VV and CV correlation effects in CVV Auger-electron and appearance-potential spectroscopy:

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Abstract. We investigate the influence of correlations among the valence-band electrons (VV correlations) and correlations between the valence-band and core electrons (CV correlations) in CVV Auger-electron spectroscopy (AES) and appearance-potential spectroscopy (APS). The AES and APS intensities are given by properly defined three-particle spectral densities, which are exactly determined for the limiting cases of the completely filled and empty valence bands. We solve the equations of motion for the corresponding three-particle Green functions within the framework of the single-band Hubbard model, which is extended to include, in addition to the on-site Coulomb interaction U among the valence-band electrons, the on-site Coulomb interaction U_c between valence-band and core electrons as well. For AES the calculation can be done analytically, yielding the same result as in the Cini–Sawatzky model except for an additional energetic shift of the spectrum by $2U_c$. For APS the calculation has to be performed numerically. The role of the core-hole potential turns out to be qualitatively different from that for AES. The APS spectrum may exhibit up to three different features, which are ascribed to effects of final-state correlations: the band-like part of the spectrum corresponds to final states in which both valence-band electrons are moving independently through the lattice. In the case of strong correlations two satellites are additionally observed. The first one corresponds to two-electron bound states that are more or less localized at the site where the transition takes place. It has a small width and takes almost the whole spectral weight as soon as it is split off. The second one has a width equal to the width of the free Bloch band and quite a small spectral weight. It is interpreted as belonging to final states in which one electron is localized in the core-hole potential while the other one is moving through the lattice. Apart from this rather weak satellite feature, the APS line shape is qualitatively well described within the Cini–Sawatzky model, provided that the coupling parameter U is replaced by an effective coupling $U_{eff} = U - 2U_c$.

1. Introduction

In recent years growing interest has been focused on the ability of Auger-electron spectroscopy (AES) and appearance-potential spectroscopy (APS) for studying the electronic structure of solids [1–6]. Since it is known that the presence of strong electron correlations for many systems prevents an interpretation of the AES or the APS line shape within a one-particle scheme [7], the discussion has been about how the effects of electron correlations on the spectra have to be included in the theoretical analysis. For CVV transitions most attempts in this direction are based on a many-body calculation of the two-particle valence-band spectral density, which gives the AES and the APS line shape, if only correlations among the valence-band electrons are taken into account [8–22]. For the general case of

the partially filled valence band the complexity of such many-body approaches inevitably implies the need for approximations in the calculation. In this context it is a remarkable fact that for the limiting cases of the completely filled and the empty valence band the calculations can be done rigorously and nevertheless yield non-trivial results.

Based on Kanamori's solution [23] of the two-particle problem, it was first shown by Cini and Sawatzky [8, 9] that in the case of the completely filled band the Auger line shape can be derived exactly for Hubbard-type Hamiltonians. In the following the Cini–Sawatzky model has served as a basis for further studies that have enlarged the range of applicability. The limit of completely filled bands for AES has been investigated by Presilla and Sacchetti [14] and Kotrla and Drchal [16] within the framework of multi-band Hubbard-type Hamiltonians. For the Hubbard model [17] and for a generalized multi-band model [20], which additionally includes direct and exchange inter-band interactions, rigorous results may be derived for the cases of completely filled bands (AES) and empty bands (APS).

In all these attempts the resulting AES and APS line shapes are decisively influenced by the model parameters, yielding sharp satellite features in the case of strong correlations. Since for the mentioned limiting cases the results are exact within the considered model, AES and APS seem to be just the methods to study electron-correlation effects. Furthermore, the results for the limiting cases may serve as a test for model calculations in the general case of arbitrary band filling.

In search of an adequate theoretical model for CVV AES and APS however, the correlations among the valence-band electrons (VV correlations) and the calculation of their effects on the spectra are only one part of the problem. The strong inherent perturbation of the system due to the core-hole potential must not be forgotten. So in general we additionally have to deal with the correlations between the valence-band electrons and the core electrons (CV correlations). In the initial state for AES the primary core hole causes the valence-band electrons to rearrange themselves and to screen the core-hole potential partially. In the final state the valence-band electrons adjust to the sudden destruction of the core hole. For APS the valence-band electrons are scattered at the core-hole potential present in the final state. Surely, the inclusion of both VV and CV correlations generates a different kind of problem, since for the additional description of the core-hole dynamics a three-particle spectral density has to be considered at least. Moreover, one has to bear in mind that the localized core hole implies a breakdown of translational symmetry in the distribution of the valence-band electrons.

Most probably because of these complications, there has been only little work on the effects of CV correlations in AES and APS in the past. Neglecting VV correlations altogether Natta and Joyes [24] worked out an *ansatz* in analogy to the problem of x-ray emission in metals [25, 26]. For the low-hole-density case in AES and for a simplified model with interactions on one lattice site only, Cini [27] demonstrated that the three-particle Green function is merely a convolution of the two-particle valence-band Green function with the Green function of the core state. In a recent paper [22] the present authors proposed a temperature-dependent theory for AES and APS including VV and CV correlations for the general case of arbitrary band filling. In this approach the CV correlations are treated by means of perturbation theory within the Matsubara formalism.

The purpose of this paper is to generalize the rigorous treatment available for the limiting cases of the completely filled and empty valence band towards a formulation in terms of three-particle Green functions in order to study electron-correlation effects on AES and APS, attaching equal importance to both VV and CV correlations.

We start from a general formulation for the AES and APS intensities as properly defined

three-particle spectral densities and consider a Hubbard model that has been extended to include the Coulomb interaction between valence-band and core electrons on every lattice site (section 2). We proceed by solving the equation of motion for the three-particle Green functions in the case of AES (section 3) and APS (section 4) and summarize the results in section 5.

