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A fully relativistic theory for magnetic EXAFS – formalism and applications

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A fully relativistic theory for magnetic Extended X-ray Absorption Fine Structure (MEXAFS) is presented that is based on the Dirac equation for spin-polarized systems and relativistic multiple scattering theory. This scheme not only allows one to treat spin-polarization and all relativistic effects on the same level but can also be applied to go beyond the standard muffin-tin construction by using non-spherical potentials. Results of applications to Fe_3Pt are presented and discussed on the basis of the so-called sum-rules.

Keywords: EXAFS; magnetic dichroism; multiple scattering theory.

1. Introduction

Relativistic effects may influence X-ray absorption spectra in a rather pronounced way. The most common example for this is the splitting of the absorption edge due to the spin-orbit splitting of initial core state giving rise for example to the $L_{2,3}$-edges for 2p-initial states. The influence of the spin-orbit coupling on the final states is also convincingly seen in many cases. The most prominent examples are the $L_{2,3}$-edge spectra of the late 5d-transition metal elements – in particular those of Pt. For these it is found that the so-called white line at the L_3-edge, which stems primarily from $5d_{5/2}$-states, is more pronounced than at the L_2-edge, where $5d_{3/2}$-states dominate.

The mentioned influences of relativistic effects on the X-ray absorption spectra, which also influence the complementary X-ray emission spectra, are already known for quite a long time. Accordingly corresponding theoretical descriptions of X-ray absorption and emission have been developed already in the 70s by various authors (Weinberger & Rosicky, 1978) on the basis of the Dirac equation. In addition, a relativistic version of the conventional EXAFS theory (Schaich, 1984) has been developed recently by Tyson (Tyson, 1994). This approach is also based on the Dirac equation and has a more or less unrestricted applicability because of the use of multiple scattering theory.

About a decade ago another important consequence of the spin-orbit coupling for the X-ray spectra of magnetic materials could be demonstrated by Schütz and coworkers in the XANES- (Schütz *et al.*, 1987) as well as in the EXAFS-region (Schütz *et al.*, 1989). The observed magnetic circular dichroism, i.e. the dependency of the absorption coefficient on the polarization of the radiation, was already predicted years before by Erskine and Stern (Erskine & Stern, 1975). Furthermore, it was noted by them that the effect is caused by the reduction in symmetry that occurs if spin-orbit coupling and spin-ordering are present at the same time. This complex situation cannot be dealt with by the various theoretical approaches mentioned above because they are applicable exclusively to non-magnetic solids. In contrast to this, a fully relativistic approach to deal with the magnetic dichroism in X-ray absorption has been developed by Ebert *et al.* (Ebert *et al.*, 1988) and has been applied to calculate XANES-spectra for a wide variety of systems (Ebert, 1996*a*). Later on, alternative schemes have been developed (Brouder & Hikam, 1991; Ankudinov & Rehr, 1997) that make use of certain approximations when dealing with relativistic effects in the presence of spin-ordering. Applying multiple scattering theory to a finite cluster of atoms calculations could be performed straightforwardly for the EXAFS-region. Recently the approach of Ebert and coworkers has been extended to deal also with atomic clusters, leading to a consistent fully relativistic description of magnetic dichroism that is applicable to the XANES- as well as to the EXAFS-region. Since then this approach has successfully been applied to a great variety of systems. Combining the relativistic magnetic EXAFS (MEXAFS) formalism with the Coherent Potential Approximation (CPA) alloy theory it became possible to treat disordered alloys as well (Popescu *et al.*, 1998). Furthermore, because for certain systems a spherical potential construction may be insufficient, a full-potential version of relativistic multiple scattering theory for magnetic systems was also developed (Huhne *et al.*, 1998) and combined with the MEXAFS-formalism (Huhne & Ebert, 1998).

In the following a short overview is given for the fully relativistic treatment of (M)EXAFS together with some hints concerning its full-potential version. To illustrate the application of the formalism, results are presented for the $L_{2,3}$-(M)EXAFS spectra of Pt in Fe_3Pt and compared with experiment. To supply a detailed interpretation of the dichroic spectra the so-called sum rules are introduced in their differential form and applied to the MEXAFS-spectra.

