Exciting core-level spectroscopy

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An ab initio approach is delineated for obtaining X-ray absorption spectra as provided by many-body perturbation theory, together with its realization within an all-electron framework. Employing the Bethe–Salpeter equation, excitations from different absorption edges in a broad range of material classes are addressed, analysing exciton binding strengths and character. Situations in which the supercell core-hole approach is likely to fail are also discussed.

1. Introduction

While density-functional theory (DFT) is the workhorse of computational materials science that concerns the ground-state properties of materials, theoretical spectroscopy requires excited-state methods beyond DFT. The state-of-the-art methodology for extended systems is provided by many-body perturbation theory (MBPT), taking DFT results as a starting point. One- and two-particle Green functions are employed to obtain the quasi-particle eigenvalues and optical spectra accounting for electron–hole interaction in the excitation process, respectively. Here, we focus on the Bethe–Salpeter equation of MBPT, which is typically used for computing absorption spectra in the visible and UV range of light, to explore core excitations. We sketch the theoretical background and its implementation in a full-potential all-electron framework, as realized in the exciting code. For a broad range of materials, we highlight the physics behind the particular spectral features, or the added value compared with experimental investigations. In all cases, we refer to the original literature for further reading.

2. exciting: an all-electron full-potential code

exciting is an electronic structure package that solves the Kohn–Sham (KS) equation of DFT using linearized augmented plane waves (LAPW) as a basis set. By LAPW, we mean various ways of linearizing the KS eigenvalue problem, including their extension by local orbitals of any kind (Gulans et al., 2014). Beyond ground-state DFT methods, exciting implements time-dependent DFT as well as MBPT for treating excitations, the latter comprising the \( GW \) approach to obtain quasi-particle bands and the Bethe–Salpeter equation that allows the inclusion of excitonic effects in the description of spectra. Besides its capability to compute optical absorption, Raman scattering and electron loss, exciting has a particular focus on core-level excitations. Owing to the fact that the LAPW method does not require any shape approximation for the potential, density or wavefunction, it can describe all electrons on the same footing, and excitations from any edge can be handled explicitly. More specifically, at present, core
3. Methodology

The Bethe–Salpeter equation is an effective two-body equation for the electron–hole interaction, based on a two-particle Green functions approach. It can be written in terms of an eigenvalue problem in matrix form, 

\[ \sum_{\mathbf{c},\mathbf{u}',\mathbf{k}} \hat{H}^{\mathbf{c} \rightarrow \mathbf{u}'} \mathbf{k} A_{\mathbf{c} \rightarrow \mathbf{u}'}^\mathbf{k} = E^\mathbf{k} A_{\mathbf{c} \rightarrow \mathbf{u}'}^\mathbf{k}. \]

In the context of X-ray spectroscopy, we consider only transitions from core (c) to unoccupied (u) states; \( \mathbf{k} \) and \( \mathbf{k}' \) are wavevectors of the first Brillouin zone.

The two-body Hamiltonian consists of three terms, \( \hat{H}^{\mathbf{c} \rightarrow \mathbf{u}'} = \hat{H}^{\text{diag}}_{\mathbf{c} \rightarrow \mathbf{u}'} + \hat{H}^{\text{dir}} + \hat{H}^{\text{ex}} \). The diagonal term \( \hat{H}^{\text{diag}} \) describes single-particle transitions. Considering only this term corresponds to the independent-particle approximation (IPA). The exchange term, \( \hat{H}^{\text{ex}} \), accounts for local-field effects, while the direct term, \( \hat{H}^{\text{dir}} \), incorporates the attractive screened Coulomb interaction \( W \). In the adopted plane-wave representation, the latter is expressed by

\[ W_{\text{GG}}(\mathbf{q}) = \frac{4\pi e^{-1}}{|\mathbf{q} + \mathbf{G}|}. \]

More details on the BSE formalism and its implementation in the LAPW framework can be found elsewhere (Puschnig & Ambrosch-Draxl, 2002; Sagmeister & Ambrosch-Draxl, 2009; Vorwerk et al., 2017, 2019). The eigenvalues, \( E^k \), represent exciton energies, while the eigenvectors, \( A^k \), carry information about their character and composition. They enter the imaginary part of the macroscopic dielectric function, \( \text{Im} \varepsilon_M \), renormalizing the oscillator strength compared with the IPA. With the the momentum operator \( \mathbf{p} \) accounting for the dipole selection rules, the diagonal components read

\[ \text{Im} \varepsilon_M = \frac{8\pi^2}{\Omega} \sum_{\mathbf{k} \mathbf{c} \mathbf{k}'} A^\mathbf{c} \mathbf{k} \frac{\langle \mathbf{c} | \mathbf{p} | \mathbf{k} \rangle}{\varepsilon^\mathbf{c} - \varepsilon^\mathbf{k}} \delta(\omega - E^\mathbf{k}). \]

This is the quantity used for comparison with experimental spectra and shown below for prototypical materials.

