

High-Energy Photoexcitation in Solids

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We formulate an expression for the single-electron photoexcitation cross section, $\sigma(\omega)$, exploiting the orthogonality of the final electron eigenstate to the occupied states of the excited solid. We find that σ depends significantly on the final-state angular momentum. The predictions of a simple model calculation correspond closely with experimental photoabsorption in several metals, as shown explicitly for the K shell in Li and the K and L shells in Al.

The cross section, $\sigma(\omega)$, for the photoexcitation of an electron from a deep core state to a continuum state in a complex molecule or solid has recently received a considerable amount of attention as a potential source of information about the local environment of particular atom species. This possibility hinges on two properties of the excitation: The threshold energy identifies the atom species of the core electron; the energy dependence of σ above threshold is sensitive to only the immediate environment of that atom because of the short mean free path of the excited electron. In the following formulation of an expression for σ , we depart markedly from previous treatments¹⁻⁵ in that we exploit the orthogonality of the final electron eigenstate to the occupied states of the excited solid. To evaluate the resulting expression, we introduce a simple model which exhibits the primary structural information contained in σ . Each crystal structure yields its own distinct signature. We find a significant dependence of σ on the angular momentum of the final state. This explicit l dependence has not been reported in previous formulations, although observed experimentally.⁶ The relative positions and shapes of the oscillations in our expression correspond closely to those in the experimental cross sections for photoabsorption in a number of metallic solids, as shown explicitly for excitations from the K shell in Li and from the K and L shells in Al.

The total cross section for the photoexcitation of a single electron from a core state j with energy E_j by the absorption of a quantum $\hbar\omega$ from the radiation field is⁵

$$\sigma_j(\omega) = 4\pi^2\alpha\hbar\omega [1 - f(E)] \langle j | \hat{\epsilon}_{\vec{k}\lambda} \cdot \vec{r} \{ - (2\pi i)^{-1} [G^+(E) - G^-(E)] \} \hat{\epsilon}_{\vec{k}\lambda} \cdot \vec{r} | j \rangle, \quad (1)$$

where α is the fine structure constant, $\hat{\epsilon}_{\vec{k}\lambda}$ is the unit electric field vector associated with propagation vector \vec{k} and polarization λ , \vec{r} is the position operator, $E = E_j + \hbar\omega$, and G is the Green's function of the full solid Hamiltonian, H . We have neglected all multielectron excitations. The Fermi factor, $f(E)$, has been introduced to exclude explicitly all excitations to occupied states, and we are free to modify or eliminate their contributions to G . Accordingly, we will depart from previous treatments¹⁻⁵ by replacing G with QGQ in Eq. (1), where

$$Q = 1 - \sum_c |c\rangle\langle c|. \quad (2)$$

The sum in Eq. (2) extends over all of the core states of H , taken to be the eigenstates of isolated atomlike potentials and nonoverlapping when associated with different sites. Let us introduce a more general operator R , where

$$R = 1 - \sum_c |g_c\rangle\langle c| \quad (3)$$

and the $|g_c\rangle$ are arbitrary vectors. Finally, let

$H = H_0 + V$, where H_0 is the Hamiltonian of an electron in the presence of the excited core and V is the contribution of the remainder of the system. With these definitions, it is straightforward to demonstrate that

$$QGQ = QG_0Q + QG_0T_RG_0Q, \quad (4)$$

where G_0 is the Green's function of H_0 and T_R is the T matrix of the potential VR ,

$$T_R \equiv [1 - VRG_0]^{-1}VR. \quad (5)$$

When QGQ is substituted for G in Eq. (1), the effect of Q is to "orthogonalize" G_0 to the occupied states of H , modifying substantially the dipole matrix element between the initial state and G_0 . For example, the presence of Q typically suppresses strongly the $2p$ transition to ϵs relative to ϵd , consistent with experiment.³

The effect of R on σ depends upon the choice of the $|g_c\rangle$, which can be selected to optimize the convergence of the procedure used to calculate

T_R . For the purposes of this work it is sufficient to consider the effect for R equal to Q , a case which has been examined often in pseudopotential theory.⁷ The relevant back-scattering matrix elements, $\langle -k | V Q | k \rangle$, are usually positive over most of the range of interest here, as can be verified readily for a single core with a simple calculation. This repulsive interaction is in sharp contrast with the attractive first-order interaction expected everywhere for a simple electrostatic potential (V). It will be seen that this repulsion is completely consistent with experiment.