2. Theoretical framework

To arrive at a most general expression for the X-ray absorption coefficient $\mu^{\vec{q}\lambda}$ one starts from the expression (Schaich, 1984; Ebert, 1996*a*):

$$\mu^{\lambda}(\omega) \propto \sum_{i\ occ} \langle \Phi_i | X^{\times}_{\vec{q}\lambda} \Im G^{+}(E_i + \hbar\omega) X_{\vec{q}\lambda} | \Phi_i \rangle \ , \qquad (1)$$

where all the possible final states at energy E_f are represented by the electronic Green's function $G(\vec{r}, \vec{r}\,', E)$. The involved initial core states i are represented by atomic-like wave function Φ_Λ (Ebert, 1989). Transitions from these initial to the final states are due to absorption of photons with wave vector $\vec{q}$, frequency ω and polarization λ and are described by using the electron-photon interaction operator $X_{\vec{q}\lambda}$. Using multiple scattering theory the Green's function $G(\vec{r}, \vec{r}\,', E)$ can be expressed in terms of the wave functions Z_Λ and J_Λ as well as the so-called scattering path operator $\tau^{nm}_{\Lambda\Lambda'}$:

$$\begin{aligned} G^{+}(\vec{r}_n, \vec{r}_m, E) &= \sum_{\Lambda\Lambda'} Z_\Lambda(\vec{r}_n, E) \tau^{nm}_{\Lambda\Lambda'}(E) Z^{\times}_{\Lambda'}(\vec{r}_m, E) \\ &- \sum_{\Lambda} Z_\Lambda(\vec{r}_<, E) J^{\times}_{\Lambda}(\vec{r}_>, E) \delta_{nm} \ . \qquad (2) \end{aligned}$$

Inserting this expression into Eq. (1) leads for the absorption coefficient to (Ebert, 1996*a*):

$$\mu^{\vec{q}\lambda}(\omega) \propto \sum_{i\ occ} \sum_{\Lambda\Lambda'} M^{\vec{q}\lambda *}_{\Lambda i}(E_f) \tau^{nn}_{\Lambda\Lambda'}(E_f) M^{\vec{q}\lambda}_{\Lambda' i}(E_f) \ , \qquad (3)$$

where $M^{\vec{q}\lambda}_{\Lambda i}$ are matrix elements and the atomic contributions $I^{\vec{q}\lambda}_{\Lambda i}$ connected to J_Λ have been omitted. If the underlying electronic structure is dealt with in a non-relativistic way – i.e. Z_Λ and J_Λ are the regular and irregular, respectively, solutions to the Schrödinger equation and a spherical symmetric potential is used – Eq. (3) leads to the standard expression obtained within EXAFS theory (Schaich, 1984). However, using the relativistic Dirac instead of the Schrödinger equation and solving for a spherical symmetric potential, the corresponding relativistic version (Tyson, 1994) is obtained.

A more complex situation is encountered if the potential within the Dirac equation is spin-dependent. Even if the spatial symmetry of the potential is taken to be spherical, the explicit coupling to the spin leads to a reduction in symmetry. This property has significant consequences. First of all one has to note that the four-component wave functions Φ_Λ, Z_Λ and J_Λ in general have no unique spin-angular character Λ. This means that they are a superposition of several partial waves, e.g. $Z_\Lambda = \sum_{\Lambda'} Z_{\Lambda'\Lambda}$. Closely connected to the properties of the wave functions is the fact that the corresponding single-site t-matrix $t_{\Lambda\Lambda'}$ is not diagonal with respect to the spin-angular index Λ and that the diagonal elements are all non-degenerate. This property has quite important consequences for the calculation of the scattering path operator $\tau^{nn}_{\Lambda\Lambda'}$ which is determined by:

$$\underline{\tau}^{nm}(E) = \underline{t}^{n}(E)\delta_{nm} + \underline{t}^{n}(E)\sum_{k\neq n}\underline{G}^{nk}(E)\underline{\tau}^{km}(E) \ . \qquad (4)$$

Here $\underline{G}^{ij}$ is the free electron propagator connecting sites j and i and a matrix notation is used with the matrix elements labeled by Λ. For ordered infinite systems this equation can be solved exactly by means of a Fourier transformation (Ebert, 1996*b*). For the EXAFS-region a restriction to a cluster of atoms is sufficient and a solution can be obtained by inversion of the real-space multiple scattering or Korringa-Kohn-Rostoker (KKR) equation:

$$\underline{\underline{\tau}} = \left(\underline{\underline{t}}^{-1} - \underline{\underline{G}}\right)^{-1} \ , \qquad (5)$$

where double underlines indicate matrices with respect to the site and spin-angular indices, i and Λ, respectively. As an alternative to the above matrix inversion technique one may also solve Eq. (4) by the scattering path expansion approach:

$$\underline{\tau}^{nn} = \underline{t}^{n} + \underline{t}^{n}\sum_{k\neq n}\underline{G}^{nk}\underline{t}^{k}\underline{G}^{kn}\underline{t}^{n} + \dots \ . \qquad (6)$$

