Final-state and other approximations in x-ray spectra

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The final-state rule (due to von Barth and Grossman and to Mahan) for the calculation of x-ray absorption and emission spectra of a metal is considered. Limiting forms of the exact Mahan, Nozières, and de Dominicis theory, valid far from threshold, are derived and compared to this rule. It is shown for a simple model that the use of "orthogonalized final-state" orbitals provides more accurate results.

Mahan[1] has shown that the x-ray spectrum (absorption or emission) of metals can be approximated away from the threshold by the single-particle spectrum calculated using the final-state potential. That is, for absorption the x-ray transitions are to single-particle states calculated in the presence of the core hole; for emission, the potential is the same as that of the ground state. Mahan's evidence for this rule comes from numerical studies of the exact (not asymptotic) Mahan, Nozières, and de Dominicis (MND) theory[2,3] using the formulation of Combescot and Nozières.[4] Von Barth and Grossman[5] originally proposed the final-state rule, likewise from numerical studies.

In this Comment, we derive limiting forms for both absorption and emission, valid far from threshold, and compare them to the final-state rule. Our simple derivation provides insight as to why the final-state rule is reasonable. Further, we show that it can be improved by orthogonalization of the final states to the occupied initial states.

The Hamiltonian[3] for the conduction electrons in the absence of a core hole is

$$H_i=\sum_k \epsilon_k a_k^\dagger a_k , \tag{1}$$

where k denotes wave vector, band index, and spin; $a_k^\dagger$ is a creation operator for the kth orbital whose energy is ϵ_k. When the core hole is present,

$$H_f=\sum_k \epsilon_k a_k^\dagger a_k+\sum_{kk'} V_{kk'} a_k^\dagger a_{k'} , \tag{2}$$

where $V_{kk'}$ represents the interaction with the core hole.

For absorption, the initial state is the ground state

$$\Phi_g=\prod_{k=1}^{L} a_k^\dagger|0\rangle , \tag{3}$$

where $k=1,2,\ldots,L$ are the L lowest energy orbitals and $|0\rangle$ is the vacuum. The ground-state energy is

$$E_g=\sum_{k=1}^{L}\epsilon_k . \tag{4}$$

The final states are eigenfunctions of H_f which can be put into one-electron form by letting

$$a_k=\sum_n S_{kn} c_n , \tag{5}$$

where

$$(\epsilon_k-\omega_n)S_{kn}+\sum_{k'} V_{kk'}S_{k'n}=0 . \tag{6}$$

Then

$$H_f=\sum_n \omega_n c_n^\dagger c_n . \tag{7}$$

A final state is (letting α stand for the set $\{n_1,n_2,\ldots,n_{L+1}\}$)

$$\phi_\alpha=b^\dagger\prod_{i=1}^{L+1} c_{n_i}^\dagger|0\rangle , \tag{8}$$

with energy

$$E_\alpha=\sum_{i=1}^{L+1}\omega_{n_i}-\epsilon_c , \tag{9}$$

where $b^\dagger$ creates a core electron with orbital energy ϵ_c.

Let the dipole transition operator be

$$H_1=\sum_k \langle k|T|\text{core}\rangle a_k^\dagger b+\text{H.c.} \tag{10}$$

The transition rate for absorption is (E is the photon energy)

$$W(E)=(2\pi/\hbar)\sum_\alpha |\langle\phi_\alpha|H_1|\Phi_g\rangle|^2\delta(E+E_g-E_\alpha) . \tag{11}$$

The transition matrix element is

$$\langle\phi_\alpha|H_1|\Phi_g\rangle=(-1)^{L+1}\begin{vmatrix}\langle\tilde{n}_{L+1}|T|\text{core}\rangle & \langle\tilde{n}_1|T|\text{core}\rangle & \langle\tilde{n}_2|T|\text{core}\rangle & \cdots & \langle\tilde{n}_L|T|\text{core}\rangle\\ S^*_{1n_{L+1}} & S^*_{1n_1} & S^*_{1n_2} & \cdots & S^*_{1n_L}\\ S^*_{2n_{L+1}} & S^*_{2n_1} & S^*_{2n_2} & \cdots & S^*_{2n_L}\\ \cdots & \cdots & \cdots & \cdots & \cdots\\ S^*_{Ln_{L+1}} & S^*_{Ln_1} & S^*_{Ln_2} & \cdots & S^*_{Ln_L}\end{vmatrix}, \tag{12}$$

where

$$\langle\tilde{n}|T|\text{core}\rangle=\sum_{k=L+1}^{N}S^*_{kn}\langle k|T|\text{core}\rangle \tag{13}$$

and N is the number of ground-state orbitals.

