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Photoemission and Auger spectra of incompletely filled bands: intermediate-coupling theory and application to palladium metal

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Abstract. The theoretical analyses of photoemission and Auger XVV spectra of incompletely filled bands are developed in a coherent fashion, based on the same model Hamiltonian. The model, which had been justified previously for cases when the hole density is small, is generalised to account for band degeneracy and multiplet splittings. Accordingly, we extend the graph theoretical expansion of the self-energy in the low-density approximation and that of the two-hole Green function in the bare ladder approximation. We work in the intermediate-coupling scheme, in order to include the spin–orbit interaction. Assuming that to a good approximation the total angular momentum J is conserved, we apply the formalism to Pd metal; we use the same Coulomb matrix and Christensen's independent-particle density of states for both spectroscopies and obtain good agreement with the experimental lineshapes.

1. Introduction

Much progress has been obtained in recent years in the theory of the photoemission and Auger XVV spectra of transition metals including hole–hole interaction effects. However, we need to extend the previous theoretical treatments in several ways, if we want to achieve a quantitative understanding in complex cases when the bands are degenerate and partially filled, and further they display important spin–orbit effects. Orbital degeneracy has already been dealt with by one of us [1], but the treatment was restricted to filled bands and included no relativistic corrections. On the contrary, the open-bands problem has been discussed by several authors [2–10]. Although the general problem remains formidable, a reliable treatment exists at least for non-degenerate bands in the case when the hole density n_h is fairly small; in this case the theory was developed as a generalisation of the closed-band limit, which is solved exactly [1, 11, 12]. However, existing theories [4, 6] of multiplet effects in photoemission from partially filled bands contain approximations that we wish to avoid. Moreover, for both Auger and photoemission lineshapes, we need to include the spin–orbit interaction that was neglected in previous treatments. In § 2, we review the theoretical framework of the open-band problem and discuss the formalism that we wish to generalise. In § 3, we present the extended formalism. In § 4, we summarise some relevant data concerning

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Pd metal, which is taken in § 5 as a testing ground for these new developments. Our main conclusions are summarised in § 6.

2. The open-bands problem

We briefly outline here previous theoretical treatments of Auger and photoemission spectra from unfilled bands. The model [2] proposed long ago by one of us considers non-degenerate bands which are almost completely filled, i.e. the hole density n_h is small. The assumption of small 'unfilling' plays a main role in formulating the model as well as providing an approximate solution. In the Auger lineshape the primary hole shake-up effects can be separated from the final-state dynamics. Moreover, we may use a model Hamiltonian of the Anderson form, including hole–hole interactions at a single site (say, site 0), where Auger decay is taken to occur. (This makes no difference in practice when the bands are filled [13]; for incompletely filled bands, however, this is an approximation which can only be justified for small 'unfilling'.) The photoemission spectrum is also consistently described starting with the same model Hamiltonian, which means that we calculate the local density of states (LDOS) and neglect matrix element effects. In both cases, however, we want to describe approximately a periodic solid by a model in which site 0 is privileged; therefore we need to compensate for the average level shift due to the interaction and we modify the energy of site 0 by an amount $\varepsilon_0 = \varepsilon_0(U, n_h)$, to be specified below. Therefore the model Hamiltonian is taken to be

$$\boldsymbol{H} = \boldsymbol{H}_{TB}(\varepsilon_0) + U\boldsymbol{n}_{0\uparrow}\boldsymbol{n}_{0\downarrow} \tag{1}$$

where $\boldsymbol{H}_{TB}(\varepsilon_0)$ is a non-interacting tight-binding model term. The second term on the right-hand side of (1) is the correlation term, with $n_{0\sigma} = a_{0\sigma}^{+}a_{0\sigma}$, and where $a_{0\sigma}$ annihilates an electron on site 0 with spin σ. For low unfilling, we may relate the Auger spectrum to the two-hole equilibrium Green functions computed with (1); the photoemission spectrum is related to the one-particle propagator. The quantities of interest are $S_\sigma(t)$ and $\Phi(t)$, defined by

$$S_\sigma(t) = \langle g|T[\boldsymbol{a}_{0\sigma}(0)\boldsymbol{a}_{0\sigma}(t)]|g\rangle \tag{2a}$$

$$\Phi(t) = \langle g|T[\boldsymbol{a}_{0\uparrow}^{+}(t)\boldsymbol{a}_{0\downarrow}^{+}(t)\boldsymbol{a}_{0\downarrow}(0)\boldsymbol{a}_{0\uparrow}(0)]|g\rangle. \tag{2b}$$

No general solution is available; however, for low unfilling, i.e.

$$n_h = \lim_{t\to 0^-} S_\sigma(t) \ll 1 \tag{3}$$

the model can be solved in the low-density approximation [2]; by a graph theoretical analysis [14] it is shown that the relevant terms which enter the self-energy allow mutual repeated scattering between the holes, with the virtual electron propagating freely. In this scheme of approximation, the expression for the self-energy is

$$\Sigma^{LDA}(\omega) = -iUn_h + \frac{1}{\pi}\int_0^T d\omega'\, T(\omega+\omega')\,\mathrm{Re}[S^0(\omega)] + \frac{1}{\pi}\int_0^{2T} d\omega'\, \sigma(\omega'-\omega)\,\mathrm{Re}\,T(\omega')] \tag{4}$$

where $S^0(\omega)$ is the one-body (non-interacting) propagator, and

$$T(\omega) = \frac{iU}{1+iU\Phi^0(\omega)} \qquad \Phi^0(\omega) = \int_{-\infty}^{+\infty} d\omega'\, S^0(\omega')S^0(\omega-\omega')$$

$$\sigma(\omega) = -|\mathrm{Re}[S^0(\omega)]| + i\,\mathrm{Im}[S^0(\omega)]. \tag{5}$$

