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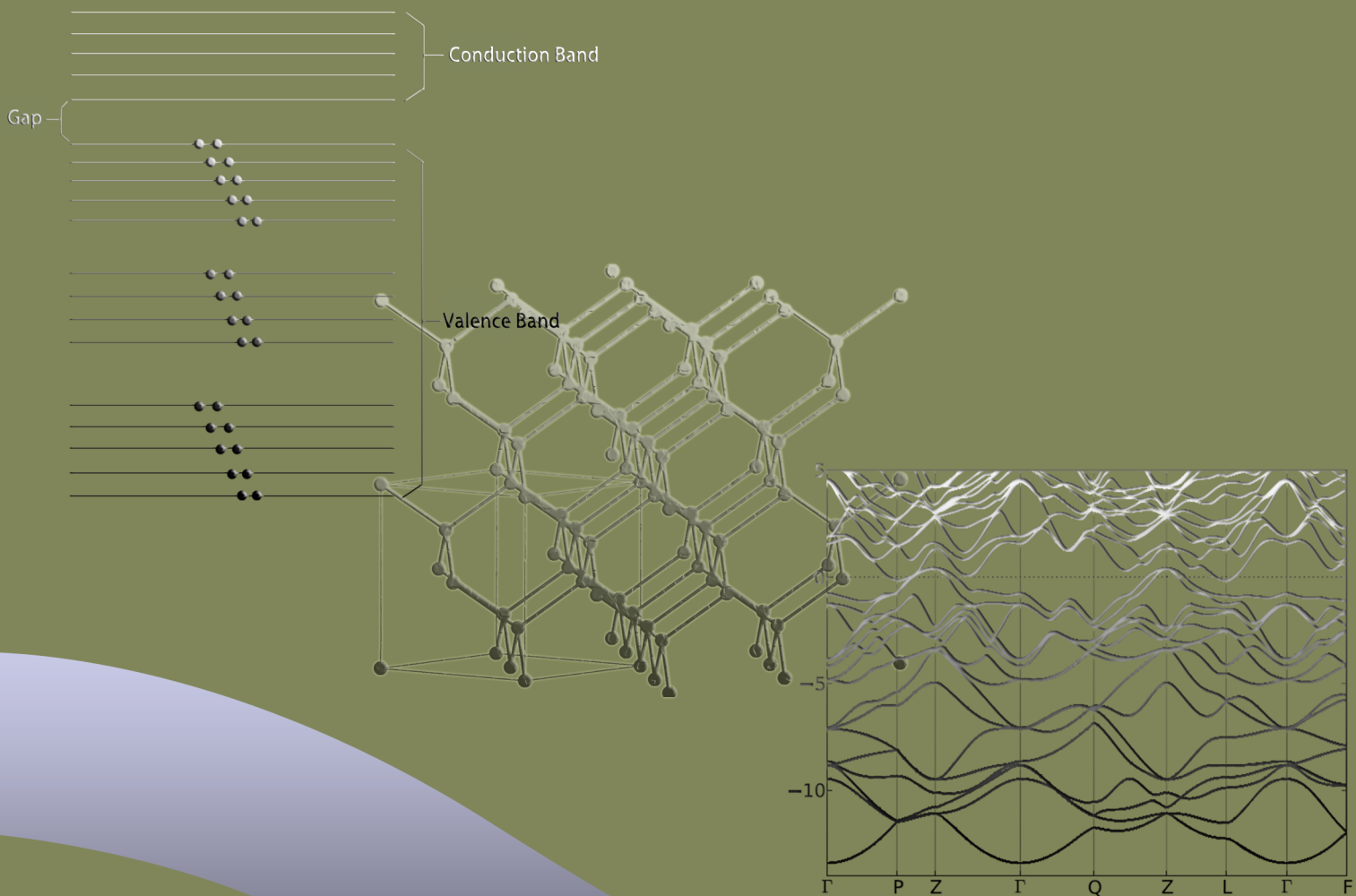
School of Physics and Astronomy

