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Branching ratios for ionization processes

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The ionization of open-shell electronic systems produces ionic multiplets of various symmetry species. The associated intensity ratios (or branching ratios) are investigated theoretically. Based on three well-defined approximations a method is presented to determine the branching ratios from the one-particle densities in the initial states. This method allows one to take initial-state correlation into account and contains the so-called geometrical branching ratios as a special case. The method is demonstrated for several examples of systems in *LS*, *J*, and *LSJ* symmetry.

I. INTRODUCTION

The ionization spectra of open-shell electronic systems, e.g., molecules,[1-4] atoms,[5-12] negative ions[13-17] exhibit characteristic differences to the spectra of closed-shell systems. In the latter case the ionization process is in general well described by the picture of ionizing an electron out of a specific occupied shell of degenerate one-particle states. At lower binding energies the ionization from a single shell usually leads to a main ionic state accompanied by weak satellite states. For higher binding energies strong final-state correlation effects may change the situation significantly and several ionic states with comparable intensities can appear (breakdown of the one-particle picture of ionization[18]). In any case, all ionic states usually share the intensity available for the specific ionized shell and are characterized by the symmetry of the hole state. For open-shell systems the picture of ionizing an electron out of a shell is equally well applicable. In general, however, even at lower binding energies the ionization out of a specific shell produces several ionic states of different symmetry due to the different coupling possibilities within and between the occurring open shells. This so-called multiplet splitting obviously provides for a rather complex structure of the ionization spectra.

The interesting quantities are the magnitudes of the energy splittings and the relative intensities of the multiplets. The energy splittings often differ profoundly from the first-order results and have to be calculated by methods taking final-state correlation into account.[19,20] Calculations of photoionization cross sections using various methods have been reported for open-shell atoms[21-27] and ions[28,29] providing the theoretical intensities of the ionic states in dependence of the photon energies. Often, however, there is no need to perform elaborate cross-section calculations when one is only interested in the relative intensities or intensity ratios of the ionic multiplets produced by ionizing a specific shell. Under certain conditions the intensity ratios are well described by "geometrical" *a priori* rules, as have first been worked out by Cox *et al.*[30-32] These geometrical ratios may be given by the ratios of the statistical weights of the ionic multiplets, but often differ from them. A different approach to geometrical multiplet ratios has been presented by Rau.[33] The validity of Rau's results, however, may be limited to a special case only, as is discussed below.

The purpose of this paper is to present a complementary and more general method for determining theoretical multiplet ratios. The approach is, in particular, capable of incorporating the effects of initial-state correlation into the geometrical intensity ratios. Much emphasis is placed on clarifying the approximations which have to be introduced in order to obtain geometrical intensity rules. The disposition of this paper is as follows. In Sec. II an expression for the ionic intensities is derived. For the special case of *LS* symmetry (atoms with a spin-independent Hamiltonian) the theoretical multiplet ratios or branching ratios are introduced and discussed in Sec. III. An extension to the important case of additional spin-orbit coupling (*LSJ* symmetry) is given in Sec. IV. Some applications and comparison with experiments are presented in Sec. V. A discussion of our results follows in Sec. VI.

II. INTENSITIES FOR THE IONIZATION OF DEGENERATE INITIAL STATES

We consider the ionization process for an electronic system with degenerate initial states $|\psi_0(\Lambda M)\rangle$, $M = 1, \ldots [\Lambda]$. In this general notation the quantum number Λ assigns the irreducible representations of the symmetry group for the considered system and the "magnetic" quantum numbers M distinguish between the different members of the basis of Λ. The number of degenerate states is denoted by the symbol $[\Lambda]$. Correspondingly, the ionic states can be written $|\psi(n\Lambda'M')\rangle\rangle$, where n is an additional quantum number for the different ionic states with equal symmetry $\Lambda'M'$. In the usual experimental situation, one deals with a statistical mixture of the states $|\psi_0(\Lambda M)\rangle\rangle$, each state contributing with equal weight. In addition the magnetic quantum numbers of the final ionic states and of the free electron states are usually not measured. Starting from Fermi's golden rule we thus obtain for the spectral intensity $P^{n\Lambda'}$ of a final ionic multiplet $n\Lambda'$ the expression (apart from factors depending only on energy and intensity of the ionizing particles)

$$P^{n\Lambda'}=\sum_{\epsilon\lambda m}\frac{1}{[\Lambda]}\sum_{M,M'}|\langle\psi(n\Lambda'M'),\epsilon\lambda m|\hat{\tau}|\psi_0(\Lambda M)\rangle\rangle|^2 \times\delta(\omega_0+E_0^N-E_{n\Lambda'}^{N-1}-E_\epsilon)\,. \tag{1}$$

Here the final states are assumed to be products of the ionic states $|\psi(n\Lambda'M')\rangle\rangle$ with energy $E_{n\Lambda'}^{N-1}$ and the free electron states $|\epsilon\lambda m\rangle$ with kinetic energy E_ϵ and symmetry λm:

$$|\psi(n\Lambda'M'),\epsilon\lambda m\rangle=|\psi(n\Lambda'M')\rangle\rangle\,|\epsilon\lambda m\rangle\,. \tag{2}$$

The δ function in Eq. (1) introduces the energy conservation $\omega_0+E_0^N=E_{n\Lambda'}^{N-1}+E_\epsilon$ into the summation over the free electron states, ω_0 being the energy absorbed from the ionizing particle, e.g., the photon energy. The transition operator for the ionization process is denoted by $\hat{\tau}$.

By writing the final states according to Eq. (2) we have made use of the approximation—henceforth referred to as approximation (a)—that the correlation between the continuum electrons and the bound electrons of the ionic and initial states is neglected. This is, in particular, justified for the case of large kinetic energy of the ejected electron, whereas, in general, threshold processes and processes involving resonances and autoionizing states are not adequately described. It should be noted, that for detachment of negative ions, where the remaining systems is electrically neutral, approximation (a) may be valid already in the vicinity of the thresholds.

In order to further evaluate Eq. (1) we shall rely on the means of second quantization. Although this is not indispensable, it allows for a very convenient and compact notation. For a basis of one-particle states $|p\rangle$, where the indices p represent a complete set of one-particle quantum numbers (e.g., $p=p\lambda m$) we define creation (destruction) operators $c_p^\dagger(c_p)$ for electrons in the states $|p\rangle$. These operators fulfill the common anticommutation relations

$$\begin{aligned}&[c_p^\dagger,c_q]=\delta_{pq}\,,\\&[c_p^\dagger,c_q^\dagger]=[c_p,c_q]=0\,.\end{aligned} \tag{3}$$

The transition operator $\hat{\tau}$ is assumed to be a one-particle operator. In second quantized notation $\hat{\tau}$ is given by

$$\hat{\tau}=\sum\tau_{pq}c_p^\dagger c_q\,, \tag{4}$$

where τ_{pq} are the one-particle matrix elements of $\hat{\tau}$. In the case of photoionization one may employ, for example, the matrix elements of the interaction operator with the electromagnetic field in the dipole approximation:

$$\tau_{pq}=\left\langle p\left|-\frac{1}{c}\vec{n}\cdot\vec{P}\right|q\right\rangle.$$

Here $\vec{n}$ denotes the polarization vector of the photons and $\vec{P}$ is the momentum operator.

Making again use of approximation (a), we obtain via Eqs. (3) and (4) from Eq. (1) the following expression for the intensity of the final state $n\Lambda'$:

$$P^{n\Lambda'}=\sum_{pq}T_{pq}^{n\Lambda'}R_{pq}^{n\Lambda'}\,. \tag{5}$$

Here the "transition coefficients" are given by

$$T_{pq}^{n\Lambda'}=\sum_{\epsilon\lambda m}\tau_{\epsilon\lambda m,p}\tau^*_{\epsilon\lambda m,q}\delta(\omega_0+E_0^N-E_{n\Lambda'}^{N-1}-E_\epsilon) \tag{6}$$

and the "relative intensities" are given by

$$R_{pq}^{n\Lambda'}=\frac{1}{[\Lambda]}\sum_{M,M'}\langle\psi_0(\Lambda M)|c_q^\dagger|\psi(n\Lambda'M')\rangle\rangle \times\langle\psi(n\Lambda'M')|c_p|\psi_0(\Lambda M)\rangle\rangle\,. \tag{7}$$

The formulation according to Eqs. (5)–(7) is conceptually very appealing. It allows to separate the calculation of intensities into two well-defined parts. The first part consists of calculating the transition coefficients, containing the details of the considered ionization mechanism. The second part is independent of the specific ionization process and depends only on the electronic properties of the initial and ionic states. If one is interested in relative intensities, it is often sufficient to compute the latter part of the intensity only.