This is the starting point for the highly efficient scheme used in the FEFF-code (Rehr & Albers, 1990) which uses several simplifying transformations. However, not all of these steps can be exploited in the spin-polarised relativistic case because of the non-diagonal form of the t-matrix. From the above considerations it is obvious that the symmetry-reduction caused by the simultaneous presence of spin-polarization and spin-orbit coupling makes the corresponding calculations of the matrix elements and the solution of the multiple scattering equations more tedious and time consuming than for a standard muffin-tin-type potential. This of course also applies if the reduced symmetry of the potential is not (only) caused by spin-dependency but due to a non-negligible anisotropy in real space (Huhne *et al.*, 1998). In particular one may note that the use of a non-spherical symmetric potential within (spin-polarized) relativistic (M)EXAFS-calculations does not increase the complexity and numerical effort when one is dealing with the multiple scattering equations – only the evaluation of the matrix elements gets more complex (Huhne & Ebert, 1998).

Most experimental investigations on the magnetic dichroism in X-ray absorption spectroscopy use circularly polarized radiation. To allow for a sound interpretation of the corresponding dichroic signal $\Delta\mu = \mu^{+} - \mu^{-}$, given by the difference in absorption of left and right circularly polarized radiation, a set of so-called sum rules have been derived by several authors (Wienke *et al.*, 1991; Thole *et al.*, 1992; Schütz *et al.*, 1993; Carra *et al.*, 1993). The main virtue of these rules is that they should allow one to obtain a reasonable estimate for the spin and orbital magnetic moments, $\langle\sigma_z\rangle$ and $\langle l_z\rangle$, respectively, of an absorber atom from its energy integrated dichroic signals $\int \Delta\mu(E)dE$. In applying these rules one of the main problems is to fix the upper integration limit. For that reason it is suggested to apply the sum rules in their differential form and to discuss the dichroic spectra $\Delta\mu(E)$ directly. For the $L_{2,3}$-edges these are given by (Ebert *et al.*, 1998):

$$3\left[\Delta\mu_{L_3} - 2\Delta\mu_{L_2}\right] = C_d\left(\frac{d}{dE}\langle\sigma_z\rangle_d + 7\frac{d}{dE}\langle T_z\rangle_d\right) \qquad (7)$$

$$2\left[\Delta\mu_{L_3} + \Delta\mu_{L_2}\right] = C_d\frac{d}{dE}\langle l_z\rangle_d \ . \qquad (8)$$

Here C_d is a normalization constant and T_z is the magnetic dipole operator, that often can be ignored. Thus the basic information to be deduced from the dichroic signal are the spin- and orbital polarization, $\frac{d}{dE}\langle\sigma_z\rangle_d$ and $\frac{d}{dE}\langle l_z\rangle_d$, respectively, of final states with d-character.

3. Application to Fe_3Pt

The magnetic dichroism of the $L_{2,3}$-edge spectra of Pt in disordered Fe_xPt_{1-x} alloys has been studied experimentally as well as theoretically (Ebert *et al.*, 1993) in great detail in the past. Typically for Pt $L_{2,3}$-spectra it was found that the white lines at the L_2- and L_3-edges are quite different because of the influence of the spin-orbit coupling acting on the final states. This finding makes clear that a fully relativistic approach is indispensable to achieve a quantitative description of the $L_{2,3}$-absorption spectra of Pt. In the following, results of corresponding calculations of MEXAFS spectra of Pt in ordered Fe_3Pt are presented to illustrate the application of the above scheme. As a first step for these investigation the potential was calculated self-consistently. The scattering path operator $\tau^{nn}_{\Lambda\Lambda'}$ entering expression for the absorption coefficient $\mu^{\vec{q}\lambda}$ was calculated using the matrix inversion technique for a cluster of 135 atoms in the XANES and 55 atoms in the EXAFS region, respectively, including the central absorber site. The effects of self-energy corrections have been accounted for after calculating the spectra.

The top panel of Fig. 1 shows the results of calculations for the L_2-edge EXAFS-spectra of Pt in ordered Fe_3Pt. Corresponding experimental data, obtained by Ahlers and coworkers (Ahlers, 1998) for an ordered but slightly off-stoichiometric sample, are added. As one can see, the agreement of the theoretical and experimental spectra is quite satisfying, demonstrating in particular that the experimental sample is indeed ordered (Popescu *et al.*, 1998).

The circular dichroic spectrum $\Delta\mu_{L_2}$ for the L_2-edge is shown in the bottom panel of Fig. 1. Again a very satisfying agreement with the corresponding experimental results could be achieved. The results for $\Delta\mu_{L_2}$ clearly demonstrate that the occurrence of magnetic dichroism is by no means restricted to the white line region. Although the amplitude for $\Delta\mu_{L_2}$ is quite small compared to the white line region, it is present throughout the whole EXAFS-range.

