Multiplet ligand-field calculation of Co L-edge X-ray absorption spectrum using parameters from DFT Wannier functions

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The conventional multiplet theory is one of the most successful methods for computing X-ray spectra of metals. However, its quality is much dependent on the choice of several semi-empirical parameters. We introduce here a feasible approach that allows to derive the key parameters from systematic first-principle calculations. Its applicability is demonstrated by multiplet calculations of Co L-edge X-ray spectra of CoO system. Density functional theory calculations have been carried out to obtain optimized structure and the related energy bands of CoO, which is then followed by an optimization of maximally localized Wannier functions for the concerned Co-3d and O-2p bands. The analysis of these Wannier functions provide most of the key parameters that are required for the ligand field and charge transfer multiplet calculations. The resulted X-ray spectra are in excellent agreement with their experimental counterparts.

INTRODUCTION

The core level X-ray spectroscopy of transition-metal and rare-earth elements is an important tool to investigate the electronic structure of various related novel materials, such as clean energy and battery materials[1, 2], transition metal corroles in coordination chemistry[3], catalysts[4, 5], magnetic materials[6, 7], micro-electronics[8], etc. In order to interpret the experimental X-ray spectral features of 3d elements, different theoretical methods that take into account of multiplet and/or charge transfer effects have been developed in past years, including multiplet theory[9–12], time-dependent density functional theory (TDDFT)[13], GW approach[14], and Bethe-Salpeter approach[15, 16]. In general, the multiplet theory, due to its computational advantage and clear physical picture, has become one of the mostly applied methods that are capable of reproducing experimental observations. The other more advanced methods are computationally very expansive and yet to be fully explored. In the multiplet calculations, several semi-empirical parameters need to be employed to fit the experiments. The finding of these optimized semi-empirical parameters enables not only a good agreement with the experimental spectra, but also a good understanding of the characters of the electronic states involved. However, the fitting procedure has apparently severely weakened the predicting power of the multiplet calculations. It is thus highly desirable to obtain the key parameters in the multipole calculations from first-principle calculations.

Over the years, several attempts have already been
made. For instance, Sugano and Shulman[17] used linear combination molecular of orbitals to obtain the crystal field parameters. Zaanen et al.[18] combined first-principle band structure calculations and charge transfer effects to compute L_{2,3}-edges X-ray absorption spectrum (XAS) of lighter 3d transition metals. Bagus and Ilton[19] carried out first-principle calculation to describe all atomic multiplet and covalent effects in both initial and final states but neglecting the explicit charge-transfer effects. Martins et al.[20] performed first-principle atomic calculations of free transition metal ions to obtain the 3p XAS and XPS spectra, without considering the crystal field effect. Josefsson et al.[21] incorporated atomic multiplet and molecular orbital effects via configuration interaction for transition metal L-edge X-ray spectra in aqueous ions and molecule. It has been shown[22, 23] that DFT method incorporated with Wannier functions are able to provide realistic values for parameters in Anderson impurity model, such as state energies, hopping parameters and Coulomb interactions. Haverkort et al.[24] employed the similar idea for multiplet calculations of X-ray spectra. In their approach, the DFT calculations at LDA level with linear augmented plane waves basis set implemented in Wien2K code were performed to generate band structures of the studied system. The crystal potential from the DFT calculation were then used to derive a set of localized Wannier functions (WFs) by using the Nth-order muffin-tin orbital method[25]. From the generated Wannier functions, the parameters for multiplet calculations of X-ray spectra could then be obtained. In practice, the charge transfer multiplet (CTM) approach[26] was applied to X-ray absorption spectra, while the Quanty approach[27, 28] was employed for the resonant X-ray inelastic scattering spectra (RIXS).

In this work, a systematic modus operandi is introduced to obtain the key parameters for multiplet calculations from DFT method. The general idea is similar to what was stated above, but with different computational procedure. This computational scheme enables to incorporate both crystal field and charge transfer effects into the multiplet calculations, while remaining the flexibility to work with crystal field effect alone. Its applicability is illustrated by computing Co L_{2,3}-edge X-ray absorption spectrum of CoO system, as well as corresponding XPS and RIXS.