If the sum on k in (13) were from 1 to N, $\langle\tilde{n}|T|\text{core}\rangle$ would be the single-particle matrix element between the nth orbital (in the final-state potential) and the core level. In fact, $|\tilde{n}\rangle$ is the nth orbital with its projection on the ground-state Fermi sea removed:

$$|\tilde{n}\rangle=|n\rangle-\sum_{k=1}^{L}S_{kn}|k\rangle\,. \tag{14}$$

Note that $\langle\tilde{n}|\tilde{n}\rangle\neq1$. Of course, the sum can be extended to all k in (13) without changing the value of the determinant in (12); however, from numerical studies we have found form (14) preferable to use in the approximate formulas which follow.

For E far above the threshold energy $E_T=E_0-E_g$ (E_0 is the minimum E_α), the states E_α which contribute to (11) have $n_{L+1}\gg L$ (i.e., $\omega_{n_{L+1}}\gg\epsilon_L=\epsilon_F$) with the remaining $n_i\ll n_{L+1}$, $i=1,2,\ldots,L$. (If some of the n_i are large compared to L, the overlap of $\{n_1,n_2,\ldots,n_L\}$ with $\{k=1,2,\ldots,L\}$ is negligible.) The elements of the first column of (12) of the form $S^*_{kn_{L+1}}$, $k=1,2,\ldots,L$, are small and can be set equal to zero. In this case (12) becomes

$$\langle\phi_\alpha|H_1|\Phi_g\rangle\simeq(-1)^{L+1}\langle\tilde{n}_{L+1}|T|\text{core}\rangle\begin{vmatrix}S^*_{1n_1} & S^*_{1n_2} & \cdots & S^*_{1n_L}\\ S^*_{2n_1} & S^*_{2n_2} & \cdots & S^*_{2n_L}\\ \cdots & \cdots & \cdots & \cdots\\ S^*_{Ln_1} & S^*_{Ln_2} & \cdots & S^*_{Ln_L}\end{vmatrix}. \tag{15}$$

Denoting the set $\{n_1,n_2,\ldots,n_L\}$ by β and letting

$$E_\beta=\sum_{i=1}^{L}\omega_{n_i}-E_g\,, \tag{16}$$

$W(E)$ can be written as

$$W(E)=\int d\omega\,W_1(\omega)\rho(E-\omega)\,, \tag{17}$$

where

$$W_1(\omega)=(2\pi/\hbar)\sum_{n=L+1}^{N}|\langle\tilde{n}|T|\text{core}\rangle|^2\delta(\omega+\epsilon_c-\omega_n) \tag{18}$$

and

$$\rho(E)=\sum_\beta|\langle\beta|\Phi_g\rangle|^2\delta(E-E_\beta)\,. \tag{19}$$

The matrix element $\langle\beta|\Phi_g\rangle$ is the determinant in (15). $W_1(\omega)$ is almost the same as the absorption given by the final-state rule; the latter can be found by replacing $\tilde{n}$ by n in (18). $\rho(E)$ is the spectral weight function[6] for core x-ray photoemission (XPS) and contains the relaxation of the Fermi sea due to interaction with the core hole:

$$E_R=\sum_{k=1}^{L}\epsilon_k-\sum_{n=1}^{L}\omega_n\,. \tag{20}$$

Equation (17) is the limiting form of $W(E)$ for $E\gg E_T$.

If the shake-up transitions inherent in $\rho(E)$ do not spread out the intensity too much compared to variations in $W_1(\omega)$, $\rho(E)$ can be replaced by $\delta(E+E_R)$ and

$$W(E)\simeq W_1(E+E_R) \tag{21a}$$

$$=(2\pi/\hbar)\sum_{n=L+1}^{N}|\langle\tilde{n}|T|\text{core}\rangle|^2\times\delta(E-(\omega_n-\epsilon_c-E_R))\,. \tag{21b}$$

