Inelastic Losses and Multi-Electron Excitations in X-Ray Spectra

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Abstract. An approach is discussed for ab initio calculations of inelastic losses and multi-electron excitations in core level x-ray absorption spectra (XAS). The approach is based on first principles calculations of dielectric response using a real-space Green’s function formalism. Extrinsic losses are calculated in terms of the photoelectron self-energy using a many-pole representation of the dielectric response function and the GW approximation. Multi-electron excitations correspond to satellites in the spectral function, which is obtained from similar ingredients using a quasi-boson model. The theory accounts for extrinsic and intrinsic losses as well as interference terms, and yields quantitative estimates of inelastic mean free paths and the many-body amplitude factor $S^2_0$. These results improve both the near edge and the extended fine structure.

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INTRODUCTION

The effects of inelastic losses and multi-electron excitations are crucial to a quantitative understanding of x-ray absorption spectra (XAS) [1]. In the extended XAS fine structure (EXAFS), for example, these effects are characterized by the mean-free path $\lambda_k$ and the many-body amplitude factor $S^2_0$ in the EXAFS formula

$$\chi(k) = S^2_0 \sum_R \frac{|f_{\text{eff}}(k)|^2}{kR^2} \sin(2kR + \Phi_k) e^{-2k^2/\lambda_k} e^{-2\sigma_k^2/k^2}.$$  

(1)

However, due to the difficulty of practical calculations, current treatments of the mean-free path [1, 2] often utilize simplified models, e.g., the plasmon-pole model for the electron gas dielectric function, while $S^2_0$ is taken to be a phenomenological constant fit to experiment.

In an effort to overcome these difficulties, we have introduced an ab initio approach for calculations of $\lambda_k$ and $S^2_0$ [3, 4, 5]. This paper is intended to summarize those developments. The first is an extension of the real-space Green’s function (RSGF) formalism in the FEFF8 XAS code [1, 6] for calculations of dielectric response over a broad spectrum. For example, the energy loss function $-\text{Im} \varepsilon^{-1}(\omega)$ for fcc Ag vs photon energy $\omega$ from Ref. [4] (solid), and from experiment (dots) [7].

FIGURE 1. Calculated energy loss function $-\text{Im} \varepsilon^{-1}$ for fcc Ag vs photon energy $\omega$ from Ref. [4] (solid), and from experiment (dots) [7].

calculated using a quasi-boson model and a generalization of the GW approximation, with ingredients similar to those for the GW self-energy. This procedure has now been implemented, based on extensions to FEFF8 [3, 5]. The approach includes the effects of intrinsic losses and interference and also explains how the theory crosses over from the adiabatic limit at threshold to the sudden approximation at very high energies. We illustrate the approach with calculations for the K-shell XAS of Cu and Ag. We obtain values of $\lambda_k$ and $S^2_0$ in good agreement with experiment and find that the method can lead to improvements in both the near edge and the EXAFS.
EXTRINSIC LOSSES

We first discuss our treatment of extrinsic losses [5], i.e., inelastic losses incurred in the propagation of the photoelectron. These losses give rise to the EXAFS mean free path $\lambda_k$. This quantity is related to the photoelectron self energy $\Sigma(E)$ which can be calculated using the “GW approximation” [10], as given by

$$
\Sigma(E) = i \int \frac{d\omega}{2\pi} G(E - \omega) W(\omega) e^{-i\delta\omega}. \tag{2}
$$

Here $W = \epsilon^{-1}(\omega)V$ is the screened coulomb interaction, and matrix indices $(\mathbf{r}, \mathbf{r'})$ in $\Sigma$, $G$, and $W$ are suppressed. For XAS calculations, it is sufficient to calculate the average self-energy, so we can use the free Green’s function for $G(E)$ in Eq. (2), ignoring multiple scattering (MS) contributions. The difficult part lies in obtaining a good approximation for the inverse dielectric matrix $\epsilon^{-1}(\omega)$ over a broad range of energies. This generally requires a system dependent treatment going beyond the independent particle approximation. Thus current GW implementations for core spectra [1] often use approximate models, e.g., the plasmon pole approximation for the dielectric function based on the electron gas. Although computationally efficient, Fig. 1. shows that a single pole is not generally a good representation of the energy loss spectrum.

