

Auger spectra of 3d transition metals with orbital degeneracy

C Presilla and F Sacchetti

Dipartimento di Fisica, Università di Perugia, Perugia, Italy

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Abstract. The equation of motion approach is employed to derive the two-body Green function, relevant for the calculation of Auger spectra, in the case of systems well described by the Hubbard Hamiltonian with many bands. The results have been used to calculate the M_{1VV} (M_1 valence–valence) Auger rate of copper, which has been shown to be well described by the present theory, as distinct contributions belonging to different bands are clearly present.

1. Introduction

Recently a great deal of attention has been devoted to both theoretical and experimental study of Auger spectra of 3d transition metals and alloys (Weightman 1982). This large amount of work is connected to the fact that Auger spectra contain information about the electron–electron interaction in metals. It is well established that the naive theory, which accounts for the Auger spectrum as the self-convolution of the single-particle density of states, only gives an approximate description of the spectrum. This happens to be true in simple metals as well as in transition metals. Therefore the electron–electron interaction must be taken into account in calculating the two-electron Green function relevant in Auger transition.

In the case of transition metals and alloys a complex situation occurs as both atom-like and band-like behaviour are present. To deal with such a situation a single-band Hubbard Hamiltonian has been employed by various authors (Cini 1977, 1978, Drchal and Kudrnovsky 1984, Sawatzky 1977). Using such a Hamiltonian and various decoupling procedures for the two-particle Green function the general shape of the Auger spectrum has been obtained.

However, a detailed examination of the experimental spectrum M_{1VV} in the case of Cu suggested that the Auger spectrum contains contributions from different bands (Jennison 1978); therefore a many-band Hubbard Hamiltonian seems to be more appropriate to describe transition metals. The same fact is probably important in Fe–Ni alloys too, though further investigation is needed in this case (Cubiotti *et al* 1986).

We have also to remark that a many-band Hubbard Hamiltonian is able to reproduce with great accuracy bulk magnetic properties in transition metal alloys (Leoni and Sacchetti 1974, Menzinger and Sacchetti 1979), thus indicating the importance of using many bands having different characters.

Bearing this in mind we extended the previous works (Sawatzky 1977, Cini 1977) to calculate the two-particle Green function, employing the equation of motion approach to deal with a many-band Hubbard Hamiltonian. Though the present approach is quite

general we limit ourselves to the case of energy independent matrix elements, but different matrix elements have been employed for various bands. The proposed model results are a surprisingly good fit to the experimental data, as will be shown in the subsequent sections.

2. Many-band model and the two-particle Green function

To describe the valence electrons of a transition metal we shall employ the following Hamiltonian:

$$H = \sum_{nks} \varepsilon_{nk} d_{nks}^{\dagger} d_{nks} + \frac{1}{2} \sum_{ln_1 n_2 n_3 n_4 ss'} U_{n_1 n_2 n_3 n_4} d_{n_1 ls}^{\dagger} d_{n_2 ls}^{\dagger} d_{n_3 ls} d_{n_4 ls} \quad (1)$$

where n , k , s indicate the band index, the wavevector in the first Brillouin zone and the spin index respectively. d_{nks} (d_{nks}^{\dagger}) annihilates (creates) an electron in the single-particle state $|nks\rangle$ the eigenenergy of which is ε_{nks} ; l is a site index, while d_{nls} (d_{nls}^{\dagger}) annihilates (creates) an electron in the state

$$|nls\rangle = N^{-1/2} \sum_k \exp(i\mathbf{k} \cdot \mathbf{R}_l) |nks\rangle$$

N being the number of unit cells in the crystal. $U_{n_1 n_2 n_3 n_4}$ is the screened Coulomb or exchange interaction among the bands n_1 , n_2 , n_3 and n_4 . The Hamiltonian (1) appears to be useful in describing the electron interaction relevant to the magnetic behaviour of transition metals and alloys (Leoni and Sacchetti 1974, Menzinger and Sacchetti 1979, Hodges *et al* 1966). However it should be emphasised that the Hubbard Hamiltonian including the interatomic interactions is of only little use in describing the effect of electron–electron interaction on the band structure itself. Therefore the single-particle eigenenergies ε_{nks} should be determined by means of more sophisticated methods. No spin–orbit interaction is considered in (1), so that the electron spin is a good quantum number and no spin–orbit splitting is assumed in the single-particle energy spectrum.