Expressions (5)–(7) can be evaluated further by performing the summations over magnetic quantum numbers. To be specific we now confine our considerations to the familiar case of LS symmetry where the initial states, the final ionic states and the one-particle states are denoted by $|LSM_LM_S\rangle$, $|nL'S'M_L'M_S'\rangle$, and $|plm_lm_s\rangle$, respectively. It should be stressed, however, that the following results are general and can be transferred to other cases, e.g., J symmetry or molecular symmetry. As is shown in Appendix A the relative intensities are diagonal with respect to the one-particle indices l, m_l, m_s and independent of m_l and m_s:

$$R^{nL'S'}_{plm_lm_s,p'l'm_l'm_s'} = \delta_{ll'}\,\delta_{m_lm_l'}\,\delta_{m_sm_s'}\,R^{nL'S'}_{pl,p'l}. \tag{8}$$

Here the m-independent relative intensities $R^{nL'S'}_{pl,p'l}$ are given by

$$R^{nL'S'}_{pl,p'l} = \frac{1}{[\frac{1}{2},l,L,S]}\,(nL'S'\|\,c_{pl}\,\|LS)(nL'S'\,\|\,c_{p'l}\,\|LS)^*, \tag{9}$$

where $(nL'S'\|c_{pl}\|LS)$ denotes the reduced matrix element of the operator $c_{plm_lm_s}$ for the initial and ionic states $|LSM_LM_S\rangle$ and $|nL'S'M_L'M_S'\rangle$, respectively. For notational brevity here and in the following the symbol $[j_1,\ldots,j_n]=(2j_1+1)\cdots(2j_n+1)$ is used. As can be seen from the properties of the reduced matrix elements, Eq. (9) also implies selection rules for the symmetries of the ionic states: Nonvanishing contributions arise only if the triangle conditions for the spins $\frac{1}{2}$, S, S' and for the angular momenta l, L, L' are fulfilled. With the help of Eq. (8) the intensity $P^{nL'S'}$ of Eq. (5) can be expressed by m-independent quantities only:

$$P^{nL'S'} = \sum_{p,p',l} 2(2l+1)\,T^{nL'S'}_{pl,p'l}R^{nL'S'}_{pl,p'l}. \tag{10}$$

Here we have defined m-independent transition coefficients by

$$T^{nL'S'}_{pl,p'l} = \frac{1}{2(2l+1)}\sum_{m_l,m_s} T^{nL'S'}_{plm_lm_s,p'lm_lm_s}. \tag{11}$$

An explicit expression for the diagonal transition coefficient $T^{nL'S'}_{pl,pl}$ is easily derived for the dipole-transition operator $\hat{r}=(\hat{x},\hat{y},\hat{z})$:

$$T^{nL'S'}_{pl,pl} = \frac{1}{2l+1}{\sum_{l''}}'\ \tfrac{1}{3}|(l''\,\|\,\hat{z}\,\|pl)|^2. \tag{12}$$

The prime at the summation symbol restricts the summation over continuum states l'' to those states fulfilling the energy conservation with respect to the considered ionic state $nL'S'$.

For a given ionic state $nL'S'$ the diagonal relative intensities $R^{nL'S'}_{pl,pl}$ characterize the intensity contribution resulting from the specific orbitals pl. If two (or more) orbitals pl and $p'l$ contribute intensity there also occur nonvanishing nondiagonal relative intensities $R^{nL'S'}_{pl,p'l}$. Often, however, the picture of ionizing from a single shell is valid. This means that every ionic state $nL'S'$ obtains its intensity from one particular orbital, say pl, and the only nonvanishing relative intensity is $R^{nL'S'}_{pl,pl}$. In this case the right-hand of Eq. (10) reduces to the simple product

$$P^{nL'S'} = 2(2l+1)T^{nL'S'}_{pl,pl}\,R^{nL'S'}_{pl,pl}. \tag{13}$$

The picture of ionizing from a single shell is henceforth termed approximation (b). It is obvious that the justification of approximation (b) is closely connected with the choice of an adequate one-particle basis.

The dependence of the transition coefficients $T^{nL'S'}_{pl,pl}$ for an orbital pl on the final ionic states $nL'S'$ is only due to the restriction of energy conservation as can be seen at the example of Eq. (12). For close-lying ionic states, as is the case for the ionic multiplets resulting upon ionization of a single shell, this energy dependence is weak and it is justified to assume a constant transition coefficient $T_{pl,pl}$ for each shell pl. This is called approximation (c). The quantities $R^{nL'S'}_{pl,pl}$ are then indeed the relative intensities and the intensity ratio of two multiplets $nL'S'$, $n''L''S''$ arising from the same shell pl is given by $R^{nL'S'}_{pl,pl}/R^{n''L''S''}_{pl,pl}$.

III. THEORETICAL BRANCHING RATIOS

A natural starting point for the determination of theoretical branching ratios is provided by the approximations (a)–(c) introduced in the preceding chapter. Again we restrict ourselves for the moment to the case of LS symmetry. Let us consider the ionization of a shell pl producing the ionic multiplets $nL'S'$ with relative intensities

$$R^{nL'S'}_{l} = \frac{1}{[\frac{1}{2},l,L,S]}\,|(nL'S'\,\|\,c_l\,\|LS)|^2. \tag{14}$$

Here we have simplified the notation of the relative intensities according to $R^{nL'S'}_{pl}\equiv R^{nL'S'}_{pl,pl}$. In addition we omit the orbital index p, whenever unambiguous. It may happen that among the multiplets arising from the shell l there occur two or more multiplets having the same symmetry. The distribution of intensity among such multiplets can certainly not be predicted by *a priori* rules, but is subject to strong final-state correlation. In this case we consider the partial relative intensity

$$R^{L'S'}_{l} = \sum_{n} R^{nL'S'}_{l} \tag{15}$$

associated with the ionic symmetry $L'S'$ rather than the relative intensity of a single multiplet $nL'S'$. The branching ratios are defined as the ratios of the partial intensities $R^{L'S'}_{l}/R^{L''S''}_{l}$. As we shall see, these quantities are completely determined from the properties of the initial states.

It is useful to introduce the so-called weight factor $g(l,LS,L'S')$ being defined by

$$g(l,LS,L'S')=\frac{1}{[L',S']}\sum_{n}|(nL'S'\|c_l\|LS)|^2 . \tag{16}$$

The partial intensity then simply reads

$$R_l^{L'S'}=\frac{[L',S']}{[\frac{1}{2},l,L,S]}g(l,LS,L'S') . \tag{17}$$

From Eq. (16) it is clear that $g(l,LS,L'S')$ and hence $R_l^{L'S'}$ is nonvanishing only for the case that the triangular conditions for (l,L,L') and $(\frac{1}{2},S,S')$ are fulfilled. This means that for ionization from a shell l of initial states LS the ionic symmetries $L'S'$ with $|L-l|\leqslant L'\leqslant L+l$ and $|S-\frac{1}{2}|\leqslant S'\leqslant S+\frac{1}{2}$ are allowed. One further notes that the branching ratios are determined by the statistical values $[L',S']$ if all weight factors are identical.