Our calculations of $\epsilon^{-1}(\omega)$ are obtained in terms of the local atomic polarizabilities $\alpha(\omega)$

$$
\alpha(\omega) = \int d^3r d^3r' \chi(\mathbf{r}, \mathbf{r'}, \omega) d(\mathbf{r}) = \sum_{i, \mathbf{L}, \mathbf{L'}} \bar{M}_{i, \mathbf{L}} G_{\mathbf{L}, \mathbf{L'}}(E) \bar{M}_{i, \mathbf{L'}}. \tag{3}
$$

Here, $\chi(\mathbf{r}, \mathbf{r'}, \omega)$ is the dielectric response function the operator $d(\mathbf{r})$ represents the dipole coupling to photons of energy $\hbar\omega$, and $E$ is the photoelectron energy $E = \omega + E_o$. In the RSGF approach $\alpha(\omega)$ is calculated in terms of Green’s functions using a generalization of FEFF8 which includes contributions from all absorption edges [4]. This leads to the second expression in Eq. (3), where $\bar{M}_{i, \mathbf{L}}$ are screened dipole matrix elements between occupied core states $|i\rangle$ and final scattering states $|\mathbf{L}, 0\rangle$, and $G_{\mathbf{L}, \mathbf{L'}}(E)$ are the elements of the photoelectron Green’s function in an angular momentum and site basis [6]. From $\alpha(\omega)$, we then obtain $\epsilon(\omega) = 1 + 4\pi\alpha(\omega)$ where $n = N/V$ is the atomic number density, and hence the energy loss function $-\text{Im}[\epsilon^{-1}(\mathbf{q}, \omega)] = \frac{\pi}{2} \sum_j g_j \omega_j \delta(\omega - \omega_j(\mathbf{q}))$. \tag{4}

Here $g_j = (2\Delta\omega_j/\pi\omega_j) \text{Im}[\epsilon^{-1}(\omega_j)]$ is the strength of pole $j$ and $\Delta\omega_j$ is the pole spacing. For simplicity, the momentum dependence of each pole is approximated by a polynomial in $\omega^2$, as in the plasmon-pole approximation $\omega_j(\mathbf{q}) = (\omega_0^2 + q^2/3 + q^4/4)^{1/2}$ [11]. This approximation is roughly consistent with explicit calculations [12], but the precise dispersion is not critical since $\mathbf{q}$ and $\omega$ are integrated over [11]. Many-pole models [13] and other methods [14] have been developed for more accurate self-energy calculations. However, these approaches are computationally demanding and not applicable at high photoelectron energies, e.g., for EXAFS. Our model is similar to that of Ref. [2], but does not rely on empirical optical constants. Thus by using Eq. (4) in Eq. (2), we obtain an efficient expression for the self-energy as a sum over single-pole models with excitation energies $\omega_j$, i.e.,

$$
\Sigma(E) = \sum_j g_j \Sigma(E, \omega_j).
$$

The EXAFS mean free path can now be calculated using the relation $\lambda_k = k/|\text{Im}\Sigma(E_k) + \Gamma/2|$, where $E_k = (1/2)\hbar^2$ and $\Gamma$ is inverse core-hole lifetime. The quantity $\lambda_k$ is closely related to the inelastic mean free path IMFP $\lambda = (E/2)^{1/2}/|\text{Im}\Sigma(E)|$ which is generally shorter by a factor of about two. The IMFP has been calculated for various materials using our method, and examples have been tabulated on the WWW [15]. For example, Fig. 2 shows $\lambda$ for fcc Cu using a 100-pole model matched to the loss function in Fig. 1. Clearly this model corrects the excessive loss of the single-pole model below 100 eV, and yields good agreement with semi-empirical fits to experiment [16, 17]. Our self-energy is also in reasonable agreement with that of Ref. [13].