To deduce the Auger rate we start from the first-order perturbation theory result:

$$\frac{dN}{d\varepsilon} = \frac{2\pi}{\hbar} \sum_f |\langle f | V_{\text{int}} | i \rangle|^2 \delta(E_i - E_f - \varepsilon) \quad (2)$$

where ε is the energy of the Auger electron, $|i\rangle$ is the initial state with one hole in a core state, $|f\rangle$ is the final state including the Auger electron, while E_i and $E_f + \varepsilon$ are the initial and final state energies respectively. V_{int} is the electron–electron interaction. Assuming that the core states are almost completely decoupled from the valence states the cvv (core–valence–valence) Auger rate can be written in the usual form:

$$\frac{dN}{d\varepsilon} = \frac{2\pi}{\hbar} \sum_{k_1 k_2 k_3 k_4} M_{k_1 k_2}^* M_{k_3 k_4} \langle d_{k_1}^{\dagger} d_{k_2}^{\dagger} d_{k_3} d_{k_4} \rangle_{\omega} \quad (3)$$

where the k are the appropriate quantum numbers, i.e. wavevector, band index and spin; $M_{k_1 k_2}$ are appropriate matrix elements of the Coulomb interaction and $\langle d_{k_1}^{\dagger} d_{k_2}^{\dagger} d_{k_3} d_{k_4} \rangle_{\omega}$ is a correlation function that describes the propagation of two particles. We have

$$\langle d_{k_1}^{\dagger} d_{k_2}^{\dagger} d_{k_3} d_{k_4} \rangle_{\omega} = \frac{1}{2\pi} \int dt e^{i\omega t} \langle 0 | d_{k_1}^{\dagger}(t) d_{k_2}^{\dagger}(t) d_{k_3}(0) d_{k_4}(0) | 0 \rangle \quad (4)$$

where $\hbar\omega = -E_c - \varepsilon$, E_c being the core hole energy, and $|0\rangle$ is the exact valence-electron ground state. To derive the correlation function of (4) we make use of the two-time Green function (Zubarev 1960), the equation of motion of which yields:

$$\begin{aligned}
 &(\hbar\omega + \varepsilon_{n_1 k_1} + \varepsilon_{n_2 k_2} - Z_{n_1 n_2}) \langle\langle d_{k_1}^+ d_{k_2}^+ ; d_{k_3} d_{k_4} \rangle\rangle_\omega \\
 &= A + \frac{1}{N} U_{n_1 n_2 n_2 n_1} \sum_{\mathbf{q}} \langle\langle d_{n_1 k_1 - \mathbf{q} s_1}^+ d_{n_2 k_2 + \mathbf{q} s_2}^+ ; d_{k_3} d_{k_4} \rangle\rangle_\omega
 \end{aligned} \tag{5}$$

with

$$A = \frac{1}{2\pi} (1 - \langle n_{k_1} \rangle - \langle n_{k_2} \rangle) (\delta_{k_1 k_3} \delta_{k_2 k_4} - \delta_{k_2 k_3} \delta_{k_1 k_4})$$

$\langle n_{k_i} \rangle$ being the occupation number of the state $k_i = n_i k_i s_i$. An RPA-like pairing approximation has been employed to simplify the higher order Green function. Such an approximation amounts to writing

$$\langle d_{k_1}^+ d_{k_2} \rangle \simeq \delta_{k_1 k_2} \langle n_{k_1} \rangle \tag{6a}$$

$$d_1^+ d_2^+ d_3 d_4 \simeq d_1^+ \langle d_2^+ d_3 \rangle d_4 - d_1^+ \langle d_2^- d_4 \rangle d_3 - d_2^- \langle d_1^+ d_3 \rangle d_4 + d_2^+ \langle d_1^+ d_4 \rangle d_3. \tag{6b}$$