In the integrals in equation (4), T is the top of the band, while 0 is the Fermi energy, assumed as the origin of the energy scale. Here, $\varepsilon_0 = iUn_h$ and, since we are already compensating for the first-order self-energy corrections through the inclusion of ε_0, its opposite occurs in the self-energy (4). The results of the above theory [2] explained the satellite peak which is observed in photoemission spectra of transition metals such as Ni. A similar explanation was independently proposed in [3].

The theory [2] of the Auger lineshape was formulated with the dressed one-body propagator as input; the two-particle Green function Φ was calculated in the ladder approximation:

$$\Phi(\omega) = \frac{\Phi_D(\omega)}{1 + iU\Phi_D(\omega)} \qquad \Phi_D(\omega) = \int_{-\infty}^{+\infty} d\omega' \, S(\omega')S(\omega - \omega')$$

$$S(\omega) = \frac{S^0(\omega)}{1 - \Sigma^{LDA}(\omega)S^0(\omega)}. \tag{6}$$

In a simplified version of the above theory, which was proposed in [4], the self-energy was calculated including terms only up to second order in U; it was claimed that the approach was valid for arbitrary unfilling and for a wide range of U-values. In order to assess the validity of these different treatments, we applied [8] the Hamiltonian (1) to model clusters of $N \times N \times N$ sites and compared exact and approximate propagator results. We studied 27- and 125-atom clusters; the unfillings in the initial state were $n_h = 0.25$ and $n_h = 0.10$, respectively. To make a consistent comparison, the compensating procedure for exact results consisted in determining ε_0 such that

$$\frac{d}{dt}S(t)|_{t=0^-} - \frac{d}{dt}S(t)|_{t=0^+} = \int_{-\infty}^{+\infty} d\omega \, |\mathrm{Re}[S(\omega)]| \, \omega = 0 \tag{7}$$

which amounts to the removal of the energy-independent part of the self-energy. We summarise the main results of our cluster approach.

(i) Cluster calculations simulate the macroscopic case fairly well (this is especially true for $5 \times 5 \times 5$ cluster).

(ii) For an exact one-body LDOS, the effect of correlations are essentially a band narrowing for intermediate U-values, plus the presence of a satellite structure for higher U-values (atomic-like regime).

(iii) The low-density approximation gives very good agreement for $n_h = 0.1$ including the satellite structure in the whole range of U-values of physical interest for transition metals (and in less wide range for $n_h = 0.25$). We made no attempt to use the self-consistent version of the low-density approximation [7], but the results that we found show that the simpler non-self-consistent version is already quite accurate.

(iv) The second-order self-energy is adequate in a subset of U-values. With increasing U, the correlations cause an excessive broadening of the band in the high-binding-energy region; moreover, the second-order approach is not capable of providing a satellite structure, this one arising from out-of-band poles in the **T**-matrix analytical structure.

(v) For the two-body propagator, the analytical path (6) is inadequate; in fact, a new approximate scheme, the bare-ladder approximation (BLA) [8], was found to be superior and actually quite accurate in a wide range of parameters. In the BLA, bare propagators S^0 are used instead of the dressed ones S. We wish to stress here that the procedure (6) follows the standard prescriptions for approximating two-body propagators and does not fail because of a trivial double counting of the interaction; rather, our analysis

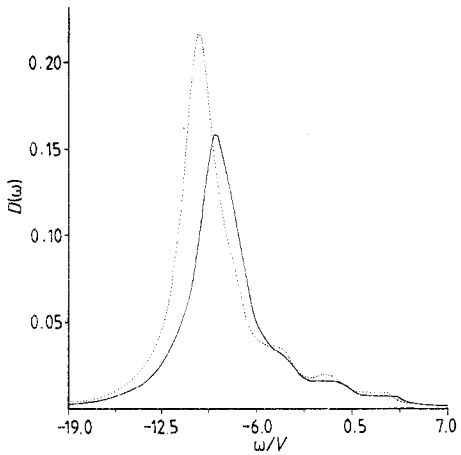

Figure 1. Comparison between the exact (———) and BLA (· · · ·) results for the two-hole interacting LDOS in the 27-atom cluster ($U/W = 1.179$; $n_h = 0.25$). The centre of mass of the one-particle spectrum is assumed to be the origin of the energy scale, and W is the band width for the closed-band case. Here ε_0, the compensation parameter, is equal to $-8.006V$, where V is the hopping parameter in the tight-binding Hamiltonian (see [8]). A Lorentzian broadening has been introduced (FWHM, 2.6V).

shows that, for low unfilling, the two-body propagator reflects the mutual scattering of 'undressed' holes. In other words, if we could carry on the systematic vertex correction expansion, this would cause a sort of 'undressing' of the two independently renormalised holes, to screen them jointly.