In order to examine the primary structural information contained in $\sigma(\omega)$, we will introduce a model which is especially appropriate for isotropic simple metals. The potential of the excited core will be neglected. We will include in G_0 , however, a factor of $\exp[-\mu(E)r_s]$,^{4,5} which can be shown to represent quite well the effect of an imaginary self-energy correction for lifetime or mean-free-path limiting effects. With regard to T_R , we will neglect multiple-site scattering and replace the array of single-site scatterers with spherically symmetric δ -function shells of strength $N_s V_0$ (N_s atoms of strength V_0 in shell s). The radii of these shells, r_s , are chosen to equal the appropriate excited-core to atom distances. These approximations yield the following simple expression for photoabsorption from the nl core shell:

$$\sigma_{nl}(\omega) = \sum_{l' = l \pm 1} \sigma_{nl l' 0}(\omega) [1 + \Delta_{l'}(\omega)] \quad (6)$$

where

$$\Delta_{l'}(\omega) = \frac{-V_0 k}{2\pi} \sum_s N_s \exp[-\mu(E)r_s] \times \text{Im}[h_{l'}^+(kr_s)]^2, \quad (7)$$

$h_{l'}^+$ is the spherical Hankel function of the first kind,⁸ and $k = (2E)^{1/2}$. These expressions differ from the results of other treatments⁹ by the presence of an explicit functional dependence on the angular momentum of the final state through $h_{l'}^+$. The agreement between our formulation and experiment depends critically on the combined effect of this l dependence and the introduction of orthogonalization.

The σ^0 factor in Eq. (6) contributes a broad, atomlike background to the cross section, essentially featureless except for the threshold.³ The only short-period oscillations in σ come from Δ , and are a manifestation of the local environment through the shell radii. In the following, we will

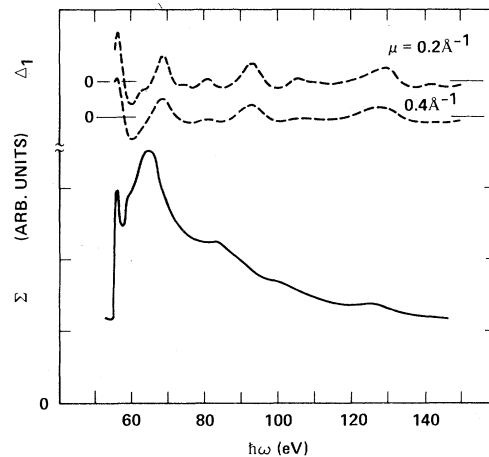


FIG. 1. Δ_1 calculated for the K shell in Li (bcc) with μ as indicated, plotted together with the experimental Σ (see Ref. 9) as a function of photon energy.

compare Δ directly with the experimental cross sections.

Δ is completely determined to within an arbitrary scale factor (V_0) by the shell radii of the appropriate structure and by μ . In Figs. 1 and 2 we have plotted Δ_l for constant μ together with the experimental cross sections, Σ , for K -shell absorption in Li (bcc)¹⁰ and for both K - and L -shell absorption in Al (fcc).^{10,11} For the case of L -shell absorption, we have plotted Δ_2 since the $2p$ -to- ϵd transition is expected to dominate.³ Examining the short-period oscillations superimposed on the smooth background, note the strong correlation between theory and experiment in the relative positions and shapes of the oscillations—the signature of the spectrum. We have found a similar correspondence for the K shell of Be (hcp) and the L shells of Na (bcc) and Mg (hcp). Each structure considered was found to have its own distinct signature, a critical property from the standpoint of structure determination.

