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Theory of Auger lineshapes of solids

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Abstract. Because of the advent of high-resolution instruments and new theoretical models, Auger spectroscopy has evolved into Auger lineshape analysis, a local probe of the electronic structure. This short introduction is devoted to some of its main physical ideas and current theoretical problems.

1. Introduction

Because of a combination of relativistic and many-electron effects, the detailed theory of the Auger spectra is quite involved even for free atoms [1]. In solids, even for $CC'C''$ transitions involving inner levels only, extra complications arise, although core states are mildly perturbed by the chemical environment. Moreover, in core–core–valence ($CC'V$) transitions, one of the final-state holes is in the valence shell and, in core–valence–valence (CVV) transitions, both holes belong to valence states which are of course highly perturbed. It is thus quite remarkable that Auger lineshape analysis (ALA) is useful to understand the physics of molecules and solids [2]. Indeed, much useful information can usually be gained rather easily. The models used in ALA are based on the idea that we may disentangle the solid state aspects from the atomic aspects; although idealised, they can be realistic and many situations have been accurately described by exact analytic solutions. However, the approximate disentangling of atomic and solid state features is not a simple matter. For example, much useful work has been done, to date, using atomic matrix elements or atomic intensities. However, the potentials seen by the Auger electron emitted by a free ion or by a solid state ion are different, and the change in matrix elements can affect the lineshape [3]; appropriate matrix elements must then be computed. Further, most of the work was done in a *two-step description* of the Auger process, neglecting core-hole lifetime effects; however, in complex atoms where the core levels are wide and many decay channels are open for a given primary hole, the theory should explicitly describe the production of the primary hole and its decay through all the various channels (*one-step description* [4]). The work with models must always be assisted by physical insight.

2. Valence spectra and two-hole resonances

In 1953 it was proposed [5] that the Auger CVV lineshape should be proportional to the self-fold of the valence band density of states, weighted by the energy dependence of

the Auger matrix elements. 20 years later, it was pointed out [6] that the CVV spectra of Al and Ag are drastically different, the former being band like and the latter atomic like. Band-like spectra were qualitatively consistent with the theory in [5], but atomic-like lineshapes were not. Various workers found that the CVV spectra of transition metals such as Cu [7], In [8], Zn [9], Cd and Ni [10] are quasi-atomic, while those of Li [11] and Si [12] are band like. This was explained by a simple model [13], restricted initially to filled non-degenerate s orbitals in entirely filled bands. It was realised that a closed band does not have excitations that preserve the memory of the primary hole and allows use of the *two-step description*; inter-band excitations contribute to dielectric screening. The holes are created by the Auger transition in a localised state because the matrix elements overwhelmingly favour *intra-atomic* over *inter-atomic* transitions. (Note, however, that the validity of this statement may depend crucially on the circumstance that the local orbital be full. The case of partially filled orbitals is discussed below.) Then, let us take the atom with the primary hole as site 0 in the lattice, and let $|00\rangle$ be the final state with two valence holes localised there. In a valence band, the holes are free to hop, and therefore $|00\rangle$ is not an eigenstate; the Auger spectrum turns out to be proportional to the square of the matrix element multiplied by the *local* two-hole density of states (LDOS), which is already an important change with respect to the theory in [5]. Next, let H_0 denote the independent-particle Hamiltonian that we would use to calculate the one-hole LDOS; the total Hamiltonian is $H = H_0 + H_r$, where H_r accounts for hole-hole interactions. Since both holes are created on site 0, it is reasonable to include in H_r the short-range part of the repulsion only, since the holes will hardly interact significantly any more if they diffuse into the solid. Therefore we borrow H_r from the Anderson Hamiltonian and write

$$H = H_0 + Un_{0+}n_{0-}. \quad (1)$$

We do not need to specify the free part H_0 further, because our solution depends on it only through the one-hole LDOS $\rho(\omega)$. Letting $N^0(\omega)$ denote its self-convolution $\rho \otimes \rho$, the interacting LDOS turns out to be

$$N(\omega) = N^0(\omega) / \{ [1 - UI_0(\omega)]^2 + [\pi UN^0(\omega)]^2 \} \quad (2)$$

where I_0 is the Hilbert transform:

$$I_0(\omega) = \int_{-\infty}^{\infty} d\omega' \frac{N_0(\omega')}{\omega - \omega'}. \quad (3)$$