Concerning the range of validity of BLA, results for $n_h = 0.25$ and atomic-like U-values show that in such severe conditions it still accounts qualitatively for the two-hole dynamics, the main discrepancy with exact results being the overestimate of the total spectrum intensity (figure 1). This can be supported by observing that, evaluating the propagators in time, e.g. in the non-magnetic case ($n_{h\sigma} = n_{h-\sigma}$), gives

$$\text{total intensity} = \Phi(0^+) + \Phi(0^-) = 1 - \langle g|(\boldsymbol{n}_{0+} - \boldsymbol{n}_{0-})^2|g\rangle = K. \tag{8}$$

In the exact result, K decreases with increasing U and consequently $\langle g|\boldsymbol{n}_{0+} - \boldsymbol{n}_{0-})^2|g\rangle$ increases. This last quantity is the variance of the observable $\mathbf{0} = \boldsymbol{n}_{h+} - \boldsymbol{n}_{h-}$, where $\langle g|\mathbf{0}|g\rangle = 0$. So the variation in total intensity is related to the variance of net magnetic moment, and this is a ground-state correlation effect. In other words, we can say that BLA is unable to account for the ground-state properties in the strong-correlation regime and for significant unfilling, but even in these cases it is fairly capable of describing the dynamics of the two extra holes after they have been added to the system.

As remarked above, the BLA amounts to evaluating the two hole propagator from S^0, very much in the spirit of the closed-band theory, although partial accupancy of the band is of course taken into account. Recently, new approaches [9, 10] imply that the inclusion of extra corrections have been proposed. These theories are generalisations of the Sawatzky scheme [12] and rest on different prescriptions for truncating the hierarchy of higher Green functions arising from the equations of motion. While such proposals are very interesting, there is no way to assess their merits *a priori*, and one should compare them with exact results. Nevertheless, the BLA proves to be so good in the range of parameters that we have in mind here that we do not need to wait for such comparisons to proceed.

The applicability of the present approach is probably more severely limited by the above-described assumptions inherent in (1) than by the accuracy of the BLA. In [15] an approximation for the two-hole LDOS in a partially filled Hubbard chain, which is free from such assumptions, was proposed. Actual calculations were performed for six-atom

chains and a phenomenological argument was used in [16] to extrapolate to infinitely long chains. However, when we look at the figures in [16], it appears questionable to us whether these results show much agreement with the exact results already for $U = 0$. At any rate, it would be very hard to extend this approach to degenerate orbitals. Moreover, since in one dimension there is no critical U and localisation problems are very different from those in three dimensions, the calculation is not really relevant here. Although our scheme is still provisional, at present it can only be validated by comparison with experiment. This is done below for Pd.

3. Generalised theory including spin–orbit coupling

In this section, we extend the graph theoretical expansions of the low-density approximation and BLA theories to degenerate orbitals and bands. This extension is of course also needed for closed bands when heavy elements are involved. Working in the intermediate-coupling scheme, we are able to include the effects of spin–orbit coupling in the absence of crystal field effects for both photoemission and Auger spectra *without having to resort to further simplifying assumptions*. Let us first deal with the simpler problem of Auger spectroscopy of completely filled bands. The model Hamiltonian is

$$H = H_0 + \sum_J \sum_{L,S} U(L,S)|LSJ\rangle\langle LSJ| \tag{9}$$

where $H_0 = \boldsymbol{H}_{\mathrm{TB}} + H_{\mathrm{S\text{-}O}}$ represents all one body contributions, including the spin–orbit interaction $H_{\mathrm{S\text{-}O}}$. The second term in (9) is the usual two-body Coulomb interaction H_r written in the LSJ picture, where $|LSJ\rangle$ is a two-hole state localised on site 0, and $U(L, S)$ is the Coulomb integral.

The non-interacting two-hole Green function is first computed in the jj picture, namely

$$\boldsymbol{K}^J(j_1j_2, j_3j_4|z) = \delta_{j_1j_3}\delta_{j_2j_4}\int_{-\infty}^{+\infty}\frac{\mathrm{d}\omega'}{2\pi}S^0_{j_1}(\omega')\,S^0_{j_2}(z-\omega') = \varphi^0_{j_1j_2}(z)\delta_{j_1j_3}\delta_{j_2j_4} \tag{10}$$

and then is cast in the LSJ picture by

$$(\boldsymbol{\Phi}^0_J(z))_{LS,L'S'} = \sum_{(j_1j_2)}\sum_{(j_3j_4)}\langle j_1j_2J|LSJ\rangle\langle L'S'J|j_3j_4J\rangle\boldsymbol{K}^J(j_1j_2, j_3j_4|z). \tag{11}$$

In (10) and (11) all couples (j_mj_n) are two-hole determinantal states, with fixed ordering, in the jj picture. In addition, (10) and (11) involve only non-interacting quantities; S^0_i, S^0_j are bare propagators, related to the non-interacting one-body LDOS, already spin–orbit projected. The Coulomb interaction is diagonal in the LS basis, with elements

$$(\mathbf{U}_J)_{L'S',LS} = -\mathrm{i}\,U(LS)\delta_{L'S',LS}. \tag{12}$$

Its effects are included, as usual, by solving the matrix equation [1]

$$(\mathbf{1} - \boldsymbol{\Phi}^0_J\mathbf{U}_J)\boldsymbol{\Phi}_J = \boldsymbol{\Phi}^0_J \tag{13}$$

for the interacting quantity

$$(\boldsymbol{\Phi}_J(z))_{L'S',LS} = -\mathrm{i}\langle L'S'J|(z+H)^{-1}|LSJ\rangle \qquad \mathrm{Im}\,z = 0^+. \tag{14}$$

