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Polarization of fluorescence radiation subsequent to inner-shell photoionization: *LS*-coupling formulas

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The polarization and angular distribution of fluorescence radiation subsequent to inner-shell photoionization in atoms are presented here in the important special case that dynamic amplitudes are calculated in *LS* coupling taking full account of anisotropic electron-ion interactions. The resulting formulas require for their evaluation no more dynamical information than is usually obtained in an *LS*-coupling calculation of the photoionization cross section. Exact geometrical relationships which are obscured in more general treatments become apparent in an *LS*-coupling formulation. Thus it is shown that in *LS* coupling the fluorescence resulting from photoionization of an *s* subshell in an atom having an initial orbital angular momentum $L_0 = 0$ has an *analytically known* constant polarization. Analytic predictions for the linear polarization of fluorescence radiation resulting from ionization of atoms with $L_0 = 0$ by unpolarized light are given and illustrated explicitly for nitrogenlike atoms. Experimental measurements of fluorescence polarizations which deviate from these theoretically exact predictions in *LS* coupling are thus a sensitive probe of relativistic and certain weak electron correlation interactions.

I. INTRODUCTION

Photoionization of an atom leads in general to an alignment and/or orientation of the resulting ion, even in the case of unpolarized incident radiation.^{1,2} That is, the magnetic quantum states M_J of the ion have an unequal probability distribution which may be detected, in the case of inner-shell photoionization, either by measurement of the anisotropic angular distribution of the subsequent Auger electrons¹ or by measurement of the polarization of the subsequent fluorescence radiation.²⁻⁹ The theoretical description of the fluorescence radiation is complicated by the large number of required summations over the atomic and ionic magnetic quantum numbers. Jacobs² has given a very general description in terms of density matrices. A much more intuitive description has been given by Fano and Macek³ in terms of a tensorial expansion of the emitted light intensity. However, the coefficients of this expansion are not determined theoretically, but are regarded as parameters to be determined experimentally. Caldwell and Zare⁴ have presented an *LS*-coupling description in the independent-electron model, which ignores anisotropic electron-ion interactions. Berezhko *et al.*⁵ also present an *LS* coupling, independent-electron-model description for the special case of closed-shell atoms. Finally, Klar⁸ has given a very general description which employs the tensorial expansion of the emitted light intensity of Fano and Macek³ and which analyzes the photoionization amplitudes in terms of the angular-momentum-transfer expansion of Dill and Fano.¹⁰⁻¹² The general treatments^{2,8} are of course the most detailed, but this complexity often ob-

scures geometrical relationships that are apparent when only the dominant electronic interactions, which may be described in *LS* coupling, are treated.

In this paper we present the angular distribution and polarization of fluorescent radiation subsequent to inner-shell photoionization for the important special case in which the photoionization amplitudes are calculated in *LS* coupling, i.e., ignoring spin-orbit and other relativistic interactions.^{13,14} We employ the same general angular momentum analysis used by Klar.⁸ The *LS*-coupling results for the emitted fluorescence intensity, however, are simpler: We obtain only a threefold summation over the photoionization amplitudes in contrast to a fivefold summation in the case of an arbitrary coupling scheme.⁸ Furthermore, we relate the photoionization amplitudes to the reduced electric-dipole matrix elements which are commonly obtained in the calculation of the associated photoionization cross section. In contrast to the *LS*-coupling results of Caldwell and Zare,⁴ we take full account of anisotropic electron-ion interactions. Thus, unlike Caldwell and Zare,⁴ we find that even photoionization of *s* subshells may lead to a nonzero polarization of the subsequent fluorescence radiation. In particular we show that in the special case of *s*-subshell photoionization of an atom having initial orbital angular momentum $L_0 = 0$, the polarization of the fluorescence radiation is an *analytically known* constant. Explicit values for these constants are given for the special case of nitrogenlike atoms ionized by unpolarized incident radiation. Experimental measurements of fluorescence polarizations which deviate from these exact *LS*-coupling predictions

are thus a sensitive probe of relativistic and/or certain weak electron correlation interactions, as discussed below.

