Supercell approach to core-level excitonic effects

Evaluation of the Supercell Core-Hole Method for X-ray Absorption Spectrum and Exciton Calculations

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In Short

- Benchmark of supercell core-hole (SCH) for X-ray absorption spectra as a viable alternative to the more computationally demanding Bethe-Salpeter equation (BSE).
- Development of practical guidelines for applying SCH to large-scale systems.

X-ray Absorption Spectroscopy (XAS) is a powerful experimental technique for probing the electronic structure of materials [1]. Since XAS concerns the excitation of electrons from core levels, the resulting spectra are highly sensitive to the specific element and core states involved. However, interpreting XAS spectra can be challenging due to their complex features. In this sense, theoretical calculations play a crucial role, enabling a deeper understanding of several aspects, such as the origin of individual peaks and the fine structure of X-ray Absorption Near Edge Structure (XANES) [2].

One of the most straightforward computational approaches for studying XAS is the Supercell Core-Hole (SCH) method [1,3], which is based on density-functional theory (DFT). In SCH, an electron is removed from a core level of a selected atom and promoted to unoccupied states, simulating the core excitation. To minimize spurious interactions between periodic images of the core hole, a sufficiently large supercell is required.

Beyond DFT-based methods, the Bethe-Salpeter Equation (BSE) offers an accurate framework for modeling core-level excitations [4]. BSE explicitly incorporates electron-hole interactions via the two-particle Green's function formalism, and its combination with GW is regarded as the state-of-the-art method for the theoretical modeling of XAS [4]. However, the high computational cost and unfavorable scaling ($\mathcal{O}(N^4)$ or $\mathcal{O}(N^5)$, where N is the number of atoms) can be a serious limitation, particularly when aiming to explore exciton dynamics, lattice distortions induced by excitons, or higher-order excitations such as trions. On the other hand, as a DFT-based method, SCH presents substantially lower numerical complexity (scaling of $\mathcal{O}(N^3)$).

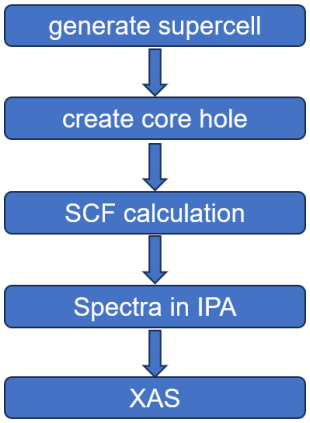

Figure 1: *Workflow of computing XAS with SCH in exciting*

In this project, we propose a systematic study of XAS calculations using the SCH approach, along with a detailed comparison with BSE. We aim to establish a solid theoretical foundation for the SCH method, required for applying SCH in more advanced calculations, such as those involving trions and exciton dynamics.

All calculations will be performed using `exciting`, an all-electron, full-potential code based on the linearized augmented plane wave plus local orbital (LAPW+lo) method. The code supports both DFT and many-body perturbation theory, including core-level spectroscopy and exciton calculations via BSE formalism. The accurate treatment of core and valence states achieved with `exciting` makes it particularly suitable for XAS simulations. The developed methodology will be implemented in the `exciting` code and made available to the community.

WWW

https://sol.physik.hu-berlin.de/

More Information

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