Electron Core-Hole Interaction in the X-Ray Absorption Spectroscopy of 3d Transition Metals

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A fully relativistic scheme is presented that allows one to deal with the electronic band structure of a solid and the influence of the electron core-hole interaction on its x-ray absorption spectra on the same level. This is achieved in a parameter-free way by working throughout in the framework of the time-dependent density functional theory and linear response formalism. Application to the $L_{2,3}$-absorption spectra of 3d transition metals demonstrates that the electron core-hole interaction intermixes the L_2 and L_3 partial spectra, strongly affecting the so-called branching ratio. The consequences of this for the magnetic circular x-ray dichroism sum rules are discussed. [S0031-9007(98)06033-5]

X-ray absorption spectroscopy is an important tool for investigating the electronic structure of solids. One of its attractive features is that one can expect in many cases the absorption coefficient to be proportional to some properly projected local density of states [1], which makes the interpretation of the spectra quite simple. Unfortunately this direct proportionality holds only as long as the absorption process can be described within the independent particle approximation (IPA), which assumes that the involved excited states can be described reasonably well in terms of the single particle energies and orbitals of the corresponding ground state.

Fink *et al.* [2] could demonstrate experimentally that the IPA is not sufficient when dealing with the x-ray absorption spectra of early 3d metals. In particular, these authors found that the so-called branching ratio at the $L_{2,3}$ edge, i.e., the ratio of the jumps of the absorption coefficient at the L_3 and L_2 edges, strongly deviates from the ideal ratio of 2:1.

This breakdown of the IPA was ascribed by Zaanen *et al.* [3] to the interaction of the excited electron with the created core hole. A simple way to account for this situation in an *ad hoc* manner is to use for the description of the excited state energies and orbitals from a system where the absorber atom has one additional positive charge by increasing its nuclear charge Z by 1 ($Z + 1$ approximation [4,5]). Another approximate approach is to calculate the final state wave functions in the presence of a hole in the core level which is involved in the absorption process (final state approximation [6,7]).

Both procedures mentioned are not able to reproduce the strong deviation from the ideal branching ratio for the $L_{2,3}$ edges of the early 3d metals [8]. In contrast to this, Zaanen *et al.* [3] could achieve fairly good agreement with experiment by taking the electron core-hole interaction into account within a model based on atomic considerations. Their approach, however, uses a number of adjustable parameters and is restricted to the early transition metals where a two-particle picture (electron and core hole) is expected to be sufficient.

The aim of the present work is to get rid of these restrictions by working in the framework of linear response theory (LR) on the basis of time-dependent density functional theory (DFT) [9]. The approach presented below is somewhat similar to that developed by Zangwill and Soven [10] to calculate the photo absorption spectra of noble-gas atoms. In contrast to this, our approach is meant to deal with x-ray absorption in solids. In addition, because of the crucial role of spin-orbit interaction for the initial states in the case of the $L_{2,3}$ spectra of the early 3d metals, it is formulated in a fully relativistic way.

Our starting point for the calculation of the x-ray absorption coefficient μ is its relationship to the current correlation function χ ($\hbar = 1$):

$$\mu(\omega, \vec{q}) = \frac{4\pi c e^2}{\omega V} \text{Im} \int d^3 r \int d^3 r' a^{\mu*} e^{-i\vec{q}\cdot\vec{r}}$$
$$\times \chi_{\mu\nu}(\vec{r}, \vec{r}\,'; \omega) e^{i\vec{q}\cdot\vec{r}\,'} a^\nu. \tag{1}$$

Here $\omega/2\pi$ is the frequency and $\vec{q}$ the wave vector of the incoming radiation, which is described by the four-potential $A^\mu = a^\mu e^{i\vec{q}\cdot\vec{r}}$. In the radiation gauge, which we use, a^0 is set to zero and a^i for $i = 1, 2, 3$ represents the usual three dimensional polarization vector. Furthermore, we use the dipole approximation, where $e^{i\vec{q}\vec{r}} \approx 1$ is assumed. This way the $\vec{q}$ dependency of the absorption coefficient drops out. Within the dipole approximation an alternative choice for the gauge leads to $A^0 = i\frac{\omega}{c}\vec{a}\cdot\vec{r}$ and $\vec{A} = \vec{0}$. This gauge is used, e.g., in Ref. [10]. Finally, V in Eq. (1) is the volume of the unit cell and all other quantities have there usual meaning.

