

Single-scattering theory of x-ray absorption

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We describe an independent-particle theory of x-ray absorption in condensed matter, which is similar to extended x-ray-absorption fine-structure theory in only retaining a single backscattering from near neighbors but which properly treats the spatial variation of the scattered wavelets. This slight modification yields a good description of the relevant features of the spectra down to the absorption edge, without increasing the computational burden. This success is illustrated by a model calculation for the *K*-edge spectrum of copper.

With the increasing number of synchrotron radiation sources there has been a growing interest in the x-ray-absorption structure due to core excitations. For historical reasons, the theoretical and conceptual viewpoints applied to this problem have been quite different depending on whether one is considering structure far above threshold: EXAFS (extended x-ray-absorption fine structure) or near threshold: XANES (x-ray-absorption near-edge structure). Within a single-particle treatment of the final electron state, the former is considered to be due to short-range order while the latter is attributed to long-range order.¹ Corresponding to these views, the theoretical approach to EXAFS is via a few single-scattering events from the near neighbors for the outgoing final electron²⁻⁴ while for XANES one resorts to band-structure calculations.⁵ It has been shown, however, that a complete treatment from either point of view should lead to the same result.⁶ This was substantiated by Durham *et al.* who extended the short-range approach beyond the standard EXAFS formula by including multiple-scattering events.⁷ The improved scheme was recently applied successfully to calculate the XANES of copper among other systems.⁸ Although this scheme has clear advantages compared with the band-structure method (e.g., it can be applied to disordered materials⁹) it is still computationally involved.

In this Brief Report we present a single-scattering theory of x-ray absorption valid for any energy above threshold. It reduces to the standard EXAFS formula in the high-energy region, but it provides an appreciable improvement at low energies without increasing the computational burden. We illustrate the usefulness of the formula with a calculation of the *K*-edge absorption spectrum of copper. We compare the single-scattering result with that of a band-structure calculation and of a standard EXAFS calcu-

lation, all three done for the same structure, the same scattering potential (which we take to be a periodic muffin-tin potential), and with the same broadening function. Note that this is only a comparison between single-particle theories. Our aim is not to assess possible many-body effects at this time, but instead to examine whether single-particle computations can be speeded up with little loss in accuracy. We show that the single-scattering approach not only yields results of useful accuracy over the entire energy range, but also offers a different conceptual view of the source of the near-edge structure. For the case of copper, for example, we find that the XANES can actually be explained without invoking multiple scattering as suggested in Ref. 8.

For the sake of brevity we shall not derive our formulas here but, instead, merely show how their final form differs from that of the standard EXAFS theory. In fact, although the explicit results are new, equations equivalent to ours have been studied before well above threshold. The quantity of interest is μ_c , the contribution to the x-ray-absorption coefficient due to dipole excitation of a deep core level. When the absorbing atoms are in a cubic environment or when one is considering a polycrystalline sample, it is appropriate to average over the x-ray polarization, obtaining^{3,4}

$$\mu_c = A \hbar \omega N_0 [l M_{l-1}^2 \chi_{l-1} + (l+1) M_{l+1}^2 \chi_{l+1}] \quad (1)$$

where l is the orbital angular momentum of the core level and the sum over its azimuthal quantum number m has been done. The constant out front is given by $A = (16\pi^3/3)(e^2/\hbar c) n_c$, where n_c is the density of absorbing atoms, ω is the x-ray frequency, and $N_0 = mk/\pi^2 \hbar^2$ is the free-electron density of states, with k determined by the final-state kinetic energy $E = \hbar^2 k^2/2m$. The M 's are atomic radial in-

tegrals and the χ 's incorporate the influence of the neighboring atoms, i.e., if the χ 's were unity, (1) would describe the absorption of isolated atoms. The standard EXAFS formula for χ_l is given by²⁻⁴

$$\chi_l = 1 + (-)^l \sum_j N_j \text{Im} \left(e^{2i\delta_l} \frac{e^{2ikR_j}}{kR_j^2} f(\pi) \right), \quad (2)$$

where Im denotes imaginary part and the sum on j is over shells of neighbors, each containing N_j atoms at a distance R_j from the origin. The δ_l are the scattering phase shifts of the absorbing atom and $f(\pi)$ is the backscattering amplitude of a single neighboring atom. All these scattering properties are to be evaluated at the energy E , which is measured from the muffin-tin zero of the potential.