In (5) we put

$$Z_{n_1 n_2} = U_{n_1 n_1 n_1 n_1} + U_{n_2 n_2 n_2 n_2} - 2 \sum_n (U_{n_1 n n n_1} + U_{n n_2 n_2 n}).$$

Equation (5) can be solved exactly to yield

$$\begin{aligned}
 &\langle\langle d_{n_1 k_1 s_1}^+ d_{n_2 k_2 s_2}^+ ; d_{n_3 k_3 s_3} d_{n_4 k_4 s_4} \rangle\rangle_\omega \\
 &= \frac{A}{\hbar\omega + \varepsilon_{n_1 k_1} + \varepsilon_{n_2 k_2} - Z_{n_1 n_2}} \\
 &\quad \times \left(1 - \frac{1}{N} U_{n_1 n_2 n_2 n_1} \sum_{\mathbf{q}} (\hbar\omega + \varepsilon_{n_1 k_1 - \mathbf{q}} + \varepsilon_{n_2 k_2 + \mathbf{q}} - Z_{n_1 n_2})^{-1} \right)^{-1}.
 \end{aligned} \tag{7}$$

This exact result has been obtained using a series expansion in terms of the interaction strength $U_{n_1 n_2 n_2 n_1}$ and then summing the single contributions. The result of equation (7) is a generalisation of that by Sawatzky (1977) and reduces to it in the case of a single-band Hubbard Hamiltonian. It should be emphasised that equation (7) holds independently of the location of the Fermi level or the occupancy of the bands, within the accuracy of equation (6), while it holds exactly when the bands are fully occupied. Therefore it is useful to treat any transition metal, taking into account the orbital degeneracy and hence connected crystal-field effects.

In principle the evaluation of equation (7) can be done exactly. However the matrix elements cannot be calculated consistently with the Hubbard Hamiltonian and even unrenormalised energies must be determined using some approximation. Therefore we shall use an approximate procedure to derive the Auger rate, taking the effect of matrix elements into account in an approximate way.

3. Calculation of the M_{1VV} Auger rate in copper

In this section we shall present the M_{1VV} Auger rate in copper, as compared to the experimental data. We choose copper as the prototype transition metal, though the

presence of an almost full d band can partly reduce crystal effects with respect to other transition metals.

To reduce the computational effort and to make equation (7) more transparent we introduce an approximation similar to that proposed by Cini (1978), thus making the Auger rate only dependent on the densities of states. To do this we put

$$\sum_{\mathbf{q}} \frac{1}{\hbar\omega + \varepsilon_{n_1, \mathbf{k}_1 - \mathbf{q}} + \varepsilon_{n_2, \mathbf{k}_2 + \mathbf{q}} - Z_{n_1 n_2}} \simeq \frac{1}{N} \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{1}{\hbar\omega + \varepsilon_{n_1, \mathbf{k}_1} + \varepsilon_{n_2, \mathbf{k}_2} - Z_{n_1 n_2}}. \quad (8)$$

Moreover we observe that

$$D_{n_1 n_2}(\omega) = \frac{1}{N^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{1}{\hbar\omega + \varepsilon_{n_1, \mathbf{k}_1} + \varepsilon_{n_2, \mathbf{k}_2} - Z_{n_1 n_2}} = \int d\varepsilon d\varepsilon' \frac{\rho_{n_1}(\varepsilon)\rho_{n_2}(\varepsilon')}{\hbar\omega + \varepsilon + \varepsilon' - Z_{n_1 n_2}} \quad (9)$$

where $\rho_n(\varepsilon)$ is the density of states of the n th band, so that the Auger rate can be calculated by means of the following approximation:

$$\frac{dN}{d\varepsilon} \simeq \frac{2\pi}{\hbar} \sum_{n_1, n_2} |M_{n_1 n_2}|^2 \text{Im} \frac{D_{n_1 n_2}(\omega)}{1 - U_{n_1 n_2} D_{n_1 n_2}(\omega)}. \quad (10)$$

As we can see, equation (10) is more suitable for computational purposes. In equation (10) energy-independent matrix elements have been included. This approximation is not very crude in view of the use of the Hubbard Hamiltonian.