All of the above expressions are evaluated by using the LAPW basis set. This dual basis is based on the partitioning of the unit cell into atomic spheres around the nuclei and an interstitial region in between. For details, we refer the reader to Puschnig & Ambrosch-Draxl (2002), Sagmeister & Ambrosch-Draxl (2009), Gulans et al. (2014) and Ambrosch-Draxl & Sofo (2006).

Before showing the performance of this method in terms of various examples, we would like to add the following notes.

(i) The BSE improves over the supercell core-hole approach in particular for excitations from semicore states where electron–hole correlation becomes significant (Olovsson, Tanaka, Puschnig et al., 2009; Rehr et al., 2005), but also in the sense that within the many-body formalism the electron–hole binding does not depend on the approximate functional employed for the ground-state calculation (see the example of LiF and Olovsson, Tanaka, Mizoguchi et al., 2009).

(ii) So far, the core excitations based on the BSE have often relied on the description of the core states with the help of local orbitals (added to the valence range) rather than accounting for the spinor wavefunctions obtained from the solution of the Dirac equation, with exceptions being Laskowski & Blaha (2010) and Vorwerk et al. (2017). The latter becomes critical in case of small \( 2p_{\alpha/\beta}/2p_{\alpha'\beta'} \) splitting (see the example of TiO\textsubscript{2} below).

(iii) In contrast to optical spectra, the GW step for obtaining the quasi-particle energies is typically avoided when it comes to core excitations, since the GW results do not match core levels well. Therefore, the spectra are typically aligned with respect to experiment. The quasi-particle correction applied to the conduction states (see, for example, Vinson et al., 2011; Vinson & Rehr, 2012; Gilmore et al., 2015) may, however, improve the spectra, especially when the self-energies of the unoccupied bands exhibit a pronounced dependence on \( k \)-point or band index.

4. Selected systems

4.1. Graphene: an unusual metal

The X-ray absorption spectrum from the carbon K edge (Fig. 1) is characterized by a sharp near-edge peak, corresponding to the resonance between the C 1s electron and the lowest unoccupied \( \pi^* \) orbital, followed by intense features at higher energies. The measured spectrum (Pacilé et al., 2008) is very well reproduced by the BSE approach, while the IPA is in qualitative disagreement. This result indicates that even in a metallic material such as graphene, the Coulomb interaction between the core hole and the conduction electrons can be relevant. It should be noted that a quantitative description of the experimental features is only obtained by taking into account spin–orbit interaction in a second-variational scheme. A fully relativistic treatment with spinor wavefunctions is currently under development.
account the laboratory setup. In the experiment (Pacilé et al., 2008), the impinging beam is at grazing incidence (16°) with respect to the sample. This configuration is reproduced by calculating the absorbance with LayerOptics (Vorwerk et al., 2016), a computational tool for solving Fresnel’s equations for anisotropic layered materials (Yeh, 1980; Puschnig & Ambrosch-Draxl, 2006). For comparison, we also plot in Fig. 1 the in-plane (xx) and out-of-plane (zz) components of the macroscopic dielectric function obtained from the BSE. It is evident that the shoulder appearing in the experimental spectrum at about 292 eV comes from the peak in the xx component of ImεM, which enters the absorbance at grazing incidence.

4.2. LiF: a wide-gap material

LiF exhibits dominant excitonic features, as demonstrated by the Li K edge absorption spectrum shown in Fig. 2. Although the Li 1s electron is a very shallow core state, the importance of core-hole effects is already evident by the failure of the IPA to reproduce the experimental features (Handa et al., 2005). The sharp peak at the absorption onset is well captured by the BSE as well as by the supercell core-hole approach. However, the latter substantially underestimates the exciton binding energy. As pointed out in Olovsson, Tanaka, Mizoguchi et al. (2009), this can be traced back to the fact that in this method the electron–hole interaction is handled on the level of the exchange-correlation functional of the underlying DFT calculation, in contrast to the BSE, where the Coulomb interaction is treated explicitly.

4.3. AlN: fingerprints of structural phases

The NEXAFS spectra of rock-salt (rs), wurzite (w) and zincblende (zb) AlN from the aluminium K-edge are shown in Fig. 3, comparing theory with experiments (Mizoguchi et al., 2003; Sennour & Esnouf, 2003; Olovsson et al., 2011). The calculated results impressively demonstrate the power of the BSE to correctly predict the particular features due to different atomic configurations. While the rock-salt phase shows a sharp peak at the absorption edge, both the wurzite and the zincblende structures display a smoother onset. How these features are related to the underlying electronic states and are reflected in the nature of the electron–hole wavefunctions of the lowest-energy excitations is discussed in detail in Olovsson et al. (2011).