As the double integral in Eq. (1) is the expression for the forward scattering amplitude of a photon, the whole expression represents nothing but the optical theorem, which connects the imaginary part of the forward scattering amplitude to the total cross section.

Application of the independent particle approximation consists in approximating the correlation function χ in Eq. (1) by that of a suitable noninteracting system (χ^0), that is described, for example, within the framework of DFT (Kohn-Sham system). Using the relativistic

Korringa-Kohn-Rostoker (RKKR) band structure formalism χ^0 is given for high energies by [8]

$$\chi_{ij}^0(\vec{r},\vec{r}\,';\omega) = \frac{1}{\pi} \sum_{k(E_k<E_F)} \sum_{\Lambda,\Lambda'} \int_{E_F}^{\infty} dE \frac{\psi_k^\dagger(\vec{r})\alpha_i Z_\Lambda(\vec{r};E)\,\mathrm{Im}\,\tau_{\Lambda\Lambda'}Z_{\Lambda'}^\times(\vec{r}\,';E)\alpha_j\psi_k(\vec{r}\,')}{\omega - (E - E_k) + i\epsilon}, \tag{2}$$

for $i,j \in \{1,2,3\}$. If one of these indices is zero, the corresponding Dirac matrix α_i has to be replaced by the unit matrix. The index k labels the involved initial core states with wave functions ψ_k. The final band states above the Fermi energy E_F are represented by the wave functions Z_Λ and the scattering path operator $\tau_{\Lambda,\Lambda'}$ with $\Lambda = (\kappa,\mu)$ standing for the spin-orbit and magnetic quantum numbers [1]. Inserting this expression for χ^0 into Eq. (1) results in the usual formula for the absorption coefficient $\mu(\omega)$ [1].

To go beyond this approximation, one has obviously to find a more accurate expression for χ. This is achieved by using the linear response formalism together with time-dependent DFT [9]. Within this framework the correlation functions χ and χ^0 are connected by the following integral equation:

$$\chi_{\mu\nu}(\vec{r},\vec{r}\,';\omega) = \chi_{\mu\nu}^0(\vec{r},\vec{r}\,';\omega) \int d^3\vec{r}\,'' \int d^3\vec{r}\,'''$$
$$\times \chi_{\mu\mu'}^0(\vec{r},\vec{r}\,'';\omega)K^{\mu'\nu'}(\vec{r}\,'',\vec{r}\,''';\omega)$$
$$\times \chi_{\nu'\nu}(\vec{r}\,''',\vec{r}\,';\omega). \tag{3}$$

The integral kernel K describing the electron core-hole interaction, can be split into a Coulomb and an exchange-correlation part:

$$K^{\mu\nu}(\vec{r},\vec{r}\,';\omega) = \delta^{\mu 0}\delta^{\nu 0}\left\{\frac{e^2}{|\vec{r}-\vec{r}\,'|} + f_{xc}(\vec{r},\vec{r}\,',\omega)\right\}. \tag{4}$$

For the exchange-correlation part f_{xc} we use the local approximation

$$f_{xc}(\vec{r},\vec{r}\,';\omega) \approx \delta(\vec{r}-\vec{r}\,')f_{xc}^{\text{hom}}(q=0,\omega,\rho)|_{\rho=\rho_0(\vec{r})} \tag{5}$$

in the limit $\omega \to \infty$ as proposed by Gross and Kohn [11].

To solve the integral equation (3) we assume that the normalized wave function

$$\hat{Z}_\Lambda(\vec{r};E) = \frac{Z_\Lambda(\vec{r};E)}{\|Z_\Lambda(E)\|} \tag{6}$$

varies only slowly with energy around $E = \omega + E_k$. This is well justified and allows one to factor χ^0 in the following way:

$$\chi_{ij}^0(\vec{r},\vec{r}\,';\omega) = \sum_{k,k'(E_k,E_{k'}<E_F)} \sum_{\Lambda,\Lambda'} \psi_k^\dagger(\vec{r})\alpha_i \hat{Z}_\Lambda(\vec{r};\omega+E_k)$$
$$\times \hat{\chi}_{k\Lambda;k'\Lambda'}^0(\omega)\hat{Z}_{\Lambda'}^\times(\vec{r}\,';\omega+E_{k'})\alpha_j\psi_{k'}(\vec{r}\,'), \tag{7}$$

with

$$\hat{\chi}_{k\Lambda;k'\Lambda'}^0(\omega) = \frac{1}{\pi}\int_{E_F}^{\infty} dE$$
$$\times \frac{\|Z_\Lambda(E)\|\mathrm{Im}\,\tau_{\Lambda\Lambda'}\|Z_{\Lambda'}(E)\|}{\omega - (E - E_k) + i\epsilon}\delta_{kk'}. \tag{8}$$

