The line shape of $L_2 - L_2 L_3 M_{4,5} - M_{4,5} M_{4,5} (M_{4,5})$ satellites in the Auger Spectra of Solids

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Abstract. We propose the foundations of an extended Auger Line Shape Analysis aiming to include the Coster-Kronig (CK) satellites in solid state spectra. In many solids like Cu and Zn metals they show up as intense high binding energy satellites of the Core-Valence-Valence (CVV) lines. Our theory covers the whole range between weak and strong correlation. We find that the satellites display three-hole and distorted two-hole features along with uncorrelated band-like continua.

1. Introduction
The Auger Line Shape Analysis (ALA) of solids gives a good understanding of the profiles of the diagrammatic CVV transitions [1], although some problems are still unsolved about half filling (see, e.g., [2]). However the hitherto uninterpreted Coster-Kronig lines from solids are also quite rich of features. For example, Thurgate and coworkers[3, 4] measured the APECS spectra of Ni, Fe, Co and Ga and compared the $L_{2,3} V V$ line shapes ($V = M_{4,5}$) taken in coincidence with the $2p_\uparrow$ photoelectrons with those in coincidence with the $2p_\uparrow$ photoelectrons. In all cases except Ga there is intensity in the $L_3 V V$ line which is due to a $2p_\uparrow$ hole undergoing the CK decay. These are $L_2 - L_2 L_3 M_{4,5} - M_{4,5} M_{4,5} (M_{4,5})$ satellites. Thurgate et al. pointed out that the satellites may be expected to be atomic-like when the final-state levels are outside the 3 hole continua, in analogy with the two-hole resonances[5, 6]; it should be a core-valence type of resonance, as first discussed in [7]. A detailed treatment of the line shapes is clearly desirable.

In this preliminary work we address the Coster-Kronig (CK) $L_2 - L_2 L_3 M_{4,5} - M_{4,5} M_{4,5} (M_{4,5})$ satellites[9] arising from closed bands, as in Zn and Cu [8], by a model which extends the previous work on two-hole resonances; we hope to be able to extend the theory to open bands later. For the sake of definiteness we concentrate on the simple case of a $^4F$ term, which is written down in terms on a single determinant of one-body spin-orbitals.

2. Theoretical Framework and Simplified Formulations
Let $H_{tot} = H + H_A + T_A + T_p$ be the system Hamiltonian, where $H_A$ denotes that part of the Coulomb interaction operator that links bound to continuum states and is responsible for the Auger transitions. The minimal description (neglecting possible extra channels) is provided by $H_A = H_A^{(1)} + H_A^{(2)}$ where $H_A^{(1)}$ produces the $L_2 \rightarrow L_2 L_3 M_{4,5}$ transition and $H_A^{(2)}$ the final
where the sum over \( k \) runs over all scattering states, the sum over \( d, d' \) runs over all deep electron states, and the sum over \( \alpha, \alpha' \) runs over all final-hole states which we assume to belong to the same shell. The operator \( T_A = \sum_k \xi_k c^\dagger_k c_k \) accounts for the kinetic energy of the Auger electrons while the operator \( T_p = \sum_p \xi_p c^\dagger_p c_p \) accounts for the kinetic energy of the photoelectron. All remaining terms are included in \( H \) which hence describes the dynamics of the system with no Auger transitions.

We need a one-step expression extending the one by Gunnarsson and Schönhammer [10] for the Auger current \( J_k \) to the case with two Auger electrons, when the first Auger electron is not detected. Let \( |\phi_g\rangle \) denotes the ground state of \( H \) with energy \( E \), \( h\omega \) the photon energy and \( z = E + \omega + i\eta \). Neglecting contributions which are off-diagonal in the deep hole states we get to the second-order in the radiation-matter interaction \( \tau_{pd} \) connecting the photoelectron to the deep electron state