Some workers regard this as an approximate solution of their own models; others have confused it with the exact solution of the Hubbard model with two fermions, which was first given in [14]. Nevertheless, equation (2) is just the exact solution of our simple model, with an arbitrary H_0 and the Anderson-like interaction term in the Hamiltonian. It holds for any shape of the LDOS ρ and yields band-like and quasi-atomic spectra as limiting cases. Let W be the width of ρ . Then, for $U \ll W$, equation (2) predicts band-like spectra, whose lineshape is the self-fold of the one-particle LDOS. However, when U/W exceeds a critical value of order unity, which depends on the detailed shape of ρ , a quasi-atomic peak develops outside the continuum. For larger U/W the band-like residuum gradually loses weight, and eventually only a quasi-atomic spectrum remains. This ' U/W criterion' and the existence of band-like residua in quasi-atomic spectra, predicted by the model, have been confirmed experimentally in many cases, starting with Cu [15] and Ag [16]. These quasi-atomic peaks correspond to a vanishing denominator in

equation (2) and represent *two-hole resonances*; the two holes form a localised state, owing to their intense repulsion, by a purely quantum effect. Such resonances also play a key role in ionic desorption [17]. CC'V spectra may also represent resonant states, with the valence hole bound to the localised core hole; in simple metals and wide-band materials, the lineshape can be understood in terms of the valence LDOS, distorted by the presence of the core hole [18].

'Extensions' of the simple model that have been published to deal with impurities and chemisorbates do not really differ from it. Various genuine extensions exist that are still exactly soluble. A model of Auger lineshapes of perfect elemental solids with non-degenerate bands, based on the Hubbard Hamiltonian was proposed in [19]; an identical repulsion U exists between up- and down-spin holes on the filled s valence orbitals at every site. The exact solution essentially coincides with that in [14] and is more complicated than that of the simple model. The physics are the same, except that now the quasi-atomic resonances can delocalise as bound states in the solid and have a width of the order of V^2/U , where V is the nearest-neighbour hopping integral [20]. This is not important for closed bands [21], because the width is generally quite small, but for open bands the two-hole dispersion is assisted by background holes and may become important [22]. Both models have been generalised [23] to degenerate orbitals and bands; often, ρ is a matrix $\rho(m_1, m_2)$, where the indices are hole magnetic quantum numbers; accordingly, we define the local two-hole states $|m_1 m_2 \sigma\rangle = c_{m_2, \sigma}^+ c_{m_1, +}^+ |\text{vacuum}\rangle$, the Coulomb integrals $U(m_1, m_2, m_3, m_4)$ and the interaction matrix \mathbf{W} with elements $W(m_1, m_2, m_3, m_4, -) = U(m_1, m_2, m_3, m_4)$ and $W(m_1, m_2, m_3, m_4, +) = U(m_1, m_2, m_4, m_3) - U(m_1, m_2, m_3, m_4)$. Similarly, we introduce the two-hole Green function Φ with elements

$$\Phi(m_1, m_2, m_3, m_4, \sigma) = -i\langle m_3 m_4 \sigma | (\omega - H)^{-1} | m_1 m_2 \sigma \rangle \quad (4)$$

whose real part is π multiplied by the interacting two-hole LDOS matrix. In terms of its non-interacting counterpart Φ^0 , we can find Φ by solving

$$(\mathbf{I} - \Phi^0 \mathbf{W}) \Phi = \Phi^0. \quad (5)$$

If the crystal field is weak (as in most metals) or highly symmetric (as in cubic crystals), ρ is diagonal and equation (5) yields decoupled scalar equations in the $|LSJ\rangle$ representation. This means that we need to solve only the simple model for each multiplet component, multiply by the (essentially) atomic intensities and add. This special case has been widely used to analyse experiments, mainly on transition metals and alloys [24], and extended to include the *spin-orbit interaction* [25], working in the intermediate-coupling scheme. This is good for transition metals. Accurate ALA on insulating compounds are needed, since the existing data are too few to provide sufficient evidence that we understand the lineshapes in great detail. The assumption of a diagonal ρ does not generally apply to insulating compounds, which complicates the analysis, but not in an essential way. The ALA of Si and O in SiO_2 in [26] is based on a model similar to the previous ones, the main difference being the use of numerical solutions on finite clusters rather than analytic results. However, a more important complication is that, although the bands are closed, the orbitals are partially filled. Not only the LDOS must be normalised to the actual occupancy, but other modifications may be needed. Recently, I have proposed a new modification [27] to take into account the orbital shrinkage of negative ions when they lose electrons. The hopping matrix element V between site 0, where the primary core hole is produced, and its nearest neighbours in a tight-binding

