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Physical content of the orthogonalized final-state rule of Davis and Feldkamp

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The orthogonalized final-state rule for x-ray absorption and emission is discussed in the light of an earlier paper by Friedel, and in the light of subsequent papers by Ramaker, and by von Barth and Grossman. It is pointed out that the orthogonalized final-state (OFS) rule deals only with the excitonic enhancement of the final-state-rule transition probability. For the models used by Davis and Feldkamp, von Barth and Grossman, and Friedel, it is shown that the orthogonalized final-state rule yields an excitonic Fermi-edge singularity which is the logarithm of the generally accepted one, and thus underestimates the excitonic enhancement near the Fermi edge. Away from the Fermi edge, the OFS rule should provide a useful evaluation of the excitonic enhancement, as was shown by Davis and Feldkamp and in their paper proposing the OFS rule.

I. INTRODUCTION

Davis and Feldkamp[1] demonstrated numerically for a simple model of x-ray emission and absorption[2] that an improvement on the well-known final-state rule could be obtained for absorption by orthogonalizing the final-state one-electron orbital to all the occupied initial-state one-electron orbitals. In emission, the orbital of the electron missing in the final state is orthogonalized to the orbitals which are unoccupied in the initial state. The numerical examples given in Figs. 1 and 2 of Ref. 1 show that this orthogonalized final-state (OFS) procedure, when used in the one-electron Fermi-golden-rule formula, is indeed an improvement on the final-state (FS) rule, compared to an exact evaluation of the many-electron formula.

Since the OFS prescription is quite simple compared to the exact calculation and since the model used to exhibit the properties of the OFS rule is a rather restricted one, a more complete discussion of the OFS rule in relation to the exact theory is warranted. That is the purpose of this paper, and it will be accomplished by deriving explicit formulas for the OFS absorption and emission matrix elements which apply to several of the models currently being used in the discussion of x-ray edge effects.

Two points about the OFS rule can be made immediately. The first point, established by Ramaker,[3] is that the OFS matrix element is in error by terms of second order and higher in the off-diagonal one-electron overlap matrix elements, because terms of these orders from the many-body expression are omitted. Since these overlap matrix elements are proportional to the strength of the core-hole potential, this puts a limitation on the use of the OFS rule, a point already discussed qualitatively in Ref. 1. The second point, not discussed in Ref. 1, but implicit in it, is that the OFS rule deals only with the excitonic enhancement[4] part of the x-ray edge effects, and does not include the effect of shakeup transitions; i.e., transitions accompanied by simultaneous excitations of the other electrons in the system.[1,2,5–11] This point needs to be kept in mind in considering applications to actual systems. It is also connected with the self-consistency of the OFS rule. The OFS excitonic enhancement is proportional to the scattering phase shift induced by the core-hole potential. However, the contributions from simultaneous excitations depend on the square of the phase shift[4] and are thus of the same order as terms already neglected in the formulation of the OFS treatment of the excitonic enhancement. Thus, some care would be required to generalize the OFS approach so as to include shakeup effects.

In the next section, formulas for the OFS matrix element will be derived which establish a third point concerning the OFS rule. This point is that the OFS rule yields an excitonic Fermi-edge singularity which is the logarithm of the accepted excitonic singularity. Thus the OFS rule is bound to underestimate this aspect of x-ray emission and absorption edges.

A logarithmic excitonic Fermi-edge singularity for absorption was obtained by Friedel in Ref. 6 for a model based on a spherically symmetric coordinate-space potential using a perturbation expansion in powers of the core-hole potential. Since, as stated above, the OFS rule is correct to first order in the core-hole potential, the results presented in the next section can be viewed, in part, as the establishment of the connection between the OFS rule and Friedel's analysis. We shall, however, carry out the derivation for the separable momentum-space model used by von Barth and Grossman.[8] This model can be rather closely related to the spherically symmetric coordinate space model,[6,11] and it includes the model used in Refs. 1, 2, and 10 as a special case.