Equations (1) and (2) include fully the effect of the potential of the central atom but treat those of the neighboring atoms only via single backscattering events. Furthermore, in order to simplify the final result one has approximated the intersite propagators. These propagators are linear combinations of outgoing spherical Bessel functions $h_l^+(\rho)$ with $\rho = kR$. Using the expansion¹⁰

$$i^l h_l^+(\rho) = \frac{e^{i\rho}}{\rho} \left(1 + i \frac{l(l+1)}{2\rho} + \dots \right), \quad (3)$$

one may replace each $i^l h_l^+(\rho)$ by $e^{i\rho}/\rho$ for $\rho \gg l^2$, i.e., far above threshold.

It is precisely this last replacement that we do *not* wish to make here. In other words, we include the same scattering events as in the standard EXAFS treatments but we do not approximate the propagators that take the final-state electron from one scattering center to another. As noted above, such an improvement has already been explored in several cases well above threshold.^{4,11} However, in none of these studies was it suggested that one had thereby obtained formulas that apply in the supposed multiple-scattering regime close to the absorption edge. The purpose of this paper is to examine this intriguing possibility. The generalized expression we use for this test is

$$\chi_l = 1 + \sum_j N_j \text{Im} \left(e^{2i\delta_l} \sum_{\bar{l}} (2\bar{l}+1) e^{i\delta_{\bar{l}}} \sin \delta_{\bar{l}} H(l, \bar{l}; kR_j) \right), \quad (4)$$

where the $\delta_{\bar{l}}$ are the phase shifts of the neighboring atoms, and

$$H(l, \bar{l}; \rho) = \sum_{l'} (2l'+1) \left[\left(\frac{\bar{l}!}{l!} \right) h_{l'}^+(\rho) \right]^2, \quad (5)$$

with the first factor in the square bracket being a $3j$ symbol.¹⁰ Far from the edge, one may show that $H(l, \bar{l}; \rho) \rightarrow (-)^{l+\bar{l}} e^{2i\rho}/\rho^2$, which, in turn, converts (4) to (2). In a forthcoming paper we shall present a

detailed derivation of (4) as well as its generalization to allow for noncubic symmetry and for spin-orbit coupling in the core level.¹²

Before turning to a numerical illustration of our formulas we briefly comment on their possible *a priori* justification. From the viewpoint of single-particle theory, the only error in our approach is the omission of higher-order multiple-scattering events. These extra terms might be small for either of the following reasons: First, the scattering off neighboring atoms could be intrinsically weak over certain ranges of energy, and second, the net electron amplitude for a long multiple-scattering path may be reduced by the energy blurring due to inelastic collisions, the core-hole lifetime, and detector resolution. The first reason will always apply at high energy while the latter, which has also been invoked in low-energy-electron diffraction theory,^{13,14} is present to some extent at all energies.

Let us now consider a specific example. Figure 1 shows the single-scattering K -edge absorption spectrum of copper together with the results of a band-structure calculation and of a standard EXAFS calculation. The solid has been represented by a periodic potential with fcc structure and lattice parameter $a = 3.615 \text{ \AA}$, ignoring any effects due to the localized core hole. This is a requirement of our band-structure scheme and is also used in the other two cases for consistency. The potential, which has muffin-tin form, is constructed from a superposition of self-consistent Dirac-Slater atomic potentials using the Mattheiss prescription.¹⁵ This potential construction has been shown to be quite adequate for the cal-

