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

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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) for d and f valence metals at different absorption edges. The program runs on Linux, Windows and MacOS platforms.

I. INTRODUCTION

Multiplet ligand-field theory (MLFT) is a successful approach, for strongly correlated systems where ab-initio methods, such as density functional theory, cannot describe adequately the electronic structure. MLFT is especially well suited for calculating local properties, such as core-hole spectra or crystal-field excitations. MLFT considers a considers a d or f valence cation surrounded by neighboring ligands. A many-body Hamiltonian is constructed for the metal-ligands cluster and is diagonalized using full configuration-interaction, i.e. we take into account in the basis states any possible combination of Slater determinants. This approach has the advantage of treating accurately the Coulomb interaction in the metal ion. This approach has been used with great success to describe x-ray spectra.

The multiplet model accounts for the atomic interactions (Coulomb and spin-orbit). The interaction with the neighbouring ligands is taken into account by including crystal-field and hybridization terms in the Hamiltonian. Many conventions exist for parametrizing the effect of the ligand environment. In our code, for the crystal field we use a parametrization based on the point group of the ion in terms of Ballhausen or Wybourne parameters. Other available atomic multiplet programs construct an ab-initio crystal field based on the relative positions of the ligand ions and parameters that modulate the strenght of the interaction with each of the ligands.

In this paper we discuss the calculation of core-hole spectroscopy in terms of a multiplet Hamiltonian with the model implemented in Xclaim [9]. We discuss the different interactions terms taken into account in the many-body Hamiltonian and the different spectra that can be calculated form the multiplet model: x-ray absorption spectroscopy (XAS), x-ray photoemission spectroscopy (XPS), photoemission spectroscopy (PES) and inverse photoemission (IPES). We explain the usage of the graphical interface for the calculation of spectra and ground state properties.

II. MODEL HAMILTONIAN

We use a many-particle Hamiltonian accounting for atomic multiplets, crystal field and hybridization

$$H = H_{\text{atomic}} + H_{\text{CF}} + H_{\text{hybridization}}$$

(1)

The spherically symmetric atomic Hamiltonian for the electrons includes kinetic energy, potential energy created by the nucleus, coulomb repulsion between the electrons, spin-orbit coupling, and interaction with a magnetic field \( \mathbf{B} \)

$$H_{\text{atomic}} = \sum_i \frac{p_i^2}{2m} - \sum_i Z e^2/r_i + \sum_{i<j} \frac{e^2}{|r_i - r_j|} + \sum_i \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i - \mathbf{\mu} \cdot \mathbf{B}$$

(2)

where the sum over \( i \) runs over all electrons, \( \xi(r_i) \) is the radial part of the spin-orbit interaction, \( \mathbf{\mu} \) is the total magnetic moment \( \mathbf{\mu} = -\mu_B (\mathbf{L} + g_S \mathbf{S}) \) with \( g_S \approx 2 \) the spin gyromagnetic ratio. When we restrict ourselves to a shell with a given orbital angular momentum quantum number \( l \), we do not need to consider the kinetic and potential energy, since they are constant.

A. Coulomb and spin-orbit interactions

In the evaluation of the matrix elements of the Hamiltonian, the angular part resulting from the integrations 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 involves integrations over the radial part of the atomic wavefunctions and therefore explicitly depends on the effective central-field potential that an electron in a particular orbital experiences. For the calculation of the radial parts of the wavefunction and the radial matrix elements of the Coulomb interaction and spin-orbit coupling, we resort to Hartree-Fock self-consistent atomic field for an
isolated ion implemented in Cowan’s atomic multiplet program RCN \cite{4, 10}.

