DFT calculation of electronic structure: an introduction

Application to K-edge XAS

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Slide courtesy: Delphine Cabaret
probe of **structural** and electronic **properties** of materials

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**local** probe: up to 5-10 Å around the absorbing element

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1 eV shift

*coordination number fingerprint*

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tremendous amount of information

needs for calculations

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About XANES spectroscopy at the K-edge

probe of structural and **electronic properties** of materials

selection rules \(\rightarrow\) **selective** probe of **empty states** localized on the absorber

\[K\text{ edge: } 1s \rightarrow p\text{ transitions (mainly)}\]

tremendous amount of information **with variable core-hole effects**
**Basic issue:** calculation of the absorption cross section for a material, i.e., a system of $N$ electrons + $N_{at}$ nuclei

$$\sigma(\hbar\omega) = 4\pi^2 \alpha \hbar\omega \sum_{i,f} \frac{1}{d_i} |\langle f|\mathcal{O}|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

- **incident x-ray energy**
- **operator of the interaction between x-rays and the system**
- **final state:** excited state of the system of energy $E_f$
- **initial state:** ground state of the system with energy $E_i$, degenerescence $d_i$

**strong** $e^-$ - $e^-$ interaction
- **multielectronic** approach (LFM)
- ex: $L_{2,3}$ edges of 3$d$ elements

**weak** $e^-$ - $e^-$ interaction
- **monoelectronic** approach (Density Functional Theory)
- ex: $K$ edges

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Part 1
Introduction to electronic structure calculation using DFT
Basic issue

System composed of $N_{\text{at}}$ atoms:

- $N$ electrons, mass $m$, charge $q < 0$, position $r_i$ ($i = 1, \ldots, N$)
- $N_{\text{at}}$ nuclei, mass $M_I$, charge $q_I$, position $R_I$ ($I = 1, \ldots, N_{\text{at}}$)

$$H_{\text{syst.}} = T_e + T_{\text{nucl}} + V_{\text{nucl–nucl}} + V_{\text{e–nucl}} + V_{\text{e–e}}$$

$$T_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2$$

$$T_{\text{nucl}} = \sum_{I=1}^{N_{\text{at}}} -\frac{\hbar^2}{2M_I} \nabla_I^2$$

$$V_{\text{nucl–nucl}} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{I} \sum_{J \neq I} \frac{q_I q_J}{|R_I - R_J|}$$

$$V_{\text{e–nucl}} = \frac{1}{4\pi\varepsilon_0} \sum_{I} \sum_{j} \frac{qq_I}{|r_i - R_I|}$$

$$V_{\text{e–e}} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j \neq i} \frac{q^2}{|r_i - r_j|}$$
Born-Oppenheimer approximation

\[ m < M_I \quad (m / m_{\text{proton}} \approx 1836) \]

Order of magnitude of the velocity ratio

Electron: \[ \frac{1}{2} m v_e^2 = 1 \text{Ry} \approx 10 \text{ eV} \]

Nucleus: \[ \frac{1}{2} M_I v_I^2 \approx \hbar \omega_{\text{vib}} \approx 10 \text{ meV} \]

\[ \frac{v_e}{v_{\text{nuclear}}} \approx \sqrt{\frac{M_I}{m}} \frac{10 \text{eV}}{10 \text{meV}} \approx 10^3 \]

The nuclear motion is much slower than the electronic motion \( \Rightarrow \) separation

The nuclei are considered at fixed positions in the electronic motion study

Positions \( R_I \) \( \Rightarrow \) parameter
Born-Oppenheimer approximation

Electronic Hamiltonian

\[ H_e^{\{R_I\}} = T_e + V_{e-e} + V_{e-nucl} + V_{nucl-nucl} \]

\[ H_e^{\{R_I\}} |\psi_n^{\{R_I\}}\rangle = E_n^{\{R_I\}} |\psi_n^{\{R_I\}}\rangle \]
Multielectronic Schrödinger equation

\[ H \, \psi_n = E_n \, \psi_n \]

\[ e = \frac{|q|}{\sqrt{4\pi \varepsilon_0}} \]

\[ H = \sum_i \left( \frac{-\hbar^2 \nabla_i^2}{2m} + \sum_I \frac{-Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \right) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \]

\[ \psi_n \equiv \psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_N) \]