Since in the absence of crystal-field effects the total angular momentum J is a good

quantum number, we can split the problem into various subspaces arising from the different J-values for a d^8 configuration. Then, for a fixed J-value, we define the eigenvectors $|\lambda_J\rangle$ of the intermediate-coupling problem

$$|\lambda_J\rangle = \sum_{L,S} \langle LSJ|\lambda_J\rangle |LSJ\rangle \tag{15}$$

which constitute the local basis of two-hole states that diagonalise $H_{S-O} + H_r$. The local states also serve as symmetry labels for the two-hole eigenstates of H. Indeed, the assumed absence of crystal-field effects implies that H_{TB} is diagonal in any local basis, including (15). Therefore the two-hole Green function matrix is also diagonal, with elements

$$\Phi_{\lambda_J\lambda_J}(z) = \sum_{LS} \sum_{L'S'} \langle LSJ|\lambda_J\rangle\langle\lambda_J|L'S'J\rangle (\mathbf{\Phi}_J(z))_{L'S',LS}. \tag{16}$$

The absence of local field effects produces a further important simplification in computing the Auger lineshape. Generally, in the absence of core hole lifetime effects, the Auger current is given by an expression of the form

$$A(\omega) = \rho\langle g|\boldsymbol{A}_k^\dagger\, \delta(\omega - \boldsymbol{H})\boldsymbol{A}_k|g\rangle \tag{17}$$

where ρ is an approximately constant factor, $|g\rangle$ is the ground state of the system, $\boldsymbol{A}_k$ is an operator that creates two valence holes, and the index k characterises the Auger electron. $\boldsymbol{A}_k$ is an essentially local operator, and we may represent its action on a local basis of holes states $|\lambda\rangle$ in the form

$$\boldsymbol{A}_k|g\rangle = \sum_{\lambda} A(\lambda, k)|\lambda\rangle \tag{18}$$

where $A(\lambda, k)$ are suitable amplitudes. Inserting (18) in the general expression (17) and using the diagonality of the two-hole Green function on the basis $|\lambda_J\rangle$, we obtain, neglecting the constant ρ,

$$A(\omega) = \sum_{J} \sum_{\lambda_J} I(\lambda_J) \frac{1}{\pi} \mathrm{Re}[\Phi_{\lambda_J\lambda_J}(\omega)] \tag{19}$$

where

$$(1/\pi)[\mathrm{Re}\ \Phi_{\lambda_J\lambda_J}(\omega)] = \mathrm{D}_{\lambda_J\lambda_J}(\omega) \tag{20}$$

are the related two-particle interacting LDOS matrix elements and $I(\lambda_J) = |A(\lambda_J, k)|^2$ are the spectral *intensities* from atomic calculations in intermediate coupling. Thus, we do not need to recalculate the Auger amplitudes, since only the atomic intensities are needed.

The extension of the above results to open bands in the case of low unfilling is obtained according to the BLA [8]. This amounts to using the filled part of the undressed one-particle propagator to compute the non-interacting two-hole Green function.

The self-energy Σ is calculated with the same degenerate Anderson model as the Auger lineshape and is expressed in jj coupling. So, Σ is labelled by the hole angular momentum J_0 and is independent of J_{0z} by symmetry. As already remarked, the first-order contribution must be omitted, since we have to compensate for the average level shift of site 0 due to the interaction. At each order in the expansion, a direct term and

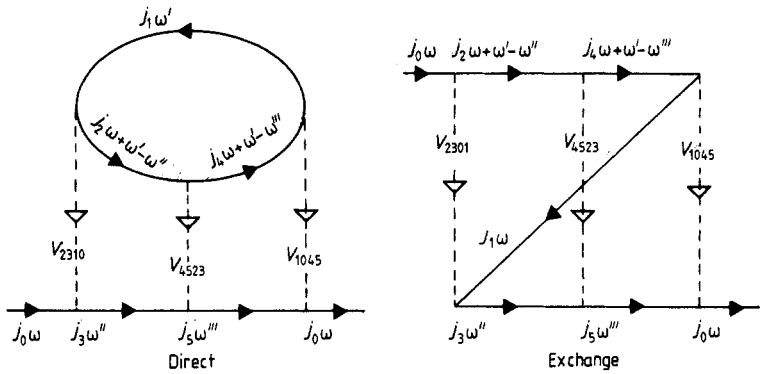

Figure 2. Diagrammatic representation of the third-order contribution to the self-energy in the low-density approximation. Here, j_0 denotes the (j_0, j_{0z}) quantum numbers of the incoming hole. The interaction term V_{ijkl} is taken between states with unconstrained angular momentum indices.