From the one particle radial wavefunctions $P_n(r)$ calculated by the Hartree-Fock method we get estimates of the spin-orbit parameter $\zeta_{nl}$

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

where $U_{nl}$ is the effective central-field potential energy for an electron in the orbital with quantum numbers $n$ and $l$ and $\alpha$ is the fine structure constant. 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 of a core-shell with $l_\sigma > 0$ 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 the Coulomb interaction, by making a multipolar expansion of $1/|r_{ij}|$ with $r_{ij} = |r_i - r_j|$, we can write the electron repulsion energy as

$$\frac{e^2}{|r_i - r_j|} = e^2 \sum_k \frac{r^{k}}{r^{k+1}} C^k(\mathbf{r}_i) \cdot C^k(\mathbf{r}_j),$$  \hspace{1cm} (4)

where $C^k$ is a tensor of normalized spherical harmonics whose components are related to the spherical harmonics $C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}; \mathbf{r} = r/\mathbf{r}$ is a shorthand for the angular coordinates $\theta$ and $\varphi$ in spherical polar coordinates. The Coulomb interaction is customarily parametrized in terms of the radial integrals

$$R_{n_l n_l l_\sigma n_l l_\sigma}^{k} = e^2 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 \frac{2r^{k}}{r_1^{k+1}}$$

$$P_{n_l l_\sigma} (r_1) P_{n_l l_\sigma} (r_2) P_{n_l l_\sigma} (r_2) P_{n_l l_\sigma} (r_1),$$  \hspace{1cm} (5)

where $P_{n_l l_\sigma} (r)$ are the radial wavefunctions of the shell $i$, and $r_<_l$ $(r_>_l)$ is the minimum (maximum) of $r_1$ and $r_2$. The integrals $R^{k}(ij; tu)$ are divided into direct $R_{nl; n'l'}$ and exchange $G^{k}_{nl; n'l'}$ parts. In addition, one has $P_{nl; n'l'} = G^{k}_{nl; n'l'}$. The direct and exchange hamiltonian contributions for the interaction of electrons in shells with angular momentum quantum numbers $l$ and $l'$ can be written

$$H_{direct} = \sum_{m_1, m_2, m_3} \sum_{m_4, \sigma, \sigma'} \sum_{k, q = -k}^{q = k} \langle m_1 | C_q^{(k)} | m_3 \rangle \langle l' m_2 | C_q^{(k)} | l' m_3 \rangle \epsilon_{m_1 \sigma}^{\dagger} \epsilon_{m_2 \sigma} \epsilon_{m_3 \sigma} \epsilon_{m_4 \sigma'}$$  \hspace{1cm} (6)

$$H_{exchange} = \sum_{m_1, m_2, m_3} \sum_{m_4, \sigma, \sigma'} \sum_{k, q = -k}^{q = k} \langle m_1 | C_q^{(k)} | l' m_3 \rangle \langle l' m_2 | C_q^{(k)} | l' m_3 \rangle \epsilon_{m_1 \sigma}^{\dagger} \epsilon_{m_2 \sigma} \epsilon_{m_3 \sigma} \epsilon_{m_4 \sigma'}$$  \hspace{1cm} (7)

where the matrix elements of normalized spherical harmonics $C_q^{(k)}$ are given by

$$\langle m | C_q^{(k)} | m' \rangle = (-1)^m [l, l']^{1/2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & q & m' \end{pmatrix}$$  \hspace{1cm} (8)

and $[l, l']$ 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. \cite{11} 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 excitation 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 \cite{12, 13} and the $O_{4,5}$ ($5d$) edges of actinides \cite{14}.

B. Crystal Field

We can express the crystal-field of an ion as a multipole expansion of the charge density around it, and use the Wybourne parametrization of the crystal-field \cite{15, 16}. For a shell with angular quantum number $l$, the crystal field is written as

$$H_{CF} = \sum_{k, q} B_{kq} C_{q}^{k}$$  \hspace{1cm} (9)

with $0 \leq k \leq 2l$, $k$ an even integer and $-k \leq q \leq k$. $B_{kq}$ are the Wybourne crystal-field parameters.

