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Abstract. McGuire has given a general expression for the evaluation of Auger transition rates in multiply ionised atoms. Simplified expressions are derived, in various coupling schemes, appropriate to the particular cases in which the multiple ionisation is restricted to those subshells directly involved in the Auger transitions. The cases in which the final state holes are inequivalent or equivalent are treated separately. The analysis is used to calculate the Auger transition rates of the Mg $KL_{2,3}$–$L_{2,3}^2 V$ Auger vacancy satellites.

1. Introduction

The study of Auger spectra has provided insight into the electronic structure of atoms, molecules and solids. For atomic systems the calculation of Auger transition rates, TR, is one of the strongest tests of electronic wavefunctions generated by independent particle models of atomic structure [1–4]. For molecules and solids the changes in the Auger spectra of atoms induced by bonding yield information on the local electronic structure [4–7]. Much of this information, on electron correlation, on the mixing between the valence states of different atoms, on charge transfer and on the screening of core holes by valence charge, cannot be obtained in any other way than from the Auger profile.

Many of the applications of Auger spectrocopy depend on detailed comparisons of experimental and theoretical Auger profiles. The theoretical calculations usually begin with a calculation of the Auger transition rate for an atom which is then modified to take account of the electronic structure of the atomic environment. Unfortunately the calculation of Auger transition rates is quite complicated and difficulties with this essential first step have limited the exploitation of the technique.

There are two main sources of information on the size of atomic Auger transition rates: the extensive tabulation of results derived from Herman and Skillman's [8] Hartree–Fock–Slater calculations of atomic structure by McGuire [2] and the more recent Dirac–Fock calculations of Chen, Crasemann and co-workers [9]. Since McGuire's results are more generally available they have tended to be more widely used and McGuire has also provided detailed descriptions [2] of the Clebsch–Gordon angular momentum algebra necessary to make use of his results for the radial matrix elements of atomic Auger transitions.

McGuire's general formalism [2] can be specialised to give expressions for transition rates in any coupling scheme for systems with both filled and unfilled shells. Due to the complexity of the problem the general expressions are necessarily complicated and several authors have provided simplified treatments for use in particular cases [2, 10–13]. Recently for example Chorkendorff [14] provided tables of Auger transition amplitudes derived from McGuire's work, but restricted his work to systems which did not involve coupling to unfilled shells in the initial state. There are, however, many interesting Auger processes which are influenced by the coupling of unfilled shells in the initial state and these are the subject of the analysis presented here. To simplify the discussion we make a distinction between the two initial and two final hole states 'active' in the Auger transition and the 'spectator' holes which influence the transition through the coupling of spin and orbital angular momentum in the initial and final states of the multiply ionised atom. Our analysis is limited to systems in which the spectator holes are confined to the same orbitals as those occupied by the hole states created in the final state of an Auger transition. We treat separately the cases in which the active final state holes are in equivalent or inequivalent orbitals. For these cases we provide simplifications and extensions of McGuire's general expression [2] in coupling schemes appropriate to the experimental situation for systems with unfilled subshells.

The expressions derived in this work are used to calculate the transition rates of the $KL_{2,3}-L_{2,3}^2 V$ Auger vacancy satellites of Mg, the experimental profiles of which have recently been measured [15].

2. The formalism

We begin with McGuire's general expression, equation (4) of reference [2], for the transition probability between an initial state described in jj coupling and a final state described in LS coupling. This jj–LS description is applicable to many systems and is usually called the mixed coupling scheme. We adopt McGuire's notation [2] for the initial and final states of the transition. In the initial state we have an inner shell l_1, with $m + 1$ holes and α_1, L_1, S_1 and J_1 quantum numbers, and a continuum hole with quantum numbers l_2 and j_2. In addition we have an l_3 shell with n holes and quantum numbers α_3, L_3 and S_3, an l_4 shell with p holes and quantum numbers α_4, L_4 and S_4, and the remainder of the holes r with quantum numbers L_R and S_R. These individual quantum numbers couple to give a total quantum number for the initial state of J. In the final state we have an l_1 shell with m holes and quantum numbers β_1, P_1, Q_1, an l_3 shell with $n + 1$ holes and quantum numbers β_3, P_3, Q_3; an l_4 shell with $p + 1$ holes and quantum numbers β_4, P_4, Q_4; and the remainder of the holes r with quantum numbers P_R, Q_R. The total final state quantum numbers are P and Q. The transition rate, using McGuire's [2] normalisation of the continuum orbital, is