As mentioned above, the applicability of the sum rules in their conventional form seems to be somewhat doubtful because of these findings. Nevertheless a clear-cut interpretation of the MEXAFS-spectra can be given making use of the sum rules in

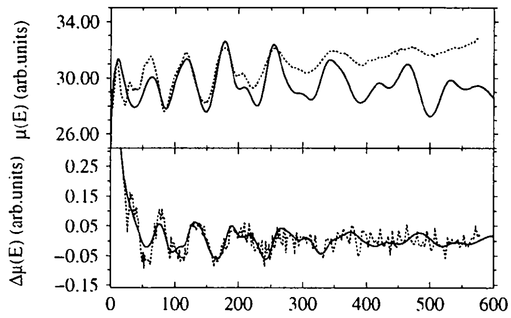

Figure 1
EXAFS- (*top*) and MEXAFS-spectra (*bottom*) at the L$_2$-edge of Pt in Fe$_3$Pt. Calculations for the ordered compound (full line), compared against the experimental data for the Fe$_{0.72}$Pt$_{0.28}$ (dotted line) (Ahlers, 1998).

their differential form. In the upper part of Fig. 2 a superposition of the theoretical magnetic dichroism spectra $\Delta\mu_{L_2}$ and $\Delta\mu_{L_3}$ according to Eq. (7) is given (here the contribution $\frac{d}{dE}\langle T_z\rangle_d$ has been neglected). This is compared to the spin polarization $\frac{d}{dE}\langle\sigma_z\rangle_d$ of the d-states that have been obtained directly from the band structure calculations. In the lower part of Fig. 2 the superposition according to Eq. (8) of the dichroic spectra is compared with the directly calculated orbital polarization $\frac{d}{dE}\langle l_z\rangle_d$ of the d-states. To compare the spectroscopic data with the band structure results the normalization factor C_d in Eq. (7) and (8) has been used as a free scaling parameter using the same value for the upper and lower part of Fig. 2.

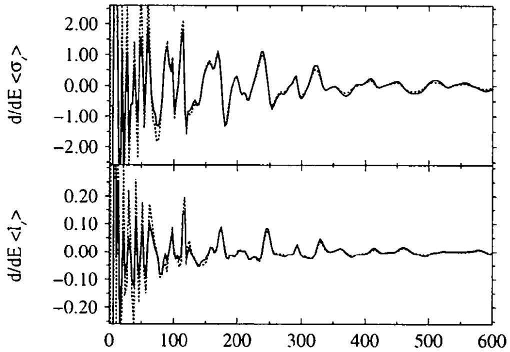

Figure 2
Top: Spin polarization $\frac{d}{dE}\langle\sigma_z\rangle_d$ for the d-states of Pt (full line) compared to those derived from the MCXD-spectra using Eq. (7) (dashed line). *Bottom*: Orbital polarization $\frac{d}{dE}\langle l_z\rangle_d$ for the d-states of Pt (full line) compared to those derived from the MCXD-spectra using Eq. (8) (dashed line).

The nearly perfect coincidence of the various curves in the upper and lower part of Fig. 2 convincingly demonstrates that the primary information that can be deduced from circular L$_{2,3}$-MEXAFS spectra is the spin and orbital polarization for the final d-like states of the absorber atom. Of course, these are no pure atomic-like properties but concerning their variation with energy they strongly depend on the bonding to their surrounding.

For that reason it is quite reasonable to perform a Fourier transform to the MEXAFS-spectra to seek for information on the magnetization distribution around the absorber atom (Ahlers, 1998). However, the relationship of the magnetic radial distribution is by no means trivial. Nevertheless, it seems to be worth to investigate this relationship in more detail to be able to deduce further magnetic information from MEXAFS-spectra in a sound and reliable way.

4. Summary

Several extensions to the conventional EXAFS-theory have been discussed. Dealing with relatively heavy elements obviously demands one to account for all possible relativistic effects; in particular the spin-orbit coupling. Investigations on systems with quite anisotropic potentials will make a full potential construction necessary. These statements apply to non-magnetic as well as magnetic materials. If the system studied posses magnetic order, a fully relativistic formalism seems to be indispensable to deal with the spin-orbit induced dichroism. It has been emphasized that from a formal point of view there is no difference concerning the treatment of anisotropic potentials and accounting for the spin-dependency of the potential for magnetic materials.

The power of a fully relativistic expression for the X-ray absorption coefficient was demonstrated by calculations for the L$_{2,3}$-edge MEXAFS-spectra of Pt in Fe$_3$Pt. Using the sum rules in their differential form it could be shown that the primary information to be deduced from circular MEXAFS-spectra are the spin- and orbital polarization.

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