Taking into account that $B_{k-q} = (-1)^q B_{kq}$ because of the hermiticity of the Hamiltonian, and separating the real and imaginary parts of the Wybourne parameters $B_{kq} = \text{Re} B_{kq} + i \text{Im} B_{kq}$, $H_{CF}$ can be written as

$$H_{CF} = \sum_{k} \left\{ B_{k0} C_{0}^{k} + \sum_{l \leq q \leq k} \left[ \text{Re} B_{kq} \left( C_{q}^{k} + (-1)^q C_{-q}^{k} \right) \\
+ i \text{Im} B_{kq} \left( C_{q}^{k} - (-1)^q C_{-q}^{k} \right) \right] \right\}$$  \hspace{1cm} (10)

The fact that the Wybourne parameters $B_{kq}$ transform under rotations like the components of an spherical tensor makes it easy to parametrize arbitrary rotations of the crystal field \cite{17}. The number of non-zero parameters, and algebraic relationships between them are determined by the point group symmetry \cite{18, 19}. The Wybourne parameters $B_{kq}$ can be easily related to the Stevens parameters \cite{13, 20}.

In the case of cubic octahedral symmetry ($O_h$), the 4-fold axis around $z$ limits the values of $q$ to $q = 0, \pm 4,$
and the invariance of the crystal field under 90-degree rotations about \( x \) or \( y \) forbids the term \( B_{20} \), since the spherical harmonic \( C_0^4 \) is not preserved for those rotations, and relates the \( q = 0 \) and \( q = 4 \) parameters for the \( k = 4, 6 \) representations:

\[
B_{44} = \sqrt{\frac{5}{14}} B_{40}
\]

\[
B_{64} = -\sqrt{\frac{7}{2}} B_{60}
\]  

(11)

The only free parameters are \( B_{40} \) and \( B_{60} \). The crystal field Hamiltonian becomes

\[
H_{\text{CF},Oh} = B_{40} \left[ C_0^4 + \sqrt{\frac{5}{14}} (C_4^4 + C_{-4}^4) \right] + B_{60} \left[ C_0^6 - \frac{7}{2} (C_4^6 + C_{-4}^6) \right]
\]  

(12)

Another common notation in the cubic case is to use the parameters \( V_4 = B_{40}/8 \) and \( V_6 = B_{60}/16 \). For an \( f \)-shell, the orbitals split into three independent representations: \( a_{2g} (f_{x^2}, t_{2g} (f_z, f_y, f_{x^2-z^2}, f_y(x^2-y^2)) \) with energies

\[
\varepsilon_{a_{2g}} = \frac{80}{143} B_{60} - \frac{4}{11} B_{40}
\]

\[
\varepsilon_{t_{2g}} = \frac{100}{429} B_{60} + \frac{2}{11} B_{40}
\]

\[
\varepsilon_{t_{2g}} = \frac{60}{143} B_{60} - \frac{2}{33} B_{40}
\]

For a \( d \)-shell \((l = 2)\) the term \( B_{60} \) does not contribute, and the orbitals split between \( e_g \) and \( t_{2g} \) orbitals at energies \( \frac{2}{7} B_{40} \) and \( -\frac{1}{21} B_{40} \). The parameter \( B_{40} \) can be related to the commonly used \( \Gamma Dq \) parameter for octahedral splitting by \( 10 Dq = \frac{19}{16} B_{40} \). We can generalize the splitting in a \( d \)-shell to tetragonal symmetry and relate \( B_{40}, B_{44} \), to the parameters \( Dq \) and \( Dt \) [122],

\[
B_{20} = -7 Ds
\]

\[
B_{40} = 21 (Dq - Dt)
\]

\[
B_{44} = 21 \sqrt{\frac{5}{14}} Dq
\]  

(13)

The splitting of the valence shell orbitals is determined by the point-symmetry group of the crystalline environment. By making a unitary transformation to a symmetry-adapted basis it is always possible to write the crystal-field Hamiltonian as a sum over irreducible representations,

\[
H_{\text{CF}} = \sum_{\Gamma \gamma} \varepsilon_{\Gamma}(\Gamma) c_{\gamma}^\dagger c_{\gamma}
\]

where \( \varepsilon_{\Gamma} \) is the energy of the \( \Gamma \) representation of the point group, and \( c_{\gamma}^\dagger \) is the creation operator for an electron in the \( \gamma \) orbital belonging to the \( \Gamma \) representation.