XANES Spectrum Calculation using Finite Difference Method

Conduction Band

Gap

Valence Band

0. Introduction

The transition of electrons from core to empty level gives rise to absorption signal, hence the absorption technique can be used to detect electronic structure of material. The excited photoelectrons propagates within specific system, and scattered back by neighbouring atoms to interfere with original out-coming photoelectrons. The interference leads to wiggles on the basis of absorption spectrum created by isolated atom, thus can be used to detect the local environment around absorption atoms. In order to determine structural information using absorption technique, it is necessary to be able to calculate the spectrum based on given reference structure. Specifically for X-ray absorption technique, the calculation mainly focuses on two ranges of absorption spectrum — near edge spectrum (X-ray Absorption Near Edge Spectrum, XANES) and extended spectrum (Extended X-ray Absorption Fine Structure, EXAFS). In EXAFS, the energy of photoelectron is up to over 50eV above the absorption edge. Due to high energy of photoelectrons, the potential around excited atoms can be spherically averaged, so the final photoelectron wavefuction (final state) can be constructed as the interference result of outgoing and backscattered wavefuctions. Basically, it is because of the short mean free electron path (hence no need to consider multiple scattering and other effects) of the excited photoelectron that is contributing to the easy approximation of potential, which then makes the exact final state calculation possible. This is just what FEFF calculation is based on. However for XANES, the lower energy of photoelectron makes it necessary to consider more details about the potential approximation because of the many body effect, multiple scattering (photoelectrons travel much longer and feels more), polarization effect, and so on. In turn, it is just because the lower energy (hence longer traveling path) of photoelectrons that makes XANES more sensitive to bonding environment hence could provide more information about local structure.[1]

1. Muffin-Tin Approximation

The commonly used potential approximation for EXAFS calculation (FEFF) and some XANES calculation is muffin-tin potential. In muffin-tin model, the potential is spherically averaged in the
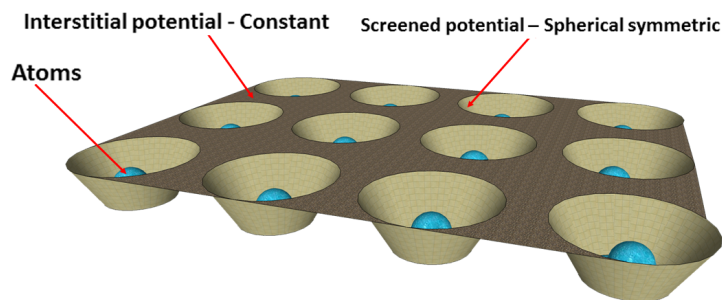

Figure. 1 Muffin-Tin approximation for potential around atoms.

atomic and outersphere regions and volume averaged (constant) in the interatomic regions, which is shown as Fig. 1.

In the atomic region, the effective screened potential felt by electrons is approximated as spherically symmetric. Here the 'screened potential' is due to the screening effect of many electrons, which makes the potential felt by electron is different from direct interaction with nucleus. In another aspect, the attraction from nucleus is screened by co-existing other electrons. As for the interstitial region between atoms, the potential is taken as constant. So the solving of final state wavefunctions becomes the solutions matching of the Schrödinger equation within each sphere with plane-wave solutions in the interstitial region. And linear combinations of these wave functions are then determined by the variational method (from Wikipedia Muffin-Tin approximation).

However, there is limitation of muffin-tin approximation when used for XANES calculation since the energy of photoelectron is close to the value of the approximation done on the potential. Moreover, the muffin-tin approximation makes the calculation result depend on the artificially selected interstitial size, which could bring pseudo-correct calculation result.[1]

2. Methods beyond Muffin-Tin

In Joly's paper[1], several methods beyond muffin-tin approximation was introduced, including the using of KKR full potential and full linear augmented plane wave (FLAWP) approach. And these two methods were restricted to periodic potential. Hence the FDM method was developed to better describe the potential, which, in another aspect, should be partly attributed to the improvement of computation capability since the FDM calculation requires significant computation power.