an exchange term exist, as exemplified for the third-order contribution in figure 2. In this case, one obtains two distinct expressions that sum to yield

$$\Sigma^{(3)}_{\mathrm{LDA}}(\omega, J_0) = (-)(-\mathrm{i})^3 \sum_{j_1} \sum_{j_2 j_3} \sum_{j_4 j_5} (\mathrm{V}_{j_2 j_3 j_1 j_0} - \mathrm{V}_{j_2 j_3 j_0 j_1}) \mathrm{V}_{j_4 j_5 j_2 j_3} \mathrm{V}_{j_1 j_0 j_4 j_5}$$

$$\times \int_{-\infty}^{+\infty} \mathrm{d}\omega'\, S^0_{j_1}(\omega') \varphi^0_{j_2 j_3}(\omega + \omega') \varphi^0_{j_4 j_5}(\omega + \omega')$$

where $V_{j_1 j_2 j_3 j_4} \propto \langle j_1 j_2 | (1/r) | j_3 j_4 \rangle$ and $\varphi^0_{j_m j_n}(\omega)$ is given by equation (10). Introducing the Coulomb matrix between determinantal states $W_{ijkl} = V_{ijkl} - V_{ijlk}$, and interchanging j_2 with j_3 and j_4 with j_5, we obtain

$$\Sigma^{(3)}_{\mathrm{LDA}}(\omega, J_0) = \frac{(-\mathrm{i})^3}{4} \sum_{j_1} \sum_{j_2 j_3} \sum_{j_4 j_5} \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega'}{2\pi} S^0_{j_1}(\omega')$$

$$\times [W_{j_1 j_0 j_4 j_5} \varphi^0_{j_4 j_5}(\omega + \omega') W_{j_4 j_5 j_2 j_3} \varphi^0_{j_2 j_3}(\omega + \omega') W_{j_2 j_3 j_0 j_1}]. \tag{21}$$

If all orders in the self-energy are included and the **T**-matrix

$$\mathbf{T}_{j_1 j_0 j_2 j_3}(\omega) = W_{j_1 j_0 j_2 j_3} + \frac{(-\mathrm{i})^2}{2} \sum_{j_4 j_5} \varphi^0_{j_4 j_5}(\omega) W_{j_4 j_5 j_2 j_3}$$

$$\times \left(W_{j_1 j_0 j_4 j_5} + \frac{(-\mathrm{i})}{2} \sum_{j_6 j_7} W_{j_1 j_0 j_6 j_7} \varphi'_{j_6 j_7}(\omega) W_{j_6 j_7 j_4 j_5} + \ldots \right)$$

$$= W_{j_1 j_0 j_2 j_3} + \frac{(-\mathrm{i})}{2} \sum_{j_4 j_5} \mathbf{T}_{j_1 j_0 j_4 j_5}(\omega) \varphi^0_{j_4 j_5}(\omega) W_{j_4 j_5 j_2 j_3} \tag{22}$$

is introduced, the self-energy assumes the form

$$\Sigma_{\mathrm{LDA}}(\omega, J_0) = \sum_{j_1} \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega'}{2\pi} S^0_{j_1}(\omega') \frac{(-\mathrm{i})^2}{2} \times \sum_{j_2 j_3} \mathbf{T}_{j_1 j_0 j_2 j_3}(\omega+\omega')\varphi^0_{j_2 j_3}(\omega+\omega')W_{j_2 j_3 j_0 j_1}. \tag{23}$$

Equation (22) can be written, in self-evident notation as

$$(\mathbf{T}(\omega))_{\alpha\beta} = (\mathbf{W})_{\alpha\beta} + \left(\frac{(-\mathrm{i})}{2}\sum_{\gamma\gamma'} (\mathbf{T}(\omega))_{\alpha\gamma}[(\varphi^0(\omega))_{\gamma\gamma'}\delta_{\gamma\gamma'}](\mathbf{W})_{\gamma'\beta}\right. \tag{24}$$

where δ is the Kronecker symbol; in operator form,

$$\mathbf{T}(\omega) = \mathbf{W}[\mathbf{1} + (\mathrm{i}/2)\boldsymbol{\varphi}^0(\omega)\mathbf{W}]^{-1}. \tag{25}$$

By using (23)–(25) and observing that $W_{ijkl} = -W_{ijlk}$, we finally obtain

$$\Sigma_{\mathrm{LDA}}(\omega, J_0) = \tfrac{1}{2}\sum_{j_1} \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega'}{2\pi} S^0_{j_1}(\omega')[\mathbf{T}(\omega+\omega')\boldsymbol{\varphi}^0(\omega+\omega')\mathbf{W}]_{j_1 j_0 j_1 j_0}. \tag{26}$$

It is instructive to study explicitly the second-order contribution $\Sigma^{(2)}$ to this expression; this turns out to be

$$\Sigma^{(2)}_{(\omega, J_0)} = \sum_{J, j_1} \frac{(2J+1)(1+\delta_{j_0 j_1})}{2j_0+1} \sum_{(j_2 j_3)} X(j_1 j_2 j_3, \omega) \times \left| \sum_{LS} U(LS)\langle j_1 j_0 J | LSJ\rangle\langle LSJ | j_2 j_3 J\rangle \right|^2 \tag{27}$$

where $X(j_1 j_2 j_3, \omega)$ is given by

$$X(j_1 j_2 j_3, \omega) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega'}{2\pi} S^0_{j_1}(\omega')\varphi^0_{j_2 j_3}(\omega+\omega'). \tag{28}$$