![CoO unit cell structure used in the calculation.](image)

The approach starts with geometric optimization and band structure calculation in a first-principle code and carried out in a unit cell with four cobalt and four oxygen atoms as shown in Fig.1. The Co^{2+} cation at site-0 and the surrounding O^{2−} anion ligands at site-(1~6) constitute a cluster to be studied in this research. The corresponding DOS and band structure are derived for a post-processing Wannier functions analysis. For the bands related to the O-2p and Co-3d orbitals in this clus-
ter, the corresponding spatially delocalized Bloch states are optimized to an alternative representation in terms of maximal localized Wannier functions (MLWFs)[29].

Since the core level X-ray spectra of transition metals and rare earth elements are related to the local electronic structure of corresponding metal cations, when the delocalized Bloch states are transformed to the localized Wannier functions, the difficult many-body problem of this local property are restricted to an easy study on orbitals of only a single metal site with few neighboring ligands. Calculation of multiplet theory parameters from these MLWFs are straightforward and the values appear to be reliable for the spectral calculation. As well known that, there would be two different sets of Wannier functions constructed corresponding to different energy windows including different bands. The first set of Wannier functions are constructed from only Co-3d orbitals related bands. The second set of Wannier functions are constructed from both Co-3d and O-2p orbitals related bands. The different sets of Wannier functions provide crystal field and charge transfer multiplet calculations parameters respectively. The crystal field effect of first set Wannier functions from only Co-3d bands already contains the contributions from charge transfer covalent interactions. While the crystal field splitting of the second set Wannier functions from both Co-3d and O-2p bands is pure electro-static interaction separated from the covalent contributions. The crystal field and charge transfer multiplet calculation with these first-principle derived parameters reproduced the Co \( ^{2}\text{p} \) electron core level related XAS, XPS and RIXS spectra very well as compared to experimental data.

The present approach adopts well developed VASP[30] and Wannier90 codes[31, 32] with the interface ready-made and easy-to-use between the two software. There are many first-principle codes such as ABINIT, Quantum-Espresso, SIESTA, FLEUR, Wien2K, OpenMX, GPAW, etc. which have comprehensive applications and ready-made interface to Wannier90 code. The present modus operandi serves as an example to the similar approaches in the future when the first-principle calculation step is completed with other code that is suitable to the system interested.

**CONSTRUCTION OF WANNIER FUNCTIONS FROM FIRST-PRINCIPLE CALCULATION**

In room temperature, CoO is in crystal structure of periclase with \( \text{Fm\ensuremath{^3m}} \) space group as shown in Fig.1. The Co\(^{2+}\) cation sites in an \( \text{O}_6 \) symmetrical local structure surrounding by six O\(^{2-}\) ligand anions. The infinite periodic structure of the CoO is optimized in non-spin-polarized first-principle DFT calculation using the VASP program package. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional[33] generated by projector augmented wave (PAW) method[34] was used for the exchange-correlation potential and pseudopotentials in which the Co(3d,4s) and O(2s,2p) semi-core states are included in the valence. Since the primitive unit cell is not large enough to constrain the final optimized Wannier functions in the correct symmetry, a large super cell with four cobalt and four oxygen atoms is used in the present calculation. In the final optimized structure Co-O bond length is about 2.043 Å, and the electronic structure is expressed in terms of Bloch states \( \psi_{mk} \) represented by band index \( m \) and crystal momentum \( \vec{k} \). The DOS and band structure are also prepared for the next step process.