3. Finite Difference Method (FDM)

This part mainly focuses on the theoretical introduction to FDM and brief description of the algorithm. First we have the Fermi Golden Rule:

$$\sigma(\omega) = \alpha \frac{4\pi}{\omega} \sum_f |\langle \psi_g | H_g | \psi_f \rangle|^2 \delta(\hbar\omega + E_g - E_f) \tag{3-1}$$

where the interaction Hamiltonian is given as:

$$H_g = \hat{\epsilon} \cdot \mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} = \hat{\epsilon} \cdot \mathbf{r} + i(\hat{\epsilon} \cdot \mathbf{r})(\mathbf{k} \cdot \mathbf{r}) + \cdots \tag{3-2}$$

in which the first term is electric dipole and second term is electric quadrupole, etc.

Given the initial and final states ψ_g (core state which is easy to calculate) and ψ_f, and considering quadrupolar approximation, the absorption amplitudes can be written as:

$$M_{gf} = \langle \psi_f | \hat{\epsilon} \cdot \mathbf{r}(1 + \frac{i}{2}\mathbf{k} \cdot \mathbf{r}) | \psi_g \rangle \tag{3-3}$$

Considering all possible combinations of initial and final which could contribute to the absorption of incoming photons, the expression for photo-absorption cross section for XANES is then given by:

$$\sigma = 4\pi^2 \alpha \hbar \omega \sum_{f,g} |M_{f,g}|^2 \delta(\hbar \omega - E_f + E_g) \tag{3-4}$$

For other absorption cross expression, more features should be taken into account such as the polarization, the distinction between outgoing and scattered-back wavefunctions and so on. For detailed information beyond XANES, refer to Ref. [1]. From the ab initio calculation, the initial core-level is easy to calculate as discussed above, and the difficulty resides in the calculation for final state. This is just where FDM mainly works.

The basic idea of FDM is to degrade the derivative functions and transform them to matrix form. The derivative (first derivative, second derivative, etc.) can be written as the expression of neighbouring functions and the function to be solved. Here for XANES calculation, the Laplacian is written as:

$$\nabla \psi_i = \frac{1}{h^2}(\frac{4}{3}\sum_{j,\epsilon}\psi_j^\epsilon - \frac{1}{12}\sum_{j,\epsilon}\psi_j^{\epsilon\epsilon} - \frac{15}{2}\psi_i) \tag{3-5}$$

where ψ_J^ϵ and $\psi_J^{\epsilon\epsilon}$ are the values of the wavefunction on the first and second neighbouring points on the grid in the directions ϵ, j, and h is the distance between the points. In general, if Laplacian is denoted as l_{ij}, the stationary Schrödinger equation of the system can be written as:

$$[(-l_{ii} + \sum_{j}^{neighbours} -l_{ij}\psi_j) + V_i]\psi_i = E\psi_i \tag{3-6}$$

which can be rearranged as:

$$(-l_{ii} + V_i - E)\psi + \sum_{j}^{neighbours} -l_{ij}\psi_j = 0 \tag{3-7}$$

While for XANES calculation, the outgoing photoelectrons are with different energy. In the atomic core (0.5Å–0.7Åaway from absorption atom), the kinetic energy of electron is higher and lower for interstitial region. So non-uniform potential should be used for the calculation (See Fig.2). In zone 1, the potential can be written as the expansion of spherical harmonics:

$$V(\mathbf{r}) = \sum_{L} V_L(r)Y_L(\Omega) \tag{3-8}$$

where $V_L(r)$ is unknown and L stands for (l, m). So the general solution for wavefunction in zone 1 can be written as:

$$\psi(\mathbf{r}) = \sum_{L} a_L \phi(\mathbf{r}) \tag{3-9}$$

where a_L is unknown. And the independent solutions can also be expanded as with spherical harmonics:

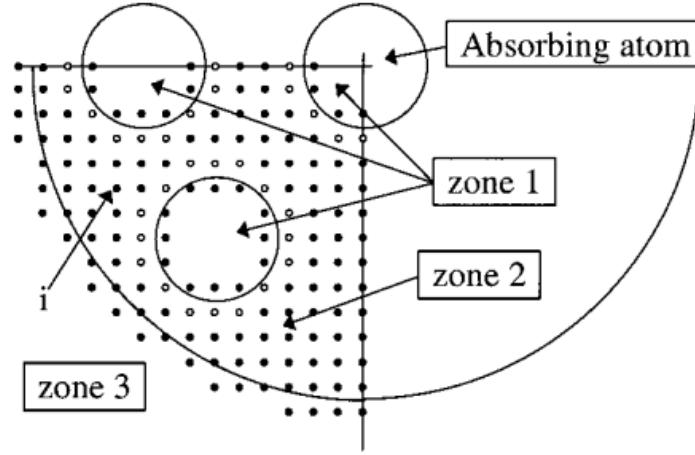$$\phi_L(\mathbf{r}) = \sum_{L'} \varphi_{L'L} Y_{L'(\Omega)} \tag{3-10}$$

Figure. 2 Non-uniform FDM calculation.

Then the expansion of potential and wavefunctions can be inserted into Schrödinger equation to get:

$$[-\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}) + \frac{l'(l'+1)}{r^2} + \sum_L V_L(r)Y_L(\Omega)]\sum_{L'}\varphi_{L'L}Y_{L'}(\Omega)$$

$$= E\sum_{L'}\varphi_{L'L}Y_{L'}(\Omega) \tag{3-11}$$

$$\Rightarrow$$

$$\sum_L V_L(r)Y_L(\Omega)\sum_{L'}\varphi_{L'L}Y_{L'}(\Omega)$$

$$= [\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}) + E - \frac{l'(l'+1)}{r^2}]\sum_{L'}\varphi_{L'L}Y_{L'}(\Omega) \tag{3-12}$$

Left multiply $Y^*_{L''}$ on both sides and integrate for Ω, equation-(3-12) turns to:

$$[\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}) + E - \frac{l'(l'+1)}{r^2}]\varphi_{L'L}$$

$$= \sum_{L'L} C^{L''}_{L'L}V_L(r)\varphi_{L'L} \tag{3-13}$$

where the coefficient $C^{L''}_{L'L}$ is:

$$C^{L''}_{L'L} = \int Y^*_{L''}(\Omega)Y_{L'}(\Omega)Y_{L''}(\Omega)d\Omega \tag{3-14}$$

Through solving equation-(3-13), independent solution can be obtained, hence the only left unknowns for wavefunctions is a_L in expression-(3-9). To obtain the final wavefunction, more equations should be established. Here for zone-2, the common finite difference method is used to establish the 'more equations', and the continuity between atomic core and region just outside the core is then considered. The continuity includes that of wavefunction and also the Fourier Transform (See Ref. [1]).

As for the outer space (zone 3 in Fig. 2), considering the Laplacian - 3-5 and the approximate constant potential, the solutions can be given as Neumann and Bessel (or Hankel) form:

$$\psi^f(\mathbf{r}) = J_{L_f}(\mathbf{r}) + i \sum_L \tau_L^f H_L^{(1)}(\mathbf{r}) \tag{3-15}$$

where J_L and $H_L^{(1)}$ are the generalized Bessel and Hankel functions (See Ref. [1]). As is the same procedure for atomic core region, continuity (including that of Fourier Transform) again should be considered to establish functions for unknown τ_L^f.

Following the prodedures above, one finally gets a general matrix containing all unknowns for the wavefunctions (both atomic core and outer space) as is shown in Ref. [1]. Hence we can obtain the solution for final states based on FDM methods with full potential taken into consideration, which is obviously beyond muffin-tin approximation.

References

[1] Y. Joly. *Phys. Rev. B*, 63:125120, 2001.