II. ANGULAR DISTRIBUTION OF FLUORESCENCE

II. RADIATION

We assume that spin-orbit and other relativistic interactions may be ignored and thus use the quantum numbers *LSJM* to identify the atomic and ionic states. We specify our notation by writing the photoionization and fluorescence reactions for an arbitrary atom *G* as follows:

$$G(L_0 S_0 J_0 M_0) + \gamma(\omega, q) \rightarrow G^*(L_c S_c J_c M_c) + e^-(\vec{p}, m_s) \quad (1a)$$

$$G^*(L_c S_c J_c M_c) \rightarrow G(L_f S_f J_f M_f) + \gamma'(\vec{k}, \hat{\epsilon}) \quad (1b)$$

$$I_q(\vec{k}, \hat{\epsilon}) = \frac{C}{[J_0]} \sum_{M_0 M_f m_s} \int d\hat{p} \left| \sum_{M_c} \langle L_f S_f J_f M_f | \hat{\epsilon}^* \cdot \vec{r} | L_c S_c J_c M_c \rangle \langle L_c S_c J_c M_c | S | J_0 M_0 j_r = 1q \rangle \right|^2 \quad (2)$$

Here the amplitude *S* describes the photoionization process (1a) while the amplitude $\hat{\epsilon}^* \cdot \vec{r}$ describes the fluorescence transition (1b), both being treated in the electric-dipole approximation (e.g., the incident radiation is assumed to impart an angular momentum $j_r = 1$ to the atom). All unobserved magnetic quantum numbers are summed incoherently in the final state and coherently in the intermediate state and averaged incoherently in the initial state. The unobserved photoelectron's ejection direction \hat{p} is integrated over. *C* represents a normalization constant which is not needed to describe the angular distribution or the polarization of the fluorescence radiation. We use the notation $[x] \equiv 2x + 1$ throughout this paper.

A. *LS*-coupling result for $I_q(\vec{k}, \hat{\epsilon})$

We have reduced Eq. (2) using the assumption that the amplitudes *S* depend on the total-angular-momentum quantum numbers J_c and J_0 only geometrically. Otherwise the reduction is carried out, as discussed in detail by Klar,⁸ by using the tensorial expansion of the emitted light intensity of Fano and Macek³ and by analyzing the amplitudes *S* in terms of the angular-momentum-transfer expansion of Dill and Fano.¹⁰⁻¹² The assumption that the amplitudes *S* do not depend dynamically on the total angular momentum J_c of the intermediate state of the ion permits an analytical summation over the quantum number J_{cs} , which is the sum of J_c and the spin $s = \frac{1}{2}$ of the photoelectron. [The angular momentum J_{cs} is defined in the course of reducing Eq. (2)

In Eq. (1) ω is the energy of the incident photon γ in atomic units ($e = \hbar = m = 1$) and q specifies the spherical tensor component of the incident photon's polarization ϵ_q . The incident photon beam direction defines the *z* axis in the case of circularly polarized incident radiation (i.e., $q = \pm 1$), while the electric vector defines the *z* axis in the case of linearly polarized incident radiation (i.e., $q = 0$). (Unpolarized incident radiation is represented as an incoherent superposition of right and left circularly polarized incident radiation.) The photoelectron is described by its momentum \vec{p} and spin projection m_s . The fluorescence photon γ' is described by its wave vector \vec{k} and its polarization vector $\hat{\epsilon}$.

The intensity of fluorescence radiation is equal to

using the angular-momentum-transfer expansion.¹⁰⁻¹² As the overall amplitude in Eq. (2) is squared, there are two such rather complex summations over J_{cs} and J'_{cs} which we have evaluated using the graphical angular momentum techniques of Yutsis *et al.*¹⁵ Our result for the intensity of fluorescence radiation has the same form, of course, as obtained in the general case by Klar⁸; the dynamical coefficients A_{K0} , defined below, have, however, a somewhat simpler form due to our assumption of *LS* coupling for the transition amplitudes *S*.

