle, and spin of the photoelectron. Our organizing principle is to determine how the single unit of angular momentum brought into the system by an incident circularly polarized, ionizing photon is partitioned in the form of spin and orbital angular momenta of the residual ion and the emitted electron during the photoionization. Any measured value of the z component of the total spin of the final state of the system that is different than the initial component must result from relativistic interactions. The absorption of the incident circularly polarized photon transfers one unit of angular momentum to an atomic electron. This electron exchanges energy and angular momentum with other electrons depending upon the nature of the interactions that take place. As a result, z components of orbital and spin angular momentum reside in different electronic structures of the final state of the system. We measure the helicity difference of the fluorescence radiation of the excited ion emitted in the direction of the initial photon propagation, as illustrated in Fig. 1. Using angular momentum conservation and recoupling, we extract from the helicity measurements the z components of the spin and orbital angular momentum of all structural components of the system. Since pure Coulomb interactions conserve spin, any transfer of angular momentum of

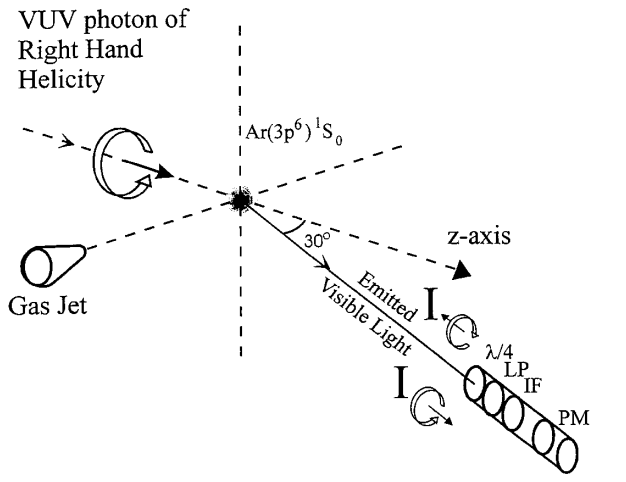

FIG. 1. Experimental setup. The linear polarization of incident ionizing radiation from Beam Line 10.0.2 of the Advanced Light Source is transformed into >99.7% right hand helicity using a four-reflector quarter-wave retarder (not shown). The visible photon at 465.8 nm emitted by the residual excited ion after photoionization is detected at 30° with respect to the quantization axis defined by initial beam direction. $\lambda/4$ denotes the quarter-wave retarder for the visible radiation, LP is the linear polarizer, IF is an interference filter with 0.3 nm FWHM bandpass, and PM is the photomultiplier.

the incident photon into the third component of the total spin of the ion-photoelectron system is indicative of relativistic interactions during the photoionization.

We define the degree of helicity P_3 in terms of the Stokes parameter definition $P_3 = (I_{\mathrm{LHH}} - I_{\mathrm{RHH}})/(I_{\mathrm{LHH}} + I_{\mathrm{RHH}})$ where I_{LHH} and I_{RHH} are the measured intensities of fluorescence radiation with left hand and right hand helicity, respectively. From the measured helicity we determine the expectation value of the z component of the spin and orbital angular momentum of all electronic structural constituents of the final state of $(\mathrm{Ar}^+)^* + e^-$ system, where the incident photon direction is taken as the quantization axis.

Measurements were performed at the Advanced Light Source where linearly polarized vacuum ultraviolet (VUV) radiation from the U-10 undulator was converted into circularly polarized radiation using reflection from a gold mirror retarder based on earlier designs and prototypes [4]. In a separate experiment we determined that the retarder produced no less than 99.7% circularly polarized light in the 35.5 to 37 eV ionizing photon energy range with a transmission efficiency of about 1%. In this energy range, an excited Ar^+ ion is formed by either direct ionization to the continuum or via the formation of an intermediate, doubly excited resonance [5–7]. With circularly polarized VUV radiation of right hand helicity, conservation of angular momentum dictates that this final ion-photoelectron system must have a total angular momentum of $J_t = 1$ and $M_{J_t} = +1$.