As is demonstrated in Appendix B the weight factors $g(l,LS,L'S')$, $L'=|L-l|,\ldots,L+l$, $S'=|S-\frac{1}{2}|$, $S+\frac{1}{2}$ are completely determined by the initial-state wave functions. In particular there is a unique relationship to the one-particle densities

$$n_{lm_lm_s}=\langle LSLS|c^\dagger_{lm_lm_s}c_{lm_lm_s}|LSLS\rangle , \tag{18}$$

i.e., the occupation numbers of the one-particle states lm_lm_s with respect to the special initial state $|LSLS\rangle$ with maximum magnetic quantum numbers $M_L=L$, $M_S=S$. For practical purposes most useful are the following implicit equations[34] for the weight factors (see Appendix B):

$$\sum_{L',S'}\left(\begin{array}{cc|c} l & L & L' \\ m_l & L & L+m_l \end{array}\right)^2\left(\begin{array}{cc|c} \frac{1}{2} & S & S' \\ m_s & S & S+m_s \end{array}\right)^2 g(l,LS,L'S')=n_{l,-m_l,-m_s},\quad m_l=l,l-1,\ldots,-l,\quad m_s=\tfrac{1}{2},-\tfrac{1}{2} . \tag{19}$$

These equations constitute a system of $2(2l+1)$ linear equations for the weight factors $g(l,LS,L'S')$ with $|L-l|\leqslant L'\leqslant L+l$ and $|S-\frac{1}{2}|\leqslant S'\leqslant S+\frac{1}{2}$. The coefficients on the left-hand sides are products of squared Clebsch-Gordan coefficients,

$$\left(\begin{array}{cc|c} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array}\right)\equiv(l_1m_1l_2m_2|l_1l_2l_3m_3)$$

in the notation of Edmonds.[35] When the rows of Eqs. (19) are ordered according to $(m_l,m_s)=(l,\frac{1}{2})$, $(l,-\frac{1}{2})$, $(l-1,\frac{1}{2}),\ldots$ and the columns according to $(L',S')=(L+l,\,S+\frac{1}{2})$, $(L+l,S-\frac{1}{2})$, $(L+l-1,S+\frac{1}{2}),\ldots$, the matrix of coefficients is of triangular shape, as can be seen by inspection of the Clebsch-Gordan coefficients. As an example, the system of equations (in matrix notation) for the case of ionization out of a p orbital $(l=1)$ of a ${}^3P$ ground state $(L=S=1)$ is presented in the following:

$$\begin{pmatrix} 1 & & & & & \\ \frac{1}{3} & \frac{2}{3} & & & & \\ \frac{1}{2} & 0 & \frac{1}{2} & & & \\ \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & \frac{1}{3} & & \\ \frac{1}{6} & 0 & \frac{1}{2} & 0 & \frac{1}{3} & \\ \frac{1}{18} & \frac{1}{9} & \frac{1}{6} & \frac{1}{3} & \frac{1}{9} & \frac{2}{9} \end{pmatrix}\times\begin{pmatrix} g(2,\frac{3}{2}) \\ g(2,\frac{1}{2}) \\ g(1,\frac{3}{2}) \\ g(1,\frac{1}{2}) \\ g(0,\frac{3}{2}) \\ g(0,\frac{1}{2}) \end{pmatrix}=\begin{pmatrix} n_{-1,-1/2} \\ n_{-1,1/2} \\ n_{0,-1/2} \\ n_{0,1/2} \\ n_{1,-1/2} \\ n_{1,1/2} \end{pmatrix} .$$

Here the notation is simplifed according to $g(L',S')\equiv g(l,LS,L'S')$ and $n_{m_lm_s}\equiv n_{lm_lm_s}$. From the triangular shape of the matrix of coefficients of Eqs. (19) it is immediately clear that the weight factors are uniquely determined by the one-particle densities $n_{lm_lm_s}$ and that Eqs. (19) can be solved easily by hand once the one-particle densities are given. The required Clebsch-Gordan coefficients may be taken from tables[36] or can be calculated with the simple recursion equations

$$\left(\begin{array}{cc|c} l & L & l+L \\ l & L & l+L \end{array}\right)=1 , \tag{20a}$$

$$\left(\begin{array}{cc|c} l & L & L' \\ m-1 & L & L+m-1 \end{array}\right)^2 =\frac{(l+m)(l-m+1)}{(L'-L-m+1)(L'+L+m)}\left(\begin{array}{cc|c} l & L & L' \\ m & L & L+m \end{array}\right)^2 \tag{20b}$$

together with the orthogonality relation

$$\sum_{L'}\left(\begin{array}{cc|c} l & L & L' \\ m & L & L+m \end{array}\right)^2=1 . \tag{21}$$

It should be noted that for the case $l>L$ only the first $2(2L+1)$ equations (19) are needed. The remaining equations are linearly dependent. Similarly for the case $S=0$ the equations with $m_s=-\frac{1}{2}$ can be dropped.

Equations (17) and (19) establish a simple means for calculating relative intensities and branching ratios for general initial states, e.g., correlated states, states with several open shells. The use of this method is demonstrated for several examples in Sec. V. For the important case of a uniformly filled shell l with $n_{lm_lm_s}=\bar{n}_l$ for all m_l, m_s the general solution of Eqs. (19) is immediately obtained. Recalling the orthogonality relation (21) (for the coefficients of a row) we see that $g(l,LS,L'S')=\bar{n}_l$ solves Eqs. (19). Here the partial intensities are proportional to the statistical weights of the ionic symmetries:

$$R_l^{L'S'}=\frac{[L',S']}{[\frac{1}{2},l,L,S]}\,\bar{n}_l\,. \tag{22}$$

In particular, this result applies to the case of the ionization out of a closed shell of an uncorrelated initial state (all $n_{lm_lm_s}=1$). It states that here ionic states with symmetry $L'S'$, $L'=|L-l|,\ldots,L+l$, $S'=|S-\frac{1}{2}|$, $S+\frac{1}{2}$ are produced, their branching ratios given by the statistical weights. For nonuniformly filled shells there apparently occur deviations from this simple result. Nonuniform one-particle densities are caused by partly filled shells and (or) by initial-state correlation. If no initial-state correlation is allowed the resulting partial intensities and branching ratios are entirely geometrical, i.e., they do not depend on any radial wave functions. It should be stressed that geometrical ratios and statistical ratios are not necessarily the same—a point that is often confused.

The geometrical branching ratios for the important case of an initial state with one open shell has been discussed by Cox *et al.*[8] We would like to relate both methods for this case. The initial states $|LSM_LM_S\rangle$ can be constructed from the ionic states $|nL'S'M_LM_S'\rangle$ and the one-particle states $|lm_lm_s\rangle$ of the considered shell with the help of so-called coefficients of fractional parentage[37] (CFP):

$$|LSM_LM_S\rangle=\sum_{nL'S'}f(l,LS,nL'S')\,|(nL'S')lLSM_LM_S\rangle\,. \tag{23}$$

Here we adapt the notation $f(l,LS,nL'S')\equiv[l^{r-1}(nL'S')lLS|\}l^rLS]$ for the CFP's. The state $|(nL'S')lLSM_LM_S\rangle$ which in general is not antisymmetric is constructed by simply coupling the ionic states $|nL'S'M_L'M_S'\rangle$ and the one-particle states $|lm_lm_s\rangle$ to a state with symmetry L, S, M_L, M_S. There exists an important relationship between the CFP's and the reduced matrix elements of the second-quantized operators[38] for the considered cases:

$$(nL'S'\,\|\,c_l\,\|\,LS)=(r[L,S])^{1/2}f(l,LS,nL'S')\,. \tag{24}$$

Here r is the number of the electrons in the shell to be ionized. According to Eq. (24) the relative intensity for the final state $nL'S'$ is given by

$$R_l^{nL'S'}=\frac{r}{[\frac{1}{2},l]}\,f^2(l,LS,nL'S')\,. \tag{25}$$

This is apart from a somewhat different normalization the result of Cox *et al.*[30,31] Again it should be stressed that for the case of several ionic states with equal symmetry $L'S'$, the single relative intensities of Eq. (25) have no meaning, since in general there is strong mixing for the final states of equal symmetry. The invariant quantity is the partial intensity $R_l^{L'S'}$ of Eq. (17). The corresponding weight factor is related to the CFP's by

$$g(l,LS,L'S')=r\,\frac{[L,S]}{[L',S']}\sum_n f^2(l,LS,nL'S')\,. \tag{26}$$

The CFP for several l^n configurations can be found in the tables of Ref. 37.

From Eq. (19) a simple sum rule for the partial intensities can be derived. By making use of the modified orthogonality relation (for the column coefficients)

$$\sum_m\begin{bmatrix} l & L & L' \\ m & L & L+m\end{bmatrix}^2=\frac{2L'+1}{2L+1}\,, \tag{27}$$

one arrives at the equation

$$\sum_{L'S'}R_l^{L'S'}=\bar{n}_l\,, \tag{28}$$

where

$$\bar{n}_l=\frac{1}{2(2l+1)}\sum_{m_l,m_s}n_{lm_lm_s} \tag{29}$$

is the mean one-particle density of the considered shell.

