DFT calculation of **electronic structure**: an introduction

*Application to **K-edge XAS***

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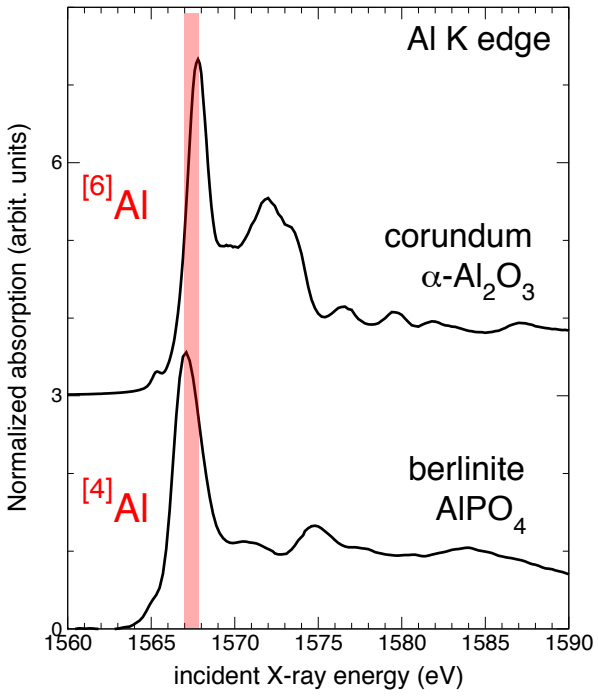
About XANES spectroscopy at the K-edge

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

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

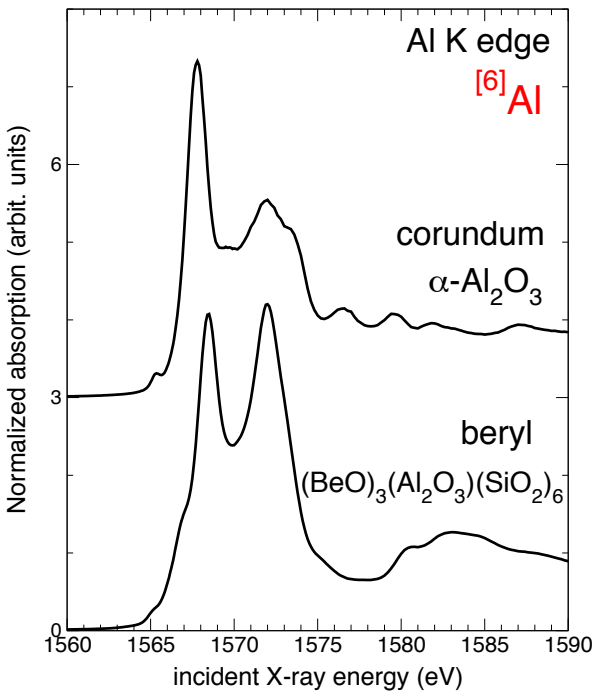
isotropic spectra



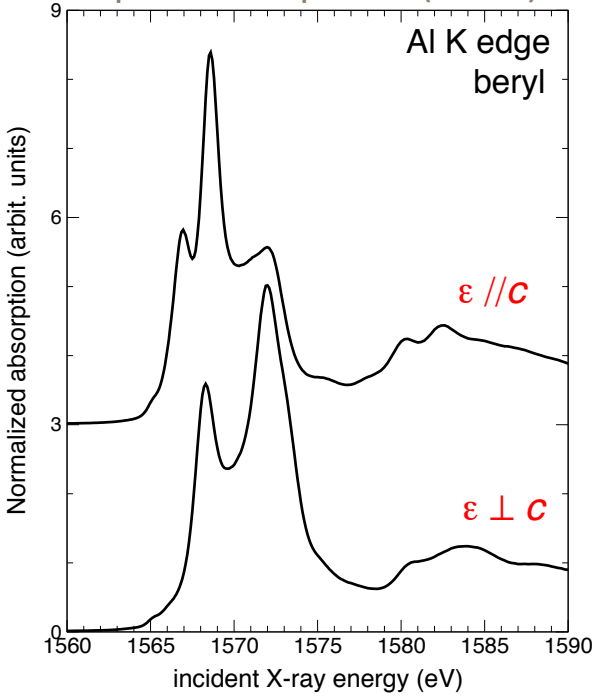
1 eV shift

coordination number fingerprint

isotropic spectra



polarized spectra (XNLD)