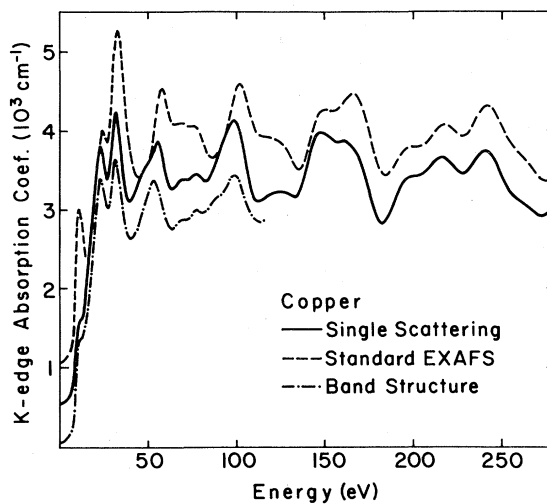


FIG. 1. Comparison between the single-scattering, the standard EXAFS, and the band-structure K -edge absorption spectra of copper. The energies are measured with respect to the muffin-tin zero of the potential, whereby the threshold energy is $E_F = 8.96 \text{ eV}$.

ulation of unoccupied states in close-packed metals.⁵

The band-structure calculation is based on a linearized version of the augmented plane-wave method, especially designed to cover large energy ranges.¹⁶ The crystal potential enters the scheme through energy-dependent logarithmic derivatives at the muffin-tin radius, which have been calculated including all scalar relativity terms. Using 180 basis functions, a k -space integration mesh with 252 points in the irreducible part of the Brillouin zone, and a partial-wave expansion carried up to $l_{\max}=6$, we have verified that the energies are converged to 0.1 eV and the wave functions to 1%.

In both the single-scattering and the standard EXAFS calculations we include the contribution of the first 11 shells of neighbors and partial waves up to $l_{\max}=10$. The partial-wave sum is quite converged, while the inclusion of more shells of neighbors gives rise to rapid oscillations in the spectra that do not survive the lifetime broadening. For the calculation of the phase shifts we use the same differential equation solver as for the logarithmic derivatives of the band-structure calculations.

The dipole matrix elements, calculated using a self-consistent Dirac-Slater atomic $1s$ wave function, show very weak energy dependence, so that the structure observed in the calculated spectra is entirely due to solid-state effects. This structure was broadened by convoluting the part of the spectra above the Fermi energy ($=8.96$ eV above the muffin-tin zero) with a Lorentzian broadening function whose width is the sum of the inverse lifetimes of the core hole¹⁷ and of the excited electron.¹⁸

The band-structure spectrum on the low-energy side of Fig. 1 represents essentially the exact solution for our model potential, in the sense that it contains all multiple-scattering contributions and all shells of

neighbors. Observe that the single-scattering results reproduce all the features of the exact solution both in energy position and in amplitude down to the absorption edge, while the standard EXAFS results show discrepancies which grow larger as one gets close to threshold. On the other hand, for high energies, where the approximation (3) becomes valid, the single-scattering and the standard EXAFS spectra show close agreement, as expected.

We have studied other close-packed systems with different lattice structures in the same way, and found in each case that all major features of the exact spectra are fairly well reproduced by the single-scattering formula.¹² We have also corroborated that the agreement between single scattering and exact results improves substantially with increasing broadening of the spectra. This may indicate that multiple-scattering events give rise mostly to rapid oscillations in the spectra and that *all* major structures of the spectra arise from single-scattering events off the first few neighboring shells of atoms.¹⁹ Similar results were also found in a study of a one-dimensional model.²⁰

In summary, we have shown that for an independent-particle calculation the correct single-scattering result for x-ray absorption appears for close-packed metals to give a fairly accurate representation of the exact result. This fact allows one to use with confidence our tractable formulas over the entire energy range, thus facilitating a comparison between theory and experiment.

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