RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 39, NUMBER 7 APRIL 1, 1989

Angular distributions of electrons in resonant Auger spectra

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(Received 17 November 1988)

Recent measurements have shown that the angular distribution of Auger electrons observed in near threshold resonant excitation with energy resolution adequate to partially resolve the multiplet structure corresponding to final core states exhibited a marked change in the angular distributions as a function of final electron energy. A method of calculating these angular distributions is proposed that extends the formalism developed for treating angular distributions in photoeffect via a separation into parity-favored and -unfavored components. As an example of the use of the method, calculations are presented for the $2p$-$4s$ resonant Auger process in argon and compared with recent experiments.

In a recent paper[1] an unusual degree of angular anisotropy in the resonant Auger spectrum of Kr following $3d_{5/2}$-$5p$ excitation was reported and it was conjectured that parity-unfavored transitions might be responsible for these results. It was also pointed out that a satisfactory theoretical treatment of the resonant Auger process was not available and would require further development. It is the purpose of this Rapid Communication to report the needed development for calculation of the angular distributions of Auger electrons in resonant Auger processes via an extension of the angular momentum transfer theory of Fano and Dill.[2] As an example of the application of the formalism, results for the angular distribution of Auger electrons in the resonant Auger process $2p_{3/2}$-$4s$ will be presented and compared with recent experimental data.[3] This example also serves to define the channels of outgoing partial waves and to show how the angular distribution can be calculated from the outgoing-wave amplitudes.

Since there has been considerable work recently on the angular distribution of Auger electrons,[4] it is important to make a clear distinction between "normal" Auger processes and resonant Auger processes. In a normal Auger process an electron is ejected creating an inner-shell vacancy which then can be filled by a two-electron transition from an outer subshell with ejection of an Auger electron. In a near threshold resonant Auger process an inner-shell electron is excited to a resonant state and the excited state then decays via a two-electron transition which fills the vacancy created in the excitation process. For the case of photon excitation the two processes can be represented as

$$h\nu + A \rightarrow A^+ + e_1 \rightarrow A^{++} + e_2 , \quad (1)$$

$$h\nu_r + A \rightarrow A^* \rightarrow A^{*+} + e_3 , \quad (2)$$

where A is a randomly oriented atom or molecule and e_i represents ejected electrons. In dipole approximation with linearly polarized light the angular distribution of all outgoing electrons is restricted to be of the form[5]

$$d\sigma_c(E_c)/d\Omega = \sigma_c(E_c)/4\pi[1+\beta_c(E_c)P_2(\cos\theta)] , \quad (3)$$

where the subscript c refers to a particular final state of ion core and thus a definite final-state electron energy E_c. The angle θ is defined relative to the direction of polarization.

In normal Auger processes the asymmetry parameter $\beta_c(E_c)$ will be a function of the incident energy $h\nu$ and measurements of the angular distribution of photoelectrons (e_1) or Auger electrons (e_2) can be alternatively used to obtain information on the energy dependence of the alignment produced in the initial photoionization process. In contrast, in the resonant Auger process, angular distribution measurements define the alignment of the excited-ion core A^{+*} at a well-defined resonant energy $h\nu_r$. There is thus no reason to consider the process as excitation followed by decay; it can be treated as a single-step process producing an excited ion and an ejected photoelectron. The only difference is that additional channels are accessible due to configuration interaction with the excited resonant state. The procedure for calculating angular distributions is then formally the same as in resonant processes in direct photoionization, the difference being that in direct photoionization both the resonance and continuum states may be reached by photon excitation, whereas in the resonant Auger process the continuum channels corresponding to Auger processes are accessible via configuration interaction.

As an illustration of this approach, consider the resonant process in argon:

$$2p^6 3s^2 3p^6 \rightarrow 2p^5 3s^2 3p^6 (2P_{3/2}) 4s \rightarrow 2p^6 3s^2 3p^4 4s + \epsilon 1 . \quad (4)$$

The resonant state A^{+*} lies at 244.4 eV above the $^1S_0$ ground state and recent measurements of the Auger spectrum at this incident energy have been made.[3,6] The first step is to define all outgoing-wave channels that can be reached by photoionization. These will be of two types; channels that can be reached by direct photoionization of outer subshell electrons and channels that can be reached via Auger decay. Both types of channels are defined by the selection rules for dipole excitation, i.e., $\Delta J = 1$ and a change in parity. The direct channels for ionization of $3s$ and $3p$ electrons are well known and arise from alternative coupling of an outgoing electron with the $^2P_{3/2}$, $^2P_{1/2}$, and $^2S_{1/2}$ cores.[7] The channels for Auger decay are defined in

exactly the same way. In the case of a $3p^4 4s$ core there are eight core states; ${}^4P(\frac{5}{2},\frac{3}{2},\frac{1}{2})$, ${}^2P(\frac{3}{2},\frac{1}{2})$, ${}^2D(\frac{5}{2},\frac{3}{2})$, and ${}^2S(\frac{1}{2})$. Parity restricts outgoing waves to $l=1,3$; p and f waves and since the final state must be $J=1$ there will be 21 possible outgoing channels corresponding to alternative couplings of the core states with outgoing p and f waves. These channels along with the seven channels for direct photoionization are listed in Table I. There will, of course, be alternative channels corresponding to Auger processes involving a single s and p or two s electrons (L_3-M_1M_{23} and L_3-M_1M_1 transitions). The angular distributions for Auger electrons resulting from these processes can be calculated in the same way.