\[
J_k = 2\pi f^2 \sum_{p,d} |\tau_{pd}|^2 |\phi_g\rangle c^\dagger_d z^* - H - T_A - \xi_p \xi_p c_d|\phi_g\rangle,
\]

where \( f \) is the amplitude of the external electromagnetic field. To proceed, provided that \( H_A \) can be treated as a perturbation, we may neglect the virtual transitions and the mixing with other channels and write:

\[
H_A(z - H - T_A - \xi_p c_d|\phi_g\rangle) \sim H_A(2) z - H - T_A - \xi_p c_d|\phi_g\rangle \sim H_A(1) z - H - \xi_p c_d|\phi_g\rangle.
\]

The Hermitian conjugate expression is also needed to complete the approximate matrix element. Reading Eq. (3) from the right, the evolution of the deep hole is followed by the Auger decay and the creation of the first Auger electron, that then evolves with the system. The second Auger electron is finally created by \( H_A(2) \). This is still involved and we feel that for a first orientation in this complex problem a further simplification can be useful at the present stage. In this paper we explore what could be termed as three-step model where, up to a constant,

\[
H_A(2) z - H - T_A - \xi_p h|\phi_g\rangle \sim H_A(1) z - H - \xi_p c_d|\phi_g\rangle \sim c_{\alpha_1} c_{\alpha_2} c_{\alpha_3}|\phi_g\rangle
\]

and the Auger spectrum is proportional to the three-final-hole density of states provided the energy dependence of the matrix elements is weak.

3. Preliminary results

Here we discuss the solution of the above problem in the case of a three-level model for the final holes. As in previous works, we shall assume an Anderson-like model \( H = H_{at} + H_S + V \), where \( H_{at} \) is the atomic term, \( H_S \) describes the solid and \( V \) accounts for one-body hoppings between the atom and the solid. The atomic Hamiltonian is given by the sum \( H_{at} = H_{at}^{(0)} + H_C \), with \( H_{at}^{(0)} = \sum_{\alpha} \varepsilon_{\alpha} c^\dagger_\alpha c_\alpha \) the one-body term, and \( H_C \) the Coulomb repulsion. The Hamiltonian describing the solid is modeled as \( H_S = \sum_{\alpha} \sum_k \varepsilon_{k\alpha} c^\dagger_{k\alpha} c_{k\alpha} \). We assume that a hole in the
atomic state $\alpha$ can only hop into the corresponding continuum of states $\{k\alpha\}$, meaning that $V = \sum_{\alpha} \sum_{k} V_{k\alpha} \left( c_{k\alpha}^\dagger c_{\alpha} + c_{\alpha}^\dagger c_{k\alpha} \right)$. For the sake of simplicity we specialize the discussion to the sector of total spin $S = 3/2$. Accordingly, we consider only three spin-orbital atomic states which, we assume, all have the same energy $\varepsilon_0$ and the same (real) hopping integrals $V_k$ with the continuum. We further assume that the Coulomb interaction is diagonal in our basis so that

$$H_C = U_0 c_1^\dagger c_2^\dagger c_1 + U_1 c_0^\dagger c_2^\dagger c_2 + U_2 c_0^\dagger c_1^\dagger c_1 c_0. \quad (5)$$

The density of states for the three-hole satellite can be obtained within the three-step model from a three-hole Green’s function $\Phi$. The latter satisfies an integral equation which can be numerically solved by discretizing the continuum of states of the solid[11]. The integral equation allows to treat the Coulomb interaction perturbatively to all orders. Alternatively, one can treat the hopping Hamiltonian as a perturbation and try to sum all terms of the series. Below we propose a closed approximate formula which gives a good approximation in all cases and an excellent approximation for band-like and atomic-like spectra. The merits of the formula are the transparent physical meaning and the computational simplicity of its implementation as no matrix inversion is required. The generalization to more complicated Hamiltonians would certainly be of interest.