In (27), the sum over j_2 and j_3 is constrained in such a way that the two indices occur in the same arbitrary but fixed order used to define the two-hole states as Slater determinants. The index j_1 is coupled in a similar way to the angular momentum index j_0 of the hole. Since S^0 depends on its index j because of the spin–orbit interaction, Σ also contains such effects. The second-order result (27) already shows that orbital degeneracy entails non-trivial changes with respect to the non-degenerate result (4 and 5). In the absence of degeneracy, there is no ambiguity concerning the smallness criterion (3) for n_{h} for the low-density approximation expansion to apply. In the present case, one cannot directly apply Galitzkii's expansion as it stands, and this has been perplexing for some people. However, once the expansion is applied to the present case in detail, it should be clear that the relevant n_{h} is the number of holes per $|j, j_z\rangle$ quantum state. Nevertheless it must be said that the low-density approximation does not contain an explicit estimate of the useful range of n_{h}-values, and the ultimate test of its validity must rely on comparisons with exact results or experiment. Of course, it is the degenerate theory that lends itself to experimental tests. However, the range of validity in n_{h} is very sensitive to the size of the interaction, and this is actually magnified by orbital degeneracy.

To see that, let us consider a trivial limit of (27) in which U is taken to be diagonal in the magnetic quantum numbers of both holes. In this case, the self-energy is independent of j_0; in addition, the quantity $X(j_1 j_2 j_3, \omega)$ becomes a scalar in the indexes j. Thus, after having summed both members of (27) with respect to j_0, we obtain

$$\Sigma^{(2)}(\omega)\left(\sum_{j_0}(2j_0+1)\right) = X(\omega)\left(\sum_{J}(2J+1)\sum_{j_0 j_1}(1+\delta_{j_0 j_1})\sum_{(j_2 j_3)}\left|\langle j_1 j_0 J\left|\frac{1}{r}\right|j_2 j_3 J\rangle\right|^2\right). \tag{29}$$

Remembering that $j_0 = \frac{3}{2}, \frac{5}{2}$ and exploiting the completeness of the set $j_2 j_3 J$, we obtain

$$10\,\Sigma^{(2)}(\omega) = X(\omega)\sum_{JJ_z}\sum_{j_1 j_0}(1+\delta_{j_1 j_0})\left|\langle j_1 j_0 J J_z\left|\frac{1}{r}\right|j_1 j_0 J J_z\rangle\right|^2 = X(\omega)2\,\mathrm{Tr}\left(\frac{1}{r^2}\right). \tag{30}$$

By calculation of the trace in the $LSJJ_z$ basis (there are 45 $|LSJJ_z\rangle$ states) and if we remember that $U(LS) = U$ for each LS-value, the resulting expression for the self-energy is

$$\Sigma^{(2)}(\omega) = 9U^2\int_{-\infty}^{+\infty}\frac{\mathrm{d}\omega'}{2\pi}S^0(\omega')\varphi^0(\omega+\omega'). \tag{31}$$

This would of course be a gross oversimplification, and we would no longer obtain any multiplet splitting, since the results would be characterised by a single U-value. Its merit is to show that band degeneracy effectively enhances correlation effects and that, for d bands, U would become multiplied by a factor of 9. This limit was proposed by Treglia *et al* [4].

4. Application to Pd metal

We wish to apply the above formalism to $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions and $N_{4,5}$ photoemission from Pd metal. We needed of course some input data, first of all the theoretical uncorrelated LDOS. Each S_j^0 is obtained from a 'bare' one-hole density of states $N_j^0(\omega)$, which is normalised such that

$$\int_B^T \mathrm{d}\omega\,|N_j^0(\omega)| = 1 \qquad j = \tfrac{3}{2}, \tfrac{5}{2} \tag{32}$$

where B and T are the bottom and top of the band, respectively; integrating between the Fermi level and T yields n_h. The 'bare' N^0 actually can be obtained from self-consistent calculations and contains interaction effects in so far as they are contained, for example, in calculations at the Hartree–Fock or even local-density level. The self-energy correction Σ that we are considering here is due to the local hole–hole scattering correlations of the ladder type which are not included in the standard treatments. Thus, there is no risk of counting the interactions twice. We used the results of Christensen [17] which are obtained by a relativistic generalisation of the linear muffin-tin orbital method in the (l, m) representation and within the atomic-sphere approximation. As is evident from figure 3, there is a discernible difference between the two one-particle LDOS, due to the spin–orbit interaction, but Pd is non-magnetic and we may take $n_h =$

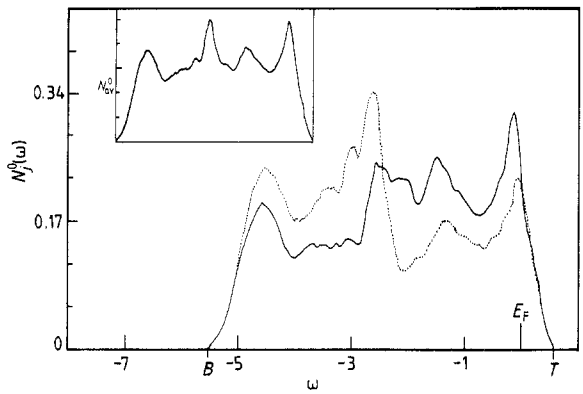

Figure 3. Spin–orbit-projected d LDOS of Pd for $j = \frac{3}{2}$ (. . . .) and $j = \frac{5}{2}$ (———) ($n_h = 0.0475$; $T = 0.56$; $B = -5.6$). In the inset, the weighted average LDOS (equation (33)) is shown on the same scale. All LDOSs are normalised to unity. The value for n_h is obtained by integrating between the Fermi level and T.