For each of the 21 indirect channels shown in Table I there will be a dipole amplitude D_{clj} and phase δ_{clj}, where c defines the core level, and l and j refer to the outgoing wave orbital and total momentum, respectively. For excitation of a single isolated resonance, each dipole amplitude can be expressed as the product of two factors, a common factor representing excitation of the resonant state and an Auger amplitude representing the interaction of the resonance with the various continuum channels. The relative probabilities of Auger decay to the different multiplet states depends only on these amplitudes and the procedure for calculating these probabilities is exactly the same as in normal Auger processes. The angular distributions will however, depend on the relative phases.

The momentum-transfer theory of Fano and Dill[2] can be used to provide explicit formulas to calculate the angular distributions. In this formalism the cross section for excitation to a particular core state is separated into two components representing alternative couplings of the total angular momentum of the core with the spin of the outgoing electron. The formalism has the advantage of separating the angular distributions of outgoing electrons into two components, parity favored and unfavored, and the unfavored components always have an asymmetry parameter $\beta_c=-1$ independent of all phases and amplitudes. In the present case, core total momentum values of $\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$, the allowed values of angular momentum transfer are $j_t=0$–3. Since the parity of the core is the same as the parity of the initial ground state, even values correspond to parity-favored transitions and odd values to parity unfavored. In a standing-wave representation, assuming a $J=0$ initial state, the cross sections for parity-favored and -unfavored transitions are defined in terms of the scattering factors

TABLE I. Final-state channels for direct photoionization and resonant Auger processes with $2p$-$4s$ excitation.

Final ion core state		Possible continuum electron partial waves		
		Direct channels		
$3p^5$	${}^2P_{3/2}$	$s_{1/2}$	$d_{3/2}$	$d_{5/2}$
$3p^5$	${}^2P_{1/2}$	$s_{1/2}$	$d_{3/2}$	
$3s3p^6$	${}^2S_{1/2}$	$p_{3/2}$	$p_{1/2}$	
		Auger channels		
$3p^4 4s$	${}^4P_{5/2}$	$p_{3/2}$	$f_{5/2}$	$f_{7/2}$
$3p^4 4s$	${}^4P_{3/2}$	$p_{1/2}$	$p_{3/2}$	$f_{5/2}$
$3p^4 4s$	${}^4P_{1/2}$	$p_{1/2}$	$p_{3/2}$	
$3p^4 4s$	${}^2P_{3/2}$	$p_{1/2}$	$p_{3/2}$	$f_{5/2}$
$3p^4 4s$	${}^2P_{1/2}$	$p_{1/2}$	$p_{3/2}$	
$3p^4 4s$	${}^2D_{3/2}$	$p_{1/2}$	$p_{3/2}$	$f_{5/2}$
$3p^4 4s$	${}^2D_{5/2}$	$p_{3/2}$	$f_{5/2}$	$f_{7/2}$
$3p^4 4s$	${}^2S_{1/2}$	$p_{1/2}$	$p_{3/2}$	

$$S_{cl}(j_t)=(-i)^{-l}(-1)^{j_t+J_c}\sum_j(-1)^j(2j+1)^{1/2}\begin{pmatrix}\frac{1}{2} & l & j\\ 1 & J_c & j_t\end{pmatrix}D_{clj}e^{i\delta_{cj}}, \tag{5}$$

where J_c is the core momentum. The cross sections for angular momentum transfer resulting in a given final core state will be

$$\sigma_c(j_t)=C(2j_t+1)\sum_l|S_{cl}(j_t)|^2, \tag{6}$$

where C is a constant factor.

The asymmetry parameter for parity favored transitions to a given core state will be

$$\beta(j_t)=\frac{(j_t+2)|S_+(j_t)|^2+(j_t-1)|S_-(j_t)|^2-3[S_+(j_t)S_-^*(j_t)+\text{c.c.}]}{(2j_t+1)|S_+(j_t)|^2+|S_-(j_t)|^2}, \tag{7}$$

where $+$ and $-$ refer to the larger and smaller l values. Finally, the asymmetry parameter for transitions to a given core state is

$$\beta_c(j_t)=\sum_{j_t}\sigma_c(j_t)\beta_c(j_t)\Big/\sum_{j_t}\sigma_c(j_t). \tag{8}$$

Equations (6)–(8) are the same as those used in treating direct photoionization,[8] the only difference being that a number of core states are involved and the dipole amplitudes D_{clj} represent both initial excitation and decay via configuration interaction.