\( \text{antisymmetric (electrons are fermions)} \)
We can solve it for a system of non-interacting electrons!

\[ H \psi_n = E_n \psi_n \]

\[ H = \sum_{i=1}^{N} H_{\text{mono}}^{(i)} \quad \text{with} \quad H_{\text{mono}}^{(i)} = T^{(i)} + V_{\text{nucl}}^{(i)} \]

\[ H_{\text{mono}} \phi_\alpha = \epsilon_\alpha \phi_\alpha \quad \alpha = 1, \ldots, \infty \]

\[ \psi_n : \text{Slater determinant (SD)} \quad - 1929 \]

\[ \text{build from } N \text{ spinorbital functions } \phi_\alpha \]
Slater Determinant

Ground state

\[ \psi_{gs} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1^{(1)} & \phi_2^{(1)} & \cdots & \phi_N^{(1)} \\ \phi_1^{(2)} & \phi_2^{(2)} & \cdots & \phi_N^{(2)} \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1^{(N)} & \phi_2^{(N)} & \cdots & \phi_N^{(N)} \end{vmatrix} \]

\[ E_{gs} = \sum_{i=1}^{N} \epsilon_i \]

Properties:

- antisymmetric
- Pauli exclusion principle satisfied
The Slater determinants form a **basis** in the $N$-electrons Hilbert space

\[ H \psi_n = E_n \psi_n \]

\[ H = \sum_i \left( -\hbar^2 \nabla_i^2 \right) + \sum_I -\frac{Z_I e^2}{|r_i - R_I|} \right) + \frac{1}{2} \sum_i \sum_{j \neq i} e^2 \left| r_i - r_j \right| \]

\[ \psi_n \equiv \psi_n(r_1, r_2, \ldots, r_N; s_1, s_2, \ldots, s_N) \]

\[ C_{\alpha_{\text{max}}}^N = \frac{\alpha_{\text{max}}!}{N!(\alpha_{\text{max}} - N)!} \]

- $N = 5$
  - $\alpha_{\text{max}} = 10 \implies 252 \text{ SD}$
  - $\alpha_{\text{max}} = 20 \implies 15, 504 \text{ SD}$
  - $\alpha_{\text{max}} = 50 \implies 2, 118, 760 \text{ SD}$
- $N = 20$
  - $\alpha_{\text{max}} = 30 \implies 3, 004, 015 \text{ SD}$

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Mean-field approximation

Non-interacting electrons

**Exact solution**: SD

Mean-field approximation

Approximative solutions

Interacting electrons

**Exact solution**: ∞ LC of SD

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**Exact multielectronic Hamiltonian**

\[
H = \sum_i \left[ T^{(i)} + V_{\text{nucl}}^{(i)} \right] + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \]

\[
V_{\text{e-e}}
\]

---

**Effective multielectronic Hamiltonian**: mean-field Hamiltonian

\[
H_{\text{eff}} = \sum_{i=1}^{N} H_{\text{mono}}^{\text{eff},(i)}
\]

\[
H_{\text{eff}}^{\text{mono}} = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{\text{eff}}(\mathbf{r})
\]

**Solutions**: Slater determinants

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Monoatomic Schrödinger solved \textbf{self-consistently} (SCF)

\[
\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{[\rho]}(\mathbf{r})\right] \phi_i^{\text{eff}}(\mathbf{r}) = \epsilon_i^{\text{eff}} \phi_i^{\text{eff}}(\mathbf{r})
\]

with \[
\langle \phi_i^{\text{eff}} | \phi_j^{\text{eff}} \rangle = \delta_{ij}
\]

electron density

\[
\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^{\text{eff}}(\mathbf{r})|^2
\]
Mean-field methods: examples

- Hartree (H)
- Hartree-Fock (HF)
- Density Functional Theory (DFT)
Hartree (H) - 1927

\[
\left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{[\rho]}^{\text{eff}}(\mathbf{r}) \right] \phi_i^{\text{eff}}(\mathbf{r}) = \varepsilon_i^{\text{eff}} \phi_i^{\text{eff}}(\mathbf{r})
\]

\[
V_H(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'
\]

