X-Ray Spectroscopy

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Abstract

Many different techniques currently exist to classify materials, most of which are spectroscopic in nature. X-Ray Absorption Spectroscopy (XAS) and X-Ray Emission Spectroscopy (XES) are common methods for identifying different molecular strucutres, rather than only their elemental constituents. At certain incoming x-ray energies there are distinct discontinuities "edges" in the absorption coefficient of the materials, around which the analysis of XAS is referred to as X-Ray Absorption Near Edge Structure (XANES), and Extended X-Ray Absorption Fine Structure (EXAFS). Advances in computational modeling of the spectrums that come from XAS and XES have come from novel theoretical approaches in describing the interaction using the quantum mechanical propogator of the electron, departing from the old-but-gold Fermi's Golden Rule.

1 Introduction

The study of the relative absorption strength of photons in the x-ray range has the ability to extract elemental, electronic, and other information about substances. Removal of core electrons from atoms requires energies on the x-ray scale, which allows us to probe the inner atomic/ionic structure of substances without chemically altering the substance. With advances in computing, it is now possible to theoretically calculate and predict XANES spectras, as well as other varieties of x-ray spectroscopies, which is what my group has been working on successfully for the past three decades. In this paper, we will explore some theoretical techniques for the prediction of x-ray spectras, as well as modern theoretic-computational advances in approximation techniques that circumvent some computational difficulties in previous techniques involving the use of Fermi's Golden Rule.

2 Theory

2.1 Core-level x-ray spectroscopy

The identification and characterization of material has seen great results from many x-ray spectroscopies, due to their probing of core-level electrons and the following excitations.

Two general classes of core-level spectroscopies are first and second-order processes, referring to the number of distinct photons involved in an individual scattering event. Respectively, these processes are what consitute X-ray

Absorption Spectroscopy (XAS) and X-ray Emission Spectroscopy (XES). We will restrict ourselves to the discussion of first-order XAS in this paper.

In an XAS measurement, photons of variable frequencies (ranging from 100 eV to 100 keV) are launched towards a sample and strike many electron shells, resulting in an emitted photoelectric current. Since the photon energy is known and electron binding energies can be calculated, the photoelectron kinetic energies are then measured to filter for only deep-core electrons. This is known as electron-yield detection.

The fundamental characteristic, or "fingerprint", of a sample is it's absorption spectrum, $\mu(\omega)$, where $\hbar\omega$ is the incoming photon's energy. Using Beer's law, we obtain an experimental method for determining the absorption spectrum of a sample: $\mu(\omega) \propto \log[I_0/I]$, with proportionality depending on the thickness of the sample. This is known as transmission spectroscopy.

2.2 Calculation of absorption spectrum

To be able to theoretically predict an absorption spectrum, one must understand the nature of the quantum mechanical mechanisms that result in the absorption of light. "Simply", a photon of energy $\hbar\omega$ is absorbed by a core electron if there is an available final state with an equal energy difference. Fermi's Golden Rule can be used to approximate the absorption spectrum as follows:

$$\mu(E) \propto \sum_f |\langle f|\hat{\epsilon} \cdot \mathbf{r}|i\rangle|^2 \delta(E - E_f)$$

Therein lies the difficulty of predicting absorption, with the multitude of final states introducing computational bottlenecks due to the necessary calculation of their eigenstates, transition probabilities, and projected density of states. However, this produces a good first step for the prediction of XAS and builds a decent qualitative image of the spectrum. This description of XAS is elucidated by the matchup of peaks between an XAS and the projected densities of final states.

Beyond the first order discontinuities due to the energy level jump, which can be almost calculated by hand, the available final energy levels depend on the system's constituents and geometry. After a photoelectron reaches/leaves an ion's conduction band, its available states depend on the potential wells created by the neighboring atoms/ions' conduction bands. These potentials determine the "trajectories" of the photoelectrons and probabilistically predict their scattering processes, which directly affect the likelihood of their absorbtion of a photon of the necessary energy.

Conveniently, there is another method of computing this process which arises from the path integral formulation and uses the propagator of the electron. The propagator, also sometimes referred to as the Green's function $G(r, r', E)$, evaluates the probability of a particle of energy E moving through a potential from one postion to another $r \to r'$, similar to the wavefunction of a particle $\Psi(r)$ determining the probability of finding it at r.

The Green's function could then be used to find probabilities of many different paths and scatterings and sum over them to produce a transition probability.

Mathematically, there is a theorem that relates the projected densities of final states to the electron's Green's function:

$$-\frac{1}{\pi}\mathrm{Im}\,G(r, r', E) = \sum_f |f\rangle\,\langle f|\,\delta(E - E_f)$$

Thus, by expanding $|\langle f|\hat{\epsilon}\cdot\mathbf{r}|i\rangle|^2$ and utilizing the theorem, we get the following relationship:

$$\mu(E) \propto \sum_f |\langle f|\hat{\epsilon}\cdot\mathbf{r}|i\rangle|^2\delta(E - E_f) \tag{1}$$

$$= \sum_f \langle i|\hat{\epsilon}\cdot\mathbf{r}'|f\rangle\,\langle f|\hat{\epsilon}\cdot\mathbf{r}|i\rangle\,\delta(E - E_f) \tag{2}$$

$$= -\frac{1}{\pi}\mathrm{Im}\,\langle i|\hat{\epsilon}\cdot\mathbf{r}'\,G(r, r', E)\,\hat{\epsilon}\cdot\mathbf{r}|i\rangle \tag{3}$$

Rather than only a theoretically advancement of our understanding of the underlying phenomena, this approach of calculating absorption spectra via Green's functions, also known as propagators, rather than Fermi's golden rule offers significant computational advantages. With Fermi's golden rule, one must calculate many final state eigenfunctions as a prerequisite for the single-particle approximation, adding on many other state functions for the many-body golden rule approximation. However, the introduction of the real-space Green's function method reduced the problem mostly to a large matrix inversion problem.
This problem can further be parallelized over different processors to drastically speed up the calculation.

3   Conclusion

The recent advances in mathematical techniques for modelling the absorption probability have resulted in major improvements in computational accuracy and efficiency. Progress is constantly being made, with the most recent approach in the past few years relying on the Bethe-Salpeter Equation that describes the bound states of a 2-particle system, such as the emergent excitons (electron-hole pairs) during x-ray absorption. However, the Bethe-Salpeter formalism is beyond the scope of this article and is only mentioned as the next step in computational modelling of x-ray spectroscopies.

References

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