RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 56, NUMBER 4 15 JULY 1997-II

# Relativistic calculations of spin-dependent x-ray-absorption spectra

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(Received 25 February 1997)

An efficient interpolative approach is presented for relativistic calculations of polarized x-ray-absorption spectra (XAS) including spin and spin-orbit interactions. The method is based on a spinor-relativistic Dirac-Fock treatment of atomic densities and dipole matrix elements, and a nonrelativistic treatment of propagation using high-order multiple scattering theory. This approach is implemented in an automated code FEFF7 which gives quantitative agreement with experiment for x-ray magnetic circular dichroism of Gd and Fe, and for polarized XAS of Cd, including both $\ell \to \ell \pm 1$ dipole transitions. [S0163-1829(97)51028-9]

The problem of x-ray-absorption spectroscopy (XAS) involves two steps, first the production of a photoelectron typically from a deep core level, and second the propagation and scattering of that electron by other atoms in a material. A relativistic approach including spin-orbit (SO) interaction is often needed for an accurate description of the first step, i.e., for dipole matrix elements and core excitation energies, which depend on the structure of the inner core of atoms and on photon polarization. The second step is essentially nonrelativistic in nature, even for photoelectrons of moderate kinetic energy (~1000 eV). This part is described by x-ray-absorption fine structure (XAFS) which is now well understood.[1] In this work we take advantage of this separation to simplify the treatment of relativistic spin-dependent XAS calculations. For example, there is now considerable interest in spin-dependent spectroscopies, such as x-ray magnetic circular dichroism (XMCD), for probing the properties of magnetic materials.[2] It has been argued that a relativistic treatment of XMCD is essential at $\ell = 0$ edges (e.g., $K$, $L_1$).[3] Although it is straightforward to generalize nonrelativistic theory for either spin or SO interaction alone, a fully relativistic theory for magnetic systems involves coupled equations,[4] which greatly increases the computational effort and complexity of the problem. To overcome this difficulty we suggest an interpolative approach which avoids solving coupled equations without significant loss of accuracy, and hence is a considerable computational advantage. At the same time, the approach provides a natural spinor-relativistic formalism which illuminates the relativistic physics involved and overcomes several limitations of current theoretical methods for XAS calculations while extending their capabilities. As shown below, the approach gives the first quantitative treatment of $\ell = 0$ XMCD spectra, whereas previous calculations[5,6] overestimate the XMCD signal. The method has been implemented in an automated high-order multiple-scattering (MS) XAS code FEFF7, which is a generalization of the FEFF6 code[1] and hence makes such relativistic calculations in arbitrary clusters widely accessible. The new code has a number of other improvements including the inclusion of both $\ell \to \ell \pm 1$ dipole transitions, and an improved treatment of excitation energies, potentials, and other atomic properties based on a spinor-relativistic single-configuration Dirac-Fock atom code[7] with fractional ionization capabilities.

The key features of our approach are: (1) a fully relativistic treatment of atomic properties and dipole matrix elements via the Dirac equation, which is solved for $j = \ell \pm 1/2$ orbitals in spin-up and -down potentials; (2) interpolation between the above four solutions of the Dirac equation via Clebsch-Gordan (CG) coefficients; (3) a nonrelativistic treatment of propagation based on the high order MS expansion; (4) semirelativistic $t$ matrices (i.e., $j$ average to cancel SO interaction[8]); and (5) spin-dependent free propagator and $t$ matrices based on overlapped atom potentials.[9] This approach thus builds in both spin and SO effects in a natural way, without the need for relativistic perturbation theory.[5] Within this approach the expression for XAS is directly analogous to the nonrelativistic spin-independent form, apart from additional spin indices. Thus the method provides a generalization, which is also applicable to general calculations of XAS including polarization dependence. Several illustrative applications are presented. First the theory is applied to XMCD calculations for the Gd $L_1$ and Fe $K$ edge. These calculations provide a severe test of our approach, since the calculated XMCD signal must vanish if either the spin or SO interaction in the final state is neglected. Second, the theory is applied to polarization-dependent XAS of hcp Cd. Further details will be given elsewhere.[10]

The relativistic expression for the absorption coefficient of x rays with energy $\hbar\omega$ and polarization $\hat{\epsilon}$, that produce photoelectrons with energy $E$, is given in a Green's-function formalism within the dipole approximation and the golden rule by

$$\sigma(\omega) = -\frac{4\pi c}{\omega} \mathrm{Im} \sum_{I,Js,J's'} \langle I | d_{\epsilon}^{*} | R_{Js} \rangle G_{Js,J's'} \langle R_{J's'} | d_{\epsilon} | I \rangle . \tag{1}$$

