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Xclaim: A graphical interface for the calculation of core-hole spectroscopies

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ABSTRACT

Xclaim (X-ray core level atomic multiplets) is a graphical interface for the calculation of core-hole spectroscopy and ground state properties within a charge-transfer multiplet model taking into account a many-body Hamiltonian with Coulomb, spin–orbit, crystal-field, and hybridization interactions. Using Coulomb and spin–orbit parameters calculated in the Hartree–Fock limit and ligand field parameters (crystal-field, hybridization and charge-transfer energy) the program calculates X-ray absorption spectroscopy (XAS), X-ray photoemission spectroscopy (XPS), photoemission spectroscopy (PES) and inverse photoemission (IPES). The program runs on Linux, Windows and MacOS platforms.

1. Introduction

Multiplet ligand-field theory (MLFT) or small cluster calculations [1–4] are useful approaches for calculating X-ray spectroscopy on strongly correlated materials where the spectral lineshape is dominated by strong multiplet effects arising from the Coulomb interactions between the valence electrons and between the valence electrons and the core hole. Since the eigenfunction of a Coulomb multiplet often involves several Slater determinants, they are often poorly described by effective single-particle models, such as density functional theory. For MLFT, one considers a single ion and the effects of the ligands are described by an effective crystal field. This approach often works well when describing X-ray absorption spectroscopy. For X-ray photoemission, screening effects are stronger and the ligands have to be included explicitly. This is generally known as small-cluster calculations. The spectra are calculated by constructing a many-body Hamiltonian for the system using full configuration-interaction, *i.e.* taking into account in the basis states any possible combination of Slater determinants and has the advantage of accurately treating the Coulomb interaction in the metal ion. This approach has been used with great success to describe X-ray spectra [5–15].

In this paper we discuss the calculation of core-hole spectroscopy in terms of a multiplet Hamiltonian with the model implemented in Xclaim [16]. Xclaim is a code to calculate different types of X-ray spectra within the ionic or small-cluster limit. The program allows flexible input and output via a graphical user interface. The paper is outlined as follows. First, we give an overview of the model Hamiltonian used in the calculation of the spectra. We discuss the different interactions included in the many-body Hamiltonian. Subsequently, we describe the various spectroscopies that can be calculated: X-ray absorption spectroscopy (XAS), X-ray photoemission spectroscopy (XPS), photoemission spectroscopy (PES) and inverse photoemission (IPES). The final Section contains a description of the graphical interface for the calculation of spectra and ground state properties.

2. Model Hamiltonian

The Hamiltonian for MLFT and small-cluster calculations, can be split into the following terms

$$H = H_{\text{atomic}} + H_{\text{CF}} + H_{\text{hybridization}}, \quad (1)$$

where H_{atomic} describes the central ion where the X-ray transition takes place. The last two terms on the right-hand side describe the effects of the surrounding ions: H_{CF} describes the effects of the ligands as an effective point-charge crystal field; $H_{\text{hybridization}}$ is included for small-cluster calculations and describes the hybridization of the central ion with the nearest-neighbor ligand ions.

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The Hamiltonian for the electrons on the central ion is given by

$$H_{\text{atomic}} = \sum_i \frac{\mathbf{p}_i^2}{2m} - \sum_i \frac{Ze^2}{r_i} + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \zeta(r_i)\mathbf{l}_i \cdot \mathbf{s}_i - \boldsymbol{\mu} \cdot \mathbf{B}, \tag{2}$$

where the indices i and j run over all electrons of the ion. The first term in H_{atomic} is the kinetic energy, where $\mathbf{p}_i$ and m are the momentum and the mass of the electrons, respectively. The second term on the right-hand side is the potential energy of the nucleus, where Z is the atomic number. These two terms lead to the binding energy for the electrons. The next term is the Coulomb interaction between the electrons. The Coulomb interactions that include electrons in a closed shell lead to an effective change in the binding energy. The interaction between two electrons that are both in open shells leads to multiplet structure that can often be clearly observed in the spectral line shape. The fourth term is the spin–orbit interaction, where $\zeta(r_i)$ is the radial part of the spin–orbit interaction. The last term is an external magnetic field $\mathbf{B}$ with $\boldsymbol{\mu}$ is the total magnetic moment $\boldsymbol{\mu} = -\mu_B(\mathbf{L} + g_S\mathbf{S})$ with $g_S \approx 2$ the spin gyromagnetic ratio. The interaction is weak but plays a crucial role in lifting the degeneracy of the ground state for magnetic systems. Let us consider the interactions in H in more detail.

2.1. Coulomb and spin–orbit interactions

In the evaluation of the matrix elements of the Hamiltonian, the angular part, resulting from the integrals over the spherical harmonics of the atomic wavefunctions, can be expressed in terms of Clebsch–Gordan coefficients or 3j symbols. The radial parts of the matrix elements involve integrals over the radial atomic wavefunctions and therefore explicitly depend on the effective central-field potential that an electron in a particular orbital experiences. Whereas the angular matrix elements can be evaluated analytically, the radial matrix elements need to be calculated numerically. In the calculations, the Hartree–Fock self-consistent atomic field for an isolated ion, as implemented in Cowan's atomic multiplet program RCN [17,18], is used. The resulting radial wavefunctions $P_{nl}(r)$, where n is the principal quantum number and l is the angular momentum quantum number, can be used to evaluate the matrix elements.