Coulomb interaction between one electron and the electron density

\[
\frac{-\hbar^2 \nabla^2}{2m} \phi_i^{\text{eff}}(\mathbf{r}) + V_{\text{nucl}}(\mathbf{r}) \phi_i^{\text{eff}}(\mathbf{r}) + e^2 \sum_{j=1}^{N} \int \frac{\phi_j^{\text{eff}}(\mathbf{r}')^2}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \phi_i^{\text{eff}}(\mathbf{r}) = \varepsilon_i^{\text{eff}} \phi_i^{\text{eff}}(\mathbf{r})
\]

includes a self-interaction term (if \( i = j \))

Hartree multielectronic wave function = product of monoelectronic wave functions

Pauli exclusion principle exchange not taken into account

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exchange included: the multielectronic wave function as a (unique) SD

additional term that depends on the spin state and the antisymmetric character of the SD:

\[- \sum_{j=1}^{N} \delta_{s_i s_j} \int \frac{\phi_j^{\text{eff}}(\mathbf{r}') \phi_i^{\text{eff}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \, \phi_j^{\text{eff}}(\mathbf{r})\]

strictly compensates the self-interaction term when electrons $i$ and $j$ have the same spin state

BUT no correlation between electrons with opposite spins

Correlation energy: difference between the exact total energy of N-electrons system and the total energy obtained using HF
Density functional theory (DFT): definition

**exact** theory

for systems of \(N\) interacting electrons

within an external potential

\[
H = \sum_i -\frac{\hbar^2 \nabla^2_i}{2m} + \sum_i V_{\text{nucl}}(\mathbf{r}_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}
\]

\[
H \psi_n = E_n \psi_n
\]

\[
\psi_n \equiv \psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_N)
\]

\[
\rho(\mathbf{r})
\]
The (non-degenerate) **ground state electron density** uniquely determines (to a constant) the **external potential** (and thus all the properties of the system).

There is a **universal density functional** $F[\rho]$, not depending explicitly on $V^{\text{ext}}(r)$, defined as:

$$F[\rho] = T[\rho] + V_{\text{e-e}}[\rho] \quad \text{with} \quad \int \rho(r) \, dr = N$$
DFT: Hohenberg and Kohn (1964)

Total energy

\[ E \equiv E[\rho] = F[\rho] + \int V^{\text{ext}}(r)\rho(r) \, dr \]

Variational principle

Exact theory but

\[ F[\rho] = T[\rho] + V_{\text{e-e}}[\rho] = \text{???} \]

question 1
DFT: Kohn and Sham (1965)

Hohenberg - Kohn theorems valid for any $N$-electrons system

also valid for $N$ non-interacting electrons ($V_{e-e} = 0$)

**Kohn – Sham ansatz**

*We can find an external potential $V_{KS}(r)$ for a fictitious system of non-interacting electrons, giving the same ground state electron density as the real system*  

Exact theory **BUT**  

$V_{KS}(r) = ???$

question 2
DFT: Kohn and Sham (1965)

**Kohn-Sham fictitious system:**

System of $N$ non-interacting electrons, in an external potential $V_{KS}(r)$, which gives the same gs electron density as the real system.

**Ground state:** SD build from $N$ orbitals (monoelectronic)

Kohn-Sham orbitals solutions of:

$$\left( \frac{-\hbar^2 \nabla^2}{2m} + V_{KS}(r) \right) \phi_{\alpha}^{KS}(r) = \epsilon_{\alpha}^{KS} \phi_{\alpha}^{KS}(r) \quad (1)$$

Electron density

$$\rho(r) = \sum_{i=1}^{N} |\phi_{i}^{KS}(r)|^2$$

Kinetic energy of the fictitious system

$$T_s[\rho] = \frac{-\hbar^2}{2m} \sum_{i=1}^{N} \int \phi_{i}^{KS}(r)^* \nabla^2 \phi_{i}^{KS}(r) dr \quad (indice \ s: \ « \ single \ particle \ »)$$

$$F[\rho] = T[\rho] + V_{\text{ee}}[\rho] = T_s[\rho] + V_{\text{ee}}[\rho] + (T[\rho] - T_s[\rho])$$
DFT: Kohn and Sham (1965)

What we can write as a functional of the electron density in $V_{e-e}$:

Hartree energy:  
$$E_H[\rho] = \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} \, dr \, dr'$$

$$F[\rho] = T_s[\rho] + V_{e-e}[\rho] + (T[\rho] - T_s[\rho])$$

$$= T_s[\rho] + E_H[\rho] + (T[\rho] - T_s[\rho] + V_{e-e}[\rho] - E_H[\rho])$$

$E_{xc}[\rho]$
exchange and correlation energy

we partially answered question 1!
DFT: Kohn and Sham (1965)

Total energy

\[ E[\rho] = T_s[\rho] + V_H[\rho] + V_{xc}[\rho] + \int V^{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \]

minimization \quad \rightarrow \quad \text{Ground state total energy}

variational principle applied to \( E[\rho] \) with respect to KS orbitals with the constraint:

\[ \int \phi_i^{KS}(\mathbf{r})^* \phi_j^{KS}(\mathbf{r}) d\mathbf{r} = \delta_{ij} \]

\[
\left( \frac{-\hbar^2 \nabla^2}{2m} + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V^{\text{ext}}(\mathbf{r}) \right) \phi_\alpha^{KS}(\mathbf{r}) = \epsilon_\alpha^{KS} \phi_\alpha^{KS}(\mathbf{r})
\]

exchange and correlation potential

\[ V_{xc} = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \]
DFT: Kohn and Sham (1965)

Kohn-Sham equations

\[
\left( -\frac{\hbar^2 \nabla^2}{2m} + V_H(r) + V_{xc}(r) + V^{\text{ext}}(r) \right) \phi^{\text{KS}}_{\alpha}(r) = \epsilon^{\text{KS}}_{\alpha} \phi^{\text{KS}}_{\alpha}(r) \tag{2}
\]

Schrödinger equations of the fictitious system

\[
\left( -\frac{\hbar^2 \nabla^2}{2m} + V^{\text{KS}}(r) \right) \phi^{\text{KS}}_{\alpha}(r) = \epsilon^{\text{KS}}_{\alpha} \phi^{\text{KS}}_{\alpha}(r) \tag{1}
\]

Kohn – Sham potential

\[
V^{\text{KS}}(r) = V_H(r) + V_{xc}(r) + V^{\text{ext}}(r)
\]

We partially answered question 2!
DFT: Kohn and Sham (1965)

Ground state: self-consistent field (SCF) resolution of the Kohn–Sham equations

\[
\left( \frac{-\hbar^2 \nabla^2}{2m} + V_H(r) + V_{xc}(r) + V^{\text{ext}}(r) \right) \phi^{\text{KS}}_\alpha(r) = \epsilon^{\text{KS}}_\alpha \phi^{\text{KS}}_\alpha(r)
\]

**Exact theory:**

A $V_{xc}$ potential that **compensates** the approximations introduced by the mean-field approaches **necessarily** exist!

**In practice:**

Different forms of exchange-correlation functionals

DFT

Exact theory useless

≈

Approximate theory widely used
In the LDA, DFT is still exact for an homogeneous electron gas.

The Local Density Approximation (LDA)

\[ E_{\text{xc}}^{\text{LDA}} \equiv \int \epsilon_{\text{xc}}[\rho(r)] \rho(r) \, dr \]

- exchange - correlation energy for a particle in a homogeneous electron gas (with density \( \rho \))

\[ \epsilon_{\text{xc}}[\rho] = \epsilon_x[\rho] + \epsilon_c[\rho] \]

- known analytically (Dirac exchange energy)
- calculated using Ceperley-Alder Monte-Carlo method, or other parametrization (ex: Hedin-Lundqvist)
Generalized Gradient Approximation (GGA)

\[ E_{xc}^{GGA} \equiv \int \epsilon_{xc}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r} \]

the density gradient at \( \mathbf{r} \) is taken into account

Various parameterizations

**example:** the PBE functional

J.P. Perdew, K. Burke & M. Ernzerhof

Hybrid functionals (H-GGA)

combine the exchange correlation obtained by using GGA methods with a given proportion of the exchange described by Hartree-Fock

The most used: B3LYP (Becke - 3 parameters - Lee, Yang, Parr)

\[
E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{LDA}} + a_0 (E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_x (E_x^{\text{GGA}} - E_x^{\text{LDA}}) + a_c (E_c^{\text{GGA}} - E_c^{\text{LDA}})
\]
DFT: SCF cycle

