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Comment on quasiatomic Auger spectra in narrow-band metals

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The equivalence of the Sawatzky approach to an earlier one of the present author is proven and the extension to degenerate orbitals and bands is given.

In a recent paper[1] I proposed an exactly solvable model for the density of states of two interacting holes in a solid. As I stressed on that occasion, this quantity is important for establishing the relationship between the Auger spectra of solids, involving two final-state holes in the valence band, and the one-electron density-of-states matrix. The solution was achieved by calculating all the moments of the total Hamiltonian. Subsequently Sawatzky, in a very interesting work,[2] put forward a closely related model and solved it exactly by a Green's-function equation-of-motion technique. As Sawatzky demonstrated, the interacting density of states solves the puzzle of the occurrence of quasiatomic Auger spectra in solids (see also Ref. 3).

A comparison between the two exact solutions is needed because they were achieved by very different mathematical techniques and with unessential differences in the models. Moreover, the solutions look very different at first sight. In this paper I prove that, despite the formal differences, the approaches of Refs. 1 and 2 are equivalent, and I extend the theory to the more realistic case of degenerate orbitals and bands. The extension is important since the observed more or less quasiatomic spectra consist of multiplets.

For convenience, we assume that the band is initially filled with electrons. Then the initial state is the hole vacuum $|v\rangle$. In the case of a simple orbital, the Auger transition suddenly takes the system to the state $|0\rangle = c_{0+}^{\dagger} c_{0-}^{\dagger} |v\rangle$, where $c_{0+}^{\dagger}$ creates a hole with spin up on the atomic orbital involved. The density of states is the Fourier transform of the correlation function

$$D(t) = \sum_{n=0}^{\infty} \frac{(-it)^n}{n!} h_n \quad , \tag{1}$$

where $h_n = \langle 0 | H^n | 0 \rangle$ is the nth moment of the Hamiltonian. In Ref. 1, the Hamiltonian was taken to be $H = H_S + H_I$, where H_S is a one-electron Hamiltonian describing the band of the solid and the hopping terms between the atom and the solid, and $H_I = U n_{0+} n_{0-}$ is the interaction term localized at the atomic site ($n_{0+} = c_{0+}^{\dagger} c_{0+}$), where the Auger transition occurs. Specifying H_S further is irrelevant here, but since H can be identified with an Anderson Hamiltonian, this model may be appropriate to describe impurities or chemisorbed atoms. The solution was obtained by taking the expectation value of the operator identity

$$H^n = H_S^n + \sum_{r=0}^{n-1} H_S^r H_I H^{n-r-1} \quad , \tag{2}$$

using the fact that H_I acts like $|0\rangle U \langle 0|$ and summing the Taylor series for $D(t)$. Here, it is convenient to write down the result in Laplace transformed form

$$D(s) = D^0(s) - iUD^0(s)D(s) \quad . \tag{3}$$

In Eq. (3), $D^0(t)$ is the correlation function calculated in the absence of H_I, and equals the square of a one-electron correlation function. Equation (3) involves the occurrence of localized resonances if U is large compared with the bandwidth,[3] in full analogy with Sawatzky's results.

Sawatzky considered a Hubbard model, with $H_I = U \sum_i n_{i+} n_{i-}$, with the index i running over all the atomic sites. His model is therefore more appropriate to describe an atom in a perfect crystal. With this interaction Hamiltonian, the above argument runs just as before, and Eq. (3) becomes

$$D_{00}(s) = D_{00}^0(s) - iU \sum_i D_{0i}^0(s) D_{i0}(s) \quad , \tag{4}$$

where, obviously,

$$D_{0i}(t) = \langle v | c_{i-} c_{i+} e^{-iHt} c_{0+}^{\dagger} c_{0-}^{\dagger} | v \rangle \quad . \tag{5}$$

Equation (4) holds for ordered and disordered solids as well. If we assume a periodic solid, with wave-vector-dependent single-particle energies η_q, we can define Fourier-transformed quantities like

$$D_q(s) = \sum_i D_{i0} e^{-i\vec{q} \cdot \vec{R}_i} \quad . \tag{6}$$

Let N be the total number of atoms. Then Eq. (4) becomes

$$D_{00}(s)=\frac{1}{N}\sum_{q}\frac{D_q^0(s)}{1+iUD_q^0(s)}\quad . \tag{7}$$

In view of the relationship $D(-i\omega+0)=iG(\omega)$, where G is the Green's function, Eq. (7) is identical to Eq. (9) of Ref. 2, apart from a trivial shift in the origin of energies and a factor $(2\pi)^{-1}$ arising from Sawatzky's use of Zubarev Green's functions.