tremendous amount of information

→ needs for calculations

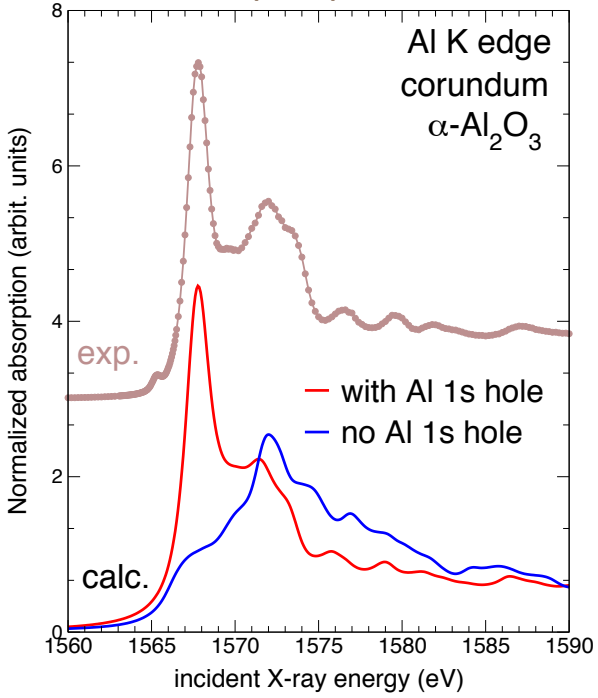
About XANES spectroscopy at the K-edge

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

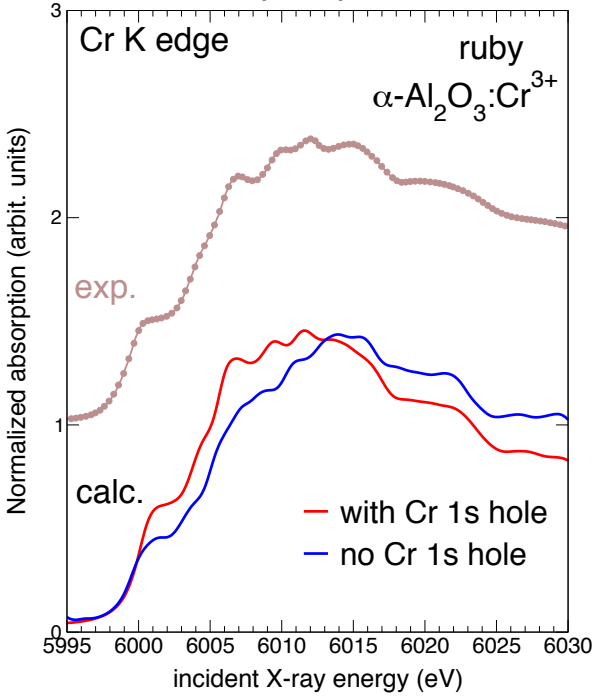
selection rules → **selective** probe of **empty states** localized on the absorber

K edge: 1s → *p* transitions (mainly)

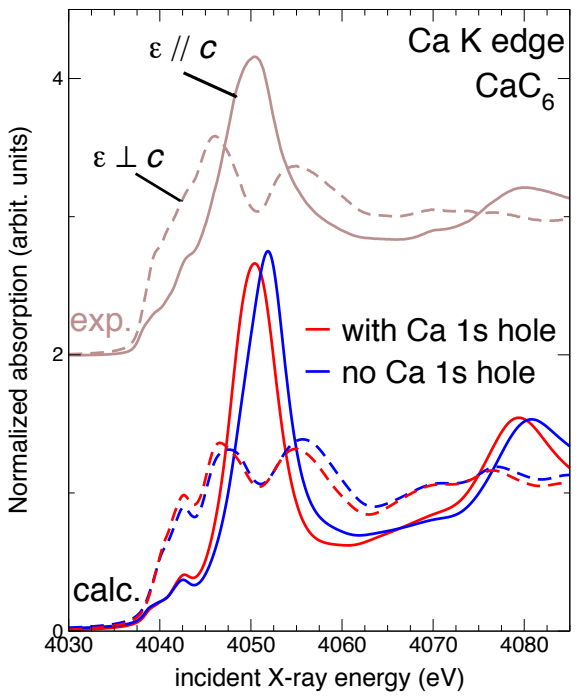
isotropic spectra



isotropic spectra



polarized spectra (XNLD)



tremendous amount of information **with variable core-hole effects**

XANES modeling

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
ex : $L_{2,3}$ edges of 3*d* elements