Here, $R_{js}$ are the radial wave functions obtained by solving the Dirac equation for orbital $j$ with the final-state potential in the presence of a screened core hole for spin $s$ at energy $E = \hbar\omega + E_I$, and $d_{\epsilon} = \vec{\alpha} \cdot \hat{\epsilon}$ is the polarization-dependent di-

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pole coupling of a photon with polarization $\hat{\epsilon}$, and $I$ represents the initial states. The capital letter for the angular momentum represents the total momentum and its $z$-axis projection, e.g., $J=(j,m_j)$, $S=(1/2,s)$. As is conventional in MS theory, the Green's-function $G_{Js,J's'}$ defined below is represented in an angular momentum basis and can be separated into central and scattering parts, $G_{Js,J's'}=G^{c}_{Js}\delta_{Js,J's'}+e^{i(\delta_{js}+\delta_{j's'})}G^{sc}_{Js,J's'}$. Equation (1) is the central approximation in our simultaneous treatment of spin and SO interaction since we do not solve coupled equations. Instead our approach uses interpolation provided by CG coefficients between the four cases, $j=\ell\pm(1/2)$ and spin-up and -down potentials,

$$G^{sc}_{Js,J's'}(E)=\langle J|LS\rangle G^{sc}_{Ls,L's'}(E)\langle L'S'|J'\rangle. \tag{2}$$

The propagator $G^{sc}_{Ls,L's'}$ can be calculated using high-order MS theory,[1] i.e., $G^{sc}_{Ls,L's'}(E)=G^{0}_{Ls,L_1s}(-\vec{\rho}_{is})\times t^{i}_{L_1s,L_2s'}G^{0}_{L_2s',L's'}(\vec{\rho}_{is'})+\cdots$, where $\vec{\rho}_{is}=k_s(\vec{R}_i-\vec{R}_{i-1})$. Here $i$ refers to the $i$th atom in the scattering path, $i=0$ corresponds to the absorbing atom, $\vec{R}_i$ are coordinates of the atom $i$, and $k_s$ is the wave number relative to the spin-dependent muffin potential.

The next approximation of our approach is to calculate the free propagators $G^{0}_{Ls,L_1s}$ nonrelativistically and to use semirelativistic scattering $t$ matrices.[9] This approximation is plausible, since the scattering of electrons with moderate kinetic energy (EXAFS) is dominated by the region where SO is small. This is the reason why SO for the final state can be treated perturbatively. Our calculations of $\delta_{js}$ are based on Loucks' Eqs. 4–87.[11] Relativistic effects in EXAFS have been discussed by Tyson.[12] However, the effect of SO and relativity on dipole matrix elements can be more important since the deep core region depends on the initial-state wave function.

We have proved that the procedure of Eqs. (1) and (2), like the coupled equation approach, is correct up to second order in perturbation theory; however, the proof is too lengthy for the present paper.[10] Here we just observe that Eq. (1) becomes exact if one neglects the spin or SO interaction separately. Thus one expects that it has a perturbation expansion around these two limits. In other words, this approach can fail only if both SO and spin dependence are large. For real systems this situation can never happen, since the SO interaction in the final state is large only for $\ell=1$ states of large $Z$ materials like actinides. However, their magnetic properties are dominated by $f$ electrons and their exchange interaction with final $p$ electrons is expected to be small. This argument is justified *a posteriori* by the good agreement of our calculations with experiment for Gd $L_1$ XMCD. Thus the relativistic expression for XAS in Eq. (1) is completely analogous to that in nonrelativistic theory except for additional spin indices, i.e., the replacement $Js\rightarrow Ls$ in each term. Hence it is straightforward to extend any relativistic spin-independent code to include both spin and relativity in this way. Moreover, the relativistic effects on free propagator matrix elements come mostly from the relativistic dispersion relation $k^2/2\approx E+E^2/2c^2$ (in atomic units) and is extremely small since $c\approx137$ and we are interested in photoelectron energies $E\leqslant50$ Hartrees. Most of the remaining relativistic corrections can be accounted for by using the same interpolative approach to include spin-flip processes or SO interaction for the $t$ matrices. This interpolation is given by

$$t_{Ls,L's'}=\sum_{j=\ell-1/2}^{\ell+1/2}\langle LS|J\rangle\frac{t_{js}+t_{js'}}{2}\langle J|L'S'\rangle. \tag{3}$$

Notice that if one neglects SO interaction, the sum over $j$ leads to zero amplitude for spin-flip processes. Both experimentally[13] and theoretically[14] this amplitude has been shown to be small compared to spin-conserving scattering. Therefore we do not use this interpolation for the $t$ matrices in the present calculations of XAS.