$$W_{if}/2\pi = \frac{(2L_1 + 1)(2S_1 + 1)(2P_3 + 1)(2Q_3 + 1)(2P_4 + 1)(2Q_4 + 1)(2j_2 + 1)(2J_{12} + 1)}{(2L_R + 1)(2S_R + 1)(2L_3 + 1)(2S_3 + 1)(2L_4 + 1)(2S_4 + 1)}$$

$$\times (2P + 1)(2Q + 1)(2J + 1) \prod_{i=1}^{4} (2l_i + 1) \sum_{A_i B_i C_4} (2C_4 + 1)$$

$$\times \prod_{i=1}^{4} (2A_i + 1)(2B_i + 1)\delta(L_R, P_R)\delta(Q_R, S_R)M^2 F_1^2 \tag{1}$$

where

$$F_1 = [(m + 1)(n + 1)(p + 1)]^{1/2}(l_1^{m+1}\alpha_1 L_1 S_1\{|l_1^m \beta_1 P_1 Q_1)$$

$$\times (l_3^{n+1}\beta_3 P_3 Q_3\{|l_3^n \alpha_3 L_3 S_3)(l_4^{p+1}\beta_4 P_4 Q_4\{|l_4^p \alpha_4 L_4 S_4). \tag{2}$$

The quantities in parentheses in F_1 are the coefficients of fractional parentage defined by McGuire [2], and

$$M = \Sigma \begin{pmatrix} f & g & d \\ f_1 & g_1 & d_1 & b \end{pmatrix} (-1)^{2f-f_1-g-g_1+d+d_1} I(KK'fg)$$

$$\times (2f+1)(2g+1)(2f_1+1)(2g_1+1)(2d+1)(2d_1+1)(2b+1)$$

$$\times \begin{Bmatrix} A_4 & g_1 & P_1 \\ l_1 & L_1 & d \end{Bmatrix} \begin{Bmatrix} B_4 & f_1 & Q_1 \\ \frac{1}{2} & S_1 & d_1 \end{Bmatrix} \begin{Bmatrix} l_2 & l_1 & g \\ g_1 & P & d \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & f \\ f_1 & Q & d_1 \end{Bmatrix}$$

$$\times \begin{Bmatrix} J & J_{12} & C_4 \\ J_1 & b & j_2 \end{Bmatrix} (-1)^\Delta \begin{Bmatrix} l_2 & \frac{1}{2} & j_2 \\ P & Q & J \\ d & d_1 & b \end{Bmatrix} \begin{Bmatrix} L_1 & d & A_4 \\ S_1 & d_1 & B_4 \\ J_1 & b & C_4 \end{Bmatrix} \begin{Bmatrix} A_1 & P_4 & P_3 \\ A_2 & L_4 & L_3 \\ g & l_4 & l_3 \end{Bmatrix}$$

$$\times \begin{Bmatrix} P & A_3 & P_R \\ g & A_1 & A_2 \\ g_1 & P_1 & A_4 \end{Bmatrix} \begin{Bmatrix} B_1 & Q_4 & Q_3 \\ B_2 & S_4 & S_3 \\ f & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} Q & B_3 & Q_R \\ f & B_1 & B_2 \\ f_1 & Q_1 & B_4 \end{Bmatrix} \tag{3}$$

with

$$\Delta = L_4 + P_4 - P_3 - L_3 + P_R - P_1 - L_1 + 2J_{12} + A_1 - A_4 + S_4 + Q_4 - Q_3 - S_3$$
$$+ Q_R - Q_1 - S_1 + B_1 - B_4 \tag{4}$$