For the spin–orbit interaction this gives

$$\zeta_{nl} = \frac{\alpha^2}{2} \int_0^\infty \frac{1}{r} \left(\frac{dU_{nl}}{dr} \right) |P_{nl}(r)|^2 r^2 dr, \tag{3}$$

α is the fine structure constant. In the matrix element the radial part of the interaction $\zeta(r_i)$ from Eq. (2) can be expressed in terms of the derivative of the effective central-field potential energy U_{nl}. The spin–orbit interaction mixes the orbital and spin quantum numbers. This can change the ground-state symmetry, which can significantly alter the spectral line shape. In the final state, the spin–orbit interaction in a core–shell with $l_c > 0$ is often large enough to separate the spectrum into two distinct edges, for example the $L_2\,(2p_{1/2})$ and $L_3\,(2p_{3/2})$ edges for transition-metal compounds.

For the electron–electron interaction, we can make a multipole expansion of $1/r_{ij}$ with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$

$$\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = e^2 \sum_k \frac{r_<^k}{r_>^{k+1}} \mathbf{C}^k(\hat{\mathbf{r}}_i) \cdot \mathbf{C}^k(\hat{\mathbf{r}}_j), \tag{4}$$

where $r_{<,>}$ is the lesser/greater of r_i and r_j; $\mathbf{C}^k$ is a tensor of renormalized spherical harmonics whose components are related to the spherical harmonics $C_q^k = \sqrt{4\pi/(2k+1)}Y_{kq}$; $\hat{\mathbf{r}} = \mathbf{r}/r$ is a shorthand for the angular coordinates θ and φ in spherical polar coordinates. The Coulomb interaction is customarily parameterized in terms of the radial integrals

$$R^k_{n_1 l_1 n_2 l_2 n_3 l_3 n_4 l_4} = e^2 \int_0^\infty dr_1\, r_1^2 \int_0^\infty dr_2\, r_2^2 \frac{2r_<^k}{r_>^{k+1}} \quad P_{n_4 l_4}(r_1) P_{n_3 l_3}(r_2) P_{n_2 l_2}(r_2) P_{n_1 l_1}(r_1), \tag{5}$$

For two atomic orbitals, the integrals are divided into direct $F^k_{nl;n'l'} = R^k_{nln'l'n'l'nl}$ and exchange $G^k_{nl;n'l'} = R^k_{nln'l'nln'l'}$ parts. In addition, one has $F^k_{nl;nl} = G^k_{nl;nl}$. The matrix element for the Coulomb interaction between two electrons with orbital angular momentum l and l' can be written in

$$\begin{aligned} &\langle nlm_4\sigma; n'l'm_3\sigma' | H | n'l'm_2\sigma'; nlm_1\sigma \rangle \\ &= \Bigg[\sum_{kq} F^k_{nl;n'l'} \langle lm_4 | C^k_q | lm_1 \rangle \langle l'm_3 | [C^k_q]^* | l'm_2 \rangle \\ &\quad - \delta_{\sigma\sigma'} G^k_{nl;n'l'} \langle l'm_3 | C^k_q | lm_1 \rangle \langle lm_4 | [C^k_q]^* | lm_2 \rangle \Bigg] \end{aligned} \tag{6}$$

where the matrix elements of the normalized spherical harmonics C^k_q are given by

$$\langle l'm' | C^k_q | lm \rangle = (-1)^m [ll']^{1/2} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix} \tag{7}$$

and $[ll']$ denotes $(2l+1)(2l'+1)$.

For ionic materials, the Hartree–Fock values of F^k and G^k are reduced customarily to 80% to account for the intraatomic configuration-interaction effects. Reductions to less than 80% can be used to mimic the effect of hybridization in a simpler crystal field model without ligand orbitals [19]. The reduction in the Coulomb parameters is related to an increase in hybridization and indicates a decrease in importance of the core-valence interaction. A strong reduction can occur when the excitonic final states in XAS are not completely pulled below the valence band continuum. Reductions of about 50% are necessary for shallow core-hole edges as the $M_{2,3}$ (3s) edges of transition metals [20,21] and the $O_{4,5}$ (5d) edges of actinides [22].

2.2. Crystal field

The spectral lineshape is generally strongly affected by solid-state effects. To lowest order, these effects can be included by an effective crystal field, H_{CF} in Eq. (1). This not only describes the point-charge crystal field, but can often also account for some of the effects of the hybridization of the central ion with the surrounding ligands. The effect of the crystal field is to lower the symmetry causing a splitting of the states that are obtained in spherical symmetry, *i.e.* by including only Coulomb and spin–orbit interactions. The spectral lineshape changes because of the energy splittings caused by the crystal field and due to the change in the symmetry of the ground state.

Many conventions exist for parameterizing the effect of the ligand environment. In our code, for the crystal field we use a parameterization based on the point group of the ion in terms of Ballhausen or Wybourne parameters [23,24]. For a shell with