Our result is

$$I_q(\vec{k}, \hat{\epsilon}) = C [L_0][S_0] \langle L_c S_c J_c || \gamma^{(1)} || L_f S_f J_f \rangle^2 \times [A_{00} X_{00}(\hat{\epsilon}, \hat{\epsilon}^*) + A_{10} X_{10}(\hat{\epsilon}, \hat{\epsilon}^*) + A_{20} X_{20}(\hat{\epsilon}, \hat{\epsilon}^*)] \quad (3)$$

Here the polarization vectors $\hat{\epsilon}$ and $\hat{\epsilon}^*$ from the two fluorescence amplitudes have been combined to form a tensor of rank *K*,

$$X_{K0}(\hat{\epsilon}, \hat{\epsilon}^*) \equiv [K]^{1/2} \sum_q \begin{pmatrix} 1 & 1 & K \\ q & -q & 0 \end{pmatrix} \epsilon_q(\epsilon^*)_{-q}, \quad (4)$$

as part of a recoupling transformation of the product of scalar products $(\hat{\epsilon} \cdot \vec{r}')(\hat{\epsilon}^* \cdot \vec{r})$ (cf. Ref. 3). The matrix element of the radius vector—which describes the electric-dipole transition producing the emission of fluorescence radiation—is given in Eq. (3) in terms of the reduced matrix element of the tensor $\gamma^{(1)}$. The coefficients A_{K0} are defined as follows: For $K = 0$,

$$A_{00} = -\frac{1}{3^{3/2}} \sum_{i j_t} [j_t] |S_i(j_t)|^2 \times P(L_0, S_0, J_0, L_c, S_c, J_c, j_t), \quad (5a)$$

where P represents a $12j$ coefficient of the second kind, which is most simply written analytically as a single summation over the dummy index x of the following product of four $6j$ coefficients¹⁶:

$$P(L_0, S_0, J_0, L_c, S_c, J_c, j_t) \equiv \sum_x [x] \begin{Bmatrix} J_c & j_t & x \\ L_0 & S_c & L_c \end{Bmatrix}^2 \begin{Bmatrix} \frac{1}{2} & J_0 & x \\ L_0 & S_c & S_0 \end{Bmatrix}^2. \quad (5b)$$

For $K=1, 2$,

$$A_{K0} = [J_c] [K]^{1/2} \begin{pmatrix} 1 & 1 & K \\ q & -q & 0 \end{pmatrix} (-1)^{J_f+2S_0+1+q} \times \sum_{i j_t j'_t} (-1)^{i+j_t+j'_t} [j_t] [j'_t] S_i^*(j'_t) S_i(j_t) \begin{Bmatrix} 1 & 1 & K \\ J_c & J_c & J_f \end{Bmatrix} \begin{Bmatrix} 1 & 1 & K \\ j_t & j'_t & l \end{Bmatrix} Q(L_0, S_0, J_0, L_c, S_c, J_c, j_t, j'_t, K), \quad (6a)$$

where Q is a $15j$ coefficient of the second kind, which is most simply written analytically as a single summation over the dummy index x of the following product of five $6j$ coefficients¹⁷:

$$Q(L_0, S_0, J_0, L_c, S_c, J_c, j_t, j'_t, K) \equiv \sum_x (-1)^x [x] \begin{Bmatrix} J_0 & \frac{1}{2} & x \\ S_c & L_0 & S_0 \end{Bmatrix}^2 \begin{Bmatrix} L_0 & S_c & x \\ J_c & j'_t & L_c \end{Bmatrix} \begin{Bmatrix} j'_t & J_c & x \\ J_c & j_t & K \end{Bmatrix} \begin{Bmatrix} j_t & J_c & x \\ S_c & L_0 & L_c \end{Bmatrix}. \quad (6b)$$