1st step

Crystal structure

atomic calculation ➔ atomic ρ

Superimposition of atomic ρ

ρ crystal = ρ_{in}
DFT: SCF cycle

Potential calculation
Poisson equation

KS orbitals calculation
Kohn and Sham equations

Calculation of $\rho_{\text{out}}(r)$

Convergence?

mixing
$\rho_{\text{in}}(r)$ & $\rho_{\text{out}}(r)$

$(1 - \alpha)\rho_{\text{in}} + \alpha\rho_{\text{out}}$

$\rho_{\text{in}}(r)$

NO

STOP

YES
### Solid state physics and quantum chemistry

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*non-exhaustive list*
DFT: softwares

real space

cluster

no periodicity constraint (amorphous and crystalline materials)

suited to molecules

or

periodic boundary conditions

infinite number of atoms

1st Brillouin zone

suited to crystals

supercell

the main differences between them
Basis to expand the Kohn-Sham orbitals

\[ \phi^K_S(r) = \sum_n c^i_n \varphi_n(r) \]

**Plane waves**
- Pseudopotentials

**Atomic orbitals**
- Gaussians
- LCAO
- **ORCA**

**Mixed basis**
- *atomic spheres*: LC of radial functions × spherical harmonics
- *interstitial region*: plane waves
- LAPW

**Muffin-tin orbitals**
- spherical waves
- LMTO, multiple scattering
- **SPR-KKR**
## Solid state physics and quantum chemistry

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*non-exhaustive list*

Part 2
Introduction to the calculation of X-ray absorption spectra

X-ray Absorption Near-Edge Structure

Near-Edge X-ray Absorption Fine Structure
Basic issue: calculation of the absorption cross section for a material, i.e., a system of \( N \) electrons + \( N_{at} \) nuclei

\[
\sigma(\hbar\omega) = 4\pi^2 \alpha \hbar\omega \sum_{i,f} \frac{1}{d_i} |\langle f | \mathcal{O} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)
\]

incident x-ray energy

**final state:**
excited state of the system of energy \( E_f \)

**initial state:**
ground state of the system with energy \( E_i \), degenerescence \( d_i \)

**strong** \( e^- - e^- \) interaction
**multielectronic** approach
ex: \( L_{2,3} \) edges of 3d elements

**weak** \( e^- - e^- \) interaction
**monoelectronic** approach
(Density Functional Theory)
ex: \( K \) edges

XANES modeling

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Interaction operator between x-rays and electrons

**incident X-ray beam**: electromagnetic wave treated as a **plane-wave** \( e^{i\mathbf{k} \cdot \mathbf{r}} \)

- \( \mathbf{k} \): wave vector
- \( \mathbf{\hat{e}} \): polarization direction

\[
e^{i\mathbf{k} \cdot \mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} + \ldots
\]

\[
\mathcal{O} = \sum_i \mathbf{\hat{e}} \cdot \mathbf{r}_i + \frac{i}{2} \sum_i \mathbf{\hat{e}} \cdot \mathbf{r}_i \mathbf{k} \cdot \mathbf{r}_i
\]

- **electric dipole transitions (E1)**
  \[
  \Delta \ell = \pm 1
  \]
  majority electronic transitions

- **electric quadrupole transitions (E2)**
  \[
  \Delta \ell = \pm 2
  \]
  observable in the \( K \) pre-edge of 3\textit{d} transition elements
**Interaction operator between x-rays and electrons**

**Electric dipole (E1) transitions**: $\Delta \ell = \pm 1$

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<tr>
<td>3</td>
<td>0</td>
<td>$M_1$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$M_{2,3}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$M_{4,5}$</td>
</tr>
</tbody>
</table>

- **Delocalised** final state (weak electron repulsion): $p$
- **Monoelectronic** theories (DFT)
- **Localized** final state (strong electron): $3d$, $4f$
- **Multielectronic** theories (multiplets)
For $K$ edges:

\[
\sigma(\hbar \omega) = 4\pi^2 \alpha \hbar \omega \sum_{i,f} |\langle \psi_f | \hat{\varepsilon} \cdot \mathbf{r} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar \omega)
\]

monoelectronic empty state (KS) calculated with a 1s core-hole in the electronic configuration of the absorbing atom.
XANES and DFT: the calculation codes

2 types

1- Those written to calculate core-level spectra

- cluster, real space

  at the beginning: multiple scattering (no self-consistency, \textit{muffin-tin} potential)
  continuum, feff, icxanes, ….