2. General theory

The fundamental steps that lead to the general formulas for the AES and the APS intensities have been outlined in [22]. The intensities

$$I_\sigma^{AES}(E_0 - \mu) = (2\pi/\hbar^2)A_\sigma^{(3),*}(E_0 - \mu) \qquad I_\sigma^{APS}(E_0 - \mu) = (2\pi/\hbar^2)A_\sigma^{(3),0}(E_0 - \mu) \quad (1)$$

are given in terms of three-particle spectral densities

$$A_\sigma^{(3),*/0}(E_0 - \mu) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp[(i/\hbar)(E_0 - \mu)t]\langle[T_\sigma^\dagger(t), T_\sigma(0)]_+\rangle^{*/0} dt \quad (2)$$

where T_σ is the transition operator:

$$T_\sigma = c_{i_c\sigma}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}. \quad (3)$$

Here $c_{i\sigma}^\dagger$ denotes the creation operator for a valence-band electron in the Wannier state with spin index σ at the lattice site i and $b_{i\sigma}$ the annihilation operator for an electron in the core state with spin index σ at the site i. The transition is thought to take place at the site i_c involving a core electron with spin index σ_c. Let $n_{i\sigma}^c = b_{i\sigma}^\dagger b_{i\sigma}$ be the core-level occupation number. Then the three-particle spectral densities $A_\sigma^{(3),*}$ and $A_\sigma^{(3),0}$ are defined as grand-canonical expectation values in the subspaces $\mathcal{H}^*$ and $\mathcal{H}^0$ of the full Hilbert space $\mathcal{H} = \mathcal{H}^* \oplus \mathcal{H}^0$ built up by all states with $n_{i_c\sigma_c}^c = 0$ and $n_{i_c\sigma_c}^c = 1$, respectively. $[\cdots, \cdots]_+$ denotes the anticommutator, and the transition operators are given in the time-dependent Heisenberg representation. μ is the chemical potential. The outgoing Auger electron (incoming electron, in the case of APS) has spin index σ and energy E_0. For the case of a non-degenerate valence band considered here, the spin of the Auger electron (APS electron) is opposite to the spin of the core electron involved in the transition: $\sigma = -\sigma_c$.

The underlying assumptions and simplifications in this formulation for the intensities have been discussed in detail in [22]. Here we shall briefly enumerate the main features of the theoretical model. The starting point has been time-dependent perturbation theory in first order for the interaction that induces the transition (Fermi's golden rule). We assume that the lifetime of the core hole is long compared with the typical relaxation time of the valence-band electrons in the presence of the core hole. So we employ a two-step model, which in the case of AES, for example, means that the initial excitation step can be treated independently from the subsequent Auger decay. Since we are interested in correlation effects only, the wave-vector and energy dependence of the transition matrix elements is neglected completely. Furthermore, we assume the contributions from an inter-atomic transition to be small and treat the transition exclusively as intra-atomic. We additionally assume that the energy of the outgoing Auger electron, or the incoming APS electron, is sufficiently high that there is only negligible interaction with the rest system (sudden approximation).

The *three-particle spectral densities will be evaluated within the model that is* characterized by the Hamiltonian

$$H = \sum_{ij\sigma}(T_{ij} - \mu\delta_{ij})c_{i\sigma}^{\dagger}c_{j\sigma} + \sum_{i\sigma}(\epsilon_{c} - \mu)b_{i\sigma}^{\dagger}b_{i\sigma} + \frac{1}{2}U\sum_{i\sigma}n_{i\sigma}n_{i-\sigma} + U_{c}\sum_{i\sigma\sigma'}n_{i\sigma}n_{i\sigma'}^{c}. \quad (4)$$

$n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$ is the valence-band occupation number at site i and for spin σ. T_{ij} denote the hopping integrals, which are connected to the Bloch-band energies $\epsilon(k)$ via

$$T_{ij} = \frac{1}{N}\sum_{k}\exp[ik(R_{i} - R_{j})]\epsilon(k) \quad (5)$$

where the sum runs over all wave vectors k of the first Brillouin zone. ϵ_{c} is the one-particle energy of the core level. The VV correlations are described by a Hubbard interaction including the on-site Coulomb interaction U among the valence-band electrons. The on-site Coulomb interaction U_{c} between the valence-band electrons and the core electrons is responsible for the CV correlation effects.

For distinctness we have chosen a model as simple as possible, considering an s-like non-degenerate core level and a non-degenerate valence band, but have retained the most important interactions that are necessary to study both VV and CV correlation effects.

3. VV and CV correlations for AES

In equation (2) the lattice site i_{c}, where the transition takes place, is distinguished from all other sites, since the grand-canonical average is restricted to a subspace with definite core-level occupation number at i_{c}. Therefore, although the Hamiltonian (4) fully reflects the lattice periodicity, the three-particle spectral density certainly does not. For the general case of the partially filled valence band this causes far-reaching complications in the calculation, which have lead us in [22] to another expression for the AES and APS intensities, in which the lattice periodicity is reestablished in a formal way. As will be shown in the following, however, for the limiting cases of the completely filled and empty valence band, this is not necessary, and we can start from equation (1) directly.

The three-particle spectral density can be calculated from the retarded three-particle Green function

$$G_{ij-\sigma_{c}}^{(3),\text{ret},*}(E_{0}) = \langle\langle b_{i_{c}\sigma_{c}}^{\dagger}c_{i\sigma_{c}}c_{j-\sigma_{c}}, c_{i_{c}-\sigma_{c}}^{\dagger}c_{i_{c}\sigma_{c}}^{\dagger}b_{i_{c}\sigma_{c}}\rangle\rangle_{E_{0}}^{*} \quad (6)$$

by use of the relationship

$$A_{-\sigma_{c}}^{(3),*}(E_{0}) = -(1/\pi)\operatorname{Im}G_{i_{c}i_{c}-\sigma_{c}}^{(3),\text{ret},*}(E_{0}). \quad (7)$$

Since $G_{ij-\sigma_{c}}^{(3),\text{ret},*}$ has to be evaluated in the subspace $\mathcal{H}^{*}$ with $n_{i_{c}\sigma_{c}}^{c} = 0$, we immediately obtain the obvious result

$$G_{ij-\sigma_{c}}^{(3),\text{ret},*}(E_{0}) \mapsto 0 \qquad I_{-\sigma_{c}}^{\text{AES}}(E_{0}) \mapsto 0 \quad (8)$$

for the case of an empty valence band ($\epsilon_{c} \ll \mu \ll \epsilon(k)$).