Finally, the amplitudes $S_i(j_t)$ may be defined in terms of the reduced dipole amplitudes for the photoionization process (1a) as follows^{13,14}:

$$S_i(j_t) \equiv \langle L_c S_c l | S(j_t) | L_0 S_0 1 \rangle = \left(\frac{4\pi\omega}{3c} \right)^{1/2} i^l \exp(-i\sigma_l) \sum_L [L]^{1/2} \begin{Bmatrix} L_c & l & L \\ 1 & L_0 & j_t \end{Bmatrix} \langle L_0 S_0 || r^{(1)} || \psi_{L_c S_c l L E}^- \rangle. \quad (7)$$

The factor $(4\pi\omega/3c)^{1/2}$ is chosen for normalization purposes.¹³ The factors $i \exp(-i\sigma_l)$ as well as the minus sign on the final-state wave function ψ^- indicate that incoming wave boundary conditions are used. The quantum number L represents the total final-state orbital angular momentum, $\vec{L} = \vec{L}_c + \vec{l}$. E represents the final-state total energy. A major advantage of defining the amplitudes $S_i(j_t)$ is that characteristically only a very few values of j_t contribute to a photoionization process.

A word here concerning the relation of our LS -coupling formulas for fluorescence radiation to a previous simpler treatment.⁴ As indicated in Eq. (7) the final-state wave function depends in general dynamically on the final-state quantum numbers L_c , S_c , l , and L . In the central-potential-independent-particle approximation, however, the final-state wave function depends only on l (as well as on the energy E). In this case (i.e., in the absence of anisotropic electron-ion interactions) the scattering amplitude reduces

to the following simple form^{13,14}:

$$S_i(j_t) \propto \delta(j_t, l_0) i^l \exp(-i\sigma_l) (-1)^{l_0-l} l_0^{1/2} [l_0]^{-1} \times \exp(-i\delta_{\epsilon l}) \int_0^\infty P_{n_0 l_0}(r) r P_{\epsilon l}(r) dr, \quad (8)$$

where $l_0 \equiv \max(l_0, l)$, $\delta_{\epsilon l}$ is the photoelectron phase shift with respect to Coulomb waves, l_0 is the initial angular momentum of the photoelectron, and $P_{n_0 l_0}(r)$ and $P_{\epsilon l}(r)$ are the initial and final radial wave functions for the photoelectron. Note that the δ function in Eq. (8) indicates that j_t may assume only the value l_0 in the independent-particle approximation. The proportionality constants are omitted in Eq. (8) since these depend on the atom studied but are constant for a given transition (1a). The results of Caldwell and Zare⁴ for the polarization of fluorescence radiation may be obtained by using Eq. (8) for the amplitudes S instead of Eq. (7). Doing so amounts to ignoring all effects of anisotropic electron-ion interactions.

B. The special case of atoms with $L_0 = 0$

The special case of atoms having zero total orbital angular momentum comprises not only all closed-shell atoms but also many states of open-shell atoms. For convenience and for use

in Sec. II we give the results for the coefficients A_{K0} in this special case:

$$A_{00}^{(L_0=0)} = \frac{-3^{-3/2} \delta(J_0, S_0)}{[S_0][S_c]} \sum_i |S_i(j_i = L_c)|^2, \quad (9a)$$

$$A_{K0}^{(L_0=0)} = \delta(J_0, S_0) (-1)^{J_f - S_c + q} \frac{[J_c][L_c]}{[S_0][S_c]} [K]^{1/2} \begin{pmatrix} 1 & 1 & K \\ q & -q & 0 \end{pmatrix} \\ \times \left\{ \begin{matrix} J_c & J_c & K \\ 1 & 1 & J_f \end{matrix} \right\} \left\{ \begin{matrix} J_c & J_c & K \\ L_c & L_c & S_c \end{matrix} \right\} \sum_i (-1)^i |S_i(j_i = L_c)|^2 \left\{ \begin{matrix} 1 & 1 & K \\ L_c & L_c & l \end{matrix} \right\}. \quad (9b)$$