In Fig. 1, we show absorption for a simple model,[6] namely, a single band (no spin) of uniform density of states and width W. The interaction $V_{kk'}$ is taken to be $-U/N$. The single-particle matrix element $\langle k|T|\text{core}\rangle$ is chosen to be constant ($T_d/\sqrt{N}$) so that in the limit $U=0$, $W(E)$ is constant. The orthogonalized final-state (OFS) approximation, using (21), produces a spectrum which is considerably closer to the exact results

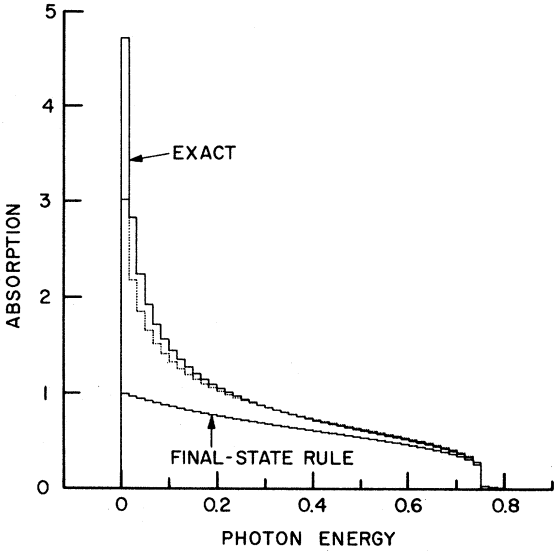

FIG. 1. Absorption spectrum for a single band (no spin) of uniform density of states with constant single-particle transition matrix elements. The absorption is in units of $(2\pi/\hbar)T_d^2/W$ and photon energy (relative to threshold) in units of W. The parameters are $N=60$, $L=15$, and $U=0.2W$. The dotted curve represents the OFS approximation. The area of the exact curve is $(N-L)/N$.

than that from the final-state rule [Eq. (21) with $\tilde{n}\to n$], which is everywhere lower. The agreement in the threshold region depends on U and would be poorer if U were increased. For larger L, the agreement is similar to that shown in Fig. 1. In the limit $L\to 0$, all three curves become identical. If the empty portion of the band were infinite in width, the replacement of $\tilde{n}$ by n for large n would have no effect and the final-state rule would agree with (21) well above threshold.

It should be noted that, for the model considered in Fig. 1, the orbital $n=1$ with energy ω_1 is a bound state. According to Ref. 4, a second threshold should occur at an energy $\omega_{L+2}-\omega_1$ above the principal threshold. The second threshold is due to system final states in which ω_1 is not occupied, whereas the first corresponds to states in which ω_1 is occupied. A second threshold does occur at a photon energy of $0.28W$ in the calculation of Fig. 1, but it is too weak to be discerned in the plot. Only if $L/N\ll 1$ and $0.1\lesssim U/W\lesssim 1.5$ do we expect to find an appreciable intensity at the second threshold. If U is small, the OFS approximation is still reasonably good above the second threshold for small L/N. However, if U is large (and L/N small), we find that the approximation which leads to (15) tends to break down, so that a different approximation may be necessary.

For emission, the initial state written in terms of holes is

$$\phi_i = b\prod_{n=L+1}^{N} c_n|\bar{0}\rangle\,, \tag{22a}$$

where

$$|\bar{0}\rangle = \prod_{n=1}^{N} c_n^\dagger|0\rangle \tag{22b}$$

and the energy is

$$E_i = \sum_{n=1}^{L}\omega_n - \epsilon_c\,. \tag{23}$$

Here $n=1,2,\ldots,L$ labels the L lowest orbitals in the presence of the core hole. The final states are of the form

$$\Phi_\nu = \prod_{i=L}^{N} a_{k_i}|\bar{0}\rangle\,, \tag{24}$$

with energy

$$E_\nu = \sum_{k=1}^{N}\epsilon_k - \sum_{i=L}^{N}\epsilon_{k_i}\,, \tag{25}$$

where ν denotes the arbitrary set $\{k_L, k_{L+1},\ldots,k_N\}$. The transition rate for emission is

$$W(E) = (2\pi/\hbar)\sum_\nu |\langle\Phi_\nu|H_1|\phi_i\rangle|^2\delta(E+E_\nu-E_i) \tag{26}$$