Finally we would like to present the central results for the case of J symmetry. Here we are concerned with an initial multiplet J, ionize from a shell j and produce ionic multiplets nJ'. The distribution of intensity on the ionic symmetries is given by the partial intensities

$$R_j^{J'}=\frac{[J']}{[j,J]}\,g(j,J,J')\,, \tag{30}$$

where the weight factors $g(j,J,J')$, $J'=|J-j|,\ldots,J+j$ are determined by the set of equations

$$\sum_{J'}\begin{bmatrix} j & J & J' \\ m & J & J+m\end{bmatrix}^2 g(j,J,J')=n_{j,-m}\,,\quad m=j,\ldots,-j\,. \tag{31}$$

The n_{jm} are the one-particle densities for the initial state $|JJ\rangle$ with the maximum magnetic quantum number.

IV. BRANCHING RATIOS FOR *LSJ* SYMMETRY

In the preceding section we have studied partial intensities for the case of LS symmetry. Here the initial and final states are classified as eigenstates of total spin and angular momentum, and the picture of ionizing an l shell is assumed to be adequate. The results also have been transferred to the complementary case of J symmetry, where the j shells provide a good one-particle description and the initial and final states are classified by the total angular momentum. In the following we shall discuss the important case where relativistic effects (represented by spin-orbit coupling terms in the Hamiltonian) cause the $(2L+1)(2S+1)$ degenerate initial states $|LSM_LM_S\rangle$ to split into sets of $(2J+1)$ states $|LSJM\rangle$ with $|L-S|\leq J\leq L+S$. The spin-orbit coupling is assumed to be small enough to ensure the spin and angular momentum to be good quantum numbers. Analogously, the resulting ionic states may be classified by $|nL'S'J'M'\rangle$ with spin S', angular momentum L', and total angular momentum J'. We consider the ionization of an l shell. Due to spin-orbit this shell splits into two j shells with $j=l\pm\frac{1}{2}$. Apparently the picture of ionizing out of a single j shell is inadequate here, since the occurring ionic states may gain intensity from both j shells. For that reason one cannot simply proceed as in the case of J symmetry.

To get the correct result for the intensity of an ionic state $nL'S'J'$ produced by ionizing the shell l one has to resume the analysis following Eqs. (5)–(7) in Sec. II. This procedure is outlined in Appendix A. In addition to the three approximations (a)–(c) introduced in Sec. II one here has to assume that the transition operator is spin-independent. Under these conditions one arrives at the simple result

$$P^{nL'S'J'} = T_{ll}R_l^{nL'S'J'} . \tag{32}$$

The total intensity again is the simple product of the transition coefficient T_{ll} for the concerned shell l—as has been given by Eq. (12)—and of the relative intensity

$$R_l^{nL'S'J'} = \frac{1}{2(2l+1)} \sum_{j=l-1/2}^{l+1/2} (2j+1)R_j^{nL'S'J'} . \tag{33}$$

The right-hand side of Eq. (33) is the (incoherent) sum of the weighted relative intensities $R_j^{nL'S'J'}$ for the two subshells $j=l\pm\frac{1}{2}$, given analogously to Eq. (14) by

$$R_j^{nL'S'J'} = \frac{1}{[j,J]} \left|(nL'S'J' \parallel c_j \parallel LSJ)\right|^2 . \tag{34}$$

Here c_{jm} is the destruction operator for the subshell states jm:

$$c_{jm} = \sum_{m_l,m_s} \left[\begin{array}{cc|c} l & \frac{1}{2} & j \\ m_l & m_s & m \end{array}\right] c_{lm_lm_s} . \tag{35}$$

The remaining task consists in evaluating the reduced matrix element of Eq. (34). It is straightforward to show the identity

$$(nS'L'J' \parallel c_j \parallel SLJ)$$

$$= (-1)^{\Delta}[j,J,J']^{1/2} \begin{Bmatrix} l & \frac{1}{2} & j \\ L & S & J \\ L' & S' & J' \end{Bmatrix} (nS'L' \parallel c_l \parallel LS) , \quad \Delta = 1+l+\tfrac{1}{2}+L'+S'+J'+L+S+J \tag{36}$$

between the reduced matrix elements in the LSJ and LS coupling scheme. The $9j$ symbols occurring here are defined according to Edmonds.[35] From Eqs. (33), (34), and (36) follows the result

$$R_l^{nL'S'J'} = \frac{2J'+1}{2(2l+1)} \left|(nL'S' \parallel c_l \parallel LS)\right|^2 \sum_{j=l-1/2}^{l+1/2} (2j+1) \begin{Bmatrix} l & \frac{1}{2} & j \\ L & S & J \\ L' & S' & J' \end{Bmatrix}^2 . \tag{37}$$

As has been discussed in Sec. III the branching ratios are defined with respect to the partial (relative) intensities of an ionic symmetry species $L'S'J'$. In the case that two or more ionic states $nL'S'J'$ with the same symmetry $L'S'J'$ occur one has to consider the sum of the individual contributions

$$R_l^{L'S'J'} = \sum_n R_l^{nL'S'J'} . \tag{38}$$

With the weight factor $g(l,LS,L'S')$ of Eq. (16) the final result for the partial intensities reads

$$R_l^{L'S'J'} = \frac{[J',L',S']}{2(2l+1)} g(l,LS,L'S') \sum_{j=l-1/2}^{l+1/2} (2j+1) \begin{Bmatrix} l & \frac{1}{2} & j \\ L & S & J \\ L' & S' & J' \end{Bmatrix}^2 . \tag{39}$$

The inspection of Eq. (39) shows that the distribution of intensity on the ionic symmetries $L'S'$ is determined by the weight-factors $g(l,LS,L'S')$. As has been discussed in Sec. III the weight factors are uniquely determined by the initial states and can easily be evaluated by means of Eqs. (19) for any given initial states. If initial-state correlation is neglected the weight factors are called geometrical. For the case of an initial state with one open shell the weight factors can be expressed by CFP's. In this case the result of Cox[32] is essentially equivalent to Eq. (37). The distribution of intensity on the ionic symmetries J' for given $L'S'$ is governed by the $9j$ symbols of Eq. (39). This part is apparently purely geometrical and not influenced by initial-state correlation. The $9j$ symbols reflect several selection rules since nonvanishing contributions require that the triangular conditions are fulfilled for the rows and the columns. The allowed symmetries $L'S'J'$ for ionization from a shell l of a state LSJ are $|L-l|\leq L'\leq L+l$, $|S-\frac{1}{2}|\leq S'\leq S+\frac{1}{2}$, $|L'-S'|\leq J'\leq L'+S'$, and $|J-j|\leq J'\leq J+j$ for $j=l\pm\frac{1}{2}$.

We finally discuss some consequences of the above results. Several sum rules can be derived for the partial LSJ intensities. With the help of the orthogonality relation for the $9j$ symbols[35] one obtains after summing over all symmetries J':

$$\begin{aligned} R_l^{L'S'} &= \sum_{J'} R_l^{L'S'J'} \\ &= \frac{[L',S']}{[\frac{1}{2},l,L,S]}\, g(l,LS,L'S')\,. \end{aligned} \tag{40}$$

This result is identical with Eq. (17) for the case of LS symmetry. It means, that the distribution of intensity on the final $L'S'$ symmetries does not depend on the specific J value of the initial state and is equal to the result of the LS case. As a consequence of the sum rule for the LS case [Eq. (28)] it follows that the sum of the partial intensities

$$\sum_{L'S'J'} R_l^{L'S'J'} = \bar{n}_l \tag{41}$$

is equal to the mean one-particle density $\bar{n}_l$ of the considered shell.

A special case of interest is the ionization of a closed-shell atom, where $L=S=J=0$ in the initial state. The ionic multiplets resulting upon the ionization of a shell with angular momentum l are the two spin-orbit splitting states with $J'=j=l\pm\frac{1}{2}$, $L'=l$, $S'=\frac{1}{2}$. The partial intensities

$$R_l^{l(1/2)j} = \frac{2j+1}{2(2l+1)} \tag{42}$$

are given by the respective statistical weights of the two subshells.