0.0475 for each (j, j_z) state. In the inset in figure 3, we also present a weighted average of the two LDOS, for later use:

$$N^0_{av}(\omega) = 10^{-1}[4N^0_{3/2}(\omega) + 6N^0_{5/2}(\omega)]. \tag{33}$$

As it concerns the relative intensities of the final multiplet structure, the values of Slater integrals $F^2(4d, 4d) = 3.92$ eV and $F^4(4d, 4d) = 6.94$ eV, the lifetime broadening (Lorentzian with FWHM = 1.0 eV) and the instrumental broadening (Gaussian with FWHM = 0.5 eV), we refer to [18]. The atomic value of the spin–orbit parameter $\zeta_{4d} = 0.18$ eV was also taken from [18] and is in good agreement with the mean across-the-band value found in [17]. For the intensity ratio we assumed that $I(M_5N_{45}N_{45}) : I(M_4N_{45}N_{45}) = 1.0 : 0.3$, which leads to good agreement with experiments [19] in the atomic limit. The theoretical Auger spectrum was obtained by considering the M_4 and M_5 contributions calculated from equation (20) and separating them by the 5.3 eV splitting of the primary hole states. Finally, we superimposed a theoretical background onto the calculated Auger spectrum, using a procedure similar to that given in [18]:

$$D(\omega) = A(\omega) + B(\omega) = (A \otimes L)_\omega \qquad L(\omega) = \delta(\omega) + \lambda\theta(-\omega). \tag{34}$$

In (34), $A(\omega)$ is the theoretical spectrum, and $L(\omega)$ is the loss function, in which λ is determined by matching the theoretical and experimental spectra on the low-kinetic-energy side. Actually, in adding the background, we replaced the θ-function part in $L(\omega)$ with a realistic inelastic part of the loss function, taken from ELS of Pd metal [20]; this cannot remove all the ambiguity that rests with the known procedures for adding a background but should improve the situation. In the photoemission case, we used strictly the same parameters as above. The Slater integral $F^0(4d, 4d)$ was our only adjustable parameter, and the same value was used for Auger and photoemission spectra.

5. Results and discussion

Fitting the theoretical Auger spectrum to the experimental spectrum [21], we found the value $F^0(4d, 4d) = 2.63$ eV. The spectrum is evidently band like and, in fact, the only

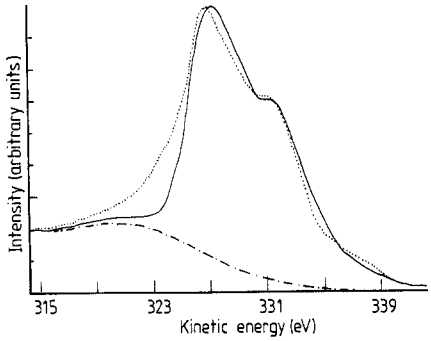

Figure 4. Comparison between calculated and experimental Pd Auger spectra: ———, theory; · · · ·, experiment; — · —, background. The theoretical spectrum is obtained from the matrix type formulation.

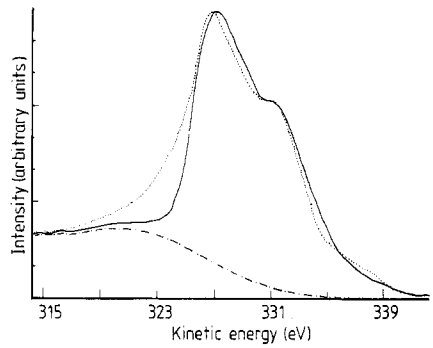

Figure 5. Comparison between calculated and experimental Pd Auger spectra: ———, theory; · · · ·, experiment; — · —, background. The theoretical spectrum is obtained using the weighted average LDOS and equation (35).

quasi-atomic contribution is due to the predominantly $^1S_0$ component of $J = 0$ subspace. We also slightly reduced the lifetime broadening to a value of 0.9 eV which is still well justified by the arguments in [18]. It may be seen in figure 4 that the 'fingerprint' is well reproduced. Some disagreement on the low-kinetic-energy side is probably due to the difficulty of properly including all loss processes and to neglect of the asymmetric shape of the core hole (see the discussion of this point in [2]). In figure 5 the Auger spectrum obtained by a simplified procedure which is used in the literature is shown. In this procedure, one takes a weighted average of the spin–orbit split N_J^0 as the LDOS but retains spin–orbit effects in the U-values. The spectrum is obtained by superimposing independent contributions:

$$\Phi(\omega) = \sum_{LSJ} I(LSJ) \frac{\Phi^0_{\mathrm{av}}(\omega)}{1 + \mathrm{i}\, U_{LSJ} \Phi^0_{\mathrm{av}}(\omega)} \qquad \Phi^0_{\mathrm{av}}(\omega) = [S^0_{\mathrm{av}} \otimes S^0_{\mathrm{av}}]_\omega$$

$$S^0_{\mathrm{av}}(\omega) = \mathrm{i} \int_{-\infty}^{+\infty} \mathrm{d}\omega' \frac{|N^0_{\mathrm{av}}(\omega')|}{\omega - \omega' + \mathrm{i}\,\delta\ \mathrm{sgn}\ \omega'} \tag{35}$$

where N^0_{av} is given by (33).