Because any realistic calculation of band structure contains the effect of electron–electron interaction we have to take into account this fact. First of all it does not appear realistic to start from band structures with no electron–electron interaction included, as such an interaction affects the shape of the density of states and the position of the bands. In principle the approximation for the two-body Green function could be used to deduce a self-consistent approximation for the single-particle self-energy and hence single-particle Green function, along the line of the work by Baym and Kadanoff (1961). Alternatively we can use a density of states with electron–electron interaction already included then subtract the effect of interaction given by the Hubbard Hamiltonian of equation (1), thus avoiding the need to introduce the electron–electron interaction twice.

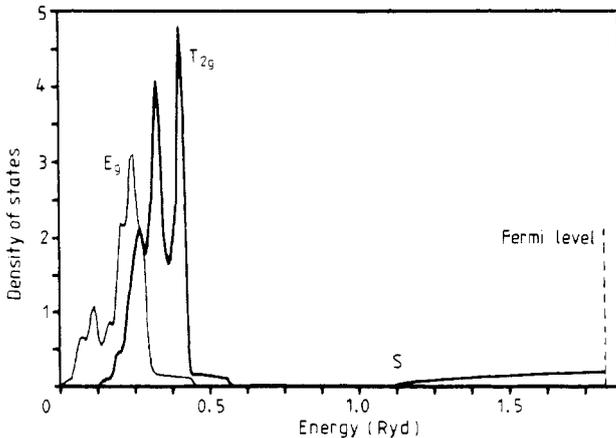


Figure 1. Densities of states of the different bands of Cu employed in calculating the Auger spectrum.

Table 1. Relevant parameters of the present calculation.

		$U_{n_1 n_2}$ (Ryd)			$M_{n_1 n_2}$		
		n_1	S	E_g	T_{2g}	S	E_g
n_2	S	0	0	0	7.5	1.94	1.94
	E_g	0	0.4	0.32	1.94	1	1
	T_{2g}	0	0.32	0.4	1.94	1	1

Following the underlined scheme we start from the rather accurate densities of states obtained by Stocks *et al* (1971), including electron–electron interaction via the local density approximation. To evaluate the electron–electron interaction contribution given by the Hubbard Hamiltonian we take the Hartree–Fock limit of equation (1), namely:

$$H_{\text{HF}} = \sum_{nks} (\epsilon_{nks} + \Delta\epsilon_n) d_{nks}^+ d_{nks}.$$

In this case the effect of the Hubbard Hamiltonian is simply a shift of the various bands which amounts to

$$\Delta\epsilon_n = \frac{1}{2} g_n U_{nn} + g_{n'} U_{nn'} \quad n = E_g, T_{2g} \quad n' \neq n \quad (11)$$

where g_n is the band multiplicity ($g_{E_g} = 2$, $g_{T_{2g}} = 3$). No shift has been assumed for s-like states, according to the assumption $U_{sn} = 0$. The densities of states resulting from the above procedure, i.e. the original densities of states (Stocks *et al* 1971) shifted according to the equation (1), are shown in figure 1. The various interaction parameters have been treated as free parameters to be fixed by comparison with the experimental Auger rate. To calculate the Auger rate we take into account also the effect of matrix elements, assuming, as already said, band-dependent and energy-independent matrix elements. Various parameters employed in the present calculation are reported in table 1. Starting from the