Assuming that the corresponding representation is also suitable for the full correlation function χ,

$$\chi_{ij}(\vec{r},\vec{r}\,';\omega) = \sum_{k,k'(E_k,E_{k'}<E_F)} \sum_{\Lambda,\Lambda'} \psi_k^\dagger(\vec{r})\alpha_i \hat{Z}_\Lambda(\vec{r};\omega+E_k)$$
$$\times \hat{\chi}_{k\Lambda;k'\Lambda'}(\omega)\hat{Z}_{\Lambda'}^\times(\vec{r}\,';\omega+E_{k'})$$
$$\times \alpha_j\psi_{k'}(\vec{r}\,'), \tag{9}$$

with a matrix $\hat{\chi}(\omega)$, one ends up with a simple matrix equation:

$$\hat{\chi}(\omega) = \hat{\chi}^0(\omega) + \hat{\chi}^0(\omega)\hat{K}(\omega)\hat{\chi}(\omega), \tag{10}$$

where the matrix $\hat{K}(\omega)$ has the elements

$$\hat{K}_{k,\Lambda;k,\Lambda'}(\omega) = \int d^3 r \int d^3 r' \psi_k^\dagger(\vec{r})\hat{Z}_\Lambda(\vec{r};\omega+E_k)$$
$$\times K(\vec{r},\vec{r}';\omega)\hat{Z}_{\Lambda'}^\times(\vec{r}\,';\omega+E_{k'})\psi_{k'}(\vec{r}\,'). \tag{11}$$

The resulting final expression for the absorption coefficient is now found to be

$$\mu(\omega) \propto \mathrm{Im} \sum_{\Lambda,k;\Lambda',k'} M_{\Lambda k}^{\lambda*}\hat{\chi}_{k\Lambda;k'\Lambda'}(\omega)M_{\Lambda'k'}^{\lambda}, \tag{12}$$

with $M_{\Lambda k}^\lambda$ denoting the appropriate dipole matrix elements for a given polarization λ [1]. In the following we are interested only in the absorption of unpolarized radiation and a corresponding average with respect to the polarization will be implied.

Using $\hat{\chi}^0$ instead of $\hat{\chi}$ in Eq. (12) results in the usual single particle expression for $\mu(\omega)$ obtained with the IPA [1]. In contrast to this approach, using $\hat{\chi}$ requires the imaginary and real part of $\hat{\chi}^0$ to be available [see Eqs. (3) and (10)]. For the applications presented below, the imaginary part of $\hat{\chi}^0$ is calculated the usual way [1] and the real part is obtained using a Kramers-Kronig transformation. For the $L_{2,3}$ spectra investigated with initial p states the dimension of the matrices in Eq. (10) is 11 when ignoring the very small p-s contribution [1]. This can be seen by simply counting the pairs of p and d states which are allowed by the dipole selection rules for left or right circular polarized radiation.

The presence of the kernel in Eq. (10) has two effects. One is the mixing of the real and the imaginary part of χ^0 which leads to a shift of the absorption peaks to higher energies and a suppression of their height. The second effect is a mixing of the contributing absorption channels. This effect plays an important role at the L_2 peak, where the L_2 channels mix with the background resulting from the L_3 peak and is responsible for the change of the branching ratio. This second effect clearly becomes weaker, when the distance of L_3 and L_2 peak, i.e., the spin-orbit splitting of the core states becomes larger. Therefore one can expect that the change of the branching ratio becomes smaller when going to higher elements in the $3d$ series.

Finally it should be mentioned that approximating the matrix $\hat{K}$ by energy independent Coulomb matrix elements taken from atomic Hartree-Fock calculations and performing a suitable basis transformation recovers from Eq. (12) the expression for $\mu(\omega)$ derived by Zaanen *et al.* [3]. However, in contrast to the approach of these authors the matrix elements of K are energy dependent and contain explicitly an exchange-correlation contribution. Furthermore, the restrictions mentioned above for the approach of these authors do not apply to Eq. (12).