2- The electronic structure codes, in which a post SCF-process code was added to calculate core-level spectra

- periodic boundary conditions, reciprocal space
Note: muffin-tin (MT) potential

ZONE I:
- atomic spheres
- spherical symmetry potentials

ZONE II:
- interstitial region
- constant potential

MT

Full Potential
XANES and DFT: the calculation codes

2 types

1- Those written to calculate core-level spectra

**cluster, real space**

- **at the beginning:** multiple scattering (no self-consistency, *muffin-tin* potential) continuum, feff, icxanes,....
- **at the end of the 90’s:** finite differences method with fdmnes

**currently:** fdmnes, feff9

2- The electronic structure codes, in which a post SCF-process code was added to calculate core-level spectra

**periodic boundary conditions, reciprocal space**

Wien2k, CASTEP, Quantum-Espresso (XSpectra),...
With codes using periodic boundary conditions (for crystals), we have to avoid spurious interaction of the excited atom with its periodically repeated images.

- **Large interaction**
  - ○ atom with a core-hole
  - ● atom without a core-hole

- **Weak interaction**
  - ○ atom with a core-hole
  - ● atom without a core-hole

To restore neutrality:
(i) Negative background charge
(ii) Excited electron in conduction band
XANES and DFT: periodic boundary conditions and core hole

**Si K edge in α-quartz**

**unit cell**

\[ a = 4.91\text{Å}, \ c = 5.40\text{Å} \]

3 Si, 6 O

**1×1×1 supercell**

= unit cell with 1 core-hole

1 Si*, 2 Si, 6 O

**2×2×2 supercell**

\[ a = 9.82\text{Å}, \ c = 10.80\text{Å} \]

1 Si*, 23 Si, 48 O

---

**without core-hole**

**interaction between core-holes**

**convergence**

---

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• DFT is dedicated to the calculation of **ground state properties** but *used here for the modeling of excited states*...
  
  ➡️ possible underestimation of the excitation energies

• **Static** modeling of the **core-hole-electron interaction** through the supercell approach or within a cluster of atoms

• Exchange and correlation **functional is not energy-dependent**
  
  ➡️ inelastic losses not calculated, the convolution factor is a parameter
• **GW + Bethe-Salpeter equation (BSE)**
  - Shirley and coll.
  - OCEAN interface
  - Olovsson, Puschnig, Ambrosch-Draxl, Lakowski : LAPW

• **TD-DFT**  (real-space approaches)
  - FDMNES
  - Quantum-Chemistry codes: Orca, ADF, Q-chem, ...
3d elements in octahedral site

**single-particle picture**

### $3d^0$

- $t_{2g}$
- $e_g$

- Ti$^{4+}$
- TiO$_2$ rutile, anatase

- $t_{2g}$, $e_g$ empty

- Favorable case

### $3d^6$

- $t_{2g}$
- $e_g$

- Fe$^{2+}$
- FeS$_2$ pyrite
- MbCO protein

- $e_g$ empty

- Acceptable case

### $3d^3$

- $t_{2g}$
- $e_g$

- Cr$^{3+}$
- ruby, emerald, spinel:Cr, pyrope:Cr

- $e_g$ empty

- Acceptable case

### $3d^2$

- $t_{2g}$
- $e_g$

- V$^{3+}$
- grossular:V

- $t_{2g}$ partially empty

- Critical case

### $3d^5$

- $t_{2g}$
- $e_g$

- Fe$^{3+}$
- MbCN protein

- $e_g$ empty

- Critical case

---

[ Cabaret et al. PCCP (2010) ]
Ti\(^{4+}\) in octahedral site

**TiO\(_2\) rutile, Ti site: centrosymmetric**

pre-edge: E2 + *non local* E1

---

**single-particle picture**

\[
\begin{array}{c}
3d^0 \\
\downarrow \\
t_{2g}
\end{array}
\]

---

Absorption (arbit. units)

- **peak A1**
  - local E2 transition 1s \(\rightarrow\) 3d \(t_{2g}\)
- **peak A2**
  - local E2 transition 1s \(\rightarrow\) 3d \(e_g\)
  + non-local E1 transition 1s \(\rightarrow\) \(p\) hybrid. 3d \(t_{2g}\) (neighb.)
- **peak A3**
  - non-local E1 transition 1s \(\rightarrow\) \(p\) hybrid. 3d \(e_g\) (neighb.)