solid is changed into $V + \eta$ if a hole of opposite spin is also present at site 0. The interaction term in the Hamiltonian is

$$H_I = Un_{0+}n_{0-} + \eta \sum_i (n_{0-}c_{0+}^+c_{i+} + n_{0+}c_{0-}^+c_{i-} + \text{HC}) \quad (6)$$

where the sum includes the nearest neighbours and HC stands for the Hermitian conjugate. The exact resolvent $G = \langle 001 | (\omega - H)^{-1} | 00 \rangle$ reads

$$G(\omega) = \frac{G^0}{\{[1 - (\eta/V)(\omega G^0 - 1)]^2 - [U + \eta^2\omega(\omega G^0 - 1)/V^2]G^0\}} \quad (7)$$

and reduces to the simple model result when η vanishes. The Auger lineshapes of negative ions should be characterised by negative values of η , that generally entail a reduction of the solid induced features. Accurate analyses of spectra of oxides and halides should reveal orbital shrinkage effects.

3. Dynamical screening and shake-up in core and valence spectra

The parameter U (or, more generally, the matrix \mathbf{W}) used in the above theories represent effective hole-hole interactions in the solid, which may differ by 10 eV or more from their 'bare' or gas phase atomic values. To describe the 'bare' interactions and the collective modes explicitly, giving rise to dynamical screening, in [28] the final-state model Hamiltonian

$$H = H_{\text{tb}} + H_I + H_P + H_{\text{h-p}} \quad (8)$$

was considered. H_{tb} is a tight-binding term; H_I is a hole-hole repulsion term of the Anderson or Hubbard form but with the 'bare' U_0 in place of the screened U ;

$$H_P = \omega_p b^+ b \quad (9)$$

represents a plasmon field with creation operator b^+ ; the hole-plasmon interaction is

$$H_{\text{h-p}} = \left[2g_0 \sum_i n_{i+} n_{i-} + 2^{1/2} g_0 \left(1 - \sum_i n_{i+} n_{i-} \right) \right] (b + b^+) \quad (10)$$

where g_0 is the hole-plasmon coupling constant. The form of (10) means that two holes are screened independently when they are on different sites but are seen by the plasmons as one charge $2e$ when they are on the same site; we have justified it provided that ω_p is larger than the hopping integrals. The model was solved exactly by the method of excitation amplitudes [29], which has been recently reviewed [30]. We found that dynamical distortions tend to be appreciable in the band-like spectra if ω_p is comparable with W . Measurements [31] were made of the CVV lineshape of graphite, and it was analysed by a simplified version of the 'static' theory. It was found that the experimental spectrum had a higher slope than that calculated at its low-binding-energy end, but this discrepancy could be cured by introducing the effects of a long-lived valence-core exciton near the Fermi level. Also, it was noted that a shoulder on the high-binding-energy side could not be understood by the static theory but appeared to be qualitatively consistent with the predictions of the 'dynamical' theory. In order to make the comparison quantitative, we generalised the above model to degenerate orbitals and bands [32]. The application of the theory to graphite was rather phenomenological in spirit, since we do not have much confidence in our understanding of Auger lineshapes in systems with

widely open bands (see below). Nevertheless, the results were rewarding, because the dynamical theory naturally predicts the shoulder and (adopting the core-valence exciton) provides a nice description of the whole lineshape.