4.4. Site selectivity in Ga2O3

The X-ray absorption spectrum from the O K edge of β-Ga2O3 (Fig. 4, bottom) is dominated by excitonic effects which are responsible for the overall spectral shape (Cocchi, Zschiesche et al., 2016). Atom-resolved contributions from chemically inequivalent O atoms of the monoclinic unit cell reveal signatures of their chemical environment that can be probed by electron loss near-edge structure (ELNES) spectroscopy under different diffraction conditions. The corresponding experimental setup is mimicked by theory by rotating the bulk dielectric tensor so as to represent the orientation of the sample with respect to the incident electron beam. This is accomplished by LayerOptics (Vorwerk et al., 2016). These results suggest that ELNES, together with ab initio many-body theory, can be successfully employed to characterize complex systems, with sensitivity to individual atomic species and their local environment.

It is also instructive to inspect the real-space extension of the exciton wavefunction (Fig. 4, top). The shape reflects the electron density related to the bottom of the conduction band, which is formed by hybridized O p and Ga s states.

4.5. Packing effects in azobenzene SAMs

Core excitations from the N K edge in azobenzene molecules and functionalized self-assembled monolayers (SAMs) at increasing packing density reveal intermolecular coupling in the excited state (Cocchi, Moldt et al., 2016). Comparison between BSE and IPA results (Fig. 5) highlights the huge exciton binding energies characteristic of organic molecular
systems. They range from up to 6 eV in isolated molecules to 4 eV in the densely packed SAM, where the screening is enhanced by molecular packing. An analogous trend was also found in the regime of optical excitations (Cocchi & Draxl, 2015, 2017). Our results, which are in very good agreement with experiment (Moldt et al., 2015), indicate the crucial role of the electron–hole attraction dominating these excitations.

4.6. Spin-orbit coupling in TiO$_2$

Rutile, TiO$_2$, is a prototypical system for studying core-level excitations from the $L_{2,3}$ edge of the metal ion. To capture multiplet effects, which are responsible for mixing the single-particle transitions from the 2$p_{1/2}$ and 2$p_{3/2}$ core states, a fully relativistic treatment together with the explicit electron–hole interaction is essential. Owing to the rather small spin–orbit splitting of the order of a few eV, the spectra arising from the $L_2$ and $L_3$ edges cannot be treated separately, as also indicated by Laskowski & Blaha (2010). We find the screened Coulomb attraction as well as the repulsive exchange interaction between the excited electron and the core hole to be crucial in order to reproduce the correct spectral features shown in Fig. 6 (Vorwerk, 2016).

5. Summary and outlook

The BSE is a powerful tool with which to explore core excitations from first principles, as demonstrated by examples that represent materials and excitations of very different character. Many-body theory is essential to complement experiments, gaining information that is inaccessible by measurements only. For a more stringent interpretation of experiments, further steps are required. These concern the incorporation of electron–phonon coupling (Karsai et al., 2018; Olovsson et al., 2019) as well as higher-order processes beyond the BSE. Also precise

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Core excitations from the oxygen $K$ edge in $\beta$-Ga$_2$O$_3$. Top: electron distribution of the lowest-energy exciton with respect to the hole whose position is marked by the cross. The dashed line indicates the unit cell. O atoms are in red and Ga atoms in grey and green. Bottom (upper panel): BSE results (solid line) and experimental ELNES spectra (circles) obtained for a sample impinged by the electron beam along the direction normal to the (200) surface; lower panel: BSE spectra for inequivalent O atoms. Results are from Cocchi, Zschiesche et al. (2016).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Near-edge X-ray absorption spectra from the nitrogen $K$ edge of an isolated azobenzene molecule (top), a diluted SAM (d-SAM, middle) and a packed SAM (p-SAM, bottom). The excitations labelled A', B' and C' in the BSE spectra (solid lines) can be traced back to peaks A, B and C, respectively, in the IPA spectra (shaded areas). Theoretical results are taken from Cocchi & Draxl (2015) and experimental data from Moldt et al. (2015).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Near-edge X-ray absorption spectrum from the titanium $L_{2,3}$ edge in rutile, TiO$_2$, computed from the BSE (solid line) and compared with experimental data (circles) taken from Kronawitter et al. (2012).}
\end{figure}
knowledge on the sample quality and experimental conditions are a must for quantitative comparison. Improvements and extensions of the *exciting* code concerning momentum transfer (Fugallo et al., 2015) as well as spin treatment have already been realized (Vorwerk et al., 2019). The latter is based on a fully relativistic description of core and valence states, also covering magnetic materials and dichroism. Additional advances entail the combination of these features for the calculations of resonant inelastic X-ray scattering (Vorwerk et al., 2020), for which the BSE treatment (Vinson et al., 2016, 2017) has been proven to be superior to the core-hole approach (Magnuson et al., 2010).

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