The Wannier functions used in present research are in a sense which is complementary to the standard defini-
\[
\omega_{n\vec{R}} = \frac{V}{(2\pi)^3} \int_{BZ} \left[ \sum_{m} U_{mn}^k \psi_m(\vec{k}) e^{-i\vec{k} \cdot \vec{R}} d\vec{k} \right]
\]

(1)

where \( V \) is the unit cell volume, the whole integral goes over the Brillouin zone (BZ). The Wannier functions WF\(s \) \( \omega_{n\vec{R}} \) are characterized by cell lattice site vector \( \vec{R} \) and number \( n \) to distinguish different Wannier orbitals in the same unit cell \( \vec{R} \). While \( U_{mn}^k \) is an arbitrary \( k \)-dependent unitary matrix that mixes the various Bloch states at each \( k \) point. Since matrix \( U_{mn}^k \) has no unique definition in equation (1), different choices of \( U_{mn}^k \) will result in various WF\(s \) with different spatial localization characteristic. In the present research, the Wannier functions are defined uniquely with Marzari and Vanderbilt (MV) method[31] that choose a \( U_{mn}^k \) to minimize the gauge variant part of total spread:

\[
\Omega = \sum_n \left[ |\langle \omega_{n\vec{R}}(\vec{r}) | \omega_{n\vec{R}}(\vec{r}) \rangle|^2 - |\langle \omega_{n\vec{R}}(\vec{r}) | \vec{r} \omega_{n\vec{R}}(\vec{r}) \rangle|^2 \right]
\]

(2)

When only the crystal field effect is taken into the multiplet calculation, only the bands with predominant Co-3d orbital characters are involved in equation (1) to derive the maximally localized Wannier functions. While if the multiplet calculation includes both crystal field and charge transfer effects, the bands with Co-3d orbital characters and bands with O-2p orbital characters are all taken into equation (1) for Wannier functions’ maximally localized optimization. The crystal potential and wavefunctions from first-principle calculation are firstly processed by the interface between Wannier90 and VASP to prepare the projection and overlap matrix. The atomic 3d and 2p orbitals centered at different Co and O sites perform as initial guess for projection matrix onto the Bloch bands. Since in the present DFT calculation

FIG. 2: In upper (a) panel, the optimized five Wannier functions of Co at site-0 remain the shape of atomic 3d orbitals. In lower (b) panel, the centered 3d orbitals hybridization interaction with nearby ligands O-2p orbitals. The red values in O-2p orbitals are hopping parameters with the corresponding 3d orbitals.

...
band structure the Co-3d related bands and O-2p related bands are in different isolated energy regions, there is no need for disentanglement procedure in the Wannier functions optimization and the number of Wannier functions is equal to that of Bloch bands involved in the calculation. The convergence tolerance is chosen to be $1.0 \times 10^{-10}$ Å$^2$ for total spread minimization.

**RESULTS AND DISCUSSION**

In crystal structure of CoO as Fig.1 the center Co$^{2+}$ cation (0) is surrounded by six O$^{2-}$ anions (1,2,3,4,5,6) which induce an $O_h$ symmetric crystal field on Co 3d orbitals. The five Co 3d orbitals 3d(xy), 3d(yz), 3d(xz), 3d(z$^2$) and 3d(x$^2$-y$^2$) will form two degenerated groups: 3d($e_g$) and 3d(t$_{2g}$). The band structure and projected densities of states (pDOS) for this CoO super cell structure are shown in Fig.3. There are 32 bands in the present study due to the super cell size, among which 12 nominal O-2p bands contains predominant O-2p orbital characters and 20 nominal Co-3d bands contains predominant Co-3d orbital characters. They are categorized into 3 groups in the focused energy region highlighted in different colors in Fig.3, which contain predominant O-2p, Co-3d(t$_{2g}$) and Co-3d($e_g$) orbital characters respectively. However, the bands with predominant Co-3d character also contains a noticeable amount of O-2p contribution and vice versa as shown in pDOS of Fig.3. This phenomenon is an indicative of partial covalence of Co-O bond which is frequently found in various TM oxides.