Now let us consider the case of a fully occupied valence band ($\epsilon_c < \epsilon(k) \ll \mu$). We start with the equation of motion for $G_{ij-\sigma_c}^{(3),\text{ret},*}$:

$$E_0 G_{ij-\sigma_c}^{(3),\text{ret},*}(E_0) = \hbar \langle [b_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}]_+ \rangle^*$$

$$+ \langle \langle [b_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c}, H]_-, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^*. \tag{9}$$

Calculating the commutator $[\cdots, \cdots]_-$ and the anticommutator $[\cdots, \cdots]_+$, we straightforwardly arrive at

$$(E_0 + \mu + \epsilon_c) G_{ij-\sigma_c}^{(3),\text{ret},*}(E_0)$$

$$= \hbar (\delta_{i_c j} \langle b_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} c_{i\sigma_c} c_{i_c\sigma_c}^\dagger \rangle^* + \delta_{i_c i} \langle c_{i_c-\sigma_c}^\dagger b_{i_c\sigma_c}^\dagger c_{j-\sigma_c} b_{i_c\sigma_c} \rangle^* + \langle c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c} \rangle^*)$$

$$+ \sum_k (T_{jk} G_{ik-\sigma_c}^{(3),*}(E_0) + T_{ik} G_{kj-\sigma_c}^{(3),*}(E_0))$$

$$+ U \langle \langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c} (n_{j\sigma_c} + n_{i-\sigma_c}) c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^*$$

$$+ U_c \sum_{\sigma'} \langle \langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c} (n_{j\sigma'}^c + n_{i-\sigma'}^c), c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^*$$

$$- U_c \sum_{\sigma'} \langle \langle b_{i_c\sigma_c}^\dagger n_{i_c\sigma'} c_{i\sigma_c} c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^*. \tag{10}$$

In this form the equation of motion is still generally valid. In the following we exploit the fact that $b_{i_c\sigma_c} |\Psi)^* = 0$ for any state $|\Psi)^*$ in $\mathcal{H}^*$ and additionally make use of $c_{i\sigma}^\dagger |\Psi)^* = 0$. Then the grand-canonical averages and the higher-order Green functions can be simplified to a great extent:

$$\langle b_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} c_{i\sigma_c} c_{i_c\sigma_c}^\dagger \rangle^* \mapsto 0$$

$$\langle c_{i_c-\sigma_c}^\dagger b_{i_c\sigma_c}^\dagger c_{j-\sigma_c} b_{i_c\sigma_c} \rangle^* \mapsto 0$$

$$\langle c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c} \rangle^* \mapsto \delta_{i_c i} \delta_{i_c j}$$

$$U \langle \langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c} (n_{j\sigma_c} + n_{i-\sigma_c}) c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^* \mapsto U(2 - \delta_{ij}) G_{ij-\sigma_c}^{(3),\text{ret},*}(E_0)$$

$$U_c \sum_{\sigma'} \langle \langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c} (n_{j\sigma'}^c + n_{i-\sigma'}^c), c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^* \mapsto U_c(4 - \delta_{i_c i} - \delta_{i_c j}) G_{ij-\sigma_c}^{(3),\text{ret},*}(E_0)$$

$$U_c \sum_{\sigma'} \langle \langle b_{i_c\sigma_c}^\dagger n_{i_c\sigma'} c_{i\sigma_c} c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} \rangle \rangle_{E_0}^* \mapsto U_c(2 - \delta_{i_c i} - \delta_{i_c j}) G_{ij-\sigma_c}^{(3),\text{ret},*}(E_0). \tag{11}$$

Now the equation of motion simply reads

$$(E_0 + \mu + \epsilon_c - U(2 - \delta_{ij}) - 2U_c) G_{ij-\sigma_c}^{(3),\text{ret},*}(E_0) = \hbar \delta_{i_c i} \delta_{i_c j}$$

$$+ \sum_k (T_{jk} G_{ik-\sigma_c}^{(3),\text{ret},*}(E_0) + T_{ik} G_{kj-\sigma_c}^{(3),\text{ret},*}(E_0)). \tag{12}$$

We notice that the valence-band–core interaction U_c merely leads to an energetic shift of the Green function by $2U_c$. Therefore, the equation of motion can easily be solved by

Fourier transformation as has been done in [17] in analogy to the method of Sawatzky and Lenselink [9]. We finally arrive at

$$I_{-\sigma_c}^{AES}(E_0 - \mu) = -\frac{2}{\hbar} \, \mathrm{Im} \left(\frac{1}{N} \sum_k \frac{\Lambda_k(E_0)}{1 + U\Lambda_k(E_0)} \right) \tag{13}$$

with

$$\Lambda_k(E) = \frac{1}{N} \sum_q \frac{1}{E + \mathrm{i}0^+ + \epsilon_c - 2U - 2U_c - \epsilon(k) - \epsilon(k - q)}. \tag{14}$$

Apart from the rather unimportant energetic shift about $2U_c$ due to the CV correlations, the result is exactly the same as that derived for the limiting case of the completely filled valence band in [17], where a two-particle valence-band spectral density has been calculated within the framework of the Hubbard model. Furthermore, it is fully consistent with the result for the considered limiting case in [22], where we have calculated the three-particle spectral density in quite a different manner, employing the Matsubara formalism and first-order perturbation theory for the U_c interaction.

Hence, we omit a detailed discussion of the result and only state the qualitative difference between the effects of VV and CV correlations on the Auger spectrum: while strong correlations among the valence-band electrons lead to the formation of two-hole bound states manifesting themselves as a sharp satellite feature in the spectrum, the CV correlations merely produce a shift of the Auger spectrum towards higher energies. Nevertheless, this is a remarkable result since it could not be expected *a priori*.

For clarity, the correlation effects on the Auger spectrum may be classified as initial-state and final-state correlations. Regarding the U interaction the effect of the *initial-state* correlations is to renormalize the one-particle Bloch energies by adding the self-energy of the valence-band electrons. In the case of the completely filled valence band the self-energy reduces to the constant value U and leads to an energetic shift of $2U$ in the Auger spectrum (cf equation (14)). The well known satellite in the Auger spectrum due to the U interaction is a consequence of final-state correlations (cf equation (13)). It can be interpreted as the two-particle density of states belonging to tightly bound pairs of holes, which propagate through the lattice *after* the transition has taken place.

Turning now to the valence-band–core interaction U_c, we surely have non-trivial initial-state correlations even in the case of the completely filled valence band, since because of the presence of the localized core hole in the initial state the valence-band density of states is site dependent. Because this initial-state effect obviously cannot manifest itself as a pure energetic shift in the Auger spectrum, we are led to the conclusion that the non-trivial effect of the *final-state* correlations almost completely cancels the non-trivial *initial-state* effect leaving the *shape* of the Auger line unaffected by the U_c interaction. Within the formalism of the equation-of-motion method, however, this distinction between initial-state and final-state correlations is not really necessary.