and

$$I(KK'fg) = \sum_K D(K) \begin{Bmatrix} l_1 & l_3 & K \\ l_4 & l_2 & g \end{Bmatrix} + (-1)^{f-g} \sum_{K'} E(K') \begin{Bmatrix} l_1 & l_4 & K' \\ l_3 & l_2 & g \end{Bmatrix}$$

$$D(K) = R_K(l_1 l_2 l_3 l_4) \begin{pmatrix} l_1 & K & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & K & l_4 \\ 0 & 0 & 0 \end{pmatrix} \tag{5}$$

$$E(K) = R_K(l_1 l_2 l_4 l_3) \begin{pmatrix} l_1 & K & l_4 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & K & l_3 \\ 0 & 0 & 0 \end{pmatrix}$$

$$R_K(l_1 l_2 l_3 l_4) = \iint \mathrm{d}r_1 \, \mathrm{d}r_2 \, \varphi_{l_1}(r_1) \varphi_{l_2}(r_2) [(r_<)^K / (r_>)^{K+1}] \, \varphi_{l_3}(r_1) \varphi_{l_4}(r_2)$$

the $\varphi_l(r)$ being single-electron radial wavefunctions.

Here J_{12} is obtained by coupling $J_1(j_1$ if $m=0)$ and j_2, and the standard notations are used for $3j$, $6j$ and $9j$ symbols.

Our analysis will use the standard relations between $6j$ and $9j$ symbols [16].

2.1. Case of inequivalent final state holes

We now proceed to rewrite equation (1) in a form which is more suitable for our purposes. We expand the $9j$ symbols containing P_R and Q_R in terms of $6j$ symbols and saturate the summations on g_1 and f_1. Then we sum on the quantum numbers J_{12}, j_2 and J and eliminate the $9j$ symbol containing P, Q and J. We obtain

$$\sum_{J_{12}j_2J} \frac{W_{\mathrm{if}}}{2\pi} = \frac{(2L_1+1)(2S_1+1)(2P_3+1)(2Q_3+1)(2P_4+1)(2Q_4+1)(2P+1)(2Q+1)}{(2L_R+1)(2S_R+1)(2L_3+1)(2S_3+1)(2L_4+1)(2S_4+1)}$$

$$\times \prod_{i=1}^{4} (2l_i+1) \sum_{bdd_1} (2b+1)(2d+1)(2d_1+1)$$

$$\times \sum_{A_iB_iC_4} (2C_4 + 1) \prod_{i=1}^{4} (2A_i + 1)(2B_i + 1)\delta(L_R, P_R)\delta(S_R, Q_R)F_1^2$$

$$\times \left| \sum_{x,y} (-1)^{x+y}(2x + 1)(2y + 1) \begin{Bmatrix} P & A_3 & P_R \\ A_2 & A_4 & x \end{Bmatrix} \begin{Bmatrix} Q & B_3 & Q_R \\ B_2 & B_4 & y \end{Bmatrix} \right.$$

$$\times \sum_{f,g} (2f + 1)(2g + 1)I(KK'fg)$$

$$\times (-1)^{2d+2d_1+f+L_4+P_4-P_3-L_3+P_R+A_1+S_4+Q_4-S_3-Q_3+Q_R+B_1+l_1+P+Q+l_2+1}$$

$$\times \begin{Bmatrix} g & A_1 & A_2 \\ A_3 & x & P_1 \end{Bmatrix} \begin{Bmatrix} f & B_1 & B_2 \\ B_3 & y & Q_1 \end{Bmatrix} \begin{Bmatrix} P_1 & g & x \\ l_2 & L_1 & l_1 \end{Bmatrix} \begin{Bmatrix} A_4 & P & x \\ l_2 & H_1 & d \end{Bmatrix} \begin{Bmatrix} Q_1 & f & y \\ \frac{1}{2} & S_1 & \frac{1}{2} \end{Bmatrix}$$

$$\times \left. \begin{Bmatrix} B_4 & Q & y \\ \frac{1}{2} & S_1 & d_1 \end{Bmatrix} \begin{Bmatrix} L_1 & d & A_4 \\ S_1 & d_1 & B_4 \\ J_1 & b & C_4 \end{Bmatrix} \begin{Bmatrix} A_1 & P_4 & P_3 \\ A_2 & L_4 & L_3 \\ g & l_4 & l_3 \end{Bmatrix} \begin{Bmatrix} B_1 & Q_4 & Q_3 \\ B_2 & S_4 & S_3 \\ f & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \right|^2. \tag{6}$$