4. The problem of partially filled orbitals and bands

The CVV spectra of simple metals are band like (see, e.g., [33]), but the general problem of ALA is considerably more difficult if open bands are directly involved. The matrix elements have to be recalculated *ex novo*, especially when the occupation of the local orbitals is widely different from the free atoms; the primary hole shake-up effects cannot be separated from the final state dynamics, and the *two-step* theory may fail. Here, I wish to concentrate on bands which are almost completely filled, i.e. the hole density n_h is small; let us start with the earliest model [34], which also assumed non-degenerate bands. For $n_h \ll 1$ we may relate the Auger spectrum to the two-hole *equilibrium* Green function $\Phi(t)$. The same theory consistently describes the photoemission spectrum, which is also distorted by correlation effects and is related to the one-particle propagator $S(t)$. Moreover, for $n_h \ll 1$ we may justify a model of the form (1), including hole-hole interactions at a single site, to describe a periodic solid; however, we must compensate for the average level shift due to the interaction by a shift $\varepsilon_0 = \varepsilon_0(U, n_h)$ of the local level such that the first moment of the one-hole LDOS is U independent. Therefore the model Hamiltonian is taken to be of the form (1), with $H_0 = H_{\text{TB}}(\varepsilon_0)$ a non-interacting tight-binding model with a parametric dependence on U . I obtained S for small n_h , using the low-density approximation (LDA) in [35] and the results explained the satellite peak which is observed in the photoemission spectra of transition metals such as Ni. (A similar theory was independently obtained in [36].) For the two-particle Green function Φ , following standard diagrammatic prescriptions, I neglected the vertex corrections to retain the lowest-order terms in n_h . The result was a ladder approximation

$$\Phi(\omega) = \Phi_{\text{D}}(\omega)/[1 + iU\Phi_{\text{D}}(\omega)] \quad (11)$$

where Φ_{D} is the self-convolution $S \otimes S$ of the dressed one-particle propagator. S is obtained from the non-interacting propagator S^0 by dressing with the LDA self-energy. In [37] a simplified version of the above theory with the second-order self-energy instead of the LDA was proposed, but the approach was presented as a generalisation to arbitrary n_h . On the contrary, in [38] the use of the self-consistent version of the LDA was advocated. In [39] the model was then applied to atom clusters, and exact results compared with the various approximations. For the one-particle spectrum, the exact calculations supported the LDA, even without self-consistency. We got very good agreement for $n_h = 0.1$ and fair agreement for $n_h = 0.25$ up to strongly atomic-like U/W ; the second-order calculation holds in a more restricted U range, as expected. For the two-body propagator, however, we found to our surprise that all the above approaches fail, because vertex corrections tend to ‘undress’ the scattering of the two holes. The ‘bare ladder approximation’ (BLA), in which bare propagators S^0 are used instead of the dressed ones S in computing Φ_{D} , gave quite accurate results in a wide parameter range. We have generalised the theory to degenerate orbitals including the spin-orbit interaction and successfully applied the BLA to $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions and the LDA to $N_{4,5}$ photoemission from Pd metal ($n_h = 0.0475$ for each (j, j_z) state). We took the theoretical uncorrelated LDOS for $j = 3/2, 5/2$ from [40] and empirical atomic data from [41, 42]. Fitting the calculated Auger spectrum to the experimental spectrum

[43], we found the Slater integral $F^0(4d, 4d) = 2.63$ eV. This was our only adjustable parameter, and the same value was used for Auger and photoemission spectra, achieving good agreement with both lineshapes. The BLA amounts to evaluating the two-hole propagator from S^0 as in closed-band theory, although the partial occupancy of the band is taken into account. Its good performance in the graphite calculation (and also in molecular spectra) suggests that it could be more generally useful than we at present understand. Corrections have been recently proposed in [44, 45], based on different prescriptions for truncating the hierarchy of higher Green functions arising from the equations of motion. While such proposals are interesting, further investigation is needed to quantify their merits.

5. Conclusions

In closed-band systems, ALA studies give information on the LDOS, on-site electron–electron interactions, electron–plasmon vertices and dielectric screening. Much of this ‘local’ information is unique and complementary to what can be obtained by photoemission and other techniques and we are often able to combine different spectroscopies into a coherent description. The theory is now supported by case studies on a variety of transition metals, alloys, semiconductors and also ionic solids, although there is a clear need for detailed tests on oxides and other compounds. Further theoretical and experimental work is needed to understand open-band systems properly and, more generally, to grasp problems where the *two-step description* is violated. However, it appears that we have already obtained a good theory of CVV spectra of partially filled bands for a small hole density, and the current research on these topics is promising. In conclusion, although ALA is certainly not always routine, it has already developed into a reliable technique for electronic structure studies.

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