**TABLE I: Crystal field splitting energies for the \( d \)-shell orbitals belonging to different representations in tetragonal symmetry \( D_{4h} \).**

| \( \Gamma \) | \( \varepsilon_{\Gamma} \) | \( d \)-orbital |
| --- | --- | --- |
| \( a_{1g} \) | \( 6Dq - 2Ds - 6Dt \) | \( 3z^2 - r^2 \) |
| \( b_{1g} \) | \( 6Dq + 2Ds - Dt \) | \( x^2 - y^2 \) |
| \( b_{2g} \) | \( -4Dq + 2Ds - Dt \) | \( xy \) |
| \( e_g \) | \( -4Dq - Ds + 4Dt \) | \( yz, z^2 \) |

In the case of octahedral symmetry \((O_h)\) for a \( d \)-shell, the \( e_g (d_{3z^2-r^2}, d_{x^2-y^2}) \) and \( t_{2g} (d_{xy}, d_{yz}, d_{xz}) \) orbitals are separated by an energy \( 10Dq \). For tetragonal symmetry \((D_{4h})\) the crystal-field splittings of a \( d \)-shell orbitals are usually given in terms of the parameters \( Dq \) and \( Dt \) (see table I).

**C. Hybridization**

We include in our model an additional shell of effective ligands and take into account configurations \( d^n, d^{n+1}L_1^1, \)

\( d^{n+2}L_2^2 \ldots \) where \( L_n^m \) denotes \( n \) holes in the ligand shell. Including additional configurations in our model will increase the computational cost of constructing and diagonalizing our Hamiltonian because of the increase in the size of the hilbert space basis. We include in the Hamiltonian a hybridization term that mixes the valence orbitals with an effective ligand shell \( L \) with the same number of orbitals as the valence shell. We consider only the linear combinations of orbitals for a particular point symmetry group that couple to the valence shell (i.e. they belong to the same irreducible representation as the valence shell orbitals).

The hybridization term is written as

\[
H_{\text{hyb}} = \sum_{\Gamma \gamma} T_{\delta L}(\Gamma)(d_{\delta \gamma}^\dagger L_{\gamma} + L_{\gamma}^\dagger d_{\delta \gamma}) + \sum_{\Gamma \gamma} \varepsilon_{L}(\Gamma) L_{\gamma}^\dagger L_{\gamma} \]  

(14)

\( \varepsilon_{L}(\Gamma) \) is the on-site energy for the electrons in the ligand shell depending on the irreducible representation \( \Gamma \) to which the ligand orbital belongs to. This displacement is produced by the hybridization between the valence orbitals. \( d_{\delta \gamma}^\dagger \) and \( L_{\gamma}^\dagger \) are the creation operators of an electron in the \( d \) and ligand shells. The transfer integrals \( T_{\delta L}(\Gamma) \) are written in terms of the Slater-Koster parameters [23]: \( (pda) \), \( (pdn) \), related to the overlap between the \( d \) and \( p \) orbitals of the ligands. An additional term \( T_{pp} = (pp) - (pp) \) will split of the \( e_g \) and \( t_{2g} \) ligand effective orbitals \( (T_{pp} \) is approximately \( \frac{2}{5} \) of the width of the ligand band).

For octahedral 6-coordinated \((\text{MO}_6)\) and planar 4-coordinated \((\text{MO}_4)\) metal-ligand clusters, the transfer integrals and ligand field splittings [24] are shown in table II. For setting the values of the Slater-Koster parameters, \( (pd\pi) \) is expected [25] to be slightly less than...
TABLE II: Hybridization parameters for the TMO₆ and TMO₄ clusters for the different representations in $O_h$ and $D_{4h}$ symmetry in terms of the Slater-Koster integrals $p\sigma$, $p\pi$.

| $\Gamma$                     | $T(\Gamma)$ | $\epsilon_L(\Gamma)$ |
|------------------------------|--------------|------------------------|
| $TMO_6 (O_h)$                |              |                        |
| $\epsilon_g$                | $\sqrt{3}(p\sigma)$ | $\Delta + T_{pp}$     |
| $t_{2g}$                     | $-2(p\pi)$  | $\Delta - T_{pp}$     |
| $TMO_4 (D_{4h})$             |              |                        |
| $a_{1g}$                     | $(p\sigma)$ | $\Delta + T_{pp}$     |
| $b_{1g}$                     | $\sqrt{3}(p\sigma)$ | $\Delta - T_{pp}$     |
| $b_{2g}$                     | $-2(p\pi)$  | $\Delta + T_{pp}$     |
| $e_g$                        | $-\sqrt{2}(p\pi)$ | $\Delta$         |