4. VV and CV correlations for APS

4.1. Theory

If only VV correlations were considered, we could derive the AES and APS intensities from a single two-particle valence-band spectral density only [17], instead of employing the two

different three-particle spectral densities in equation (1). Then, if the problem were solved exactly for AES in the limiting cases of the completely filled and empty valence bands, we might deduce the results for APS by means of an electron–hole transformation [28]. Therefore, regarding the VV correlations, Auger-electron and appearance-potential spectra are qualitatively similar.

Considering additionally the CV correlations, however, the mentioned symmetry between AES and APS no longer exists. While for AES the core hole, present in the initial state, gives rise to a site-dependent valence-band density of states, there is no non-trivial core-hole effect in the initial state for APS. On the other hand, in the final state for APS the valence-band electrons are scattered at the core-hole potential, whereas the core hole has just been filled up in the final state for AES. These qualitative physical differences between the two types of spectroscopy reveal themselves in equation (1), where the AES and APS intensities are related to different kinds of three-particle spectral density. So, in the absence of any appropriate symmetry transformation, we have to do the calculation of the preceeding section once more for the case of APS.

We again start with the retarded three-particle Green function

$$G_{ij-\sigma_c}^{(3),\text{ret},0}(E_0) = \langle\langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}\rangle\rangle_{E_0}^0 \tag{15}$$

which now has to be calculated in the subspace $\mathcal{H}^0$ of all states with $n_{i_c\sigma_c}^c = 1$. The corresponding three-particle spectral density is given by

$$A_{-\sigma_c}^{(3),0}(E_0) = -(1/\pi)\,\text{Im}\,G_{i_c i_c-\sigma_c}^{(3),\text{ret},0}(E_0). \tag{16}$$

Just as in section 3 we immediately obtain for the limiting case of the completely filled valence band

$$G_{ij-\sigma_c}^{(3),\text{ret},0}(E_0) \mapsto 0 \qquad I_{-\sigma_c}^{\text{APS}}(E_0) \mapsto 0. \tag{17}$$

Turning now to the limit of the empty valence band, we again have to derive the equation of motion for $G_{ij-\sigma_c}^{(3),\text{ret},0}$, which is exactly the same as equations (9) and (10) of section 3, provided that all expectation values are evaluated in $\mathcal{H}^0$ instead of $\mathcal{H}^*$, i.e. if all superscripts * are replaced by ^{0}.

The simplifications of the grand-canonical averages and the higher-order Green functions now read

$$\langle b_{i_c\sigma_c}^\dagger b_{i_c\sigma_c} c_{i\sigma_c} c_{i_c\sigma_c}^\dagger\rangle^0 \mapsto \delta_{i_c i}$$

$$\langle c_{i_c-\sigma_c}^\dagger b_{i_c\sigma_c}^\dagger c_{j-\sigma_c} b_{i_c\sigma_c}\rangle^0 \mapsto 0$$

$$\langle c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c}\rangle^0 \mapsto 0$$

$$U\langle\langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c}(n_{j\sigma_c} + n_{i-\sigma_c}) c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}\rangle\rangle_{E_0}^0 \mapsto U\delta_{ij} G_{ij-\sigma_c}^{(3),\text{ret},0}(E_0)$$

$$U_c \sum_{\sigma'}\langle\langle b_{i_c\sigma_c}^\dagger c_{i\sigma_c} c_{j-\sigma_c}(n_{j\sigma'}^c + n_{i-\sigma'}^c), c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}\rangle\rangle_{E_0}^0 \mapsto U_c(4 - \delta_{i_c i} - \delta_{i_c j}) G_{ij-\sigma_c}^{(3),\text{ret},0}(E_0)$$

$$U_c \sum_{\sigma'}\langle\langle b_{i_c\sigma_c}^\dagger n_{i_c\sigma'} c_{i\sigma_c} c_{j-\sigma_c}, c_{i_c-\sigma_c}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}\rangle\rangle_{E_0}^0 \mapsto 0 \tag{18}$$

and finally we are left with the following equation of motion:

$$(E_0 + \mu + \epsilon_c - U\delta_{ij} - U_c(4 - \delta_{i_c i} - \delta_{i_c j}))G^{(3),\text{ret},0}_{ij-\sigma_c}(E_0)$$

$$= \hbar\delta_{i_c i}\delta_{i_c j} + \sum_k (T_{jk}G^{(3),\text{ret},0}_{ik-\sigma_c}(E_0) + T_{ik}G^{(3),\text{ret},0}_{kj-\sigma_c}(E_0)). \tag{19}$$

Because now both the U and U_c interactions are multiplied by Kronecker deltas in the left-hand side of (19), the solving of the equation of motion is far more involved. The CV correlations no longer manifest themselves as pure energetic shifts of the spectrum as in the case of AES.

For the following let us introduce the short-hand notation

$$G^{(3)}_{ij} = G^{(3),\text{ret},0}_{ij-\sigma_c}(E_0 - \mu) \tag{20}$$

and its Fourier transform $G^{(3)}_{p\cdot q}$:

$$G^{(3)}_{ij} = \frac{1}{N} \sum_{p\cdot q} \exp(ip \cdot R_i) \exp(iq \cdot R_j)G^{(3)}_{p\cdot q}$$

$$G^{(3)}_{p\cdot q} = \frac{1}{N} \sum_{ij} \exp(-ip \cdot R_i) \exp(-iq \cdot R_j)G^{(3)}_{ij}. \tag{21}$$

After Fourier transformation of equation (19) we arrive at

$$[E_0 + \epsilon_c - 4U_c - \epsilon(p) - \epsilon(q)]G^{(3)}_{p\cdot q} = \frac{\hbar}{N} \exp[-i(p + q) \cdot R_i]$$

$$+ \frac{1}{N} \sum_{kl} \exp[-ip \cdot R_k] \exp[-iq \cdot R_l](U\delta_{kl} - U_c\delta_{i_c k} - U_c\delta_{i_c l})G^{(3)}_{kl}. \tag{22}$$