This simplified treatment of multiplets is justified for highly symmetric environments [6, 11] in the absence of spin–orbit effects, and the present results validate it for Pd; however, it might not be adequate for metals with higher ζ-values, in which case the present detailed theory should be necessary.

Since, in Pd, U-values are rather small compared with the band width and n_{h} is also quite small, we calculated the photoemission lineshape according to the second-order

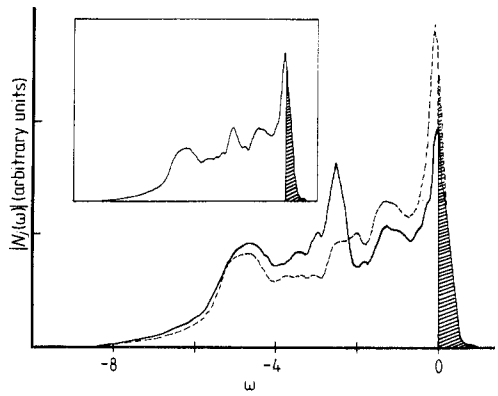

Figure 6. Spin–orbit-projected interacting LDOSs for $j = \frac{3}{2}$ (———) and $j = \frac{5}{2}$ (— — —). No experimental or instrumental broadening is introduced. In the inset, the total LDOS is shown on the same scale. The shaded areas correspond to the electron part of propagators and must be removed before comparison with the experimental photoemission spectrum.

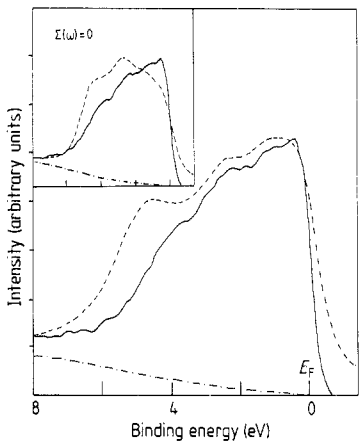

Figure 7. Comparison between the experimental photoemission spectrum [21] and the theoretical density of states including correlations: — — —, theory; ———, experiment; — · —, background. In the inset, the zero-self-energy case is shown on the same scale.

formula (27) for simplicity. We present in figure 6 the calculated LDOS for $j = \frac{3}{2}, \frac{5}{2}$. The main effects of correlations and spin–orbit interaction result in an enhancement near the Fermi level and a broadening in the band region. As far as the effects of correlations are concerned, these findings are in line with our cluster results [8]. After introducing lifetime and instrumental broadenings and adding the background contribution by the same procedure as in the Auger case, we report a comparison between theory and experiment [21] in figure 7. For comparison, we have applied the same treatment to the non-interacting density of states in the inset in figure 7. It may be seen that interaction effects are not so severe as to impair the use of the second-order self-energy seriously, but they are important for detailed lineshape analysis. The interacting theory reproduces quite well the skewness of the line and the three main experimental features, which are completely unobtainable by the 'bare' one theory. The positions of the features agree with experiment remarkably well; this is significant since we are using the same U-matrix and spin–orbit parameter as in the theory of the Auger lineshape. The intensity of the shoulders also compares well, except that the -5 eV feature is somewhat exaggerated. The calculation of intensities is not our main concern here: some distortion may be expected to occur owing to matrix element effects; matrix element calculations require wavefunctions and are beyond the scope of the present work. Furthermore, we feel that the comparison would benefit from a reduction in the broadening parameters with

respect to the reported values, and presumably the lifetime broadening should be energy dependent, which also would imply a non-standard treatment of the background. Nevertheless, the good agreement that we obtain already allows for unambiguous interpretation of the dominant spectral features and clearly supports the present treatment of correlation effects.

6. Conclusions

We have shown how the formalism must be generalised to include multiplet splittings properly. Even in the absence of crystal-field effects, when the Auger lineshape is obtained (equation (19)) from the atomic multiplet intensities $I(\lambda_J)$, the densities of states $D_{\lambda\lambda}$ depends on λ_J. Therefore, in general, $D_{\lambda\lambda}$ cannot be obtained from weighted averages of the spin–orbit split components, as in previous approaches, but must be computed by the present theory, which also leads to the correct atomic limit. The extension to open bands was performed according to the BLA and is expected to be suitable for low unfilling. Similar remarks apply to the photoemission theory, where the results for open bands cannot be simply related to the non-degenerate case; the criteria for small n_h and for the validity of the various approximations are modified. Indeed, using the intermediate-coupling scheme, the required extensions of the theory were carried out without further approximations.

We have tested the present approach against experiment for the interesting special case of Pd. By the single adjustable parameter F^0, we have succeeded in giving a good description of both photoemission and Auger lineshapes. For the first time, we have provided an interpretation for the three main structures which are seen in the photoemission spectrum and we have shown that they are due to correlation effects. The agreement achieved for the Auger spectrum is comparable with that obtained by a previous simplified approach, but at any rate is quite good and is obtained with the same parameters as in the photoemission calculation. This supports the generalised theory presented here and also confirms the ability of the BLA to describe the Auger spectra from partially filled bands. We expect the present scheme to be equally successful for a variety of transition metals and alloys, which, however, may constitute more stringent tests for the theory than Pd does because of stronger interaction effects and/or higher ζ. Such calculations are currently under way.

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