$(p\sigma)/2$. When considering changes in bond-length, we can use Harrison’s relationship [24], i.e. that the $3d-2p$ and $2p-2p$ charge transfer integrals are proportional to the power $-3.5$ and $-2$ of the bond-distance, respectively.

D. Definition of the charge transfer energy

The two parameters that determine the amount of covalent mixing between the valence shell of the metal-center and the ligands are the transfer integrals $T$ in Eq. (14) and the charge transfer energy, defined as the cost in energy of removing one electron of the ligands and transferring it to the metal center, i.e., difference between the ground state energies for the $d^n$ and $d^{n+1}\pi$ configurations,

$$\Delta = E(d^{n+1}\pi) - E(d^n).$$

In the limit of weak hybridization, and neglecting the multiplet splitting, the total energy of the system is

$$E(d^n) = E_0 + n\epsilon_d + \frac{n(n+1)}{2}U_{vv},$$

where $U_{vv}$ is the monopolar part of the valence-valence Coulomb interaction. The charge transfer energy will be

$$\Delta = \epsilon_d + nU_{vv} - \epsilon_L.$$  

In our cluster program, the energy of the ligand-shell in eq. (14) is given by the parameter $\epsilon_L$. In order to use the charge-transfer energy $\Delta$ as a parameter, we need to calculate $\epsilon_L$ for a given $\Delta$. To do so, we calculate the ground state for the $d^n$ and $d^{n+1}$ configurations without hybridization, and set the energy of the ligand orbitals as $\epsilon_L = E(d^n) - E(d^{n+1}) + \Delta$.

III. Calculation of X-ray spectra

For a one-photon process we can write the transition probability using Fermi’s golden rule and summing to all the final states.

$$I(\omega) = \sum_f |\langle f|T|g\rangle|^2 \delta(E_f - E_g - \hbar\omega).$$

$E_g$ and $E_f$ are the energies of the ground $|g\rangle$ and final states $|f\rangle$, $\hbar\omega$ is the x-ray energy and $T$ is a transition operator that connects the ground state to the final states. The particular form of $T$ will depend on the x-ray process that we are considering. Eq. (18) can be reexpressed as a Green’s function of the final state

$$I(\omega) = -\frac{1}{\pi} \mathrm{Im} \langle g|T|f\rangle \frac{1}{E_g + \hbar\omega - H_f + i\Gamma} |T|g\rangle,$$

where $\Gamma$ is the broadening due to the finite core-hole lifetime. In the calculation first the lowest energy eigenstate $|g\rangle$ of the initial state hamiltonian is obtained and the Green’s function of the final state hamiltonian is calculated by using a continued fraction expansion.

A. X-ray Absorption Spectroscopy (XAS)

In x-ray absorption a core electron is promoted to the valence shell by an x-ray photon. The transition operator in this case is $T(E1) = \epsilon \cdot r$ for dipolar transitions and $T(E2) = (\epsilon \cdot r)(k \cdot r)$ for quadrupolar transitions. $\epsilon$ is the x-ray polarization, $r$ is the position operator and $k$ is the propagation vector of the light. The transition operators for dipolar and quadrupolar transitions can be rewritten as spherical tensors

$$T(E1) = r \sum_q (-)^q \epsilon_{-q}^{(1)} \epsilon_q^{(1)} C_q,$$

$$T(E2) = r^2 \sum_q (-)^q \sqrt{\frac{3}{5}} \epsilon_{-q}^{(2)} \epsilon_q^{(2)} C_q,$$

with $[\epsilon_k^{(2)}] = \sum_q \epsilon_{q}^{(1)} \epsilon_{-q}^{(1)} (11q'q''|2q)$.