The helicity of the fluorescent photon emitted by the excited residual ion reflects the degree to which the angular momentum of the VUV photon is transferred to the excited Ar^+. Angular momentum coupling rules are used to express the ionic angular momentum in terms of spin and orbital angular momentum of the various electronic components. In this particular experiment, we measure the degree of helicity of the 465.8 nm fluorescent radiation from the $\mathrm{Ar}^+\{3p^4[^3P]4p\}^2P^{\mathrm{o}}_{1/2}$ to $\mathrm{Ar}^+\{3p^4[^3P]4s\}^2P^{\mathrm{o}}_{3/2}$ transition [8] emitted at 30° with respect to the initial angular momentum vector of the incoming ionizing photon. The measurements are performed with constant detection efficiency from the ionizing threshold of 35.561 eV of $\mathrm{Ar}^+\{3p^4[^3P]4p\}^2P^{\mathrm{o}}_{1/2}$ formation to 36.7 eV with an energy resolution of 8 meV. The $\mathrm{Ar}^+\{3p^4[^3P]4p\}^2P^{\mathrm{o}}_{1/2}$ state that emits the fluorescent photon of $\lambda = 465.8$ nm derives its label from its most dominant L-S coupled element. A more accurate representation of this fluorescent state can be written in terms of pure L-S coupled states as $c_1|3p^4[^3P]4p\,^2P^{\mathrm{o}}_{1/2}\rangle + c_2|3p^4[^3P]4p\,^2S^{\mathrm{o}}_{1/2}\rangle + c_3|3p^4[^1D]4p\,^2P^{\mathrm{o}}_{1/2}\rangle$. Statz *et al.* [9] give $c_1 = -0.834$, $c_2 = 0.4036$, $c_3 = 0.3625$, and two additional quartet states with coefficients less than 0.07 that we neglect.

For this particular state, the measurement of the degree of helicity of the fluorescence of a characteristic wavelength uniquely determines the expectation value of the z component of the total ionic angular momentum $J = \frac{1}{2}$. Using the Fano-Macek formalism, we relate the measured P_3 to the expectation value of the z component of the total angular momentum J through the use of the orientation coefficient $O_0(J)$ [10,11]:

$$O_0(J) = \frac{\langle J_z\rangle}{J(J+1)} = \frac{\sum_{M_J} M_J |\langle JM_J \mid \psi\rangle|^2}{J(J+1)} = -\frac{2P_3}{3h^{(1)}\sin\phi}, \quad (1)$$

where $h^{(1)}$ is a constant depending on the initial and final states of the ion that fluoresces ($h^{(1)} = -1/2$ for the transition studied) [12]. The symbol $|\psi\rangle$ denotes the state of the system formed by the residual ion and the photoelectron. The quantities $|\langle JM_J \mid \psi\rangle|^2$ are the probabilities for forming a residual ionic state with total angular momentum and magnetic quantum numbers J and M_J, respectively, integrated over all electron emission angles. The last equality of Eq. (1) is the application of the Fano-Macek formalism and normalization [10] to our experiment, which has cylindrical symmetry [11]. The lower graph in Fig. 2 shows the