Relativistic and polarization-dependent calculations of XAS spectra require a careful treatment of the dipole matrix elements. Here we use the relativistic form of the multipole matrix elements discussed by Grant,[15]

$$M^{n'\kappa'm'}_{n\kappa m}(\hat{\epsilon},\vec{q})=\langle n\kappa m|\vec{\alpha}\cdot\hat{\epsilon}e^{i\vec{q}\cdot\vec{r}}|n'\kappa'm'\rangle. \tag{4}$$

Here the quantum number $\kappa=\ell$ when $j=\ell-(1/2)$ and $\kappa=-(\ell+1)$ when $j=\ell+1/2$. For convenience we take the photon wave vector $\vec{q}$ ($|\vec{q}|=\omega/c$) to be along the $z$ axis, and define right ($\epsilon=+1$) and left ($\epsilon=-1$) circular polarizations as $\hat{\epsilon}_{\pm1}=\mp(\hat{\epsilon}_x\pm\hat{\epsilon}_y)/\sqrt{2}$. Grant's Eq. 6.30 for the dipole approximation can then be rewritten in the form of Wigner-Eckart theorem and $3j$ symbols,

$$M^{n'\kappa'm'}_{n\kappa m}(\hat{\epsilon}_{\epsilon},|\vec{q}|)=(-1)^{j-m}\begin{pmatrix} j & 1 & j' \\ -m & \epsilon & m' \end{pmatrix}R_{\kappa\kappa'}, \tag{5}$$

where the reduced matrix element $R_{\kappa\kappa'}$ is

$$R_{\kappa\kappa'}=i\int dr j_0(qr)[P_{\kappa}Q_{\kappa'}C^{(1)}_{\kappa\kappa'}+Q_{\kappa}P_{\kappa'}C^{(-1)}_{\kappa\kappa'}], \tag{6}$$

and $P_{\kappa}$ ($Q_{\kappa}$) is the upper (lower) component of the Dirac spinor.[15] It is straightforward to calculate all $C^{(\pm1)}_{\kappa\kappa'}$ using the appendixes of Messiah,[16] and we obtain $C^{(\sigma)}_{\kappa\kappa'}=[\sigma(-1)^{(\Delta-1)}/(2\kappa+\sigma)]\quad|(\Delta+\sigma)(2\kappa+\Delta)(2\kappa+\Delta)^2-1|^{1/2}$, where $\Delta=\kappa'-\kappa=\pm1$ or $\Delta=0$ if $\kappa=-\kappa'$. These are the only possible pairs of $\kappa\kappa'$ in the dipole approximation. Thus it is easy to calculate the relativistic dipole matrix elements using Eq. (6). Hence the smooth central atom cross section becomes

$$\sigma_0(\omega)=(8\pi ck/3\,\omega)\sum_{k'}|R_{\kappa\kappa'}|^2. \tag{7}$$

Defining normalized reduced matrix elements by $\widetilde{R}_{\kappa\kappa'}=e^{i\delta_{j'}}R_{\kappa\kappa'}/[\Sigma_{\kappa'}|R_{\kappa\kappa'}|^2/3]^{1/2}$, the equation for the fine structure $\chi=[\sigma-\sigma_0]/\sigma_0$ is

$$\chi=\sum_{\kappa'\kappa''}\widetilde{R}_{\kappa\kappa'}\widetilde{R}_{\kappa\kappa''}\begin{pmatrix} j & 1 & j' \\ m & \epsilon & m' \end{pmatrix}\begin{pmatrix} j & 1 & j'' \\ m & \epsilon & m'' \end{pmatrix}\widetilde{G}^{sc}_{J',J''}. \tag{8}$$

This expression can be used to calculate polarization-dependent XAS, including both $\ell\rightarrow\ell\pm1$ channels. These expressions are straightforward to generalize for spin-