The matrix elements of the spherical harmonics $C_q^{(k)}$ are given in [8]. The radial matrix elements $r$ are constant for a given edge. The transition operators for light with helicities $\lambda = +1$ and $\lambda = -1$ correspond to setting $q = \pm 1$ in [20]. Light with linear polarization along the z-axis corresponds to $q = 0$. For linearly polarized along the x and y axes and propagation vector along the z-axis the transition operators for dipole and quadrupole transitions become in terms of spherical harmonics

$$T(E1, e_x) = \frac{1}{\sqrt{2}} (-C_{1}^{(1)} + C_{-1}^{(1)})$$

$$T(E1, e_y) = \frac{1}{\sqrt{2}} (C_{1}^{(1)} + C_{-1}^{(1)})$$

$$T(E2, e_z) = \frac{1}{\sqrt{6}} (-C_{1}^{(2)} + C_{-1}^{(2)})$$

$$T(E2, e_y) = \frac{1}{\sqrt{6}} (C_{1}^{(2)} + C_{-1}^{(2)}).$$

(21)
The program calculates linear and circular dichroism substracting the XAS for different polarizations. X-ray magnetic circular dichroism (XMCD) is defined as the difference between the spectra for the incoming light with helicities $\lambda = +1$ and $\lambda = -1$. In the case of XMCD sum rules give a straightforward way to obtain the orbital and spin magnetic moment from the integrated values of the measured spectra \[27, 28\]. Similarly, it is possible to get the expectation value of the spin-orbit coupling ($\sum_i l_i s_i$) from the branching ratio of the isotropic spectrum \[29\–31\]. The application of sum rules is not exempt from problems. Mixing of spectral weight occurs between spin-orbit split edges (e.g. L$_2$, L$_3$) occurs as a result of the Coulomb core-valence interaction \[32–34\]. In the case of the spin sum rule an additional term added to the spin momentum comes from the magnetic dipolar term $\langle T_z \rangle$, whose value needs to be calculated \[35, 36\].

C. Photoemission and inverse photoemission

We can also calculate the electron-removal and electron-addition spectra, which can be observed in valence photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES), respectively. The angular integrated PES spectrum, as a function of the difference between the energies of the photoelectron and incident photon $\varepsilon$ is

$$I_{\text{PES}} = -\frac{1}{\pi} \text{Im} \sum_{m\sigma} \langle g | d^\dagger_{m\sigma} \frac{1}{E_g - \varepsilon - H_f + i\Gamma} c_{m\sigma} | g \rangle,$$

where $c_{m\sigma}$ annihilates an electron with spin $\sigma$ in the $m$ orbital of the core shell and $\varepsilon$ is the energy difference between the photoelectron and the incident photon.

$$I_{\text{IPES}} = -\frac{1}{\pi} \text{Im} \sum_{m\sigma} \langle g | d_{m\sigma} \frac{1}{E_g + \varepsilon - H_f + i\Gamma} d^\dagger_{m\sigma} | g \rangle,$$

where $d^\dagger_{m\sigma}$ creates an electron with spin $\sigma$ in the $m$ orbital of the valence shell.

IV. GRAPHICAL INTERFACE

When the program is started it displays a window (Fig. 1) with entries for the chemical element, ionization state and edge to be calculated, as well as different Hamiltonian parameters. Once the ion and edge are input, the initial and final state electronic configurations are automatically generated. The program shows below the reduction values for the Slater integrals for the Coulomb interactions within the valence shell, and between core and valence. The default reduction factor is 0.8.

In addition to setting the reduction factors of the Coulomb interactions, it is also possible to edit the full set of Slater integrals and spin-orbit parameters for the initial and final states by clicking in the button Hartree-Fock values: Edit. This opens a window (Fig. 2) where the Hartree-Fock parameters are separated into two different blocks for the ground and final configurations. The Slater integrals $F^K$, $G^K$ and spin-orbit parameters are labelled in terms of the different core and valence shells. After clicking Ok, the values of the parameters are saved. The values of the Slater integrals given in the window will be renormalized by the reduction factors specified in the main window.