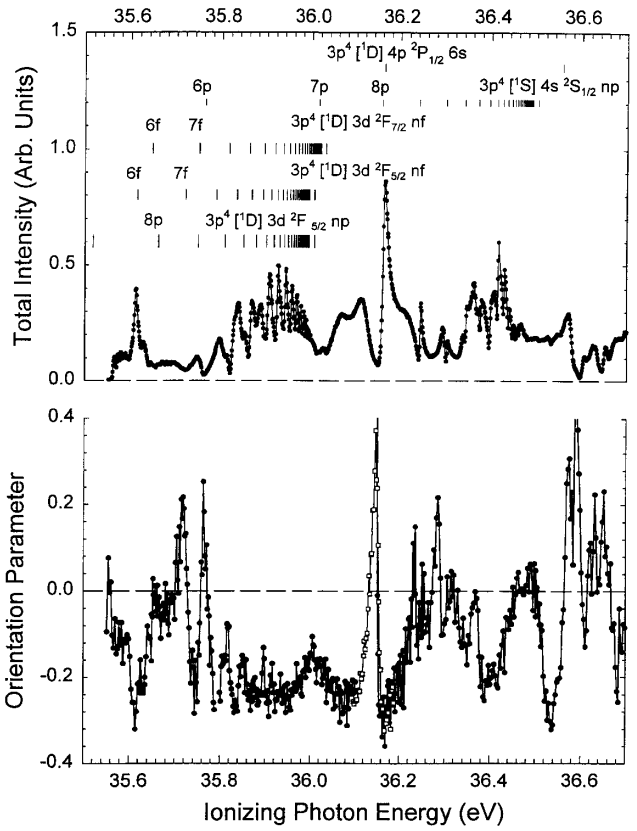

FIG. 2. Top graph: Total intensity of the fluorescence radiation at 465.8 nm from the decay of the $\mathrm{Ar}^+\{^2P_{1/2}\}$ produced by linearly polarized VUV light at a resolution of 3 meV. The vertical lines show the known doubly excited states of Ar. Bottom graph: The orientation parameter for the total angular momentum of the residual excited ion. Filled and open circles are used for data taken at different runs at ALS.

values of $O_0(J)$ for different incident photon energies calculated from the measured value of P_3. The upper half of Fig. 2 is the relative total intensity of the fluorescence radiation as a function of ionizing photon energy. The intensity spectrum was taken with linearly polarized incident photons with a resolution of 3 meV using a 1 meV step size. The vertical lines on the graph represent the position of doubly excited states of Ar. These are obtained from the known series limits and accepted ranges of quantum defects [5–8].

We denote the total, orbital, and spin angular momenta of the emitted photoelectron by j_e, l_e, and s_e, respectively. Parity and angular momentum conservation restrict the emitted photoelectron to s and d partial waves with total angular momentum $j_e = \frac{1}{2}$ and $\frac{3}{2}$, respectively. Therefore, there is a one-to-one correspondence between the total angular momentum j_e of the photoelectron and its orbital angular momentum.

To determine the expectation value of the z component of the orbital and spin angular momenta resulting from the orbital motion and the spin of the excited ion, we introduce orientation coefficients $O_0(L)$ and $O_0(S)$ in a manner similar to Eq. (1). Similarly, $O_0(s_e)$ represent the spin orientation of the photoelectron. The orientation coefficient resulting from angular momentum X is given by

$$O_0(X) = \frac{\langle X_z \rangle}{X(X+1)} = \frac{\sum_{M_X} M_X |\langle X M_X \,|\, \psi \rangle|^2}{X(X+1)}, \quad (2)$$

where $X = L$, S, or s_e.

Our goal is to determine whether the z component of the total final spin of the excited ion-photoelectron system is different from its initial component. Hence, in addition to the total spin of the ion, we also need to find the expectation value of the z component of the spin of all of the free electrons emitted to the 4π solid angle. The excited ionic state and the free electron are related through the condition that the total angular momentum of the total system $J_t = 1$ and $M_{J_t} = +1$. With the incident ionizing radiation of right hand helicity a pure s-wave photoelectron with total angular momentum $j_e = \frac{1}{2}$ must orient its spin along the propagation direction of this radiation. For a pure d wave, $j_e = \frac{3}{2}$ and its spin can be either up or down relative to this quantization axis. We can determine the probability of each partial wave by expressing the total wave function ψ of the residual excited ion plus free electron system as a linear combination of states with different j_e.