Within the present DFT calculation, CoO shows a band gap $\Delta E_{Gap}=0.00$ eV as metallic, which is contrast to the experiment value 2.6 eV[35, 36]. This is a well known inherent defect of DFT method for transition metal band structure calculation[37]. Although the present band structure from DFT calculation is not correct, the Wannier functions derived from this local electronic structure around Co are still able to provide correct parameters for multiplet calculations[24]. As a result, there is no need to consider the +U effect in present research. However in the future, the spin polarized DFT+U calculation may be studied on their effects on the multiplet calculations.

In the present research, the derived parameters from optimized Wannier functions are used in the multiplet calculation for X-ray absorption spectroscopy of Co 2p L$_{2,3}$-edges, whereby a 2p core electron is excited into the 3d valence shell. This transition is dipole allowed so that the spectral peaks are intense and clear with little noise. The spectrum contains two sets of peaks, the $2p_{j=3/2}$ L$_3$ and $2p_{j=1/2}$ L$_2$ edges, split by strong relativistic spin-orbit coupling $\zeta_{2p} = 9.75$ eV of 2p core hole. Typically there are two approaches in multiplet calculation for transition metal XAS, the crystal field multiplet approach with only crystal field effect included and the charge transfer multiplet approach with both crystal field and charge transfer effects. For these two approaches, two different sets of Wannier functions are optimized in present research to derive the corresponding calculation parameters. The first set of maximally localized Wannier functions are optimized when the 12 bands with predominant O-2p character and 20 bands with predominant Co-3d character are all included in the optimization process. The second set of maximally localized Wannier functions are optimized when only the 20 bands with predominant Co-3d character are included in the optimization process.

The Co-3d and O-2p orbital like Wannier functions are optimized simultaneously from all related bands to get the first set of Wannier functions. There are 3 Wannier functions centered at each four O$^{2-}$ anions
FIG. 3: In left panel, the band structure of CoO super cell from DFT calculation are presented in thick colored lines and the Co-3d, O-2p like Wannier functions interpolated bands are drawn in thin gray lines. The pDOS of Co atomic 3d(e_g, t_{2g}) and O atomic 2p(t_{1u}) orbitals are shown in right panel. The Fermi level is set as zero of energy.

with the shapes like atomic O-2p orbitals (2p_x, 2p_y, 2p_z) and 5 Wannier functions centered at each four Co$^{2+}$ cations with the shapes like atomic Co-3d orbitals (3d_{x^2-y^2}, 3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{z^2})). These Wannier functions reproduce the local bands perfectly the same as the DFT calculation results shown in Fig.3 while they still remain the spatial maximally localized features and include the correlation interaction. The orbital shape of Co-3d like Wannier functions contain only minimal contribution of O-2p orbital feature from surrounding ligands and vice versa.

Not all linear combination of O-2p WFs from ligands can interact with Co-3d WFs on the center, only some symmetric groups of O-2p WFs are interacted with corresponding same symmetric center Co-3d WFs as shown in Fig.2 panel (b). These linear combination groups of O-2p are so-called ligand orbitals[24]. For each Co-3d Wannier orbital there is exactly one such linear combination of O-2p Wannier orbitals to interact with. As shown in Fig.2 there are two groups of ligand orbitals L-t_{2g} and L-e_g that are coupled respectively with centered Co-3d t_{2g} and e_g orbitals. The ligand orbitals L-t_{2g} and L-e_g have an important difference in bonding types as shown in Fig.2. The L-t_{2g} orbitals are bonding between nearest O-2p Wannier orbitals and form a $\sigma$ type bond. The L-e_g orbitals are anti-bonding between nearest O-2p Wannier orbitals and form a $\pi$ type anti-bond.