Let us consider the special case of ionizing from a closed shell of an uncorrelated initial state. Here all weight factors are equal to 1 and the partial intensities are given by

$$R_l^{L'S'J'} = \frac{[J',L',S']}{[\frac{1}{2},l]} \sum_{j=l-1/2}^{l+1/2} (2j+1) \begin{Bmatrix} l & \frac{1}{2} & j \\ L & S & J \\ L' & S' & J' \end{Bmatrix}^2 . \tag{43}$$

The geometrical branching ratios in general differ from the ratios of the statistical weights J' of the ionic multiplets.

It should be mentioned that the Eqs. (33), (34), and (36) also provide a means to evaluate relative intensities for a CI (configuration interaction) calculation. Let us consider the case of strong spin-orbit coupling. Here spin and angular momentum are no longer good quantum numbers and an ionic state nJ' may be given as a linear combination

$$|nJ'M'\rangle = \sum_{n'L'S'} b_{n'L'S'}^{nJ'} \, |n'L'S'J'M'\rangle \tag{44}$$

of states $n'L'S'J'$, where $b_{n'L'S'}^{nJ'}$ denote the expansion coefficients. The relative intensity for the ionic state nJ' follows from

$$R_l^{nJ'} = \frac{[J']}{[\frac{1}{2},l]} \sum_{j=l-1/2}^{l+1/2} [j] \left| \sum_{n'L'S'} \begin{Bmatrix} l & \frac{1}{2} & j \\ L & S & J \\ L' & S' & J' \end{Bmatrix} (-1)^{L'+S'+J'} (n'L'S' \| c_l \| LS) b_{n'L'S'}^{nJ'} \right|^2 . \tag{45}$$

Here the initial states are still assumed to be given in LSJ symmetry. Of course, also the initial states may be expanded analogously to Eq. (44) leading to a straightforward extension of Eq. (45).

V. APPLICATIONS AND COMPARISON WITH EXPERIMENTAL PARTIAL INTENSITIES

The aim of this section is to demonstrate how to use the concepts presented in the preceding sections for determining partial intensities or branching ratios. In order to allow for a self-contained reading of this section we repeat the essential working equations.

For LS symmetry we are concerned with an initial multiplet LS, ionize from a shell l and produce ionic multiplets $nL'S'$, where the additional quantum number n is required for the case that more than one ionic multiplet with symmetry $L'S'$ occur. The distribution of the intensity on the final ionic symmetries, described by the partial intensities $R_l^{L'S'}$, is completely determined by the properties of the initial state. The branching ratios are given as the ratios of the partial intensities $R_l^{L'S'}/R_l^{L''S''}$. When the initial state is uncorrelated the resulting partial intensities or branching ratios are called "geometrical." The partial intensities for LS symmetry are given by Eq. (16),

$$R_l^{L'S'} = \frac{[L',S']}{[\frac{1}{2},l,L,S]} g(l,LS,L'S],$$

where the weight factors $g(l,LS,L'S')$ with $L' = |L-l|,\ldots,L+l$, $S' = |\frac{1}{2}-S|$, $S+\frac{1}{2}$ are uniquely determined from the set of $2(2l+1)$ linear equations (19):

$$\sum_{L',S'} \begin{bmatrix} l & L & L' \\ m_l & L & L+m \end{bmatrix}^2 \begin{bmatrix} \frac{1}{2} & S & S' \\ m_s & S & S+m_s \end{bmatrix}^2 g(l,LS,L'S') = n_{l,-m_l,-m_s} \quad .$$

The inhomogeneities on the right-hand side of Eqs. (19) are the one-particle densities $n_{lm_lm_s}$ of the specific initial state $|LSLS\rangle$ with maximum magnetic quantum numbers $M_L = L$, $M_S = S$. For a given wave function representation of this state the $n_{lm_lm_s}$ are readily obtained. A particularly easy care is met for the uncorrelated ground states of an open l^n shell. According to Hund's rule the ground state possess maximum spin S and maximum angular momentum L. The corresponding state $|LSLS\rangle$ is a single Slater determinant with the n electrons successively occupying the one-particle states $(m_l, m_s) = (l, \frac{1}{2})$, $(l-1, \frac{1}{2})\ldots(-l, \frac{1}{2})$, $(l, -\frac{1}{2}),\ldots$. According to this occupation scheme the one-particle densities assume the values 1 and 0.

In the case of LSJ symmetry we start from an initial multiplet LSJ resulting from coupling the LS states to a specific total angular momentum J. Ionization takes place from both $j = l \pm \frac{1}{2}$ subshells of a shell l. The ionic multiplets $nL'S'J'$ again result from states $nL'S'$ coupled to another momentum J'. The corresponding partial intensities are given by Eq. (39):

$$R_l^{L'S'J'} = \frac{[J',L',S']}{[\frac{1}{2},l]} g(l,LS,L'S') \times \sum_{j=l-1/2}^{l+1/2} [j] \begin{Bmatrix} l & \frac{1}{2} & j \\ L & S & J \\ L' & S' & J' \end{Bmatrix}^2 \quad .$$

The weight factors $g(l,LS,L'S')$ are determined by Eq. (19), as described above.

As an example for LS symmetry we consider the ${}^2P$ ground state of an open p^5 shell. For the moment we assume the case without correlation. Then the special state with $M_L = 1$ and $M_S = \frac{1}{2}$ is a single determinant, where all one-particle states are occupied except the one with $m_l = -1$ and $m_s = -\frac{1}{2}$. The corresponding one-particle densities are $n_{-1,1/2} = 0$ and $n_{m_lm_s} = 1$ otherwise. Since $L = 1$, $S = \frac{1}{2}$, and $l = 1$ the final-state symmetries allowed according to the triangular conditions are $L' = 0, 1, 2$ and $S' = 0, 1$. The linear Eqs. (19) for this particular case are in matrix notation as follows:

$$\begin{bmatrix} 1 & & & & & \\ \frac{1}{2} & \frac{1}{2} & & & 0 & \\ \frac{1}{2} & 0 & \frac{1}{2} & & & \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & & \\ \frac{1}{6} & 0 & \frac{1}{2} & 0 & \frac{1}{3} & \\ \frac{1}{12} & \frac{1}{12} & \frac{1}{4} & \frac{1}{4} & \frac{1}{6} & \frac{1}{6} \end{bmatrix} \times \begin{bmatrix} g({}^3D) \\ g({}^1D) \\ g({}^3P) \\ g({}^1P) \\ g({}^3S) \\ g({}^1S) \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} . \tag{46}$$

Here the notation of the weight factors is simplified according to $g({}^{2S'+1}L') \equiv g(l,LS,L'S')$. One easily finds the solution $g = 2$ for ${}^3P$, ${}^1D$, ${}^1S$ and, $g = 0$ for ${}^3D$, ${}^1P$, ${}^3S$. Of the six possible final multiplets only the three multiplets ${}^3P$, ${}^1D$, and ${}^1S$ occur with the relative intensities $\frac{9}{18}$, $\frac{5}{18}$, and $\frac{1}{18}$, respectively, reflecting the statistical weights of these multiplets. It should be noted, however, that in general the relative (partial) intensities for ionization from an open shell are not given by the statistical values. The relative intensities here sum up to the mean occupation number $\frac{5}{6}$ of the p^5 configuration in accordance with the sum rule of Eq. (28). The coefficients of fractional parentage for the ionic states ${}^3P$, ${}^1D$, and ${}^1S$ are $\frac{3}{15}$, $\frac{1}{3}$, and $\frac{1}{15}$, respectively, leading via Eq. (26) to the same results for the weight factors and the relative intensities.