$$|\psi\rangle = \sum_{j_e} a_{j_e} |J j_e J_t M_{J_t}\rangle, \quad (3)$$

where $J_t = 1$ refers to the total angular momentum of the residual ion plus emitted electron system and $M_{J_t} = +1$. For a given J of the ion, the allowed values of j_e are restricted by the conservation of angular momentum and parity. The quantities $|a_{j_e}|^2$ are the partial wave probabilities of the emitted electrons. The partial wave probability amplitudes a_{j_e} contain all the dynamical information of the photoionization process. We can readily express the $O_0(J)$ in terms of partial wave probabilities $|a_{j_e}|^2$ of the electrons emitted to 4π allowing us to experimentally determine the value of each partial wave probability. This is accomplished by noting the total angular momentum $\mathbf{J}_t = \mathbf{J} + (\mathbf{l}_e + \mathbf{s}_e)$ and expanding the total wave function $|\psi\rangle$ of the excited ion plus free electron in terms of $|JM_J\rangle\,|l_e m_{l_e}\rangle\,|s_e m_{s_e}\rangle$.

$$|\psi\rangle = \sum_{j_e} a_{j_e} \sum_{\substack{M_J m_{j_e} \\ m_{l_e} m_{s_e}}} \langle JM_J j_e m_{j_e} \,|\, J_t M_{J_t}\rangle \langle l_e m_{l_e} s_e m_{s_e} \,|\, j_e m_{j_e}\rangle \times |JM_J\rangle\,|l_e m_{l_e}\rangle\,|s_e m_{s_e}\rangle. \quad (4)$$

As stated above, the eigenvectors $|JM_J\rangle$ can be expressed as a linear superposition of pure L-S coupled states. A second expansion in terms of the ionic orbital and spin angular momentum eigenstates gives

$$|\psi\rangle = \sum_{j_e} a_{j_e} \sum_{i=1}^{3} c_i \sum_{\substack{M_J m_{j_e} m_{l_e} \\ m_{s_e} M_L M_S}} \langle JM_J j_e m_{j_e} \,|\, J_t M_{J_t}\rangle \times \langle l_e m_{l_e} s_e m_{s_e} \,|\, j_e m_{j_e}\rangle \langle L^{(i)} M_L^{(i)} S M_S \,|\, JM_J\rangle \times |L^{(i)} M_L^{(i)}\rangle\,|SM_S\rangle\,|l_e m_{l_e}\rangle\,|s_e m_{s_e}\rangle, \quad (5)$$

where $L^{(1)} = L^{(3)} = 1$ and $L^{(2)} = 0$, and c_i coefficients are the mixing coefficients of pure LS coupled states that form the excited ionic state as given above.

Since the probability of exciting a state with particular M_J is $|\langle JM_J \,|\, \psi\rangle|^2$, projecting $\langle JM_J|$ onto $|\psi\rangle$ in Eq. (4) and using the normalization condition $\sum_{j_e} |a_{j_e}|^2 = 1$ we obtain the measured orientation parameter in terms of the partial wave probabilities $|a_{j_e}|^2$ of the electrons emitted to 4π.

$$|a_{1/2}|^2 = O_0(J) + \tfrac{1}{3} \quad \text{and} \quad |a_{3/2}|^2 = \tfrac{2}{3} - O_0(J). \quad (6)$$

Figure 3 shows the s-wave probabilities of the electrons emitted to 4π calculated from the measurements using Eq. (6). We note from Fig. 3 that the s-wave probability is small over most of the energy range investigated, except in the regions where the total cross section is small. Since there are only two partial waves, the energy dependence of the d-partial wave is the complement of that of the s wave shown in Fig. 3. Within the energy region of the large resonant structure near 36.170 eV the partial wave probabilities $|a_{1/2}|^2$ rapidly switch from a dominant s wave on the low energy side to all d wave at the peak of the resonance. Within a span of 40 meV, the propensity of $\Delta l = +1$ for photoabsorption changes from violated to maximally adhered to. This dramatic change in the partial wave character across the resonances manifests itself in a sign change in the degree of helicity of the radiation emitted by the excited ion (see near 36.170 eV in Fig. 2).