The on-site energies of these Co-3d orbital like Wannier
FIG. 4: In left panel, the band structure of CoO super cell from DFT calculation are presented in thick colored lines and the Co-3d like Wannier functions interpolated bands are drawn in thin gray lines. The pDOS of Co atomic $3d(e_g, t_{2g})$ and O atomic $2p(t_{1u})$ orbitals are shown in right panel. The Fermi level is set as zero of energy.

functions are denoted as two degenerated values $E^{[3d+2p]}_{(e_g)}$ and $E^{[3d+2p]}_{(t_{2g})}$. The inclusion of all nominal Co-3d and O-2p bands in the Wannier functions optimization essentially removed the mixture between Co-3d and O-2p bands, as a result the optimized WFs are localized atomic-like Co-3d, O-2p orbitals and the energy splitting from on-site energies of these Co-3d like Wannier functions have no charge transfer contribution but only pure electro-static interaction. In the one-particle or LDA approximation picture, these Co-3d and O-2p WFs have hybridization interaction to each other.

As shown in table I, the parameters used for charge transfer multiplet calculation are compared with the semi-empirical values used in many previous studies. The 10Dq, $\Delta E$ and hopping parameters are derived from present DFT calculation through the analysis of optimized Wannier functions. The crystal field splitting parameter 10Dq is derived from the Wannier functions on-site energies difference: $10Dq= E^{[3d+2p]}_{(e_g)} - E^{[3d+2p]}_{(t_{2g})}=0.65$ eV which seems very reasonable as compared with previous semi-empirical values in table I. For systems with lower symmetries, there will be more parameters needed to describe the crystal field splitting and this approach

<table>
<thead>
<tr>
<th></th>
<th>10Dq</th>
<th>$\Delta E$</th>
<th>$U_{dd}$</th>
<th>$U_{pd}$</th>
<th>$T(e_g)$</th>
<th>$T(t_{2g})$</th>
</tr>
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<tbody>
<tr>
<td>present</td>
<td>0.65</td>
<td>4.94</td>
<td>6.0</td>
<td>7.0</td>
<td>1.37</td>
<td>0.72</td>
</tr>
<tr>
<td>[38]</td>
<td>0.7</td>
<td>5.5</td>
<td>5.2</td>
<td>5.3</td>
<td>2.25</td>
<td>1.2</td>
</tr>
<tr>
<td>[39]</td>
<td>0.6</td>
<td>2.5</td>
<td>7.0</td>
<td>7.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>[40]</td>
<td>0.5</td>
<td>4.0</td>
<td>7.0</td>
<td>7.0</td>
<td>2.2</td>
<td>1.1</td>
</tr>
</tbody>
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All values are in eV.
will be much more helpful than guessing semi-empirically.

The spherical part of the Coulomb repulsion in 2p and 3d shell are \( U_{pd} \) and \( U_{dd} \). The charge transfer energy \( \Delta E \) is defined as to transfer one electron from O-2p orbital to an empty Co-3d orbital in ground state. Since X-ray absorption process is a charge neutral excitation, it is not very sensitive to parameters \( U \) and \( \Delta E \). Normally \( U \) and \( \Delta E \) are treated as adjustable parameters to fit the experiment. In several previous researches the charge transfer energy \( \Delta E \) varies from 2.5 to 5.5 eV which is quite a large range. This makes it difficult to choose an appropriate value so as to work with other calculation parameters. Though the relation between \( \Delta E \) as defined in multiplet theory and on-site energy difference \( \epsilon_{3d} - \epsilon_{2p} \) is rather nontrivial, in present research \( \Delta E = \epsilon_{3d} - \epsilon_{2p} = 4.94 \text{eV} \) is chosen as a simple approximation. For other complicated system where this approximate value may be nontrivial, it can also serve as a good start point to approach a better semi-empirical value. As for \( U_{pd} \) and \( U_{dd} \) parameters there is a general rule[9]: \( U_{pd} - U_{dd} = 1 \) or 2 eV but in certain cases such as CoO as shown in Table I \( U_{pd} = U_{dd} \) are also used in many previous researches. There are several calculation methods to obtain \( U_{pd} \) and \( U_{dd} \)[23, 41–44], but these methods are not included in the present research temporarily due to their complexity. For most applications the use of simple empirical rules is a reliable choice to follow. And only the relative difference value \( U_{pd} - U_{dd} \) has the effect on calculated spectral shape. In this charge transfer multiplet calculation, \( U_{pd} = 7.0 \text{eV} \) and \( U_{dd} = 6.0 \text{eV} \) are chosen as the input values.