MULTI-ELECTRON EXCITATIONS

Multi-electron excitations refer to the many-body “shake-up” and “shake-off” processes that accompany XAS. Thus theoretical calculations require treatments going beyond the single particle approximation. In our approach these excitations correspond to satellites beyond the quasi-particle peak in a spectral function $A = (-1/\pi)\text{Im}G_{\text{off}}$ which characterizes the energy distribution of the photoelectron. Here $G_{\text{off}}$ is an effective, one-particle propagator, which can be calculated within the quasi-boson approximation using a generalization of the GW approximation and similar ingredients [9]. Thus our many-pole dielectric function also permits efficient calculations of multi-electron excitations within this model. Formally, keeping terms to second order in the electron-boson interaction $V''$, where $n$ is an excitation
index, the expression for $G_{\text{eff}}(\omega)$ is

$$G_{\text{eff}}(\omega) = e^{-\omega_0} \left[ G(\omega) + \sum_n \left( \frac{V_{nn}}{\omega_0} \right)^2 G(\omega - \omega_0) - 2 \sum_n \frac{V_{nn}^2}{\omega_0} G(\omega - \omega_0) V_n G(\omega) \right]. \quad (5)$$

The amplitudes $V^n$ are obtained in terms of many-pole model in Eq. (4) [5, 9]. The first term in Eq. (5), $G(\omega) \equiv [\omega - h' - \Sigma(\omega) + i\gamma]'^{-1}$ is the damped Green’s function calculated in the presence of a core hole potential. The second term in Eq. (5) refers to intrinsic losses within the sudden approximation. The third term in Eq. (5) which is of opposite sign, comes from the energy-dependent interference terms between extrinsic and intrinsic excitations which tend to suppress the satellites. At threshold (the adiabatic limit) the interference is complete and the quasi-particle limit is restored. At high energies, however, interference becomes small, and the sudden-approximation prevails. The characteristic energy between these regimes is the mean excitation energy (i.e., the centroid of the energy loss function) which is typically comparable to the plasmon energy.

As shown in Ref. [9], these excitations can be included in the XAS $\mu(\omega)$ in terms of a convolution of a normalized, energy-dependent spectral function $\hat{A}(\omega, \omega')$ and the quasi-particle absorption coefficient $\mu_{qp}$ (i.e., the spectrum calculated in the absence of satellites),

$$\mu(\omega) = \int_0^\infty d\omega' \hat{A}(\omega, \omega') \mu_{qp}(\omega - \omega') \equiv \langle \mu_{qp}(\omega) \rangle. \quad (6)$$

The effect of multi-electron excitations on EXAFS $\chi(\omega)$ is given by a similar a convolution of $\hat{A}(\omega, \omega')$ with the quasi-particle fine structure, i.e., $\chi(\omega) = \langle \chi_{qp}(\omega) \rangle$. The energy dependence of $\hat{A}(\omega, \omega')$ controls the cross-over from the adiabatic limit to the sudden approximation limits. This energy dependence arises from the interference terms, which are neglected in treatments based on the sudden approximation [1]. At threshold the interference terms suppress the satellites completely, yielding the adiabatic limit. At high energies interference becomes negligible, and one recovers the sudden approximation. Thus for each MS path $R$ in the path expansion for EXAFS, the convolution over the oscillatory fine structure yields a path-dependent amplitude reduction factor $S_R^2(\omega)$ and a many-body phase shift $\delta_R(\omega)$.

$$S_R^2 = \langle e^{2iR} \rangle = S_R^2(\omega) e^{2iR + \delta_R(\omega)}. \quad (7)$$

The behavior is illustrated for Cu in Fig. 3. Note that for the first shell, $S_R^2(\omega)$ and $\delta_R(\omega)$ cross-over smoothly from the adiabatic limit at threshold to nearly constant values $S_R^2 \approx 0.9$, and $\delta_R \approx -0.2$ rad, respectively in the EXAFS, roughly consistent with experiment [9]. Note also that the results for the amplitude and phase of $S_R^2$ are nearly independent of energy with the many-pole model.

**APPLICATION TO EXAFS AND XANES**

We now illustrate these results with applications to the K-shell XAS of fcc Cu and Ag. Consider first the XANES spectra (Fig. 4). Note that the fine structure amplitude calculated with the plasmon-pole approximation is too small, and is shifted in phase compared with experiment. In contrast the many-pole model is in much better agreement. Next consider the EXAFS (Fig. 5). As expected, the quasi-particle approximation with the single-pole model overestimates the EXAFS amplitudes, but generally gives good distance estimates. When the intrinsic losses and interference terms are added, the agree-
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