As a case where initial-state correlation plays a role we consider the state ${}^2P$ resulting from the p^5 configuration and an additional excited configuration p^3s^2. This state is given by a linear combination

$$|{}^2P\rangle = a_0|{}^2P(p^5)\rangle + a_1|{}^2P(p^3s^2)\rangle \tag{47}$$

with coefficients normalized by $a_0^2 + a_1^2 = 1$. Now the vector of one-particle densities is

$$(n_{-1,-1/2}, n_{-1,1/2}, n_{0,-1/2}, n_{0,1/2}, n_{1,-1/2}, n_{1,1/2}) = (0, x, x, x, x, 1)$$

where $x = a_0^2 + \frac{1}{2}a_1^2$. Inserting this vector on the right-hand side of Eq. (46) we find the solution $g = 0$ for ${}^3D$, ${}^1P$, ${}^3S$, and $g({}^3P) = g({}^1D) = 2a_0^2 + a_1^2$, $g({}^1S) = 2a_0^2 + 4a_1^2$. The branching ratios for the three occurring states ${}^3P$, ${}^1D$, and ${}^1S$ now are $\frac{9}{18} - \frac{1}{4}a_1^2 : \frac{5}{18} - \frac{5}{36}a_1^2 : \frac{1}{18} + \frac{1}{18}a_1^2$ showing a deviation from the above geometrical values $\frac{9}{18} : \frac{5}{18} : \frac{1}{18}$. The initial-state correlation here causes an enhancement of the ${}^1S$ intensity with respect to the intensities of the states ${}^3P$ and ${}^1D$. This is an example for a principal effect which apparently is important for the case of large mixing coefficients a_1.

Now we extend the previous examples to *LSJ* symmetry. Upon inclusion of spin-orbit coupling the ground state ${}^2P$ splits into the two states ${}^2P_{1/2}$, ${}^2P_{3/2}$ with $J = \frac{1}{2}$ and $\frac{3}{2}$. If the spin-orbit coupling is weak we may classify the ionic states according to ${}^3P_{2,1,0}$, ${}^1D_2$, and ${}^1S_0$. The relative intensities of these ionic states produced by ionizing the p shell of the initial state ${}^2P_{1/2}$ or ${}^2P_{3/2}$ are easily obtained from Eq. (39). The required weight factors $g(l, LS, L'S')$ already have been determined for the case of the uncorrelated state ${}^2P(p^5)$ and the correlated state of Eq. (47). The correlation effects in the latter case influence the distribution of intensity on the ionic symmetries $L'S'$ as discussed above. The relative intensities of the ionic states J' for a given symmetry $L'S'$, however, are purely geometrical and are not affected by initial-state correlation. In Table I the geometrical relative intensities (without initial-state correlation) are listed. Apparently these values differ drastically from the statistical expectations. We note that both for ${}^2P_{1/2}$ and ${}^2P_{3/2}$ the relative intensities sum up to the mean one-particle density $\frac{5}{6}$ of the p^5 configuration. In Table I also the experimental relative intensities of several photoionization spectra are presented. The agreement of the geometrical values with the data of the high precision photodetachment experiment of Breyer, Frey, and Hotop[16] for the negative ions O^- and S^- is excellent. The reported data here are obtained at a photon energy of 2.54 eV. Thus, only the ${}^3P$ final states are reached energetically. The agreement between experiment and the geometrical values is particularly interesting considering the fact that the photon energy is only slightly above the ${}^3P$ thresholds. For negative ions the approximation (a) of neglecting the continuum correlation may be adequate already for small kinetic energies of the detached electron.

The He I photoelectron spectra of Kimura *et al.*[8] exhibit for the Cl atom a good agreement between the experimental and geometrical relative intensities. For Br the spin-orbit coupling plays an increasing role. Hence the *LSJ* classification ceases to be adequate. By a small CI calculation for the ionic states of the same total angular momentum Berkowitz and Goodman[12] achieve a better description of the experimental relative intensities. We would like to mention that for the special case of the p^5 configuration Berkowitz and Goodman use an expression for the relative ionic intensities which is essentially equivalent to Eq. (45).

As an example for the ionization from a closed shell we consider the ${}^2S_{1/2}$ ground state of a $d^{10}s^1$ configuration, e.g. the $4d^{10}5s^1$ configuration of the Ag atom. The geometrical partial intensities for ionization from the d shell are obtained from Eq. (43). For the four ionic states ${}^3D_3$, ${}^3D_2$, ${}^3D_1$, and ${}^1D_2$ we find the statistical branching ratios $\frac{7}{20} : \frac{5}{20} : \frac{3}{20} : \frac{5}{20}$. The experimental intensity ratios for Ag have been measured by Süzer.[11] His ratios 7 : 4.9 : 2.9 : 4.7 are in good agreement with the geometrical results. We would like to remark that for the special case of an initial state ${}^2S_{1/2}$ the geometrical partial intensities assume the statistical values for any shell.

TABLE I. Comparison of the geometrical relative intensities with experimental intensities for the ionization of the $({}^5p)\ {}^2P_{1/2,3/2}$ states.

Ionic states	Initial state ${}^2P_{1/2}$ Geometrical Intensity	Ratios [a]	Expt. ratios [b] O^-	S^-	Initial state ${}^2P_{3/2}$ Geometrical Intensity	Ratios [a]	Expt. ratios [b] O^-	S^-	Expt. ratios [c] Cl	Br
${}^3P_2$	$\frac{5}{36}$	1.0	1.00	1.00	$\frac{25}{72}$	1.0	1.00	1.00	1.00	1.00
${}^3P_1$	$\frac{9}{36}$	1.8	2.0(2)	1.90(10)	$\frac{9}{72}$	0.36	0.367(12)	0.346(13)	0.44	0.51
${}^3P_0$	$\frac{4}{36}$	0.8	0.85(10)	0.81(5)	$\frac{2}{72}$	0.08	0.084(5)	0.082(4)	0.06	0.06
${}^1D_2$	$\frac{10}{36}$	2.0			$\frac{20}{72}$	0.8			0.81	0.71
${}^1S_0$	$\frac{2}{36}$	0.4			$\frac{4}{72}$	0.16			0.16	0.09

[a] Ratios with respect to the state ${}^3P_2$.

[b] Data of Ref. 16, $\lambda = 5145$ Å, the uncertainty with respect to the last digits is given in parentheses.

[c] Data of Ref. 8.

In order to present a complete list of geometrical branching ratios for the interesting case of ionization from the open p^n configuration Tables II–V have been compiled. The weight factors $g(l, LS, L'S')$ for the respective ground states (Hund's rule) are listed in Table II. The geometrical relative intensities for the LS case follow immediately from Eq. (17). In Tables III–V the results of the LSJ case are presented for the p^4, p^3, and p^2 configurations, respectively.

VI. DISCUSSION

Methods for determining branching ratios of ionization experiments have been presented and illustrated for several cases. The only required input data are the one-particle densities of a specific initial state. The approach considered here to determine branching ratios makes use of few well-defined approximations: (a) no correlation between bound and free electron states, (b) the picture of ionization from a single shell is valid, (c) constant transition coefficients for each shell. For the case of LSJ symmetry we also have to assume (d) small spin-orbit coupling for the transition operator and for the initial and ionic states. When initial-state correlation is neglected, one arrives at the so-called geometrical branching ratios which have been discussed in the work of Cox *et al.*[30-32] These geometrical ratios may be given by ratios of the statistical weights, i.e., the degree of degeneracy of the ionic symmetry species. Statistical ratios result for the ionization from a closed shell in the LS or J case. The geometrical ratios, in general, differ from the statistical values when the ionization takes place from an open shell. In the LSJ case the multiplet ratios, in general, do not reflect the statistical weights even when a closed shell is ionized.

We have shown that initial-state correlation introduces deviations of the branching ratios from the geometrical ratios. Hence, at least in principal, one could study initial-state correlation effects from experimental branching ratios. In particular, one could determine relative one-particle densities from the experimental branching ratios via Eq. (19). For such a purpose it is, of course, essential, that other sources of deviations from the geometrical ratios can be eliminated. Such sources clearly are provided by approximations (a)–(c). The validity of approximation (b) is itself determined by initial-state properties. The approximations (a) and (c), on the other hand, depend on the kinetic energy of the ejected electron. In particular for high kinetic energy the error introduced by approximations (a) and (c) may be neglected. Then the experimental branching ratios exclusively reflect initial-state correlation effects. Here a remark might be appropriate. The theoretical branching ratios are defined as the ratios of partial intensities, i.e., the relative intensity of a specific shell. When determining experimental branching ratios one has to make sure to collect actually the contributions of all states with the same symmetry. The relative intensities for ionic multiplets of the same symmetry are subject to final-state correlations and cannot be predicted by *a priori* rules.