The hopping parameters \( T(e_g) \) and \( T(t_{2g}) \) are always difficult to determined with the variation of other parameters and normally an empirical rule: \( T(e_g) = 2T(t_{2g}) \) with \( T(e_g) \approx 2.0 \text{eV} \), is applied as initial guess for calculation. In contrast, the present approach can provide accurate values for both \( T(e_g) \) and \( T(t_{2g}) \) from the hopping matrix elements of Wannier functions. The hopping parameter \( T(e_g) \) is chosen to be the hopping matrix element \( \langle 3d(z^2) | T \| 2p(z) \rangle \) between the center Co\(^{2+}\) and the nearest ligand O\(^{2-}\) along the z direction. The hopping parameter \( T(t_{2g}) \) is chosen to be the hopping matrix element \( \langle 3d(\pi) | T \| 2p(x) \rangle \) between the center Co\(^{2+}\) and the nearest ligand O\(^{2-}\) along the z direction[24]. The hopping matrix elements are denoted in Fig. 2 panel (b). Beware that only the absolute value of hopping parameter has effect on spectral shape. Finally absolute values \( T(e_g) = 1.37 \text{eV} \), \( T(t_{2g}) = 0.72 \text{eV} \) are chosen for charge transfer multiplet calculation and they still follow the empirical rule mentioned above approximately.

All these calculated parameters as shown in Table I are used in the charge transfer multiplet calculation for Co\(^{2+}\) L\(_{2,3}\)-edges XAS. The scale factors for Slater integral reduction in this calculation are chosen as 80% to compensate the excessive electron repulsive interaction calculated from the atomic model so as to give out a better simulation for solid crystal. The charge transfer multiplet (CTM) calculation spectrum is shown in Fig. 5 with comparison to experimental XAS data. The pre-edge peak and main features in L\(_3\)-edge are well matched with experiment. The single peak in L\(_2\)-edge is 0.3 eV less than the experimental data. In the calculation the lower energy parts of L\(_3\) and L\(_2\) edges have the better agreement with experiment than the high energy part, for example the low energy part around 775 eV and high energy part around 780 eV in L\(_3\)-edge as shown in Fig. 5. This is because in transition metals, the monopole part of 2p-3d Coulomb interaction is larger than that of 3d-3d interaction, which leads to strongly bound excitons at L\(_{2,3}\)-edges and makes the multiplet theory with small basis set in cluster applicable to reproduce the spectra in lower ener-
FIG. 5: The multiplet calculations of Co$^{2+}$ L$_{2,3}$-edge of CoO compared with experimental data. In left panel is the charge transfer multiplet (CTM) calculation compared with experiment. In right panel is the crystal field multiplet (CFM) calculation compared with experiment.

energy parts of L$_{2,3}$-edges. However besides these localized excitonic states, excitations to non-localized states are also possible in the X-ray absorption process[24]. The multiplet theory is not capable to describe these excitations, which results in poor fit at higher energy part of L$_{2,3}$-edges.