We proceed by dividing equation (22) by $E_0 + \epsilon_c - 4U_c - \epsilon(p) - \epsilon(q)$ and retransforming the result to the Wannier representation, ending up with

$$G^{(3)}_{ij} = \hbar\Lambda^{i_c i_c}_{ij} + \sum_{kl} \Lambda^{kl}_{ij}(U\delta_{kl} - U_c\delta_{i_c k} - U_c\delta_{i_c l})G^{(3)}_{kl}. \tag{23}$$

Here Λ^{kl}_{ij} denotes the free two-particle Green function in the Wannier representation:

$$\Lambda^{kl}_{ij} = \frac{1}{N^2} \sum_{p\cdot q} \frac{\exp[ip \cdot (R_i - R_k)] \exp[iq \cdot (R_j - R_l)]}{E_0 + \epsilon_c - 4U_c - \epsilon(p) - \epsilon(q)}. \tag{24}$$

From equation (23) we deduce that the three-particle Green function has the general form:

$$G^{(3)}_{ij} = \hbar\Lambda^{i_c i_c}_{ij} + \sum_k \Lambda^{kk}_{ij}\alpha_k - \sum_k \Lambda^{i_c k}_{ij}\beta_k - \sum_k \Lambda^{k i_c}_{ij}\gamma_k \tag{25}$$

where the *a priori* unknown energy-dependent functions α_k, β_k and γ_k have to be determined by the equation of motion. Inserting the *ansatz* (25) into the transformed equation of motion (23), we obtain

$$\sum_k \Lambda_{ij}^{kk}\alpha_k - \sum_k \Lambda_{ij}^{i_ck}\beta_k - \sum_k \Lambda_{ij}^{ki_c}\gamma_k$$

$$= \sum_k U\Lambda_{ij}^{kk}\left(\hbar\Lambda_{kk}^{i_ci_c} + \sum_l \Lambda_{kk}^{ll}\alpha_l - \sum_l \Lambda_{kk}^{i_cl}\beta_l - \sum_l \Lambda_{kk}^{li_c}\gamma_l\right)$$

$$- \sum_k U_c\Lambda_{ij}^{i_ck}\left(\hbar\Lambda_{i_ck}^{i_ci_c} + \sum_l \Lambda_{i_ck}^{ll}\alpha_l - \sum_l \Lambda_{i_ck}^{i_cl}\beta_l - \sum_l \Lambda_{i_ck}^{li_c}\gamma_l\right)$$

$$- \sum_k U_c\Lambda_{ij}^{ki_c}\left(\hbar\Lambda_{ki_c}^{i_ci_c} + \sum_l \Lambda_{ki_c}^{ll}\alpha_l - \sum_l \Lambda_{ki_c}^{i_cl}\beta_l - \sum_l \Lambda_{ki_c}^{li_c}\gamma_l\right). \tag{26}$$

This equation is valid for arbitrary lattice sites i and j. Considering the general properties $\Lambda_{ij}^{kl} \mapsto 0$ for $|R_i - R_k| \mapsto \infty$ and $\Lambda_{ij}^{kl} \mapsto 0$ for $|R_j - R_l| \mapsto \infty$ of the free two-particle Green function Λ_{ij}^{kl}, we look at equation (26) for three different special sets of lattice sites i and j. Firstly, we take $i = j$ and $|R_i - R_{i_c}| \mapsto \infty$. In this case $\Lambda_{ij}^{i_ck} \mapsto 0$ and $\Lambda_{ij}^{ki_c} \mapsto 0$, and the first term of the left-hand side is equal to the first term of the right-hand side of (26). Secondly, we take $i = i_c$ and $|R_j - R_{i_c}| \mapsto \infty$ observing the respective second terms to be equal in this case. Finally, for $j = i_c$ and $|R_i - R_{i_c}| \mapsto \infty$ the respective third terms of (26) are equal. Assuming that the matrices $(\Lambda_{ii}^{kk})_{ik}$, $(\Lambda_{i_cj}^{i_ck})_{jk}$ and $(\Lambda_{ii_c}^{ki_c})_{ik}$ are non-singular, we are left with three coupled linear systems of equations:

$$\alpha_k = \hbar U\Lambda_{kk}^{i_ci_c} + U\sum_l \Lambda_{kk}^{ll}\alpha_l - U\sum_l \Lambda_{kk}^{i_cl}\beta_l - U\sum_l \Lambda_{kk}^{li_c}\gamma_l$$

$$\beta_k = \hbar U_c\Lambda_{i_ck}^{i_ci_c} + U_c\sum_l \Lambda_{i_ck}^{ll}\alpha_l - U_c\sum_l \Lambda_{i_ck}^{i_cl}\beta_l - U_c\sum_l \Lambda_{i_ck}^{li_c}\gamma_l \tag{27}$$

$$\gamma_k = \hbar U_c\Lambda_{ki_c}^{i_ci_c} + U_c\sum_l \Lambda_{ki_c}^{ll}\alpha_l - U_c\sum_l \Lambda_{ki_c}^{i_cl}\beta_l - U_c\sum_l \Lambda_{ki_c}^{li_c}\gamma_l$$

which due to the relationship $\Lambda_{ij}^{kl} = \Lambda_{ji}^{lk}$ can be simplified once more:

$$\alpha_k = \hbar U\Lambda_{kk}^{i_ci_c} + U\sum_l \Lambda_{kk}^{ll}\alpha_l - 2U\sum_l \Lambda_{kk}^{i_cl}\beta_l$$

$$\beta_k = \hbar U_c\Lambda_{i_ck}^{i_ci_c} + U_c\sum_l \Lambda_{i_ck}^{ll}\alpha_l - U_c\sum_l \Lambda_{i_ck}^{i_cl}\beta_l - U_c\sum_l \Lambda_{i_ck}^{li_c}\beta_l \tag{28}$$

$$\gamma_k = \beta_k.$$

The system of equations (28) together with the *ansatz* (25) is fully equivalent to the equation of motion (19), where we started from for the limiting case of the empty valence band. Replacing $E_0 \mapsto E_0 + i0^+$ at the end of the calculation in order to obtain the retarded three-particle Green function, we obtain the APS intensity from equations (1), (16), (24), (25) and (28).