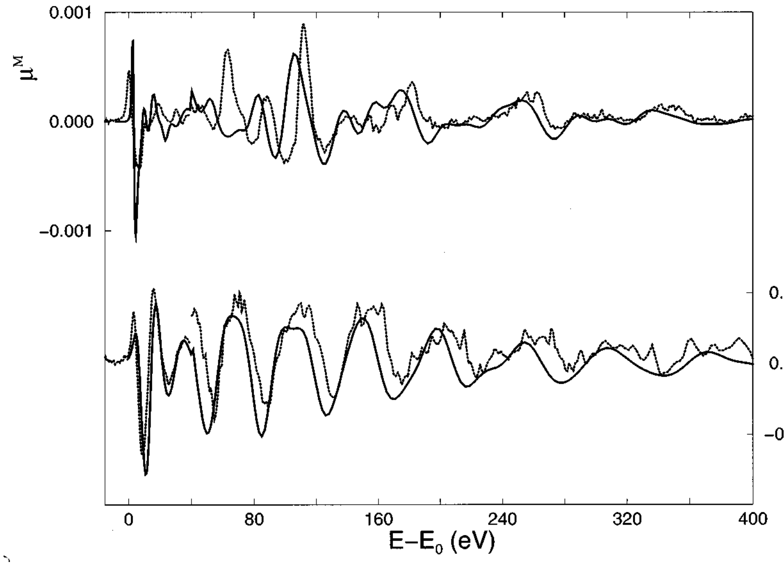

FIG. 1. Upper panel: calculated (solid) Fe $K$ edge XMCD vs experimental data (dotted) of Dartyge *et al.*; lower panel: calculated (solid) Gd $L_1$ XMCD with background subtraction vs experimental data (dotted) of Schütz *et al.* Both theory and experiment are reduced by a factor of 1/3 for $E<40$ eV.

dependent potentials with our interpolative approach. Just one spin index must be added since spin is conserved in dipole transitions.

An approximate expression for XMCD can be derived for $\ell=0$ based on Eq. (1), assuming that SO is important only for the central atom. After substitution of all $3j$ symbols one obtains

$$\sigma_c \approx \tfrac{1}{3}(\sigma_{3/2\uparrow}-\sigma_{3/2\downarrow}-\sigma_{1/2\uparrow}+\sigma_{1/2\downarrow}), \tag{9}$$

where $\sigma_{js}$ is calculated by solving the Dirac equation for the final total angular momentum $j=3/2$ or 1/2 and for spin-up ($\uparrow$) or -down ($\downarrow$) potentials. Thus the $\ell=0$ XMCD signal is roughly given by the second derivative of the nonmagnetic absorption $\sigma$. In the derivation of Eq. (9) it was important to delete cross terms. Thus, since SO in the final state is a small perturbation, we approximated the product of reduced matrix elements as $\tilde{R}_{\kappa,1}\tilde{R}_{\kappa,-2}\approx\frac{1}{2}(\tilde{R}^2_{\kappa,1}+\tilde{R}^2_{\kappa,-2})$, where spin indices are suppressed. Equation (9) explicitly shows that the XMCD vanishes if either spin or SO interaction in the final state is neglected.

We now present two applications. First we apply Eq. (1) to calculate XMCD at $\ell=0$ edges in magnetic materials. The use of $j$-independent $t$ matrices corresponds to the neglect of spin-flip processes. Therefore spin is conserved for the photoelectron and our calculations naturally separate into calculations for spin-up and -down alone. Here the spin-dependent density was constructed from overlapped spin-polarized neutral atom orbitals with appropriate occupation numbers, e.g., we assume the excess spin-up density in Fe is due to five $3d$ electrons.[9] The spin-dependent potential was then calculated using the the local spin-density prescription of von Barth and Hedin[17] together with the Hedin-Lundqvist (HL) self-energy. The energy dependence of this difference leads to a reduction of the XMCD signal at high energies (EXAFS region).[9]

Calculations of XMCD for the Fe $K$ edge, including the atomic background contribution, are compared in Fig. 1(a) to the experimental results of Dartyge *et al.*[18] at 30 K and 0.5 T. Edge energies were fixed by comparing the XAFS and no other adjustable parameters were used. Analogous calculations have been carried out by Brouder *et al.*[5] and by Ebert *et al.*[6] However, our results agree better with experiment both in EXAFS and in x-ray-absorption near-edge structure (XANES). We remark that none of these one-electron calculations reproduces the observed peak around 60 eV, which has been attributed to multielectron excitations.[19] Some additional sharp features arise due to final states with two holes that one-electron calculations do not include. Similar calculations of XMCD at the $L_1$ edge of Gd [Fig. 1(b)] give good agreement with the experimental data of Schütz.[20] These results verify that our interpolative approach to spin-dependent XAS calculations works well.