II. ANALYSIS OF THE OFS RULE

The main ingredient of the OFS rule is the overlap matrix between the one-electron orbitals calculated in the absence or presence of the core hole. Therefore, we start by defining the model[8] from which this matrix is obtained. Let the one-band Hamiltonian H in the absence of the core hole be defined by

$$H=\sum_{k=1}^{N}\epsilon_k a_k^{\dagger}a_k\ , \tag{1}$$

where $a_k^{\dagger}$ is the creation operator for the state whose

eigenvalue is ϵ_k and the number of states is N. Let the Hamiltonian $\tilde{H}$ in the presence of the core hole be defined by

$$\tilde{H}=H+\sum_{k,k'} V_{kk'}a_k^\dagger a_{k'} . \tag{2}$$

These are Eqs. (2.8) and (2.9) of Ref. 8. In Ref. 1, H is designated as H_i and $\tilde{H}$ is designated as H_f, as would be appropriate for x-ray absorption. Following Ref. 8,

$$V_{kk'}=V_0 p_{ck}^* p_{ck'} , \tag{3}$$

where

$$p_{ck}=\langle \text{core} \mid T \mid k \rangle , \tag{4}$$

and, in the notation of Ref. 1, $\langle \text{core} \mid T \mid k \rangle$ is the one-electron dipole matrix element between the core orbital and the eigenfunction $\mid k \rangle$ of H. Once N, V_0, the ϵ_k and the p_{ck} are given, the model is defined. The model used in Refs. 1 and 2 can be described by $\epsilon_k=(W/N)(k-\frac{1}{2}N-\frac{1}{2})$, where W is the bandwidth, $p_{ck}=T_d/N^{1/2}$, and $V_0T_d^2=-U$. Here T_d and U are constants. In Ref. 8, the spacing of the levels ϵ_k is assumed to vary slowly with k. Adopting a notation similar to that in Ref. 8, we define a density of states $D(\epsilon_k)=(\epsilon_{k+1}-\epsilon_k)^{-1}$.[12]

The statement of the OFS rule requires the expression for the overlap matrix elements S_{kn}. Let the eigenfunctions and eigenvalues of $\tilde{H}$ be designated by $\mid k\sim \rangle$ and $\tilde{\epsilon}_k$, respectively. From Eqs. (1)—(3) one obtains the convenient expression,

$$S_{kn}=\langle k \mid n\sim \rangle=\frac{V_0 p_{ck}^* \tilde{p}_{cn}}{\tilde{\epsilon}_n-\epsilon_k} , \tag{5}$$

which, however, still contains S_{ij} through $\tilde{p}_{cn}=\langle \text{core} \mid T \mid n\sim \rangle$. If we set $c_n \equiv -V_0\tilde{p}_{cn}$, we can find c_n from the required unitarity of the matrix $||S_{kn}||$.[13] The $\tilde{\epsilon}_n$ are sandwiched between consecutive ϵ_k ,[14] and they satisfy the eigenvalue equation,[2,5,10]

$$\sum_{k=1}^{N} \frac{V_0 \mid p_{ck} \mid^2}{(\tilde{\epsilon}_n-\epsilon_k)}=1 , \quad 1\le n\le N . \tag{6}$$

We are now in a position to discuss the OFS rule of Davis and Feldkamp.

By definition in Eqs. (14) and (28) of Ref. 1, the orthogonalized final states for absorption $\mid \bar{n}\sim \rangle$ and emission $\mid \bar{k} \rangle$ are given by

$$\mid \bar{n}\sim \rangle = \mid n\sim \rangle - \sum_{k=1}^{L} S_{kn} \mid k \rangle \quad \text{(absorption)} , \tag{7a}$$

$$\mid \bar{k} \rangle = \mid k \rangle - \sum_{n=L+1}^{L} S_{kn}^* \mid n\sim \rangle \quad \text{(emission)} . \tag{7b}$$

As in Ref. 1, the bar above n or k identifies the OFS. These OFS are used in the Fermi golden rule formula, Eqs. (21b) and (29) of Ref. 1 to find the x-ray absorption and emission rates. In these formulas, electron shakeup is neglected so $L+1\le n\le N$ and $1\le k\le L$, where L numbers the highest occupied orbital in the initial state. The final-state rule is obtained by using the states $\mid n\sim \rangle$ and $\mid k \rangle$ in the golden rule expressions. In addition to the neglect of shakeup transitions, the many-electron overlap determinant which appears in Eqs. (15) and (19) of Ref. 1 is eliminated in the formulation of the golden-rule equations, so that the Anderson nonorthogonality factor[15] has been set equal to unity. Thus, as stated in the introduction, the OFS procedure based on Eqs. (7a) and (7b), is an approximate treatment of the excitonic enhancement of the final-state rule matrix elements. When Eqs. (5), (7a) and (7b) are used to compute the dipole matrix elements. When Eqs. (7a) and (7b) are used to compute the dipole matrix elements $\langle \text{core} \mid T \mid \bar{n}\sim \rangle$ and $\langle \text{core} \mid T \mid \bar{k} \rangle$, the equations