Our approximation consists in saying that the system “remembers” the order in which the particles have hopped onto the solid and only the latest particle is allowed to hop back on the local site. Representing each three-particle state as a vertex of some lattice and drawing a line between the vertices connected by $V$ the approximation is equivalent to transform the original lattice into a Bethe lattice. We compensate this error by renormalizing the hopping amplitude $V_p$. The renormalization is fixed by imposing that the formula reproduces the exact solution for $U_0 = U_1 = U_2 = U$ in the narrow band limit, i.e., when the continuum is represented by a single $k$-level[11]. Within the above approximation the interacting three-particle Green’s function is given by

$$\Phi(z) = \frac{1}{z - 3\varepsilon_0 - W - \sum_{k} V_k^2 / (z - 2\varepsilon_0 - \varepsilon_k - U_1 - 4 \sum_{p} V_p^2 / (z - \varepsilon_0 - \varepsilon_k - \varepsilon_p - 3\Sigma(z - \varepsilon_k - \varepsilon_p))}. \quad (6)$$

where $\Sigma(z)$ is the local self-energy and is defined according to $\Sigma(z) = \sum_{k} V_k^2 / (z - \varepsilon_k)$. Equation (6) yields a strikingly good formula having the correct normalization, the Herglotz property and all peaks at the correct places.

Below we show results for the rectangular band model considered in Ref. [6]. We plot in Fig. 1 the three-particle density of states $\rho(\omega) = -(1/\pi)\text{Im}\{\Phi(\omega + i\eta)\}$ as obtained from the exact solution of the integral equation (solid line) and from Eq. (6) (dashed line) for different values of the interaction parameters $U_i$. As one can see the approximate solution is remarkably good. The intermediate case $U \sim a$ are the only ones that shows some discrepancy.

Panel a) shows the uncorrelated result $\Phi^{(0)}$ (all $U_i$ set to zero). As expected, by analogy with the two-hole resonances, the spectra remain band-like when $\gamma \equiv U/a \ll 1$ but the line shape is progressively distorted with increasing $\gamma$, see panel b). However the intermediate cases [panels c) to d)] show new features, and besides the distorted continuum one can have a non-split-off two-hole resonances around $\omega \sim U$ and three-hole resonances at energies of about $W$. For $\gamma \gg 1$ [panel e) and f)] split-off two-hole resonances and a quasi-atomic three-hole resonance develop. The two-hole resonances are not sharp but rather smeared out and their width is of the order of $2a$. This is due to the bound hole that virtually explore the valence band. We observe that the two-hole resonances have rather small and unequal intensity as compared to the pronounced three-hole peak and that the residual spectral weight of the original band is close to zero.
Figure 1. Plot of $\rho(\omega) = -(1/\pi)\text{Im}[\Phi(\omega + i\eta)]$ for the exact numerical solution (solid line) and for the approximate solution of Eq. (6) (dashed line) for different values of the Coulomb parameters $U_i$: a) $U_0 = U_1 = U_2 = 0$; b) $U_0 = 0.4$, $U_1 = U_2 = 0.8$; c) $U_0 = U_1 = U_2 = 1$; d) $U_0 = U_1 = 1.5$, $U_2 = 3$; e) $U_0 = U_1 = U_2 = 4$; f) $U_0 = 5$, $U_1 = 8$, $U_2 = 11$. The values of $U$ and $\omega$ are in units of $a$.

4. Conclusions and outlooks
The hitherto disregarded CK satellites contain information on 3-hole multiplet states of the atom and on the two-hole multiplets that result when one of the holes explores the surroundings. Such two-hole multiplets may differ from those of the Auger transitions leading to 2 valence holes. The peak positions are modified by the field of a larger screening cloud, while the intensities predicted by the present theory can be quite different: for instance, peaks corresponding to forbidden Auger transitions can be prominent in CK satellites. We have an unique opportunity to characterize the system by measuring what happens when strongly correlated system responds to a strong local perturbation. Much more computational work is needed in order to compare the above results with experiment, and such work is currently under way.

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