To demonstrate the consequences of the electron core-hole interaction results for the $L_{2,3}$ spectra of Ca are shown in Fig. 1 that were obtained within the IPA (μ^0) and the formalism presented above (μ). As a consequence of the IPA the spectrum μ^0 based on χ^0 is just a superposition of the independent L_2 and L_3 spectra that are shifted against one another by the spin-orbit splitting of the $2p_{1/2}$ and $2p_{3/2}$ subshells (upper panel of Fig. 1). These partial spectra directly reflect the structure of the d-like DOS above E_F because of the dipole selection rules and the negligible p-s contribution to μ^0. Because of the weak spin-orbit interaction for the final d states in the case of Ca, the resulting branching ratio is very close to 2:1. When going from μ^0 to μ; i.e., when taking the electron core-hole interaction into account, the structure of μ^0 essentially survives (lower panel of Fig. 1). However, for the main features of the spectrum a pronounced shift in energy occurs. In addition the amplitudes change—especially for the main peak of the former L_3 spectrum. As it is obvious from Eq. (10)
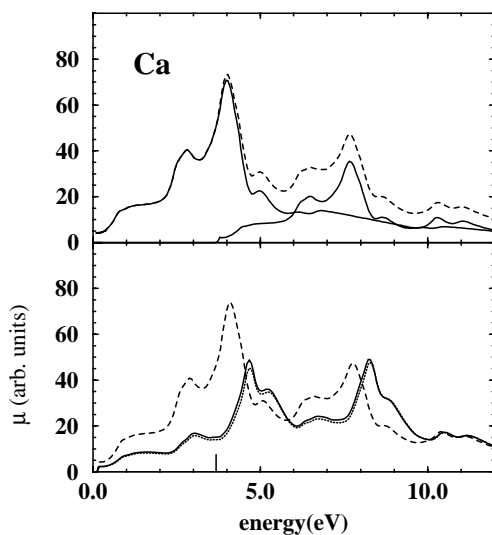
the electron core-hole interaction leads to a coupling of the partial absorption channels of the $2p_{1/2}$ and $2p_{3/2}$ subshells. For that reason it is no more possible to split μ into L_2 and L_3 spectra. Accordingly, the branching ratio is no more well defined (see below). Nevertheless, one obviously notes from Fig. 1 that the amplitude ratio for the two main peaks at 4.5 and 8.5 eV—originally belonging to the L_3 and L_2 spectra, respectively—is now roughly 1:1 instead of 2:1.

Equation (4) allows one to investigate the origin of the observed changes in the spectrum caused by inclusion of the electron core-hole interaction in more detail. Suppressing, for example, the exchange correlation contribution f_{xc} to K leads to a spectrum that is very close to that of the full calculation (lower panel of Fig. 1). This obviously implies that the Coulomb contribution to K is by far dominating in full agreement with the finding of Zangwill and Soven [10] for the photo absorption cross section of noble-gas atoms. Because of this result, f_{xc} has been ignored for the calculations presented below.

Applications of the formalism presented above to the $L_{2,3}$ spectra of hcp Ti and bcc Cr are shown in Fig. 2 together with corresponding experimental data. For a comparison with the latter ones an appropriate broadening of the theoretical spectra has been performed to account for apparative and lifetime broadening effects [1]. As one can see, inclusion of the electron core-hole interaction considerably improves agreement with experiment. This applies in particular to the branching ratio in the case of Ti. Here, one finds an influence of the electron core-hole interaction on the theoretical spectrum comparable to that found for Ca. Nevertheless, one also notes that the branching ratio is less affected for Ti than for Ca.
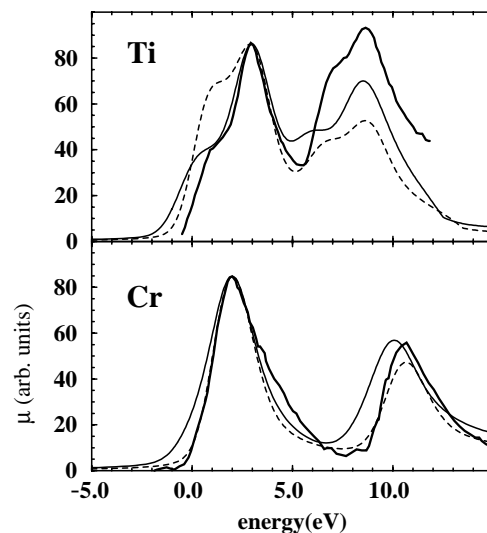

FIG. 1. Theoretical $L_{2,3}$-absorption spectra of Ca. The upper panel gives the spectrum μ^0 based on the IPA together with its decomposition into the L_3 and L_2 partial spectra. For the lower panel, the full and dotted curves give the absorption coefficient μ obtained by inclusion of the full electron core-hole interaction and only its Coulomb part, respectively [see Eq. (4)]. For comparison μ^0 has been added (dashed curve). The energy zero coincides with the edge of the L_3 spectrum and the vertical line indicates the spin-orbit splitting of the $2p$ states.