A simple manipulation of this equation yields equation (7) of [2], an expression for the transition rate in the LS–LS coupling scheme. For our purposes however it is convenient to work with equation (6), which we simplify for the case we are interested in. This is the case in which the passive shells are filled and the inner shell is filled after the transition has taken place. This is described by:

$$m = 0 \qquad J_1 = j_1 \qquad P_1 = Q_1 = L_R = S_R = P_R = Q_R = 0. \tag{7}$$

Now the only unfilled subshells are those active in the transition; l_3 and l_4 with n and p holes in the initial state respectively.

If we make the replacement $d \to L$, $d_1 \to S$ and $b \to J$, we get a TR for the initial coupling from a summation on the TRs in a scheme in which we couple P and l_2 to get $d(L)$, Q and $\frac{1}{2}$ to get $d_1(S)$ and $d(L)$ and $d_1(S)$ to get $b(J)$. A_2 is L_{34}, B_2 is S_{34} and C_4 is J_{34}, the respective resultants of coupling L_3 and L_4, S_3 and S_4 and J_3 and J_4. In order to have the TR with the initial state described by this LSJ scheme, we have to drop the summations on $d(L)$, $d_1(S)$, $b(J)$ and $C_{34}(J_{34})$ and multiply by the statistical weight

$$(2j_1 + 1)(2L_3 + 1)(2S_3 + 1)(2L_4 + 1)(2S_4 + 1)/(2J + 1). \tag{8}$$

Thus we get the TR in the LS–LS scheme as

$$(1/2\pi)W_{if}(j_1, L, S, P_3, Q_3, P_4, Q_4, J_{34})$$

$$= \tfrac{1}{2}(2L_1 + 1)(2S_1 + 1)(2P_3 + 1)(2Q_3 + 1)(2P_4 + 1)(2Q_4 + 1)$$

$$\times (2j_1 + 1)(2J_{34} + 1)(2P + 1)(2Q + 1)(2L + 1)$$

$$\times (2S + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1) \sum_{A_2B_2} (2A_2 + 1)(2B_2 + 1)F_1^2$$

$$\times \left| \sum_{x,y} (2x + 1)(2y + 1)(-1)^y I(KK'yx) \begin{Bmatrix} A_2 & P & x \\ l_2 & l_1 & L \end{Bmatrix} \begin{Bmatrix} B_2 & Q & y \\ \frac{1}{2} & \frac{1}{2} & S \end{Bmatrix} \right.$$

$$\times \left. \begin{Bmatrix} l_1 & L & A_2 \\ \frac{1}{2} & S & B_2 \\ j_1 & J & J_{34} \end{Bmatrix} \begin{Bmatrix} P & P_4 & P_3 \\ A_2 & L_4 & L_3 \\ x & l_4 & l_3 \end{Bmatrix} \begin{Bmatrix} Q & Q_4 & Q_3 \\ B_2 & S_4 & S_3 \\ y & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \right|^2. \tag{9}$$

The *TR* in a *jj–LS* coupling scheme is obtained by summing on L and S, but not on j_1 and J_{34}:

$$(1/2\pi)W_{if}^{jj}(j_1, J_{34}, J, P_3, Q_3, P_4, Q_4, P, Q)$$
$$= \tfrac{1}{2}(2L_1 + 1)(2S_1 + 1)(2P_3 + 1)(2Q_3 + 1)(2P_4 + 1)(2Q_4 + 1)(2P + 1)$$
$$\times (2Q + 1)(2j_1 + 1)(2J_{34} + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)$$
$$\times \sum_{LS} (2L + 1)(2S + 1) \sum_{A_2 B_2} (2A_2 + 1)(2B_2 + 1)F_1^2$$