The multiplet calculation discussed above is taking both crystal field and charge transfer effects into consideration. If only crystal field effect is incorporated in the multiplet calculation, then the bands with predominant Co-3d characters are included in the optimization alone without O-2p orbital related bands for the second set of Wannier functions. In the result, there are 20 optimized Wannier functions which are centered at four Co$^{2+}$ cations with atomic Co-3d orbitals (3d$_{xy}$,3d$_{xz}$,3d$_{yz}$,3d$_{x^2-z^2}$,3d$_{y^2}$) features. The Wannier functions constructed with only Co-3d related bands can be viewed as molecular orbitals that have the contribution from hybridization between ligands O-2p orbitals and centered Co-3d orbital, since the O-2p characters are not decoupled from the optimized Co-3d Wannier orbitals. As a result the on-site energies of these Co-3d like Wannier functions include both the hybridization effect from neighboring ligands and the pure electro-static interaction. The on-site energies of these Co-3d orbital like Wannier functions are denoted as two degenerated values $E_{(e_g)}^{[3d]}$ and $E_{(t_{2g})}^{[3d]}$ and the crystal field splitting value $10D_q=E_{(e_g)}^{[3d]}-E_{(t_{2g})}^{[3d]}=1.267$ eV. When crystal field multiplet calculation is performed without the charge transfer effect, the crystal field splitting energy will be considerably larger than the value used in charge transfer multiplet calculation. Because the different hopping integrals to t$_{2g}$ and e$_g$ orbitals are effectively included in the splitting parameter 10Dq of crystal field multiplet calculation. The 10Dq=1.267 eV derived from this approach for crystal field effect is almost twice larger as the value 0.6513
eV used in the previous charge transfer multiplet calculation. This large value contains the contribution from the charge transfer hopping differences as discussed above.

The crystal field parameter $10D_q=1.267$ eV with 80% scale on Slater integral reduction is used in the crystal field multiplet calculation for Co$^{2+}$ L$_{2,3}$-edges XAS. The crystal field multiplet (CFM) calculation spectrum is compared with experimental data in Fig.5. The pre-edge peak and main features in L$_3$-edge are almost perfectly matched with experiment. The single peak in L$_2$-edge shows the same energy and broadening both in calculation and experiment. In many previous crystal field multiplet calculations, this $10D_q$ values are derived in variation with many other semi-empirical parameters such as scale factors by fitting the calculation spectral features to experiment. However the present modus operandi provides this parameter a reliable value in a first-principle way.

Once the multiplet calculation parameters for ground state Co$^{2+}$ cation in CoO are set, the same set of parameters can be used for various core level X-ray spectroscopy multiplet calculations other than XAS such as XPS. The charge transfer multiplet 2p XPS calculation for Co$^{2+}$ cation in CoO at 300 K is presented in Fig.6. The calculation reproduces the experimental features[45] adequately. The XPS of Co$^{2+}$ in O$_h$ symmetric structure is also divided into two regions: L$_2$-edge (2p$_{1/2}$) and L$_3$-edge (2p$_{3/2}$). The whole calculation spectral features fit very well with most experimental peaks at 780, 785.04 and 796.84 eV. Only the peak at 800.55 eV is about 2.45 eV less than the experimental value. The calculation spectrum also reveals more detailed multiplet features which are vague in experiment due to the low spectral resolution. It is important to have such a good theoretical XPS calculation to distinguish the real CoO XPS signal in experiment and determine the pure CoO sample. Since the XPS is surface sensitive and pure CoO is hard to obtain, the surface of CoO is always oxidized to Co$_3$O$_4$ in commercial samples, the CoO XPS experiment features are always interfered by Co$_3$O$_4$ XPS signal, even in two published handbooks[46, 47]. In previous experiment research[45] only semi-empirical curve fitting procedures are carried out to interpret the spectral features, the present calculated multiplet features are more precise and meaningful to analyze the spectral features such as peak asymmetries.

As compared to XAS and XPS, RIXS provides more information about the atomic geometry and electronic structure of the sample. For example the 2p3d RIXS at Co$^{2+}$ L-edge probes 3d-3d, charge transfer (ligand-to-metal or metal-to-ligand), charge fluctuation (metal-to-metal) excitations. The present set of multiplet cal-

![FIG. 6: The charge transfer multiplet 2p XPS calculation for Co$^{2+}$ cation in CoO.](image-url)
FIG. 7: (a) The crystal field multiplet calculation of Co$^{2+}$ 2p3d RIXS at 300 K for CoO, where the line-c and -d are denoted to energy loss spectra excited at 774.40 eV and 777.62 eV incident laser energy. (b) The corresponding RIXS in 3D image. (c) The extracted energy loss spectrum at 774.40 eV incident excitation energy. (d) The extracted energy loss spectrum at 777.62 eV incident excitation energy.