III. POLARIZATION OF FLUORESCENCE RADIATION SUBSEQUENT TO PHOTOIONIZATION BY UNPOLARIZED INCIDENT RADIATION

A. General remarks

Equations (3)–(7) of the previous section define the general form of the fluorescence intensity in the LS -coupling approximation in which fine-structure effects are taken into account geometrically but are ignored in computing dynamical amplitudes. General expressions for the polarization of the fluorescence radiation may be given in terms of these formulas, but these expressions simplify greatly if the polarization of the incident radiation is specified, in which case explicit expressions for the tensors $X_{K0}(\hat{\epsilon}, \hat{\epsilon}^*)$ may be obtained. Klar⁸ has presented formulas for the polarization of the fluorescence radiation for all cases of incident-light polarization. As our purpose is merely to demonstrate that in the LS -coupling approximation one may obtain geometrically determined values for the fluorescence polarization which are obscured in a more general treatment, we consider here only one case, that of unpolarized incident light. In this case the fluorescence radiation can only be linearly polarized, as explained below. Our formulas (3)–(7) for the coefficients A_{K0} may be inserted in the polarization formulas of Ref. 8 for other types of incident-photon or fluorescence-photon polarization that may be of interest.

B. The linear polarization $P_L(\theta)$ of the fluorescence radiation

We must first define the polarization vector of the fluorescence photon. The incident unpolarized light beam defines the z axis. The wave vector \mathbf{k} of the fluorescence photon defines, together with this z axis, a scattering plane. The vectors $(\hat{\epsilon}_x, \hat{\epsilon}_y, \hat{z})$ then define a coordinate system suitable

for describing the incident beam, where $\hat{\epsilon}_y$ is chosen to lie in the scattering plane. Similarly the vectors $(\hat{\epsilon}_x', \hat{\epsilon}_y', \hat{k})$, where $\hat{\epsilon}_y'$ also lies in the scattering plane and $\hat{\epsilon}_x' = \hat{\epsilon}_x$ are suitable for describing the fluorescence photon. The most general elliptically polarized light wave moving along \hat{k} may be written as¹⁸

$$\vec{\delta}(t) = \delta_0 (\hat{\epsilon}_x' \cos \beta + \hat{\epsilon}_y' i \sin \beta) \exp[-i(\omega t - k\hat{k})] + \text{c.c.} \quad (10)$$

Here β denotes the ellipticity of the fluorescence radiation. If \mathbf{k} makes an angle θ with the incident radiation, then in terms of the unit vectors $(\hat{\epsilon}_x, \hat{\epsilon}_y, \hat{z})$ the polarization of the fluorescence radiation is

$$\hat{\epsilon} = \hat{\epsilon}_x \cos \beta + \hat{\epsilon}_y i \sin \beta \cos \theta - \hat{z} i \sin \beta \sin \theta. \quad (11)$$

Substituting Eq. (11) in Eq. (4) one obtains explicit expressions for the tensors $X_{K0}(\hat{\epsilon}, \hat{\epsilon}^*)$, i.e.,

$$X_{00} = -3^{-1/2}, \quad (12a)$$

$$X_{10} = 2^{-1/2} \cos \theta \sin 2\beta, \quad (12b)$$

$$X_{20} = 6^{-1/2} (3 \sin^2 \beta \sin^2 \theta - 1). \quad (12c)$$

The intensity of fluorescence radiation produced by an unpolarized incident beam of light may be represented as an incoherent sum of the intensities resulting from right and left circularly polarized incident radiation. Thus,