The program allows the components of the magnetic field in the $x, y, z$ directions to be specified. The two choices (exchange and magnetic field) mean that the field is acting on the spin moment $\mathbf{S}$ or on the total magnetic moment of the ion $\mu = \mu_B (L + 2S)$. The exchange fields are given by setting $\mu_B H$ in units of eV ($\mu_B = 5.79 \cdot 10^{-5}$ eV T$^{-1}$).

For setting the crystal field splitting, one can select from a list of different symmetries and parametrizations...
FIG. 1: Main input window and periodic table pop-up for the element selection. The main window contains the controls for setting up the main parameters for the spectra calculation divided into several areas: spectroscopy and ionization state, Coulomb and Spin orbit parameters, crystal field, hybridization, spectral broadenings and polarization.

FIG. 2: Pop-up window showing the default Hartree-Fock parameters for the Slater integrals $F_k$ and $G_k$ and the spin-orbit $\zeta$ of the core and valence shells. Customized values can be introduced in this window.

for the crystal field. The main window allows to the values of the octahedral ($10Dq$) and tetragonal ($Dq$, $Ds$ and $Dt$) crystal-field parameters. For other crystal-field parametrizations, the parameters are set with pop-up dialog boxes. One can specify the values of the energies of the different real $d$-orbitals, or in the case a general point group, it is possible to set the crystal field in terms of Wybourne parameters $B_{kq}$ (Fig. 3). In the case of an $f$-valence shell the only way to set up the crystal field is to specify Wybourne parameters. The selection of spherical in the pull-down menu means that there is no crystal field term in the Hamiltonian.

The pop-up dialog box for setting the Wybourne parameters contains a pull-down list to set the point-group symmetry. For high symmetry point groups (cubic, tetragonal, hexagonal) the program automatically disables the input boxes for the parameters that are required to be zero by symmetry. In the case of cubic octahedral symmetry, the only free parameters are $B_{40}$ and $B_{60}$, and the program automatically calculates $B_{44}$ and $B_{64}$. Selecting point group symmetry any in the pull-down list means that there is no constraint in the Wybourne parameters and all input boxes are activated.

The last group of parameters are the hybridization (implemented for $O_h$ and $D_{4h}$ symmetry). The first box is the maximum number of holes in the ligand shell, this is the number of different electronic configurations taken
FIG. 3: Pop-up window for entering the crystal field when it is defined in terms of Wybourne parameters $B_{kq}$. The point group (cubic, tetragonal or hexagonal) can be selected from a pull-down list. The point symmetry places constraints between the parameters and only the input boxes for the independent parameters are active. The input boxes for the parameters that are zero or constrained are inactive. For the case of a general point group all the boxes are active and will accept input.

into account $(d^n, d^{n+1}L, d^{n+2}L^2, ...)$). This will increase the computational cost of the calculation. The rest of the input boxes set the numerical values for the different parameters involved in the hybridization Hamiltonian: charge-transfer energy $\Delta$, isotropic coulomb interaction ($F^0$) for the valence shell and for the attractive potential between the core-hole and valence electrons ($F_{cv}^0$), and the Slater-Koster parameters ($(pd\sigma)$, $(pd\pi)$ and the difference $(pp\pi) - (pp\sigma)$)

From the parameters given, the program sets the Hamiltonian, and calculates expectation values of quantum operators in the ground state (energy, spin and orbital angular momentum and expected electronic occupations of the valence and ligand shells) or calculate the spectra.

The calculated spectra are shown in the output window (Fig. 4). For each of the polarizations calculated, results are placed in a separate tab in the plot window. In the case of dichroism, the difference (dichroism) and average spectra for two polarizations are shown. The multiplet model cannot account for the absolute positioning of the absorption edge energy, so the program positions the edge according to the values tabulated for the binding energies of the core-electrons in different elements [39]. The calculated spectrum is displayed as poles (vertical bars) and also convoluted with the input core-hole lifetime and experimental broadenings. There are input boxes on the plot for setting the values of the Lorentzian and Gaussian broadenings. For core-hole spin-edges, it is possible to set an energy-dependent Lorentzian broadening divided by an energy set by the user. This is to account for possible differences in core-hole lifetime broadening of the two spin-orbit split edges due to the presence of additional Koster-Kronig processes at the edge at higher energy. When the button Rebroaden is pressed, all polarization tabs in the window are recalculated. There are buttons on the plot window for loading experimental data to fit and to save the calculation results to a file.