calculation parameters can also be applied to 2p3d RIXS calculation. The Fig. 7 shows the Co$^{2+}$ 2p3d RIXS calculation result in crystal field multiplet model at 300 K using the same parameters as in crystal field multiplet XAS calculation. The detailed calculation is carried out in Crispy+Quany codes. The main features of the RIXS data are divided into 3 catalogues around 0, 1 and 3 eV in transferred energy dimension. The 3D RIXS figure is also shown in (b) demonstrating the whole 2p$^6$3d$^7 \rightarrow 2p^5$3d$^8 \rightarrow 2p^6$3d$^8$d transitions. The 2D and 3D RIXS plots shows the transferred energy or final state.
energy as a function of the incident excitation energy over the Co$^{2+}$ L$_3$-edge XAS range. The (c) and (d) are energy loss spectra extracted from RIXS data at excitation energy line-c and -d in (a), which represent the resonant X-ray emission spectra.

Most intense spectral features as bright dots in 2D-RIXS and high peaks in 3D-RIXS figures are due to the 3d-3d excitations. The elastic peak of the resonant X-ray emission spectra at 0 eV with 100 meV broadening comes from ground state, which is visible and intense in all incident excitation energy values. While the inelastic peaks above 0 eV are due to other 3d-3d excitation transitions. The elastic peak at 0 eV not only contains the non-material specific elastic scattering channels, but
also some weak inelastic resonant transitions which appear to be the asymmetric shoulder of this peak. Such peak shoulder is energy dependent and more obvious in higher excitation (d) energy loss spectra.

Compared to previous theoretical and experimental research[48], the present Co$^{2+}$ 2p3d RIXS calculation result shows similar main features but the energy gaps between peaks are different. This may be because previous experimental sample is nanoparticle and calculation conditions are different in scaling factors, tetragonal distortion in $O_h$ crystal field and low temperature effect.

Compare the 2D-RIXS figure of crystal field multiplet calculation in Fig.7 and charge transfer multiplet calculation in Fig.8, the later one shows an obvious shrinkage to lower energy in both incident energy and transferred energy dimensions. The charge transfer multiplet calculation for RIXS gives more accurate peaks energies in energy loss spectra as compared with experimental data. For example in spectrum (c) the inelastic transition peak due to 3d-3d excitation is below 1 eV in charge transfer multiplet calculation close to experimental value, but crystal field multiplet calculation overestimates this transition energy. As in spectrum (d), the second 3d-3d transition peak is around 2.5 eV in charge transfer multiplet calculation but it is shifted to 3.0 eV in crystal field multiplet calculation. The crystal field multiplet calculation for CoO RIXS is proved to be good fitting to single crystal sample when including additional tetragonal distortion and super-exchange interactions. However the charge transfer multiplet calculation for CoO RIXS is more suitable for systems with strong charge transfer effect such as nanocrystal samples.

CONCLUSION

The conventional multiplet theory for X-ray spectroscopy requires many semi-empirical parameters to perform the spectrum calculation on small cluster model. These semi-empirical parameters have to be optimized to fit with experiment, but finding the best fit is not trivial. The present research applied on CoO system shows an example that these parameters can be easily derived from the first-principle calculation via the analysis of corresponding Wannier functions. The CoO first-principle calculation is carried out in DFT theory and the corresponding band structure is also derived for the following procedure. The wavefunctions and band structure from the DFT calculation are used to construct the maximally localized Wannier functions. The Wannier functions are constructed in different set of bands, which can separate the Co-O hybridization and pure electro-static interaction in the crystal field splitting. The two different sets of Wannier functions respectively provide reliable calculation parameters for crystal field and charge transfer multiplet calculations of Co$^{2+}$ L$_{2,3}$-edges XAS, XPS, RIXS and all calculated spectra show satisfactory agreement with the experimental data. Besides this, the present modus operandi also gives out complementary information on electronic orbitals from DFT calculation of infinite crystal structure, which the conventional multiplet theory can not provide.

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