$$I_{\text{unpol}}(\theta, \beta) = \frac{1}{2} [I_{q=+1}(\vec{k}, \hat{\epsilon}) + I_{q=-1}(\vec{k}, \hat{\epsilon})], \quad (13)$$

where the angles θ and β arise from the tensors X_{K0} . Owing to the $3j$ coefficient in Eq. (6a), which is odd under a change in the sign of q , $I_{\text{unpol}}(\theta, \beta)$ does not depend on A_{10} . Hence the fluorescence radiation can only be linearly polarized. The extent of linear polarization at an angle θ with respect to the incident light beam is

$$P_L(\theta) = \frac{I_{\text{unpol}}(\theta, \beta = \pi/2) - I_{\text{unpol}}(\theta, \beta = 0)}{I_{\text{unpol}}(\theta, \beta = \pi/2) + I_{\text{unpol}}(\theta, \beta = 0)}. \quad (14)$$

Here $\beta = \pi/2$ corresponds to a linear polarization of the fluorescence radiation in the scattering plane and $\beta = 0$ corresponds to one perpendicular to the scattering plane (i.e., along the direction $\hat{\mathbf{e}}_x$). Substituting Eqs. (3), (12), and (13) in (14) gives

$$P_L(\theta) = \frac{(\frac{3}{2})^{1/2} A_{20}(q=\pm 1) \sin^2 \theta}{2A_{00}X_{00} - 6^{-1/2} A_{20}(q=\pm 1)(3 \cos^2 \theta - 1)}. \quad (15)$$

Note that as A_{20} is even with respect to a change of sign of q , either value $q = +1$ or -1 may be used.

C. Analytic result for $P_L(\theta)$ in the special case of s -subshell photoionization for atoms with zero orbital angular momentum

As shown in Eq. (9), the special case of atoms with $L_0 = 0$ restricts the summation over angular momentum transfers j_\dagger to the single value $j_\dagger = L_c$. If now we further restrict consideration to s subshells, then ordinarily the photoelectron angular momentum is restricted to the single value $l = 1$. In some cases, determinable by angular momentum conservation rules, other odd values of $l \geq 3$ may be permissible due to ground-state correlations or else final-state interchannel interactions. Ordinarily, however, these interactions are rather weak. Thus if we assume $l = 1$ is the only permissible final-state angular momentum, then only a single dynamical amplitude, $S_{l=1}(j_\dagger = L_c)$, contributes to the coefficients A_{K0} and hence this dynamical amplitude cancels in the ratio that determines $P_L(\theta)$ or any other type of fluorescence polarization resulting from ionization by any kind of polarized incident light. *Thus the polarization of fluorescence radiation resulting from s -subshell photoionization of atoms with zero orbital angular momentum is an analytically known constant.* In the special case of unpolarized incident light, for example, the linear polarization is determined analytically as

$$P_L(\theta) = \frac{3r \sin^2 \theta}{2 - r(3 \cos^2 \theta - 1)} = \frac{1}{1 + \frac{2}{3}[(1-r)/r] \csc^2 \theta}, \quad (16a)$$

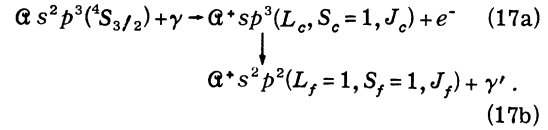
where

$$r \equiv \frac{3}{2} [L_c] [J_c] (-1)^{J_f - S_c} \times \begin{Bmatrix} J_c & J_c & 2 \\ 1 & 1 & J_f \end{Bmatrix} \begin{Bmatrix} J_c & J_c & 2 \\ L_c & L_c & S_c \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ L_c & L_c & 1 \end{Bmatrix}. \quad (16b)$$

The second form for $P_L(\theta)$ in Eq. (16a) demonstrates clearly that $-1 \leq P_L(\theta) \leq +1$ since one may show that $-\frac{1}{2} \leq r \leq +1$.