4.2. Results and discussion

The following calculations have been done for a non-degenerate tight-binding valence band of a simple-cubic crystal:

$$\epsilon(k) = T_0 + T_1 \sum_i \exp[ik \cdot R_i] + T_2 \sum_j \exp[ik \cdot R_j] \tag{29}$$

where the sums run over all lattice sites i of the first and all lattice sites j of the second shell around the site $R_0 = 0$. T_0 is the band centre of gravity, which we take as energy zero. For the hopping integrals T_1 and T_2 we choose $T_1 = 0.15$ eV and $T_2 = 0.10$ eV, resulting in a valence-band density of states (DOS) with an approximate width of $W \simeq 3$ eV, shown in the inset of figure 1.
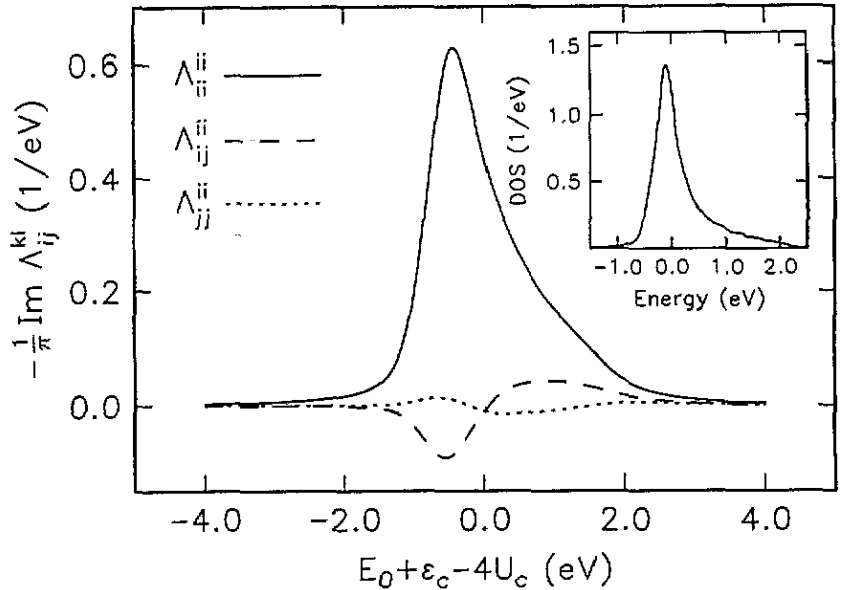

Figure 1. Free retarded two-particle Green function in the Wannier representation (diagonal element Λ_{ii}^{ii} and first non-diagonal elements Λ_{ij}^{ii} and Λ_{jj}^{ii}) as a function of energy. The inset shows the free Bloch-band DOS.

For computational reasons we use the substitution $E_0 \mapsto E_0 + \Sigma$ with a finite constant imaginary value for Σ to switch over to retarded Green functions instead of using the infinitesimal $\Sigma = i0^+$. This has the effect of convoluting the spectra with a Lorentzian, thereby smearing out sharp spectral features. All calculations have been performed with $\Sigma = i0.15$ eV.

For the double wave-vector summation in equation (24) we have chosen 701 special k points in the first Brillouin zone for each sum according to the Korobov method for the evaluation of multiple integrals [29]. For the chosen value for Σ this is sufficient for convergence. The results of the calculation of Λ_{ij}^{kl} are shown in figure 1. The imaginary part of the diagonal element Λ_{ii}^{ii} represents the self-convolution of the one-particle valence-band DOS and is proportional to the APS intensity for the case $U = U_c = 0$, i.e. in a one-particle

scheme [7]. The absolute values of the off-diagonal elements Λ_{ij}^{ii} and Λ_{jj}^{ii}, where i and j are neighbouring lattice sites, are generally much smaller than the absolute value of the diagonal element, which is a consequence of the tight-binding *ansatz* for the free Bloch band. Further elements, not shown in figure 1, are still smaller and need not be considered for the solution of (28).

The coupled linear system of equations (28) is solved numerically by restricting the lattice sums to a given number of lattice sites in the first n_{sh} shells around the site i_c, where the transition is thought to take place. For $\Sigma = i\, 0.15$ eV we have considered $n_{sh} = 11$ shells, including 171 sites. Smaller values for Σ would require the inclusion of still more shells, soon exceeding our present computational capacities.

The results of the calculation of the APS intensity are shown in figure 2. We have taken the Hubbard interaction to be $U = 8$ eV and have varied the valence-band–core interaction U_c from 0 eV to 11 eV. For this choice of the parameters all interesting features reveal themselves in the spectra.
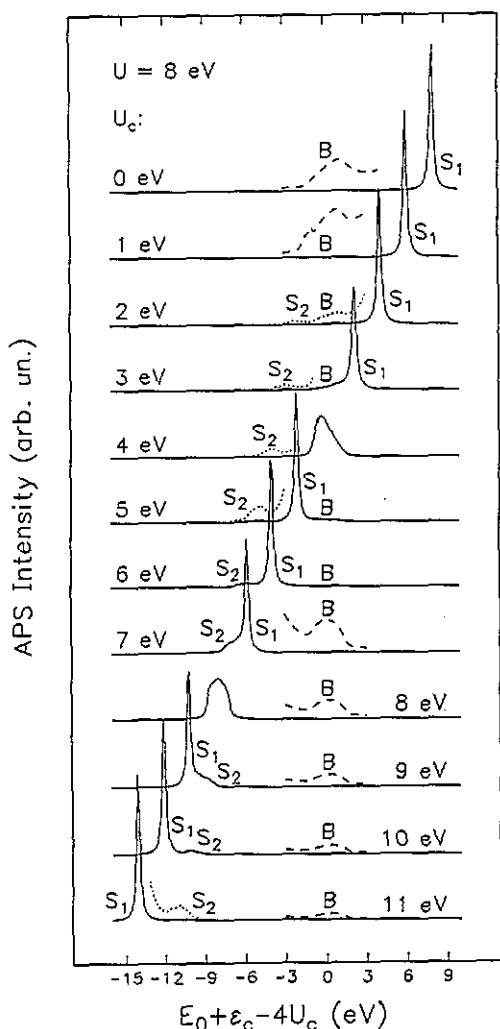

Figure 2. Calculated APS intensities (full curves) for different indicated values of the valence-band–core interaction U_c as functions of energy. The Hubbard interaction is fixed at $U = 8$ eV. Parts of the spectra are enhanced by a factor of 10 (dotted curves) and a factor of 100 (broken curves). For the meaning of the symbols see the text.