$$\frac{\langle \text{core} \mid T \mid \bar{n}\sim \rangle}{\langle \text{core} \mid T \mid n\sim \rangle}=1-\sum_{k=1}^{L} \frac{V_o \mid p_{ck} \mid^2}{\tilde{\epsilon}_n-\epsilon_k} \quad \text{(absorption)} , \tag{8a}$$

$$\frac{\langle \text{core} \mid T \mid \bar{k} \rangle}{\langle \text{core} \mid T \mid k \rangle}=1-\frac{1}{V_0}\sum_{n=L+1}^{N} \frac{\mid c_n \mid^2}{\tilde{\epsilon}_n-\epsilon_k} \quad \text{(emission)} \tag{8b}$$

are obtained. In Eq. (7a), $L+1\le n\le N$ and in Eq. (7b) $1\le k\le L$. Since in applications $V_0<0$, the sums in Eqs. (7a) and (7b) are positive. The squares of the right-hand sides of Eqs. (7a) and (7b) are the OFS rule excitonic enhancement factors to be applied to the final state rule transition rates for x-ray absorption and emission.

Equations (8a) and (8b) exhibit the logarithmic Fermi-edge singularity of the OFS excitonic enhancement factors. Since the factors $\mid p_{ck} \mid^2$, $\mid c_n \mid^2$, and $\tilde{\epsilon}_n-\epsilon_n$ are slowly varying functions, the essential part of the summands in Eqs. (8a) and (8b) is $(\epsilon_n-\epsilon_k)^{-1}$, which leads to a logarithmic singularity at the Fermi edge. This establishes the third point described in the introduction. The logarithmic Fermi-edge singularity resulting from the OFS rule was not discussed in Ref. 1. However, Fig. 1 of Ref. 1 exhibits this behavior for $N=60$.[16]

It is straightforward to relate the OFS excitonic enhancement given in Eqs. (8a) and (8b) to the result obtained by Friedel[6] for a spherically symmetric coordinate-space potential. We evaluate Eqs. (8a) and (8b) to first order in $V_{k'k}$. Then $\tilde{\epsilon}_n\approx\epsilon_n+V_0 \mid p_{cn} \mid^2$, $\mid c_n \mid^2=v_0^2 \mid \tilde{p}_{cn} \mid^2\approx V_0^2 \mid p_{cn} \mid^2$, and near the Fermi edge $\tilde{\epsilon}_n-\epsilon_m\approx(n-k)/D(\epsilon_L)$. Also,

$$-V_0 \mid P_{cL} \mid^2 D(\epsilon_L)\approx\delta(\epsilon_L)/\pi ,$$

where $\delta(\epsilon_L)$, is the scattering phase shift.[5,6,8,10] Inserting these approximations into Eq. (8a) and squaring, one obtains, for n close to L and L large,

$$\left[\frac{\langle \text{core} \mid T \mid \bar{n}\sim \rangle}{\langle \text{core} \mid T \mid n\sim \rangle}\right]^2 \approx 1+\frac{2\delta(\epsilon_L)}{\pi}\ln\left[\frac{L}{n-L}\right] . \tag{9}$$

Equation (9) exhibits the replacement collision[6,7] enhancement given in Eq. (10) of Ref. 6, where the symbol N stands for our L and N_c is a cutoff of order L. As Friedel points out, this is the first term in the expansion of the accepted edge singularity

$$\left[\frac{\epsilon_L}{\epsilon_n-\epsilon_L}\right]^{2\delta(\epsilon_L)/\pi} \approx 1+\frac{2\delta(\epsilon_L)}{\pi}\ln\left[\frac{\epsilon_L}{\epsilon_n-\epsilon_L}\right] . \quad (10)$$

Thus, the OFS rule exhibits the same logarithmic Fermi-edge singularity for absorption and emission as results from first-order perturbation theory. This is not surprising in the light of Ramaker's error estimate.[3] On this basis, one should be able to obtain the main content of the OFS rule to first order in V_0 by carrying out the appropriate simplification of the overlap determinants in the many-body theory. This is what Friedel did for absorption, and it is not hard to recognize Eq. (7a) above in Eq. (7) of Ref. 6.[17] Equation (9) was obtained here from the momentum-space model defined in Eqs. (1)—(4). It can also be obtained from the OFS rule formulated directly for a spherically symmetric coordinate-space potential,[6,8,11,15] starting with Eqs. (7a) and (7b). In place of Eq. (5) for S_{kn} one uses large N the structurally identical expression,

$$S_{kn}=\sin\delta(\epsilon_n)/[(k-n)\pi+\delta(\epsilon_n)] ,$$

derived in Refs. 6 and 15.