D. An example: analytic result for $P_L(\theta)$ for nitrogenlike atoms

As a concrete example, consider the family of atoms \mathbf{Q} having the configuration of nitrogen. The ground state has the term level $^4S_{3/2}$. Photoionization of the s subshell leads to the following photoionization and fluorescence transitions:



(Note that we have assumed the initial ionic state to have only $S_c = 1$ since in LS coupling that is the

TABLE I. Predicted linear polarization P_L for fluorescent radiation γ' emitted perpendicularly to an incident unpolarized radiation beam of photons γ in the special case of photoionization of an s subshell in an atom \mathbf{Q} having $L_0 = 0$ and the configuration $s^2 p^3$, i.e.,

$$\begin{aligned} \mathbf{Q} s^2 p^3 (^4S_{3/2}) + \gamma &\rightarrow \mathbf{Q}^+ s p^3 (L_c, S_c = 1, J_c) + e^- \\ &\rightarrow \mathbf{Q}^+ s^2 p^2 (L_f = 1, S_f = 1, J_f) + \gamma' + e^- \end{aligned}$$

L_c	J_c	J_f	$P_L(\theta = \pi/2)^{a,b}$
2	3	2	$-\frac{9}{47} (-19.1\%)$
		2	$+\frac{21}{167} (+12.6\%)$
		1	$-\frac{7}{51} (+13.7\%)$
		2	$-\frac{21}{793} (-2.6\%)$
	1	1	$+\frac{21}{167} (+12.6\%)$
		0	$-\frac{21}{73} (-28.8\%)$
	2	2	$-\frac{7}{51} (-13.7\%)$
		1	$+\frac{21}{167} (+12.6\%)$
1	1	2	$-\frac{1}{53} (-1.9\%)$
		1	$+\frac{1}{11} (+9.1\%)$
	1	0	$-\frac{1}{5} (-20.1\%)$
		1	0 (0.0%)
	0	1	0 (0.0%)
	0	2, 1, 0	0 (0.0%)

^a All predictions for P_L are based on the neglect of relativistic (spin-dependent) interactions, which in general make P_L dependent on the energy of the incident photon γ .

^b For $L_c = 2$ the predictions for P_L ignore the possibility that the photoelectron may have orbital angular momentum $l = 3$ due to final-state interchannel interactions and/or ground-state configuration mixing. Such $l = 3$ waves would make P_L dependent on the energy of the incident photon γ .

only type of state which decays by fluorescence.) The analytical values for the fluorescence polarization for a measurement perpendicular to the incident beam (i.e., at $\theta = \pi/2$) are given in Table I for the allowed values of L_c , J_c , and J_f . For $L_c = 0$ and 1 these predicted polarizations are exact in LS coupling. For $L_c = 2$, in principle, the photoelectron may have the orbital angular momentum $l = 3$ so that the LS -coupling predictions in Table I are approximate for this case as we have ignored such $l = 3$ waves. Inclusion of $l = 3$ waves in the case $L_c = 2$ would introduce a dependence of the polarization P_L on the incident photon energy. The spin-orbit and other relativistic interactions which we have neglected also serve in general to introduce multiple final-state amplitudes $S_i(j_i)$ instead of only one. The dynamical amplitudes in this case do not cancel in the ratio determining P_L and thus give a dependence of P_L on the incident-photon energy. A

measurement of P_L for one of the cases in Table I which detects a dependence on incident-photon energy is thus a sensitive measure of relativistic and, in the case of $L_c = 2$, of weak electron correlation interactions.

The photoelectron angular distribution, like the fluorescence polarization, is determined by a ratio of dynamical amplitudes $S_i(j_i)$. Hence for those cases where only a single $S_i(j_i)$ contributes, the photoelectron angular distribution is also an analytically known constant independent of incident-photon energy. These cases have been analyzed recently by Manson and Starace.¹⁹

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