The APS intensities are shown as a function of $E_0 + \epsilon_c - 4U_c$ to suppress the rather uninteresting constant energetic shift of the spectra about $4U_c$ in the picture. This shift is

clearly an effect of the initial-state correlations: since in the initial state for APS the core level is filled and since we consider the limiting case of the empty valence band, the contribution to the valence-band self-energy due to the U_c interaction can easily be calculated yielding the constant value $2U_c$, which renormalizes the Bloch-band energies $\epsilon(k)$. This self-energy contribution explains the term $4U_c$ in the expression for the free two-particle valence-band Green function Λ_{ij}^{kl} in equation (24). Regarding the U interaction we obviously have no contribution to the valence-band self-energy for an empty valence band. So in general the initial-state correlations are trivial for APS, and concerning the APS line shape, all features in the spectra that deviate from the self-convolution result have to be ascribed to effects of final-state correlations.

Let us first consider the case $U_c = 0$, which defines the Cini–Sawatzky model [8, 9, 17]. If additionally $U = 0$, the APS intensity is given by the self-convolution of the valence-band density of states as mentioned above. With increasing U the line shape is more and more distorted, and when U exceeds a certain critical value (roughly given by the width W of the free Bloch band), the spectrum separates into a rather broad band-like part with a width of $2W$ and a sharp satellite, which takes almost the whole spectral weight as soon as it is split off. This well known situation is shown in the first spectrum of figure 2 for $U = 8$ eV. The satellite (denoted by 'S_1') is located about 8 eV above the band region (denoted by 'B').

Now we switch on the valence-band–core interaction U_c. For weak coupling (see figure 2, $U_c = 1$ eV) the general form of the spectrum is still quite similar to the case $U_c = 0$. The energetic distance between the satellite S_1 and the band-like part B, however, is reduced by $2U_c$, thereby transferring some spectral weight from S_1 to B. If U_c is increased from 1 eV up to 3 eV, the band-like part of the spectrum is more and more distorted, and on the low-energetic side of B a new satellite (denoted by 'S_2') comes into existence. The satellite S_2 always lies below the band-like part of the spectrum and is separated from it by the amount U_c. The width of S_2 is nearly the same as the width W of the free Bloch band. For $U_c < U$ its spectral weight increases and for $U_c > U$ decreases with increasing U_c.

Compared with the satellite S_1, however, the spectral weight of S_2 is rather small, so it will hardly be observed in an experiment. The energetic position of S_1 is $U - 2U_c$ relative to the band-like part B. So if we forget about the satellite S_2 for a moment and about the energetic shift of $4U_c$ due to the initial-state correlations, the situation simply resembles that of the Cini–Sawatzky model with an effective coupling parameter $U_{eff} = U - 2U_c$. For $U_{eff} = 0$ ($U_c = 4$ eV) the spectrum is almost completely characterized by the self-convolution of the valence-band density of states. For $U_c > 4$ eV we have $U_{eff} < 0$, and the satellite S_1 splits off from the band region on the low-energetic side.

The interpretation of the spectra in terms of an effective coupling strength would be completely justified if it were allowable to neglect all off-diagonal elements of the free two-particle Green function Λ_{ij}^{kl} and to keep only Λ_{ii}^{ii}. In this case the coupled linear system of equations (28) can be solved analytically:

$$\alpha_{i_c} = \hbar U \Lambda_{i_c i_c}^{i_c i_c} / [1 - (U - 2U_c)\Lambda_{i_c i_c}^{i_c i_c}]$$

$$\beta_{i_c} = \gamma_{i_c} = \hbar U_c \Lambda_{i_c i_c}^{i_c i_c} / [1 - (U - 2U_c)\Lambda_{i_c i_c}^{i_c i_c}] \qquad (30)$$

$$G_{i_c i_c}^{(3)} = \hbar \Lambda_{i_c i_c}^{i_c i_c} / [1 - U_{eff}\Lambda_{i_c i_c}^{i_c i_c}].$$

If the satellites S_1 and S_2 come close together, however, a striking feature occurs, which can no longer be explained in terms of an effective interaction U_{eff}. For $U_c = U = 8$ eV the spectrum shows a broad peak of almost symmetric shape located at 8 eV below the band-like part. It has the width of the satellite S_2 and takes the whole spectral weight from the satellite S_1.

For the physical interpretation of the spectra we have to remind ourselves that all features deviating from the self-convolution model are due to final-state correlations, apart from the general shift about $4U_c$. For the limiting case considered here, the possible final states for APS are excited eigenstates of the Hamiltonian (4) with two electrons in the valence band and with all core states filled except for the core state at the site i_c with spin index σ_c. We can easily imagine three different kinds of such a final state:

(i) The two valence-band electrons are moving independently from each other on lattice sites preferably different from the site i_c. Because we have taken the Coulomb interaction between valence-band and core electrons to be on site, the two valence-band electrons are not affected by the core hole at the site i_c in this case. So apart from the overall energetic shift about $4U_c$, there is no effect of the valence-band–core interaction. Analogously there is no U interaction *between* these two electrons, since for most of the time they are moving on different lattice sites. For this quasi-free motion, each electron may occupy any state of the free Bloch band. So this type of final state reveals itself as a broad peak in the spectrum located at twice the centre of gravity of the free Bloch band $E_0 + \epsilon_c - 4U_c = 2T_0$ ($= 0$ for our choice of the energy zero) with a width $2W$, and can be identified with the band-like part B of the spectrum.

If $|i\rangle$ denotes the initial state for APS and $|f\rangle$ any final state, we obtain the contribution of $|f\rangle$ to the APS intensity from the absolute square of the matrix element $\langle f|T_\sigma|i\rangle$, where T_σ is the transition operator (3). Since we have assumed the transition to be intra-atomic, the two valence-band electrons are created at the site i_c just after the transition. On the other hand, for the final states of the first kind the two valence-band electrons are moving through the whole lattice. Therefore, the overlap of the intermediate state $T_\sigma|i\rangle = c_{i_c\sigma}^\dagger c_{i_c\sigma_c}^\dagger b_{i_c\sigma_c}|i\rangle$ with the first type of final state is small, explaining the rather small spectral weight of the band-like part B in the spectrum for those cases, in which B is clearly separated from other spectral features.