and the transition matrix element is

$$\langle\Phi_\nu|H_1|\phi_i\rangle = (-1)^{\begin{vmatrix} \langle\text{core}|T|\tilde{k}_L\rangle & \langle\text{core}|T|\tilde{k}_{L+1}\rangle & \langle\text{core}|T|\tilde{k}_{L+2}\rangle & \cdots & \langle\text{core}|T|\tilde{k}_N\rangle \\ S^*_{k_L L+1} & S^*_{k_{L+1}L+1} & S^*_{k_{L+2}L+1} & \cdots & S^*_{k_N L+1} \\ S^*_{k_L L+2} & S^*_{k_{L+1}L+2} & S^*_{k_{L+2}L+2} & \cdots & S^*_{k_N L+2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ S^*_{k_L N} & S^*_{k_{L+1}N} & S^*_{k_{L+2}N} & \cdots & S^*_{k_N N} \end{vmatrix}}\,, \tag{27}$$

where

$$|\tilde{k}\rangle = |k\rangle - \sum_{n=L+1}^{N} S^*_{kn}|n\rangle\,. \tag{28}$$

Here the complementary nature of absorption and emission is apparent, i.e., $|\tilde{k}\rangle$ has been orthogonalized to the initial-state sea of holes, whereas in (14) $|\tilde{n}\rangle$ was made orthogonal to the initial-state sea of electrons.

Approximations analogous to those given above

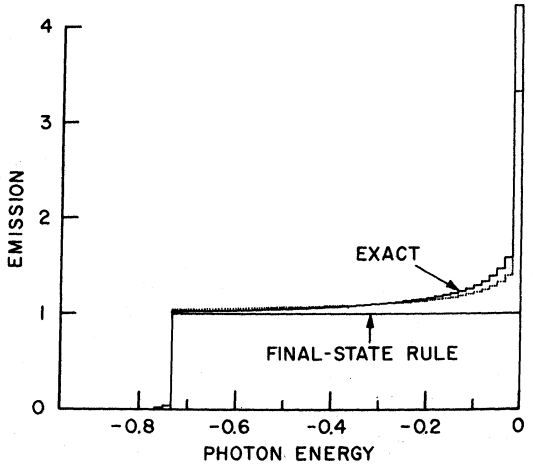

FIG. 2. Emission spectrum for a single band (no spin) of uniform density of states with constant single-particle transition matrix elements. The parameters are $N=60$, $L=45$, and $U=0.2W$. The units and labeling are the same as in Fig. 1. The area under the final-state rule curve is L/N.

for absorption may be made. For example, sufficiently far from threshold we have the following one-electron form:

$$W_1(E+E_R)=(2\pi/\hbar)\sum_{k=1}^{L}|\langle \text{core}|T|\tilde{k}\rangle|^2 \times\delta(E-(\epsilon_k-\epsilon_c-E_R))\,. \tag{29}$$

If $|\tilde{k}\rangle$ is replaced by $|k\rangle$, we obtain the final-state-rule expression.

From Fig. 2 we see that for emission, as in absorption, the proper one-electron form provides an excellent representation of the spectrum away from threshold. Use of the orthogonalized final-state orbitals [(14) for absorption and (28) for emission] produces accurate results by seemingly avoiding destructive interference artificially introduced when the bare final-state orbitals are used. Note, further, that the relationship of the final-state-rule spectrum to the exact spectrum is not, in this case, the simple multiplicative factor proposed by Mahan.[1]

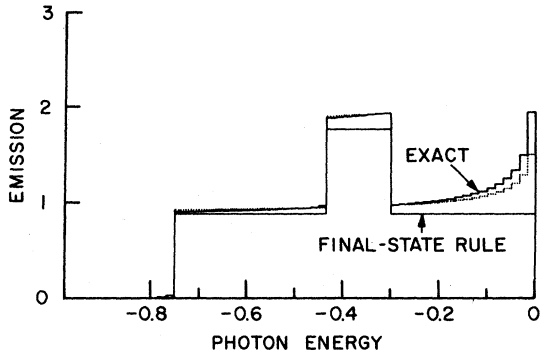

FIG. 3. Emission spectrum for a nonuniform density of states. Note that the final-state-rule results have the same shape as that of the occupied density of states. $U=0.2W$. The units and labeling are the same as in Fig. 1.

In Fig. 3, we present results for emission from a band of nonuniform density of states (ground state). The simililarity of the emission spectrum to the density of states is evident. The OFS results agree well with the exact results.

Extension of our procedures to actual potentials and densities of states should be possible.

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