To calculate $O_0(S)$ we evaluate the square of the absolute value of the projection of $\langle SM_S|$ onto $|\psi\rangle$ in Eq. (5)

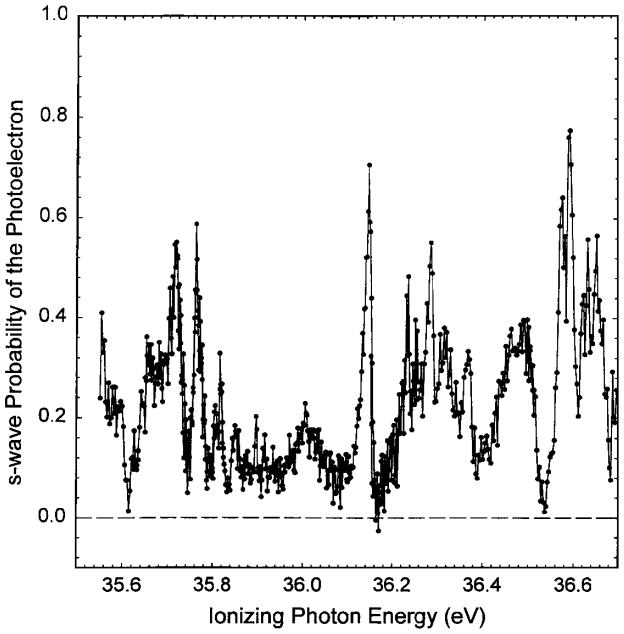

FIG. 3. s partial wave probability of the emitted photoelectron.

which gives us the probability of observing a given S and M_S. Substituting this result into (2) and using (6) gives

$$O_0(S) = -\tfrac{1}{3}(c_1^2 - 3c_2^2 + c_3^2)O_0(J). \quad (7)$$

To relate the orientation coefficient $O_0(s_e)$ to the measured $O_0(J)$, we project $\langle s_e m_{s_e}|$ onto the expansion of $|\psi\rangle$ in Eq. (4) and use Eq. (6) to eliminate $|a_{j_e}|^2$. We find

$$O_0(s_e) = O_0(J). \quad (8)$$

We can show that a nonvanishing measured value of $O_0(J)$ is a signature of relativistic interactions during the dynamic photoionization process. For the absorption of the initial VUV photon, the dipole interaction depends only on the spatial coordinates of the system and does not alter the spins. Since the initial system of Ar, designated by i, is in the ground state, it is a singlet state with $\langle M_{S_t}\rangle_i = 0$. Any measured nonzero net spin polarization of the total final system must result from relativistic interactions during the photoionization process. The expectation values of the z components of the spin of the final system of the residual ion and the photoelectron satisfy the condition

$$\langle M_S\rangle + \langle m_{s_e}\rangle = \langle M_{S_t}\rangle_f. \quad (9)$$

Expressing the expectation values in terms of orientation coefficients and using Eqs. (7) and (8) we find

$$\tfrac{1}{4}(3 - c_1^2 + 3c_2^2 - c_3^2)O_0(J) = \langle M_{s_t}\rangle_f. \quad (10)$$

For the values given in Statz *et al.* [9], $\frac{1}{4}(3 - c_1^2 + 3c_2^2 - c_3^2) = 0.665\,43 \approx \frac{2}{3} \neq 0$. Since the measured total orientation coefficient is nonvanishing over the considered energy range, except at a few crossing points where the orientation changes sign, we conclude that in the resonance region studied *the observed photoionization process displays significant relativistic interactions.*

Experimentally, other manifestations of relativistic interactions were observed for photoionization [13]. Theoretically, they were considered in the calculations of van der Hart and Greene [14]. This paper describes a new experimental way of determining the importance of the relativistic electron-electron interactions through the concept of angular momentum sharing and can be equally applied to resonant or nonresonant photoionization.

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