$$\times \left| \sum_{x,y} (2x + 1)(2y + 1)(-1)^y I(KK'yx) \times \begin{Bmatrix} A_2 & P & x \\ l_2 & l_1 & L \end{Bmatrix} \begin{Bmatrix} B_2 & Q & y \\ \tfrac{1}{2} & \tfrac{1}{2} & S \end{Bmatrix} \right.$$

$$\left. \times \begin{Bmatrix} l_1 & L & A_2 \\ \tfrac{1}{2} & S & B_2 \\ j_1 & J & J_{34} \end{Bmatrix} \begin{Bmatrix} P & P_4 & P_3 \\ A_2 & L_4 & L_3 \\ x & l_4 & l_3 \end{Bmatrix} \begin{Bmatrix} Q & Q_4 & Q_3 \\ B_2 & S_4 & S_3 \\ y & \tfrac{1}{2} & \tfrac{1}{2} \end{Bmatrix} \right|^2 \tag{10}$$

and to get the TR with the initial state described in intermediate coupling it is enough to insert inside the absolute value signs the summation on the mixing parameters [17, 18]

$$\sum_{j_1 J_{34}} C_i(j_1, J_{34}, J). \tag{11}$$

This leads to

$$(1/2\pi)W_{if}^{IC}(P, Q_3, P_3, Q_4, P_4, Q) = \tfrac{1}{2}(2L_1 + 1)(2S_1 + 1)(2P_3 + 1)$$
$$\times (2Q_3 + 1)(2P_4 + 1)(2Q_4 + 1)(2P + 1)(2Q + 1)$$
$$\times (2l_2 + 1)(2l_3 + 1)(2l_4 + 1) \sum_{LS} (2L + 1)(2S + 1)$$

$$\times \sum_{A_2 B_2} (2A_2 + 1)(2B_2 + 1)F_1^2 \left| \sum_{x,y} (2x + 1)(2y + 1)(-1)^y I(KK'yx) \right.$$

$$\times \begin{Bmatrix} A_2 & P & x \\ l_2 & l_1 & L \end{Bmatrix} \begin{Bmatrix} B_2 & Q & y \\ \tfrac{1}{2} & \tfrac{1}{2} & S \end{Bmatrix} \begin{Bmatrix} P & P_4 & P_3 \\ A_2 & L_4 & L_3 \\ x & l_4 & l_3 \end{Bmatrix} \begin{Bmatrix} Q & Q_4 & Q_3 \\ B_2 & S_4 & S_3 \\ y & \tfrac{1}{2} & \tfrac{1}{2} \end{Bmatrix}$$

$$\left. \times \sum_{j_1 J_{34}} C_i(j_1, J_{34}, J)[(2j_1 + 1)(2J_{34} + 1)]^{1/2} \begin{Bmatrix} l_1 & L & A_2 \\ \tfrac{1}{2} & S & B_2 \\ j_1 & J & J_{34} \end{Bmatrix} \right|^2. \tag{12}$$

We recall here that the mixing parameters, which give the eigenfunctions of the system in intermediate coupling in terms of the Russell–Saunders eigenfunctions, can be obtained by solving for a given J the secular equation which is given by the energy matrix [18], the particular root being specified by i.

It should be emphasised [19] that in the above derivation a hole description has been used for initial and final states. This description simplifies the formalism but requires

some attention in summing on the right quantum numbers and 'unsumming' on dummy variables.

2.2. Case of equivalent final state holes

This case can be treated by putting $L_4 = S_4 = P_4 = Q_4 = 0$ and using the proper combination of fractional parentage coefficients. Following reference [2], we have in the initial state an l_1 shell with $m + 1$ holes and quantum numbers α_1, L_1, S_1, J_1; a continuum hole with quantum numbers l_2, j_2; an l_3 shell with n holes and quantum numbers α_3, L_3, S_3; and a passive electron structure with quantum numbers L_R and S_R. In the final state we have an l_1 shell with m holes and quantum numbers β_1, P_1, Q_1; an l_3 shell with $n + 2$ holes and quantum numbers β_3, P_3, Q_3; and a passive electron structure with quantum numbers P_R and Q_R. The Auger TR is given by equation (17) of reference [2]. We manipulate this expression using procedures similar to those applied to the case of inequivalent final state holes. Simplifying for the special case in which the only unfilled subshells are those active in the transition, i.e.

$$m = 0 \qquad P_1 = Q_1 = L_R = S_R = P_R = Q_R = 0 \tag{13}$$

we obtain expressions corresponding to equations (9), (10) and (12).