As we have already mentioned, an approach to geometrical branching ratios for the case of LSJ symmetry has been presented by Rau.[33] Although Rau apparently also makes use of the approximations (a)–(d) his final formula still takes explicitly the (geometrical) coupling of the continuum electron into account. This renders a comparison to our result of Eq. (39) rather difficult. As has already been noted by Lineberger[17] the result of Rau does not correctly predict the distribution of intensity on the ionic symmetry species $L'S'$ when an open shell is ionized, since he does not antisymmetrize the state obtained by geometrically coupling the ionic state and the one-particle states. However, for a given symmetry species

TABLE II. The weight factors $g^2(l, LS, L'S')$ for the ionization from the (Hund's rule) ground states of all p^n configurations.

p^6		p^5		p^4		p^3		p^2		p^1		p^0
^1S	1	^2P	2	^3P	3	^4S	4/3	^3P	3	^2P	6	^1S
			2		3/2		0					
				^1D		^2D		^1D				
			2		3/2		0					
				^1S		^2P		^1S				

TABLE III. The geometrical relative intensities for the ionization of the $(p^4)\ ^3P_{2,1,0}$ states.

Initial states	Final states $^4S_{3/2}$	$^2D_{5/2}$	$^2D_{3/2}$	$^2P_{3/2}$	$^2P_{1/2}$
$^3P_2$	$\frac{8}{36}$	$\frac{9}{36}$	$\frac{1}{36}$	$\frac{5}{36}$	$\frac{1}{36}$
$^3P_1$	$\frac{8}{36}$	$\frac{3}{36}$	$\frac{7}{36}$	$\frac{3}{36}$	$\frac{3}{36}$
$^3P_0$	$\frac{8}{36}$	0	$\frac{10}{36}$	$\frac{2}{36}$	$\frac{4}{36}$

TABLE IV. The geometrical relative intensities for the ionization of the $(p^3)\ ^4S_{3/2}$ state.

Initial state	Final states $^3P_2$	$^3P_1$	$^3P_0$
$^4S_{3/2}$	$\frac{10}{36}$	$\frac{6}{36}$	$\frac{2}{36}$

TABLE V. The geometrical relative intensities for the ionization of the $(p^2)\ {}^3P_{2,1,0}$ states.

Initial states	Final states ${}^2P_{3/2}$	${}^2P_{1/2}$
${}^3P_2$	$\frac{10}{36}$	$\frac{2}{36}$
${}^3P_1$	$\frac{6}{36}$	$\frac{6}{36}$
${}^3P_0$	$\frac{4}{36}$	$\frac{8}{36}$

$L'S'$ the distribution of intensity on the possible J' states is not affected and should be correct. For the example of the ${}^2P_{1/2,3/2}(p^5)$ states discussed in Sec. V Rau reports geometrical ratios for the ionic states ${}^3P_{2,1,0}$ which agree with the results of Eq. (39). These ratios have been calculated for a s continuum electron. For the case of a d continuum wave these ratios—reported by Breyer *et al.*[16]—differ from those of the s wave. This is in contradiction to the general result that—provided the four approximations (a)–(d) are valid—the branching ratios do not depend on the symmetry of the continuum electron. A possible error in Rau's result might come in as follows. Rau introduces in the dipole-transition matrix element a complete set of LS coupled states LSJ of a complex of the ion and the contiuum electron. When squaring this matrix element the contributions for different values of J add incoherently. One also has to perform a summation over the different values of L (and S). In contrast to what is apparently assumed in Rau's result these contributions do not add incoherently. For s waves the summation over the angular momenta L reduces to a single term, thus explaining the fact that Rau's formula produces correct results for s waves, but incorrect results for d waves.

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APPENDIX A: RELATIVE INTENSITIES FOR *LS* AND *LSJ* SYMMETRY

We consider the relative intensities of Eq. (7) for the case of LS symmetry where the initial, ionic, and one-particle states are denoted by $|LSM_LM_S\rangle$, $|nL'S'M_L'M_S'\rangle$, and $|plm_lm_s\rangle$:

$$R^{nL'S'}_{plm_lm_s,ql'm_l'm_s'}=\frac{1}{[L,S]}\sum_{M_L,M_S,M_L',M_S'}\langle LSM_LM_S|c^\dagger_{ql'm_l'm_s'}|nL'S'M_L'M_S'\rangle\langle nL'S'M_L'M_S'|c_{plm_lm_s}|LSM_LM_S\rangle\,. \tag{A1}$$

Since the creation operators $c^\dagger_{lm_lm_s}$ and the (modified) destruction operators $(-1)^{l-m_l+1/2-m_s}c_{l,-m_l,-m_s}$ are irreducible tensor operators, the Wigner-Eckart theorem[35] may be applied to evaluate the matrix elements of Eq. (A1):

$$\langle nL'S'M_L'M_S'|c_{plm_lm_s}|LSM_LM_S\rangle$$

$$=(-1)^{L'-M_L'+S'-M_S'}(-1)^{l+m_l+1/2+m_s}\begin{pmatrix}L' & l & L\\ -M_L' & -m_l & M_L\end{pmatrix}\begin{pmatrix}S' & \frac{1}{2} & S\\ -M_S' & -m_s & M_S\end{pmatrix}(nL'S'\|c_{pl}\|LS)\,. \tag{A2}$$

Here $(nL'S'\|c_{pl}\|LS)$ is a reduced matrix element [defined by Eq. (A2)] being independent of magnetic quantum numbers. Now the summation over M_L, M_S, M_L', M_S' in Eq. (A1) can be performed yielding the simple result

$$R^{nL'S'}_{plm_lm_s,ql'm_l'm_s'}=\delta_{ll'}\delta_{m_lm_l'}\delta_{m_sm_s'}R^{nL'S'}_{pl,ql} \tag{A3}$$

with m-independent relative intensities

$$R^{nL'S'}_{pl,ql}=\frac{1}{[\frac{1}{2},l,L,S]}(nL'S'\|c_{pl}\|LS)(nL'S'\|c_{ql}\|LS)^*\,. \tag{A4}$$

From the properties of the $3j$ coefficients[35] appearing on the right-hand side of Eq. (A2) the selection rules for the ionic symmetries $|L-l|\leqslant L'\leqslant L+l$ and $|S-\frac{1}{2}S'|\leqslant S'\leqslant S+\frac{1}{2}$, are derived.

In the LSJ case we consider initial states $|LSJM\rangle$ and ionic states $|nL'S'J'M'\rangle$. For the moment both LS and $L'S'$ can be regarded as additional quantum numbers characterizing the initial and ionic states of J symmetry. We assume that the ionic states stem from the ionization of a shell l or equivalently of the both subshells $j=l\pm\frac{1}{2}$. The evaluation of Eq. (5) can be performed by using the one-particle basis $|lm_lm_s\rangle$ as well as the basis $|jm\rangle$, $j=l\pm\frac{1}{2}$. With the first choice one obtains for the intensity

$$P^{nL'S'J'}=\sum_{m_l,m_s,m_l',m_s'}T_{lm_lm_s,lm_l'm_s'}R^{nL'S'J'}_{lm_lm_s,lm_l'm_s'}\,. \tag{A5}$$

Here the dependence of the transition coefficients on the ionic state has been left out of consideration. The relative intensities are given by

$$R^{nL'S'J'}_{lm_lm_s,lm'_lm'_s}=\frac{1}{[J]}\sum_{M,M'}\langle LSJM|c^{\dagger}_{lm'_lm'_s}|nL'S'J'M'\rangle\langle nL'S'J'M'|c_{lm_lm_s}|LSJM\rangle\,. \tag{A6}$$

To proceed we introduce the destruction operator for the j subshells

$$c_{jm}=\sum_{m_l,m_s}\left(\begin{array}{cc|c} l & \frac{1}{2} & j \\ m_l & m_s & m \end{array}\right) c_{lm_lm_s} \tag{A7}$$

and the relative intensity $R^{nL'S'J'}_j$ for a shell j

$$R^{nL'S'J'}_j=\frac{1}{[J]}\sum_{M,M'}|\langle nL'S'J'M'|c_{jm}|LSJM\rangle|^2=\frac{1}{[j,J]}\,|(nL'S'J'\,\|\,c_j\,\|\,LSJ)|^2\,. \tag{A8}$$