FIG. 2. Theoretical $L_{2,3}$-absorption spectra μ^0 (dashed line) and μ (full line) calculated without and with the electron core-hole interaction, respectively, for hcp Ti and bcc Cr. The corresponding experimental spectra (thick line) have been taken from Ref. [2]. All spectra have been normalized in such a way that their main peak at the L_3 edge coincides.
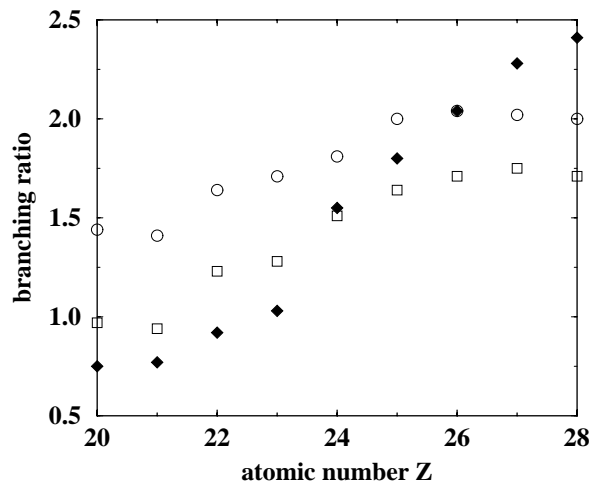
FIG. 3. Branching ratio for the $L_{2,3}$ edge of the $3d$ transition metals in the paramagnetic state obtained for the theoretical spectra μ^0 (open circles) and μ (open squares); i.e., calculated without and with the electron core-hole interaction, respectively. Corresponding experimental data (full diamonds) have been deduced from the spectra in Ref. [2].

Going to Cr, the influence is even more reduced. As mentioned above, the branching ratio is not well defined if the electron core-hole interaction is included in the calculations. For that reason the relative height of the main peaks at the L_3 and L_2 edges have been plotted in Fig. 3 to demonstrate the reduced influence of the electron core-hole interaction when going along the $3d$ transition metal series.

Although the experimental data given in Fig. 3 are influenced to some extent by the necessary background subtraction, they nevertheless clearly show a monotonous increase in the relative peak height with increasing ordering number Z. Both sets of calculations for μ^0 and μ; i.e., without and with inclusion of the electron core-hole interaction are in line with this. However, for μ the variation is much more pronounced and in much better agreement with experiment than for μ^0. As expected from the spectra shown in Figs. 1 and 2 the influence of the electron core-hole interaction decreases with the ordering number.

The scheme and results presented above clearly demonstrate that the electron core-hole interaction has the consequence that the $L_{2,3}$-absorption spectra of $3d$ transition metals cannot be separated into L_2 and L_3 partial spectra in a strict sense. Of course this applies also for the case that the absorbing system is spin polarized and exhibits magnetic circular x-ray dichroism (MCXD) for that reason. As a consequence of this, the so-called MCXD sum rules, that have been derived during the last years by various authors [12–16] and that are meant to deduce the spin and orbital magnetic moments of an absorbing atom from its dichroic spectra is not sensible or at least questionable. Fortunately,

the influence of the electron core-hole interaction decreases along the $3d$ series with increasing spin-orbit splitting of the $2p$ levels. For that reason application of the sum rules seems to be problematic for example for Cr [17] but is reasonably well justified for the late $3d$ transition metals Fe, Co, and Ni. This expectation based on the present results could indeed be supported by extending and applying the scheme described above to magnetic $3d$ transition metal systems [8]. Nevertheless, all other problems connected with the application of the sum rules [1] still remain.

In summary, a scheme has been presented that allows one to account for the influence of the electron core-hole interaction on the x-ray absorption spectra of transition metals without using any adjustable parameter. Application to the $3d$ transition metal series clearly demonstrated that its effect on the so-called branching ratio continuously diminishes along the series with the increase of the spin-orbit splitting of the $2p$ levels. As a consequence, application of the MCXD sum rules seems to be doubtful for the middle of the series but is reasonably well justified at the end of it.

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