The TR in the LS–LS scheme is

$$
W_{if}^{LS}(L, S, P_3, Q_3)/2\pi = (2P_3 + 1)(2Q_3 + 1)
$$
$$
\times (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)^2(2j_1 + 1)(2J_3 + 1)(2L + 1)(2S + 1)
$$
$$
\times \left| \sum_{\beta_3' P_3' Q_3'} F_3 \sum_{x,y} (-1)^{2L+2S+x}(2x + 1)(2y + 1) \begin{Bmatrix} L_3 & P_3 & x \\ l_2 & l_1 & L \end{Bmatrix} \right.
$$
$$
\left. \times \begin{Bmatrix} S_3 & Q_3 & y \\ \tfrac{1}{2} & \tfrac{1}{2} & S \end{Bmatrix} \begin{Bmatrix} P & P_3' & l_3 \\ l_3 & x & L_3 \end{Bmatrix} \begin{Bmatrix} Q_3 & Q_3' & \tfrac{1}{2} \\ \tfrac{1}{2} & y & S_3 \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_3 \\ \tfrac{1}{2} & S & S_3 \\ j_1 & J & J_3 \end{Bmatrix} I(KK'yx) \right|^2. \tag{14}
$$

with

$$
F_3 = \tfrac{1}{2}[(n + 1)(n + 2)]^{1/2}[(2P_3' + 1)(2Q_3' + 1)]^{1/2}
$$
$$
\times (l_3^{n+2}\beta_3 P_3 Q_3\{|l_3^{n+1}\beta_3' P_3' Q_3')(l_3^{n+1}\beta_3' P_3' Q_3'\{|l_3^n \alpha_3 L_3 S_3). \tag{15}
$$

Similarly, the TR in the jj–LS coupling scheme is

$$
W_{if}^{jj}(j_1, J_3, P_3, Q_3)/2\pi = (2P_3 + 1)(2Q_3 + 1)
$$
$$
\times (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)^2(2j_1 + 1)(2J_3 + 1)\sum_{LS}(2L + 1)(2S + 1)
$$
$$
\times \left| \sum_{\beta_3' P_3' Q_3'} F_3 \sum_{x,y} (-1)^{2L+2S+x}(2x + 1)(2y + 1) \begin{Bmatrix} L_3 & P_3 & x \\ l_2 & l_1 & L \end{Bmatrix} \right.
$$
$$
\left. \times \begin{Bmatrix} S_3 & Q_3 & y \\ \tfrac{1}{2} & \tfrac{1}{2} & S \end{Bmatrix} \begin{Bmatrix} P & P_3' & l_3 \\ l_3 & x & L_3 \end{Bmatrix} \begin{Bmatrix} Q_3 & Q_3' & \tfrac{1}{2} \\ \tfrac{1}{2} & y & S_3 \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_3 \\ \tfrac{1}{2} & S & S_3 \\ j_1 & J & J_3 \end{Bmatrix} I(KK'xy) \right|^2 \tag{16}
$$

and with the initial state expressed in intermediate coupling

$$W_{\text{if}}^{\text{IC}}(j_1, J_3, P_3, Q_3)/2\pi = (2P_3 + 1)(2Q_3 + 1)$$

$$\times (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)^2 \sum_{LS} (2L + 1)(2S + 1)$$

$$\times \left| \sum_{\beta_3' P_3' Q_3'} F_3 \sum_{x,y} (-1)^{2L+2S+x}(2x + 1)(2y + 1) \begin{Bmatrix} L_3 & P_3 & x \\ l_2 & l_1 & L \end{Bmatrix} \begin{Bmatrix} S_3 & Q_3 & y \\ \frac{1}{2} & \frac{1}{2} & S \end{Bmatrix} \right.$$

$$\times \begin{Bmatrix} P_3 & P_3' & l_3 \\ l_3 & x & L_3 \end{Bmatrix} \begin{Bmatrix} Q_3 & Q_3' & \frac{1}{2} \\ \frac{1}{2} & y & S_3 \end{Bmatrix} \sum_{j_1 J_3} C_i(j_1, J_3, J)[(2j_1 + 1)(2J_3 + 1)]^{1/2}$$

$$\times \begin{Bmatrix} l_1 & L & L_3 \\ \frac{1}{2} & S & S_3 \\ j_1 & J & J_3 \end{Bmatrix} I(KK'yx) \Bigg|^2 . \tag{17}$$