The last equality follows from an analysis analogously to Eq. (A1)–(A4) for the case of J symmetry. With the help of Eqs. (A7) and (A8) the relative intensities of Eq. (A6) can be written as

$$R^{nL'S'J'}_{lm_lm_s,lm'_lm'_s}=\sum_{jm}\left(\begin{array}{cc|c} l & \frac{1}{2} & j \\ m_l & m_s & m \end{array}\right)\left(\begin{array}{cc|c} l & \frac{1}{2} & j \\ m'_l & m'_s & m \end{array}\right)R^{nL'S'J'}_j\,. \tag{A9}$$

Apparently, the right hand of the equation is not diagonal with respect to m_l and m'_l (m_s and m'_s). Let us now consider the transition coefficients of Eq. (A5). If one can neglect relativistic effects for the transition, in particular, if the transition operator employed is spin independent, then the transition coefficients $T_{lm_lm_s,lm'_lm'_s}$ are diagonal with respect to m_s, m'_s and independent of m_s. We shall call this approximation (d). As a consequence one can perform the summation over m_s on the right-hand side of Eq. (A5). With the help of the relation

$$\sum_{m_s}\left(\begin{array}{cc|c} l & \frac{1}{2} & j \\ m_l & m_s & m_l+m_s \end{array}\right)^2=\frac{2j+1}{2l+1}\,, \tag{A10}$$

we arrive at the simple result for the ionic intensity

$$P^{nL'S'J'}=T_{ll}R^{nL'S'J'}_l$$

with the relative intensity

$$R^{nL'S'J'}_l=\frac{1}{2(2l+1)}\sum_j(2j+1)R^{nL'S'J'}_j \tag{A11}$$

and the m-independent transition coefficient T_{ll} of Eq. (12).

APPENDIX B: THE WEIGHT-FACTORS FOR *LS* SYMMETRY

In the following we show that the weight factors $g(l,LS,L'S')$ introduced in Eq. (16) are given by the normalization integrals

$$g(l,LS,L'S')=\langle L'S'M'_LM'_S|L'S'M'_LM'_S\rangle \tag{B1}$$

of the $(N-1)$-particle states

$$|L'S'M'_LM'_S\rangle=\sum_{m_l,M_L,m_s,M_S}(-1)^{l+m_l+1/2+m_s}\left(\begin{array}{cc|c} l & L & L' \\ -m_l & M_L & M'_L \end{array}\right)\left(\begin{array}{cc|c} \frac{1}{2} & S & S' \\ -m_s & M_S & M'_S \end{array}\right)c_{lm_lm_s}|LSM_LM_S\rangle\,, \tag{B2}$$

which are constructed by coupling the operators $c_{lm_lm_s}$ and the initial states $|LSM_LM_S\rangle$ to states with symmetry $L'S'M'_LM'_S$. For this purpose we start from the definition (B1) and (B2) and prove Eq. (17). According to Eq. (A1) and (A3) the partial intensity $R^{L'S'}_l$ can be written as

$$R^{L'S'}_l=\sum_n\frac{1}{[L,S]}\sum_{M_L,M_S,M'_L,M'_S}|\langle nL'S'M'_LM'_S|c_{lm_lm_s}|LSM_LM_S\rangle|^2\,. \tag{B3}$$

Using the inverse expansion of Eq. (B2),

$$c_{lm_lm_s}|LSM_LM_S\rangle=\sum_{L',M'_L,S',M'_S}\left(\begin{array}{cc|c} l & L & L' \\ -m_l & M_L & M'_L \end{array}\right)\left(\begin{array}{cc|c} \frac{1}{2} & S & S' \\ -m_s & M_S & M'_S \end{array}\right)(-l)^{l+m_l+1/2+m_s}|L'S'M'_LM'_S\rangle\,, \tag{B4}$$

Eq. (B3) becomes

$$R_l^{L'S'}=\frac{1}{[L,S]}\sum_{M_L,M_S,M'_L,M'_S}\left(\begin{array}{cc|c} l & L & L' \\ -m_l & M_L & M'_L \end{array}\right)\left(\begin{array}{cc|c} \frac{1}{2} & S & S' \\ -m_s & M_S & M'_S \end{array}\right)^2\sum_n \left|\langle nL'S'M'_LM'_S\,|L'S'M'_LM'_S\rangle\right|^2 . \tag{B5}$$

Since the summation over n runs over a complete set of normalized states with symmetry $L'S'M'_LM'_S$ we obtain

$$\sum_n \left|\langle nL'S'M'_LM'_S\,|L'S'M'_LM'_S\rangle\right|^2=g(l,LS,L'S') , \tag{B6}$$

where the weight factor $g(l,LS,L'S')$ is given by the square of the absolute magnitude of the $(N-1)$-particle state of Eq. (B2). The remaining summation on the right-hand side of Eq. (B5) is easily evaluated with the help of the orthogonality relations for the Clebsch-Gordan coefficients, yielding

$$R_l^{L'S'}=\frac{[L',S']}{[\frac{1}{2},l,L,S]}\,g(l,LS,L'S') . \tag{B7}$$

This result proves the validity of Eq. (17). From Eqs. (B1) and (B2) it is clear that the weight factors are entirely determined by the initial states $|LSM_LM_S\rangle$. Equations (19) relating the weight factors to the one-particle densities $n_{lm_lm_s}$ of Eq. (18) are readily obtained by taking the norm on both sides of Eq. (B4) for the special values $M_L=L$ and $M_S=S$ and by making use of Eq. (B1).

In addition to the procedure discussed in Sec. III an explicit solution of Eqs. (19) can be derived as follows. We start from Eq. (B1) and insert the right-hand side of Eq. (B2). To evaluate the matrix elements $\langle LSM_LM_S\,|c^\dagger_{l\bar{m}_l\bar{m}_s}c_{lm_lm_s}|LSM_LM_S\rangle$ we express the products

$$c^\dagger_{l\bar{m}_l\bar{m}_s}c_{lm_lm_s}=\sum_{l',m'_l,s',m'_s}\left(\begin{array}{cc|c} l & l & l' \\ \bar{m}_l & -m_l & m' \end{array}\right)\left(\begin{array}{cc|c} \frac{1}{2} & \frac{1}{2} & s' \\ \bar{m}_s & -m_s & m'_s \end{array}\right)(-1)^{l+m_l+1/2+m_s}\,\hat{0}^{l',s'}_{m'_l,m'_s} \tag{B8}$$

by irreducible tensor operators $\hat{0}^{l',s'}_{m'_l,m'_s}$ [defined by the inverse expansion to Eq. (B8)] and make use of the Wigner-Eckart theorem. The various summations over magnetic quantum numbers of the occurring Clebsch-Gordan coefficients can be replaced by two $6j$ symbols, yielding

$$g(l,LS,L'S')=(-1)^{L+L'-l+S+S'-1/2}\sum_{s'=0}^{1}\sum_{l'=0}^{2l}(-1)^{s'+l'}[s',l']^{1/2}$$
$$\times\begin{Bmatrix} l & l' & l \\ L & L' & L \end{Bmatrix}\begin{Bmatrix} \frac{1}{2} & s' & \frac{1}{2} \\ S & S' & S \end{Bmatrix}(LS\,\|\,\hat{0}^{l',s'}\,\|\,LS) . \tag{B9}$$

The reduced matrix element on the right-hand side of Eq. (B9) can be evaluated introducing the one-particle densities $n_{lm_lm_s}=\langle LSLS\,|c^\dagger_{lm_lm_s}c_{lm_lm_s}|LSLS\rangle$ of Eq. (18):

$$(LS\,\|\,\hat{0}^{l',s'}\,\|\,LS)=\begin{pmatrix} L & l' & L \\ -L & 0 & L \end{pmatrix}^{-1}\begin{pmatrix} S & s' & S \\ -S & 0 & S \end{pmatrix}^{-1}\sum_{m_l,m_s}(-1)^{l+1/2+m_l+m_s}$$
$$\times\left(\begin{array}{cc|c} l & l & l' \\ m_1 & -m_l & 0 \end{array}\right)\left(\begin{array}{cc|c} \frac{1}{2} & \frac{1}{2} & s' \\ m_s & -m_s & 0 \end{array}\right)n_{lm_lm_s} . \tag{B10}$$

Equations (B9) and (B10) establish an explicit relation between the weight factors and the initial-state one-particle densities.

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