Another window shows the parameters used for the calculation and the expectation values of different physical magnitudes in the ground state: number of holes in the ligand and valence shells, the components of the total spin $\mathbf{S}$ and orbital angular momentum $\mathbf{L}$ given in units of $\hbar$, spin-orbit coupling $\sum_i l_i \cdot s_i$, and the magnetic dipole operator $T_z$ that appears as an additional term in the XMCD spin sum rule [28] (see appendix A). For a $d$ valence shell the program also shows the individual occupation of the orbitals $d_{3z^2-r^2}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{yz}$, and $d_{zx}$.

V. CONCLUSION

X-ray spectroscopy is a useful tool to study the electronic structure of materials. Despite being a useful technique, multiplet effects can make its interpretation not straightforward. The model discussed allows to take into account the many-body character of the electronic structure of strongly correlated materials, and the interaction with the core hole in the final states. X-ray spectra has
been traditionally understood by the application of sum rules which give expectation values of ground state observables from experimental measurements. It is possible to go further by using multiplet ligand-field calculations of x-ray spectra, which give more detailed knowledge, aiding, for example in the quantitative determination of crystal field parameters, ground state configurations and the inclusion of charge transfer effects.

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Appendix A: Coupled tensor operators

In this appendix we define the coupled tensor operators, which are implemented in the program to calculate different quantum operators and physical magnitudes. For a shell with orbital \( l \) and spin \( s = \frac{1}{2} \) quantum numbers the unit tensor operator \( w_{\zeta \xi \eta} \) is defined as [41, 42],

\[
 w_{\zeta \xi \eta} = \sum_{m\prime \sigma \sigma'} (-1)^{l-m'} n_{l_x}^{-1} n_{s_y}^{-1} \begin{pmatrix} l & x & l \\ -m' & \xi & \eta \end{pmatrix} (-1)^{s-\sigma'} \begin{pmatrix} s & y & s \\ -\sigma' & \eta & \sigma \end{pmatrix} c_{m'\sigma} c_{m\sigma} \tag{A1}
\]

Where \( a \) and \( b \) are the unit tensor orbital and spin quantum numbers, with \(-x \leq \xi \leq x, -y \leq \eta \leq y\). The normalization factor \( n_{l_x} \) is defined as

\[
 n_{l_x} = \begin{pmatrix} l & x & l \\ -l & 0 & l \end{pmatrix} \tag{A2}
\]

From the unit tensor operator we define the coupled tensor as,

\[
 w_{xyz} = \sum_{\zeta \eta} (-1)^{x-\zeta+y-\eta} \frac{n_{xyz}^{-1}}{n_{xyz}} \begin{pmatrix} x & z & y \\ -\zeta & \xi & \eta \end{pmatrix} w_{\zeta \cdot \eta} \tag{A3}
\]

with \(-z \leq \zeta \leq z\). \( n_{xyz} \) is a normalization factor given by [43]

\[
 n_{xyz} = \begin{pmatrix} x & y & z \\ 0 & 0 & 0 \end{pmatrix} \tag{A4}
\]

The double tensor operators \( w_{xy}^{xyz} \) are used to get the ground state expectation values of physical observables: number of electrons in a shell \( n_h = w_{000} \), total spin \( S = -sw_{011} \) and orbital angular momenta \( L = -lw_{101} \), spin-orbit coupling \( \sum_i l_i \cdot s_i = lsu_{010} \), and the magnetic dipole operator \( T = \sum_i (\mathbf{r}_i \cdot \mathbf{s}_i)/\mathbf{r}_i^2 \) = \(-\frac{l}{2l+3} w_{211} \), which is relevant for the analysis of XMCD, where it appears as an additional term in the sum rule used to determine the spin angular momentum [28].
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