3. Application to Mg $KL_{2,3}$–$L_{2,3}^2$ V satellites

It is clear from studies of the KLV Auger spectra of simple metals and their alloys that Auger profiles can reveal information about the local density of states of the screening charge around core-ionised sites and, by the equivalent cores approximation, about the impurity density of states of impurities of atomic number $Z + 1$ in a host of atomic number Z [7]. In particular the observation [20] that the local s and p valence electron densities of states around core-ionised sites have very different shapes opens up the possibility that Auger profiles can be used to determine the local valence electron configuration of core-ionised sites and also act as a test of calculations of the shape of the local densities of states. In this context a crucial theoretical idea, the final state rule [4, 7, 20–22], makes it possible to separate the influence on the Auger profile of the initial state local configuration, which determines the intensity of spectral components, and the shapes of the final state densities of states which determine their lineshapes.

The extension of these studies to more complicated Auger processes has the potential to reveal corresponding information about the screening of multi-ionised species which may be related by the equivalent cores approximation to a wider range of impurity–host systems. In order to extract such information from the profiles of Auger transitions it is essential to have an idea of the relative intensity of the various components of the multiplet structure. That is the purpose of the expressions derived in this work and we illustrate the significance of such transition rate calculations by a consideration of the $KL_{2,3}$–$L_{2,3}^2$ V Auger vacancy satellite spectrum of Mg.

The spectral profile of these transitions has recently been measured for the pure metal [15] but not unfortunately for free Mg atoms. The spectrum observed from the metal is complex and shows the presence of several incompletely resolved multiplet structure components. In the free atom the transitions take place between the multiplet structure components of the $1s^1 2s^2 2p^5 3s^2$ and $1s^2 2s^2 2p^4 3s^1$ configurations. In the metal the spectra will be complicated by the presence of screening electrons which may occupy valence orbitals of p character. Of course we do not expect the valence electrons in the metal to have the same radial wavefunctions as those of the free atom. However, due to the presence in the Auger matrix element of the wavefunctions of core electrons, Auger

Table 1. Calculations of Mg K $L_{2,3}$–$L_{2,3}^2$V Auger transition rates in atomic units.

K $L_{2,3}$–$L_{2,3}^2$V$_s$			
Initial configuration	Final configuration		
$1s^12s^22p^53s^23p^2$	$1s^22s^22p^43s^13p^2$		
Term	Term and rate $\times 10^{-4}$		
	^{1}S	^{1}D	^{3}P
^{1}P	0.375	1.875	0.0
^{3}P	0.0	0.0	3.375

K $L_{2,3}$–$L_{2,3}^2$V$_p$			
Initial configuration	Final configuration		
$1s^12s^22p^53s^23p^2$	$1s^22s^22p^43s^23p^1$		
Term	Term and rate $\times 10^{-4}$		
	^{1}S	^{1}D	^{3}P
^{1}P	0.518	2.591	0.0
^{3}P	0.0	0.0	4.664

transition rates are a very local probe of the valence wavefunctions [23]. In the metal the wavefunctions of valence electrons, and of additional screening electrons, must be orthogonal to the wavefunctions of the core electrons. Since the core wavefunctions are expected to be independent of phase this constraint on the wavefunctions of metallic valence and screening electrons means that they may not deviate strongly from atomic valence electron wavefunctions in the core region. For this reason Auger matrix elements deduced from atomic structure calculations may be a quite reasonable approximation to the matrix elements of corresponding transitions in the metal.