Numerical calculations of the asymmetry parameters corresponding to Eq. (4) used the following procedure.[9] Hartree-Fock calculations of the wave functions and energy levels for the $3p^4 4s$ core configuration were performed and parameters were adjusted to obtain better agreement with known energy levels.[10] Continuum p and f waves were then calculated using these core wave functions and the Coulomb matrix elements were evaluated for each of the alternative channels shown in Table I. In applying Eq. (7) it was assumed that the phases for p and f waves were spin independent and the single p-f phase difference was

TABLE II. Results for argon $2p$-$4s$ resonant Auger angular distributions and relative cross sections. σ_{cp} and σ_{cf} represent the p and f wave contributions to the total cross section σ_T for excitation to a given core state c. $\sigma_c(\text{fav})/\sigma_T$ is the ratio of parity-favored cross section to the total for a given core state.

Ion core state	σ_{cp}	σ_{cf}	$\sigma_c(\text{fav})/\sigma_T$	β_c
$^4P_{5/2}$	15.1	0.03	1.00	2.0
$^4P_{3/2}$	16.5	· · ·	0.06	−0.82
$^4P_{1/2}$	15.9	· · ·	0.86	1.59
$^2P_{3/2}$	60.3	· · ·	0.06	−0.82
$^2P_{1/2}$	19.5	· · ·	0.04	−0.83
$^2D_{3/2}$	78.6	0.9	0.75	0.43
$^2D_{5/2}$	7.3	13.3	1.00	1.90
$^2S_{1/2}$	23.7	· · ·	0.67	1.00

TABLE III. Comparison of the averaged results for $2p$-$4s$ resonant Auger transitions with the experimental data of Ref. 3. Cross sections have been normalized to the total ^2D cross section. Two results are given for some values of the experimental data which represent alternative ways of reducing the data.

Ion core state	σ_{avg}	σ_{expt}	β_{avg}	β_{expt}
^4P	48.5	54,20	0.88	0.23, 0.47
^2P	79.8	71,96	−0.83	−0.69, −0.8
^2D	100	100	0.73	0.48, 0.45
^2S	23.7	36	1.0	0.6

evaluated from the continuum wave functions. Equations (6)–(8) were then used to calculate the relative cross sections and asymmetry parameters for each core state. The results are given in Table II and compared with the experimental data of Ref. 3 in Table III. The asymmetry parameters are simply averaged to compare with the experimental data.

In evaluating the cross sections and asymmetry parameters, it was found that except for the $^2D(\frac{5}{2}$ and $\frac{3}{2})$ states the f waves made a negligible contribution to the cross sections. Thus for the other states the asymmetry parameters are phase independent and are determined solely by the ratios of parity favored and unfavored cross sections.

There are several interesting features of these results. First, although f waves may be neglected for all except the ^2D final core states, both $p_{1/2}$ and $p_{3/2}$ waves contribute to all other final core states except for $^4P_{5/2}$ and $^2S_{1/2}$. For these states the asymmetry parameter is determined independent of matrix elements to be 2 and 1, respectively. Second, transitions to the $^2P(\frac{3}{2}$ and $\frac{1}{2})$ core states are almost entirely parity unfavored as they would be in LS coupling. However, note that the small percentage of parity-favored transitions results in a marked change in the asymmetry parameter.

The relative intensities shown in Table III agree rather well with the experimental intensities with the exception of $^2S_{1/2}$ results. The agreement for the asymmetry parameters is less satisfactory. However, the calculation does produce the same overall pattern of variations of asymmetry parameters and indicates that different fine-structure levels will in general have radically different asymmetry parameters.

The method used here is immediately applicable to other resonant Auger processes. In particular, it could be applied to all of the cases of singly excited resonances in the heavier rare gases for which experimental information is available[3] and easily extended to cases where more than one resonance is excited. However, some comments are in order concerning the approximations used here and their validity. First, dipole approximation is assumed here. For resonant Auger processes involving deep inner subshells where the outgoing Auger electrons have high velocity, contributions from higher multipoles might be expected to affect the angular distributions. Second, while it is a good approximation to assume that the phase shifts of argon Auger processes are independent of the core state and of the total angular momentum transferred to the outgoing electron, the latter is a poorer approximation for heavier systems. Some estimate of the j dependence of outgoing waves will probably have to be made either by relativistic calculations or by empirical estimates of the j dependence. Third, here the effects of electron shakeup and shakeoff have been ignored completely, although recent work[6] indicates that they make a measurable contribution to the total rate for resonant Auger decay. Finally, the effects of initial-state correlation and final-state interactions have not been included.

The author is indebted to D. W. Lindle and F. A. Grimm for calling his attention to the experimental results and for valuable discussions concerning them.

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