As a second application we consider the polarization dependence of hcp Cd. Polarization dependence is important for monocrystals with symmetry lower than cubic and for surface studies. The Cd XAS is compared with FEFF7 simulations in Fig. 2 for hcp in-plane polarization. It was argued by Le Fèvre *et al.* that the neglect of $\ell\to\ell-1$ transitions can lead to errors in distance determination as much as 0.1 Å.[21] This is surprising, considering that the difference between calculations with and without the $\ell\to\ell-1$ channel is very small (see Fig. 2). Le Fèvre *et al.* have extracted a related cross term contribution to Cd XAS $\{\chi_2(\alpha)=[\chi_{\ell\to\ell\pm1}(\alpha)-\chi_{\ell\to\ell+1}(\alpha)]/(6-9\cos^2\alpha)\}$, where $\alpha$ is the angle between the polarization vector and the hexagonal base plane of the Cd hcp structure.[21] The theoretical extraction of $\chi_2$ is straightforward and is practically angle independent. It is compared to experimental data in the insert to Fig. 2. Since $\chi_{\ell\to\ell+1}$ also has an angular dependence proportional to $(2-3\cos^2\alpha)$, the experimental extraction of $\chi_2$ is more subtle. However, both the observed amplitude and sign agreement are reasonable considering the difficulty of this experimental extraction; part of the amplitude discrepancy may be due to the overestimation of loss by the plasmon-pole HL self-energy used in FEFF.

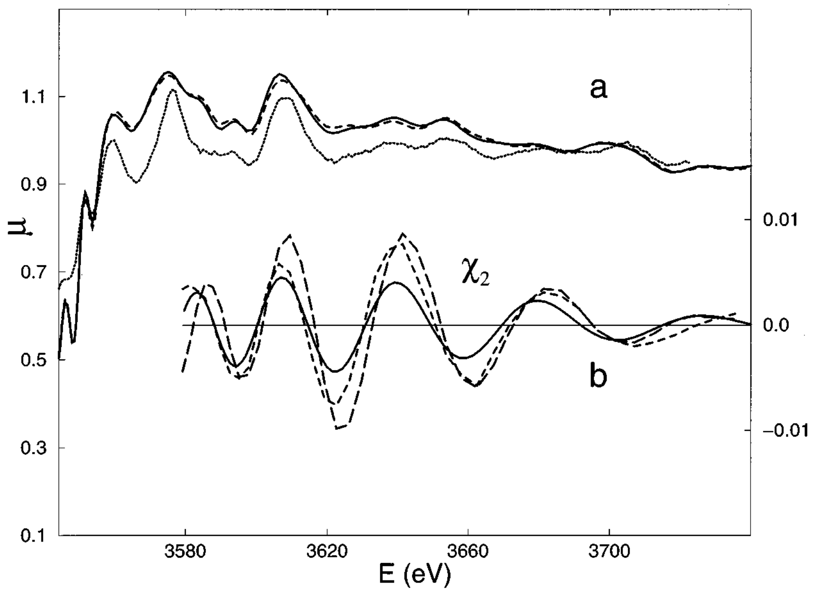

FIG. 2. hcp Cd $L_3$ EXAFS with polarization vector in the hexagonal plane; calculation (solid) vs experimental data (dotted), and calculation without $\ell \rightarrow \ell - 1$ channel (dashes); inset: comparison of calculated (solid) cross term ($\chi_2$) and that experimentally extracted at 0° (long dashes) and 80° (dashes). The difference between 0° and 80° data is a measure of the experimental uncertainty in $\chi_2$.

Finally, various self-energy models can be tested within our code. We have shown elsewhere[22] that a partly nonlocal self-energy, based on full nonlocal Fock exchange for core states and HL self-energy for valence/conduction states, gives better positions of peaks in XANES and slightly improves EXAFS analysis of Cu metal. However, this self-energy still overestimates losses in the XANES region and improvements are desirable.

In conclusion, we have developed an efficient two-step algorithm for relativistic calculations of XAS and XMCD in arbitrary systems. The method yields the best agreement with experiments to date for XMCD and provides a basis for many further developments.[10]

We are grateful to G. Schütz, M. Knülle, D. Ahlers, E. Dartyge, H. Magnan, and D. Chandesris for making their data and details of their experiments available to us. We also thank R. C. Albers, M. Alouani, Ch. Brouder, H. Ebert, D. Koelling, C. R. Natoli, and E. A. Stern for helpful comments. This work was supported in part by U.S. DOE Grant No. DE-FG03-97ER45623.

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