In order to understand the $\mathrm{KL}_{2,3}$–$L_{2,3}^2$V spectrum it is necessary to have an understanding of the multiplet splittings. A consideration of the size of the various Coulomb and exchange integrals of Mg given by atomic structure calculations [24] and the direct observation [25] of splittings in similar Mg excited states shows that the important splittings are those between the ^{1}P and ^{3}P components formed from coupling the angular momentum of electrons in the initial state 1s and 2p orbitals and the ^{1}S ^{1}D and ^{3}P components of the final state 2p orbitals. The subsidiary splitting of these components by interaction with valence 3s and 3p electrons is expected to be at least an order of magnitude smaller and is unlikely to be resolved experimentally. In view of these considerations we have performed transition rate calculations in which the influence of these multiplet components was explicitly considered. The transition rates were summed over any additional structure caused by coupling to the spin and orbital quantum numbers of valence electrons.

It only remains to determine the appropriate atomic configuration which will best represent the local configuration of the screened double core-ionised site in the metal. Studies of the energetics of core–hole states in Mg metal [26] suggest that the local configuration around a double core-ionised site is $3s^23p^2$, which is of course locally neutral. We have accordingly carried out our transition rate calculations assuming this valence configuration. The results are shown in table 1. Since the shapes of the local valence s and p densities of states, V$_s$ and V_p respectively, are expected to be different we have listed the results according to the character of the valence electron involved in the transition.

In the experimental work [15] the profile of the $KL_{2,3}-L_{2,3}^2V$ transitions was analysed by attributing the lineshape of the $KL_{2,3}V$ transition to all six transitions between the ^1P and ^3P components of the initial state and the ^1S ^1D and ^3P components of the final state. We can now see a number of failings with this approach. To begin with only three transitions are allowed by the Clebsch–Gordon algebra: those between the ^1P component of the initial state and the ^1S and ^1D components of the final state and the transition between the ^3P components of the initial and final states. However, each of these three transitions will have contributions from valence orbitals of s and p character. The ratio of valence s and p contributions to the $KL_{2,3}-L_{2,3}^2V$ Auger profile, $(KL_{2,3}-L_{2,3}^2V_s)/(KL_{2,3}-L_{2,3}^2V_p)$, is 0.72. This ratio is determined by the relative amount of valence s and p character in the valence configuration and the value required to get agreement with the experimental profile should determine the character of the screening charge.

A full analysis of the $KL_{2,3}-L_{2,3}^2V$ Auger profile of Mg metal requires calculations of V_s and V_p, the shapes of the local densities of states of s and p character around double core-ionised sites. Such calculations are in progress [27]. When they are completed it will be possible to compare the experimental and theoretical $KL_{2,3}-L_{2,3}^2V$ Auger profile of Mg metal. This should be a strong test of the density of states calculations and of the idea that the local configuration around a doubly core-ionised site is $3s^23p^2$.

4. Conclusions

We have derived expressions for Auger transition rates in multiply ionised systems in which the additional hole states occupy those subshells directly involved in the Auger transition. The cases in which the final-state holes created in the Auger process are equivalent or inequivalent are treated separately and for each case we have given expressions in the *LS–LS*, *jj–LS* and *IC–LS* coupling schemes.

We have calculated the transition rates for Mg $KL_{2,3}-L_{2,3}^2V$ Auger vacancy satellite processes assuming that the double core-ionised site in the metal is screened by a $3s^23p^2$ valence configuration. The transition rates for processes involving valence s and p orbitals have been given separately, and the distribution of the total rate between transitions from each of the initial state ^1P and ^3P terms to each of the final state ^1S ^1D and ^3P terms has been evaluated. The results of the calculations show that the only allowed transitions are those between the initial state ^1P and final state ^1S and ^1D terms and the initial state ^3P and final state ^3P terms.

A detailed comparison between the theoretical and experimental profiles of Mg $KL_{2,3}-L_{2,3}^2V$ Auger transitions must await the results of calculations of the local V_s and V_p densities of states around double core-ionised states in Mg. Such a comparison should make it possible to determine the relative importance of valence orbitals of s and p character in the screening charge.

Acknowledgments

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