A completely analogous comparison can be made with the results of Ref. 4 for x-ray emission, this time in the context of a continuous single-band spectrum. Appendix B of Ref. 4 gives the required expression for S_{kn} and all the other relations needed to evaluate Eqs. (7b) and (8b). Retaining in part a discrete notation for ease in comparison with Ref. 4,

$$\frac{\langle \text{core}\,|\,T\,|\,\bar{k}\rangle}{\langle \text{core}\,|\,T\,|\,k\rangle}=1-V_0\sum_{n=L+1}^{N}\frac{|p_{cn}|^2}{\epsilon_n-\epsilon_k}\frac{1}{F_n} , \quad (11)$$

where

$$F_n=\left[1-V_0\int\frac{A(\epsilon')d\epsilon'}{\epsilon_n-\epsilon'}\right]^2+\pi^2V_0^2A(\epsilon_n)^2 , \quad (12)$$

and $A(\epsilon_k)=|p_{ck}|^2D(\epsilon_k)$.[18] The logarithmic Fermi-edge singularity of the OFS rule is apparent. Section VI of Ref. 4 solves the excitonic enhancement problem accurately for the model considered here by evaluating the many-body overlap matrix determinants through the solution of the integral equation (6.9) of Ref. 4. The results given in Eqs. (6.14) and (6.15) of Ref. 4 are an excitonic enhancement with the correct Fermi-edge singularity analogous to the left-hand side of Eq. (10). It is readily seen that the OFS result from Eqs. (11) and (12) is equivalent to solving the integral equation (6.9) of Ref. 4 to lowest order in V_0 and using the result in Eq. (6.2) of Ref. 4 for the transition rate.

III. DISCUSSION

As shown above, the orthogonalized final-state rule of Davis and Feldkamp yields transition rates close to those obtained by an evaluation of the excitonic enhancement of the final-state rule to first order in the core-hole potential. The Fermi-level-edge singularity resulting from the OFS rule is the logarithm of the accepted singularity. Therefore, as already shown in Ref. 1, the OFS rule works best away from the Fermi level. Exact calculations are possible for the models discussed here. Therefore, the sphere of application of the OFS rule would naturally be to more complex Hamiltonians for which the overlap matrix in Eqs. (7a) and (7b) is available; for example, from self-consistent-field calculations.

If the important scattering phase shifts $\delta_l(\epsilon_L)$ are available, a completely different approach to the final-state rule is possible.[4,5,8] In this method, the final-state rule transition rates are corrected for excitonic enhancement and shakeup effects by multiplying them by the asymptotic Mahan—Nozieres—De Dominicus Fermi-edge factor.[4,5,8] In the cases studied thus far,[8] the result is a rather accurate shape for the emission and absorption bands. An independent determination of the overall normalization is required in this approach, if absolute transition rate are desired.[8]

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[14]See Fig. 1 of Ref. 2, for example.
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[16]A computer indexing problem caused the points for Fig. 2 of

Ref. 1 to be misplotted. A corrected graph is available from the authors. The last six values in the OFS bar graph should be 1.25, 1.29, 1.33, 1.40, 1.51, and 1.80, and the last six exact values should be 1.34, 1.39, 1.47, 1.58, 1.78, and 2.40, as communicated by the authors of Ref. 1. These values suffice for intercomparison of the OFS and exact results near the Fermi edge. Elsewhere, the two are in close agreement.

[17]In Eq. (7) of Ref. 6, the left-hand absolute-value bar should be placed to the left of d and u_{rn}, which corresponds to our S_{rn}, should be multiplied by (-1).

[18]Equations (11) and (12) can be obtained from the discrete formulation in Eq. (8b) by expanding Eq. (6) in powers m of $(\tilde{\epsilon}_n-\epsilon_n)/(\epsilon_n-\epsilon_k)$ for each $k\neq n$ and keeping just the powers $m=0$ and 1. By solving the resultant quadratic equation for $\tilde{\epsilon}_n-\epsilon_n$ and using the results to evaluate c_n in Eq. (8b), one obtains Eqs. (11) and (12) in the limit of large N, thanks to the result that $\sum_1^\infty k^{-2}=\pi^2/6$.