---


---

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Ti$^{4+}$ in octahedral site

TiO$_2$ rutile, Ti site: centrosymmetric

pre-edge: $E_2$ + non local $E_1$

singlet-particle picture

\[
\begin{array}{ccc}
3d^0 & & e_g \\
 & & t_{2g}
\end{array}
\]

- A1 calc. at too high energy!
- WHY?

TiO$_2$ rutile, Ti site: centrosymmetric

pre-edge: E2 + non local E1

single-particle picture

$3d^0$ --- $e_g$

--- $t_{2g}$

A1 calc. at too high energy!
The 1s core-hole is not attractive enough...

How to improve?
**Ti$^{4+}$ in octahedral site**

TiO$_2$ rutile, Ti site: centrosymmetric

pre-edge: $E2 + \text{non local } E1$

---

**Bethe-Salpeter equation**

Cr$^{3+}$ in octahedral site

MgAl$_2$O$_4$:Cr$^{3+}$, Cr site: centrosymmetric

pre-edge : E2

single-particle picture

3d$^3$

Origin?

two E2 peaks (at too high energy...)

V$^{3+}$ in octahedral site

Ca$_3$Al$_2$(SiO$_4$)$_3$:V$^{3+}$, V site: centrosymmetric

pre-edge : E2

Three E2 peaks (at 2eV too high energy...)

Origin?

occupied states

spin up + spin down

spin up

spin down


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Fe$^{2+}$ in octahedral site

MbCO protein, complex Fe site geometry

$\downarrow$ pre-edge: E2 + local E1

2 peaks essentially E1, but
- at too high energy peak
- A2 too intense

peak A1
$1s \rightarrow p_z - 3d_z^2$ mixing

local E1

peak A2
$1s \rightarrow p_z$ weakly mixed with $3d$
hybridized with $\pi^*$ of CO

off-site E1

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Cabaret et al. PCCP (2010)
Angular dependence of core hole screening in LiCoO$_2$

Electronic structure poorly described in GGA

Gap = 1.7 eV

Better described using Hubbard parameter (U) on Co 3d states

Gap = 2.3 eV
LiCoO$_2$ : the Co K pre-edge

Best agreement is obtained when including U and the 1s core hole
LiCoO$_2$ : the Co K pre-edge

pre-edge : E2 + nonlocal E1

Peak $\alpha$ : 1s$\rightarrow$3d (Co*)
Peak $\beta$ : 1s$\rightarrow$4p + O(2p) + Co (3d) n.n. in plane
Peak $\gamma$ : 1s$\rightarrow$4p + O(2p) + Li (2p)+Co (3d) n.n. out of plane
Inherent **drawbacks** of DFT-LDA/GGA for XANES calculation

- electronic repulsion modeling
- core hole-electron interaction modeling

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d^0$ (TiO$_2$)</td>
<td>~0.5 eV</td>
</tr>
<tr>
<td>$3d^6$ LS (MbCO, FeS$_2$)</td>
<td>~0.8 eV</td>
</tr>
<tr>
<td>$3d^3$ (Cr-spinel, emerald)</td>
<td>~1 eV</td>
</tr>
<tr>
<td>$3d^5$ LS (MbCN)</td>
<td>~1.7 eV</td>
</tr>
<tr>
<td>$3d^3$ (ruby) and $3d^2$ (V-grossular)</td>
<td>~2 eV</td>
</tr>
</tbody>
</table>

**E2 and E1 transitions toward $3d$ (abs) systematically at too high energy**


2.4 eV → 1.7 eV for $3d^6$ LS (LiCoO$_2$) Juhin *et al.* PRB 81:115115 (2010)

Inherent **drawbacks** of DFT-LDA/GGA for XANES calculation

- electronic repulsion modeling
- core hole-electron interaction modeling

E2 and E1 transitions toward 3d (abs) **systematically at too high energy**

However, **DFT in LDA/GGA is useful!**

- **number of pre-edge peaks** well reproduced
- **relative intensities and positions** in rather good agreement with experiment
- single-particle description of transitions with
  - E1/E2 character
  - **degree of local and non-local hybridization**
  - spin polarization
- improved with adding $U$ (NiO, LiCoO$_2$, ...)

Summary