(ii) One of the two valence-band electrons is localized at the site i_c, while the other one is moving on lattice sites preferably different from the site i_c. Again the quasi-freely moving electron may occupy any state of the free Bloch band. The localized electron, on the other hand, has a rather definite energy of $T_0 - U_c$, since it is captured in the core-hole potential and thus cannot contribute to the dispersion of the final states. Because the two valence-band electrons are separated from each other for most of the time, we again have no effects of the Hubbard interaction U. Transitions that leave the system in final states of this second kind create a satellite at the energy $E_0 + \epsilon_c - 4U_c = 2T_0 - U_c$ with an energetic width of W. This is precisely the satellite that we have denoted above by S_2. For situations in which all spectral features are well separated from each other (see figure 2, $U_c = 6$ eV and $U_c = 11$ eV, for example), S_2 has clearly higher spectral weight than B. This has to be expected from the above discussion: Since for final states of the second kind there is one electron localized at the site i_c, the overlap of the intermediate state $T_\sigma|i\rangle$ with these final states is higher than the overlap with final states of the first kind.

(iii) The two valence-band electrons are localized at the site i_c. In this case both electrons are affected by the core-hole potential, shifting the energy of such final states downwards by an amount $2U_c$. Since both electrons are on the same lattice site, we furthermore have to consider the Coulomb repulsion between them, resulting in a shift by U to higher energies. Therefore, if the system is left in this third kind of final state, we have for the energy E_0 of the incoming APS electron $E_0 + \epsilon_c - 4U_c = 2T_0 - 2U_c + U$. So we identify these final states with the satellite that we have denoted above by S_1.

Since the two valence-band electrons are localized, the dispersion of the final states is weak. Consequently, the satellite S_1 has a much smaller width than the satellite S_2 and the

band-like part B, if S_1 is well separated from them. While for the creation of the satellite S_2 we need a non-zero valence-band–core interaction U_c, the satellite S_1 is already known from the Cini–Sawatzky model, i.e. for $U_c = 0$. In [17] it has been shown (for $U_c = 0$) that S_1 has a small but finite width and has therefore been interpreted as a bound pair of electrons *propagating* through the lattice. Nevertheless, because the width is rather small compared with the width W of the free Bloch band, the two electrons *preferably* stay at the site i_c. For $U_c \neq 0$ it is difficult to determine the width of S_1 from our results, since it is broadened as a consequence of the finite value for Σ, so we can only state that the final states belonging to S_1 are localized, and are not able to obtain information about the degree of localization. The localization of the considered final states very obviously explains the high spectral weight of the satellite S_1: the intermediate state $T_\sigma |i\rangle$, for which there are two valence-band electrons at the site i_c, has maximal overlap with the final states of the third kind.

5. Concluding remarks

One of the main advantages of AES and APS is their direct sensitivity to electron-correlation effects. Especially for CVV transitions there can be no doubt that for many systems electron-correlation effects even dominate the general form of the line shape. For this reason, and because of their comparatively simple experimental set-up, AES and APS appear as attractive methods for studying the electronic structure of solids. Since correlation effects alone prevent us from a simple interpretation of the measured line shape (e.g. within a self-convolution model), however, there is an urgent need for a general theory of AES and APS, from which we can extract the information on the electronic structure via comparison of experimental and theoretical results.

Concerning the description of VV correlation effects, the Cini–Sawatzky model has served as a paradigm for CVV AES and, to a lesser extent, APS line-shape analysis. CV correlation effects, however, are not considered within this model. On the other hand, in the only approach that seriously deals with CV correlations in CVV Auger transitions [24], VV correlations are neglected altogether. Therefore, our main interest is focused on the question of whether it is possible to formulate a theory in which both types of correlation effect are treated with equal importance and which additionally allows for a future inclusion of other important effects due to band degeneracy and the energy and wave-vector dependence of the transition matrix elements. For the general case of arbitrary band filling this seems to be quite a difficult task, so in our recent work [22] we could treat the U_c interaction only by means of perturbation theory. A more general approach, which works for arbitrary strengths of both the U and U_c interactions, will be presented in a forthcoming paper.

In our present work we have tackled the problem, restricting ourselves to the limiting cases of the fully occupied and the empty valence band. These cases are of special importance, since they can be treated exactly. The AES and APS intensities are given by properly defined three-particle spectral densities, which are determined solving the equations of motion for the corresponding three-particle Green functions within a simple model of a non-degenerate valence band and a non-degenerate core level.

For AES and for the limiting case of the completely filled valence band, the calculation is performed analytically. The result for the Auger spectrum is exactly the same as in the Cini–Sawatzky model, apart from a rather unimportant shift of the whole spectrum about $2U_c$ towards higher energies. For AES in the limit of the fully occupied valence band, this shift is the only effect that is due to the valence-band–core interaction U_c. This result may

be interpreted in terms of initial-state and final-state correlations. The electron correlations due to U_c, in both the initial state and the final state for AES, are non-trivial. However, they almost completely cancel each other leaving the *shape* of the Auger line unaffected by the U_c interaction.

For APS the calculation has to be performed numerically. In the case of the empty valence band the APS spectra may exhibit up to three different features. These have to be ascribed exclusively to final-state correlation effects, since now both the VV and the CV correlations are trivial for the initial state for APS, yielding a constant energetic shift of the spectrum about $4U_c$ towards higher energies only. The band-like part B of the spectrum, which is located at $E_0 = 2T_0 - \epsilon_c + 4U_c$ and which has a width of $2W$, where W is the width of the free Bloch band, corresponds to final states in which both electrons are moving independently through the lattice. Furthermore, the spectrum exhibits a satellite S_2 located at an amount U_c below the band-like part. It has the width of the free Bloch band and belongs to final states in which one electron is captured in the core-hole potential, while the other one propagates through the lattice. Finally, the strong satellite S_1 lies at an energy $U - 2U_c$ relative to B and has a rather small width. It is interpreted as reflecting final states in which both valence-band electrons are more or less localized at the site where the transition has taken place.

If the coupling parameters U and U_c are chosen in such a way that all three spectral features are well separated from each other, the satellite S_1 takes almost the whole spectral weight. The spectral weight of S_2 is only small, so it will be hardly observed in an experiment, but is still higher than the spectral weight of the band-like part.

Apart from the satellite feature S_2 and apart from the overall energetic shift about $4U_c$ due to the initial-state correlations, we have the same situation as in the Cini–Sawatzky model, provided that the coupling parameter U is replaced by an effective coupling $U_{eff} = U - 2U_c$. This surely has to be taken into account if one tries to determine the value for U from the energetic difference between the positions of the band region and the satellite.

Acknowledgments

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