The experimentally observed variation in Σ between the K and L shells of Al is accounted for quite well by our theory. The predicted zeroth-order l dependence is evident in the leading term in $\text{Im}[\rho h_{l'}^+(\rho)]^2$ in powers of $1/\rho$: $(-1)^l \sin(2\rho)$. Although Shiraiwa, Ishimura, and Sawada¹ were cautious about the l dependence and noted that their expression for Δ was applicable only to K -shell absorption, there is no evidence that either Ritsko, Schnatterly, and Gibson³ or Ashley and Doniach⁵ took account of this effect. The importance of explaining the observed dependence of Σ on the angular momentum of the final state has been stressed by Fano.⁶

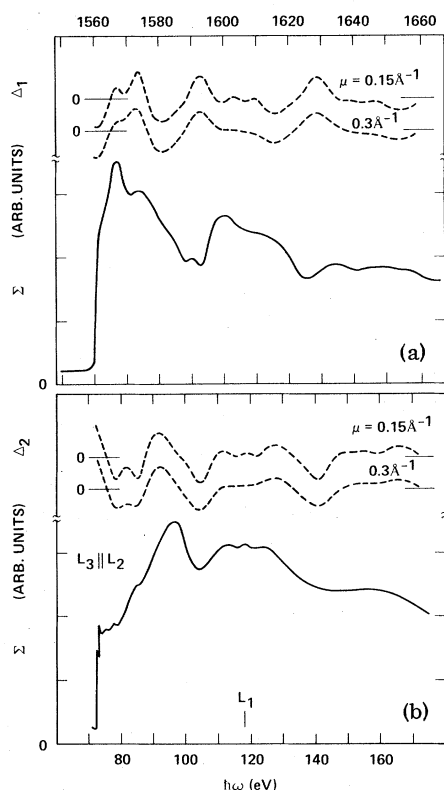


FIG. 2. (a) Δ_1 calculated for the K shell in Al (fcc) with μ as indicated, plotted together with the experimental Σ (see Ref. 10) as a function of photon energy. (b) Δ_2 and Σ for the L shell in Al (fcc) (see Ref. 9) plotted as in (a).

We let V_0 be a positive constant in each calculation of Δ , equivalent to a repulsive interaction between the outgoing electron and the surrounding atoms. Having treated the l dependence properly, we found that this choice of V_0 corresponds well with experiment over most of the energy range of interest. As discussed earlier, this finding is consistent with our considerations of orthogonalization.

In each figure, we have plotted Δ for that constant value of μ which gives the best overall fit to experiment, and also for a μ of one-half that magnitude in order to show the signature in more detail. The same values of μ are used for both K and L shells in Al. As expected, increasing the value of μ decreases the rapid oscillations due to more distant shells. An energy-dependent μ would have no effect other than allowing more structure at very low and very high energies, where experiments indicate that the mean free

paths are the longest.¹² The sensitivity of Δ to the value chosen for μ suggests the possibility of obtaining an experimental estimate of μ from Σ . In Li, for example, μ appears to vary from approximately 0.2 \AA^{-1} at 5–10 eV to 0.4 \AA^{-1} at 25 eV above threshold. Finally, note that the small values of μ expected in the immediate vicinity of threshold should produce very sharp variations of Δ with energy. The neglect of this variation in treatments of the “edge singularity” in metals¹³ is a potentially serious omission.

We have shown that most features of the photoabsorption cross section can be understood qualitatively through proper treatment of two aspects of the final electron state—its angular momentum and its orthogonality to the occupied states of the excited solid. A quantitative treatment of the photoexcitation background, σ^0 , and of the backscattering potential of individual atoms will be needed to establish a detailed correspondence between theory and experiment. Understanding the experimental manifestations of these and other effects will be greatly facilitated by the essential simplicity of our approach.

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