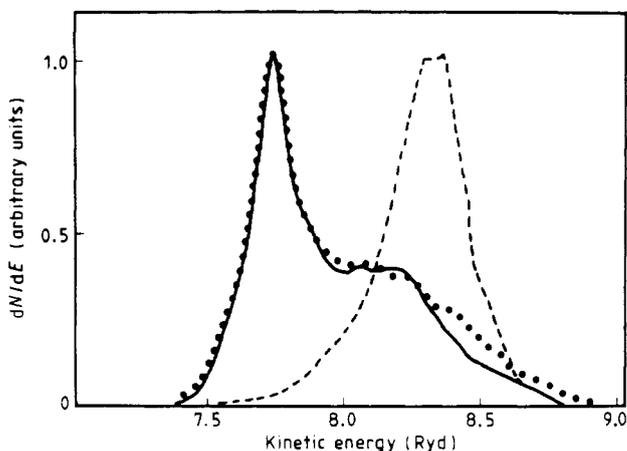


Figure 2. Auger rate as determined using present theory (full curve), self-convolution of density of states (broken curve) and experimental results (dots). The energy scale is absolute.

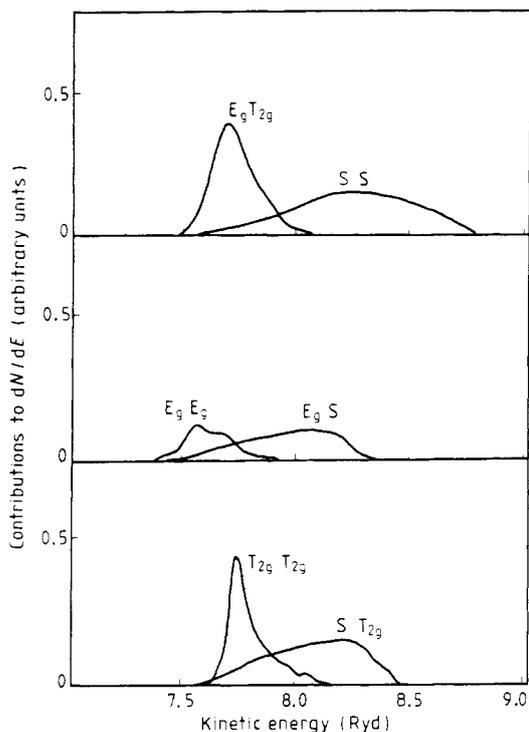


Figure 3. Contributions to the Auger rate belonging to different bands as well as to mixed terms.

densities of states of figure 1 and using the parameters of table 1 we calculate the Auger rate, employing equation (10). In principle the core hole energy should be taken into account; however, in view of the approximations introduced in treating the unperturbed densities of states, the present energy scale cannot be regarded as absolute. Therefore we choose the final energy scale in such a way that experimental and theoretical peaks coincide. The results of the calculation are shown in figure 2, where the experimental data reported by Jennison (1978) are also shown. As we can see the agreement is surprisingly good. Of course the close agreement between theory and experiment point by point should probably be regarded as accidental, though the overall agreement is in any case an indication that present theory indeed includes most of the relevant physics. In figure 3 we report the contributions to the Auger rate due to different bands. As we can see the high-energy tail observed in the experimental spectrum is directly connected to the presence of several bands and, while an almost atomic behaviour is typical of d-like bands, the s-like band gives rise to almost free-electron behaviour. However a non-negligible contribution is due also to mixed terms which contribute to both the atomic-like peak and the high-energy tail.

4. Concluding remarks

As a conclusion we want to observe that, apart from the obvious validity of the present model in accounting for the many-band effect on the Auger rate, our equation of motion approach appears to be rather powerful also in treating different problems connected to a

two-body correlation function. In fact the procedure we employed to solve the equation of motion is not connected to the actual form of the interaction potential, but any potential can be treated resulting in a solution of the same form.

Finally we observe that the basic approximation of equation (6) holds exactly in the case of full bands or in the case of independent electrons, i.e. when $U_{n_1 n_2 n_3 n_4} = 0$, while equation (6) loses its validity when an electron–electron interaction is present. Therefore any improvement of the present approach, still using the Hubbard Hamiltonian, should remove the approximation connected to equation (6), as equation (7) is the exact solution of equation (5).

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