Also, we can readily verify that

$$D_q^0(s)=\frac{1}{N}\sum_{q_1}\left[s+i(\eta_{q_1+q/2}+\eta_{q_1-q/2})\right]^{-1} . \tag{8}$$

Thus, the relationship between the two solutions is established. We can now extend Eq. (3) to the case of degenerate orbitals and bands without special difficulty. Let L be the angular momentum of the atomic orbital where the two holes are produced. Then, we are interested in calculating the spin-dependent two-particle correlation function

$$D_{m_1m_2,m_3m_4,\sigma}(t)=\langle m_3m_4\sigma|e^{-iHt}|m_1m_2\sigma\rangle\ , \tag{9}$$

where $|m_1m_2\sigma\rangle=c^{\dagger}_{m_2\sigma}c^{\dagger}_{m_1+}|v\rangle$ and the m_j are magnetic quantum numbers. The interaction Hamiltonian now reads

$$H_I=\frac{1}{2}\sum_{\sigma\sigma'}\sum_{m_1m_2}\sum_{m_3m_4}U_{m_1m_2m_3m_4}c^{\dagger}_{m_1\sigma}c^{\dagger}_{m_2\sigma'}c_{m_3\sigma'}c_{m_4\sigma}\ , \tag{10}$$

where

$$U_{m_1m_2m_3m_4}=(\phi_{m_1}\phi_{m_2}|r_{12}^{-1}|\phi_{m_4m_3})$$

is a Coulomb integral. The noninteracting correlation functions are related to the single-hole density matrix $\rho_{m_1m_2}(\omega)$ as follows:

$$\begin{aligned}D^0_{m_1m_2,m_3m_4,-}(t)&=\rho_{m_1m_3}(t)\rho_{m_2m_4}(t)\ ,\\ D^0_{m_1m_2,m_3m_4,+}(t)&=\rho_{m_1m_3}(t)\rho_{m_2m_4}(t)\\ &\quad-\rho_{m_3m_2}(t)\rho_{m_4m_1}(t)\ .\end{aligned} \tag{11}$$

The calculations can be carried out just as before and Eq. (3) becomes the matrix equation

$$\hat{D}_\sigma(s)=\hat{D}^0_\sigma(s)-i\hat{D}_\sigma(s)\,\hat{W}_\sigma\hat{D}^0_\sigma(s)\ , \tag{12}$$

where the matrix $\hat{W}_\sigma$ has elements

$$\begin{aligned}W_{m_1m_2,m_3m_4,-}&=U_{m_1m_2m_4m_3}\ ,\\ W_{m_1m_2,m_3m_4,+}&=U_{m_1m_2m_4m_3}-U_{m_1m_2m_3m_4}\ .\end{aligned} \tag{13}$$

In general, Eq. (12) is equivalent to a rather big system of linear equations. If, however, the solid does not distort the spherical symmetry of the atom too much, the off-diagonal ρ_{mn} vanish. Then, the equations for different total angular momenta L_t decouple and become identical to Eq. (3), each with its own value of the repulsion U_{Lt}. For narrow bands, the spectrum clearly becomes a quasiatomic multiplet.

Finally, let us consider a transition metal, composed of identical atoms with valence shells of angular momentum L. The interaction Hamiltonian is now

$$\begin{aligned}H_I=\frac{1}{2}\sum_{i}\sum_{\sigma\sigma'}\sum_{m_1m_2}\sum_{m_3m_4}&U_{m_1m_2m_3m_4}\\ &\times c^{\dagger}_{m_1i\sigma}c^{\dagger}_{m_2i\sigma'}c_{m_3i\sigma'}c_{m_4i\sigma}\ ,\end{aligned} \tag{14}$$

that is the sum of the interaction Hamiltonians at all the atomic sites (the notation is obvious). In order to extend Eqs. (4)–(7) to angular momentum L, we just define matrices $\hat{D}_{0i\sigma}$ with components

$$\begin{aligned}D_{m_1m_20,m_3m_4i,\sigma}(s)=\langle v|c_{m_3i+}c_{m_4i\sigma}&(s+iH)^{-1}\\ &\times c^{\dagger}_{m_20\sigma}c^{\dagger}_{m_10+}|v\rangle\ ,\end{aligned}$$

and introduce their Fourier transform as in Eq. (6). The final result is

$$\hat{D}_{00,\sigma}(s)=\frac{1}{N}\sum_{q}\hat{D}^0_{q\sigma}(s)[\hat{E}+i\hat{W}_\sigma\hat{D}^0_{q\sigma}(s)]^{-1}\ , \tag{15}$$

where $\hat{E}$ is the unit matrix. Equations (12) and (15) should allow for a detailed comparison with experiment, and this work is currently under way.

As a closing remark, I should like to note that generalizing the theory to alloys is a rather easy task and the simple method proposed here and in Ref. 1 leads to exact solutions to a variety of problems involving localized interaction terms in the Hamiltonian. For instance, we can deal with x-ray-photoemission-spectra or Auger experiments that produce holes in valence states, while allowing for the coupling of the holes with a plasmon field. A paper dealing with such problems is forthcoming.[4]

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[1] M. Cini, Solid State Commun. 20, 605 (1976).

[2] G. A. Sawatzky, Phys. Rev. Lett. 39, 504 (1977).

[3] M. Cini, Solid State Commun. 24, 681 (1977).

[4] M. Cini, Phys. Rev. B (to be published).