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

Part 1
Introduction to electronic structure calculation using DFT

Basic issue

N_{at} atom system :

+ N electrons, mass m, charge $q < 0$, position $\boldsymbol{r}_i$ (i = 1, …, N)

N_{at} nuclei, mass M_I, charge q_I, position $\boldsymbol{R}_I$ (I = 1, …, N_{at})

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

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

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

$$V_{\mathrm{e–e}} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_i \sum_{j \neq i} \frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V_{\mathrm{e–nucl}} = \frac{1}{4\pi\varepsilon_0} \sum_i \sum_I \frac{q q_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

$$V_{\mathrm{nucl–nucl}} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_I \sum_{J \neq I} \frac{q_I q_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Born-Oppenheimer approximation

$m < M_I$ (m / m_{proton} ≈ 1836)

*Order of magnitude of the **velocity ratio***

Electron : $\frac{1}{2} m v_e^2 = 1\mathrm{Ry}$ ≈ 10 eV

Nucleus : $\frac{1}{2} M_I v_I^2 \approx \hbar\omega_{vib}$ ≈ 10 meV

$$\frac{v_e}{v_{noy}} \approx \sqrt{\frac{M_I}{m}\frac{10\mathrm{eV}}{10\mathrm{meV}}}$$

≈ **10^3**

The nuclear motion is much slower
than the electronic motion ➔ **separation**

The nuclei are considered at fixed positions in the electronic motion study
Positions R_I ➔ **parameter**

Born-Oppenheimer approximation

Electronic Hamiltonian

parameter

$$H_{\mathrm{e}}^{\{\mathbf{R}_I\}} = T_{\mathrm{e}} + V_{\mathrm{e-e}} + V_{\mathrm{e-nucl}} + \underbrace{V_{\mathrm{nucl-nucl}}}_{\text{constant}}$$

$$H_e^{\{\mathbf{R}_I\}} |\psi_n^{\{\mathbf{R}_I\}}\rangle = E_n(\{\mathbf{R}_I\}) |\psi_n^{\{\mathbf{R}_I\}}\rangle$$

Multielectronic Schrödinger equation

$$H\ \psi_n = E_n\ \psi_n$$

$$H = \sum_i \underbrace{\left(\underbrace{\frac{-\hbar^2 \nabla_i^2}{2m}}_{T^{(i)}} + \underbrace{\sum_I \frac{-Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}}_{V_{\text{nucl}}^{(i)}} \right)}_{} + \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V_{\text{e-e}}}$$

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

↳ antisymmetric (electrons are fermions)

Multielectronic Schrödinger equation

$$H\ \psi_n = E_n\ \psi_n$$

We can solve it for a system of non-interacting electrons !

solution

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

$$H_{\text{mono}}\ \phi_\alpha = \epsilon_\alpha\ \phi_\alpha \qquad \alpha = 1, ..., \infty$$

↳ spinorbital

ψ_n : Slater determinant (SD) - 1929

build from N spinorbital functions ϕ_α

Slater Determinant

Ground state

$$\psi_{\mathrm{gs}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1^{(1)} & \phi_2^{(1)} & \dots & \phi_N^{(1)} \\ \phi_1^{(2)} & \phi_2^{(2)} & \dots & \phi_N^{(2)} \\ . & . & . & . \\ . & . & . & . \\ \phi_1^{(N)} & \phi_2^{(N)} & \dots & \phi_N^{(N)} \end{vmatrix}$$

$$E_{\mathrm{gs}} = \sum_{i=1}^{N} \epsilon_i$$

Properties :

- antisymmetric
- Pauli exclusion principle satisfied

Multielectronic Schrödinger equation

$$H\ \psi_n = E_n\ \psi_n$$

solution

$$H = \sum_i \left(\underbrace{\frac{-\hbar^2 \nabla_i^2}{2m}}_{T^{(i)}} + \underbrace{\sum_I \frac{-Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}}_{V_{\text{nucl}}^{(i)}} \right) + \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V_{e-e}}$$

$$\psi_n \equiv \psi_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N; \mathbf{s}_1, \mathbf{s}_2, ..., \mathbf{s}_N)$$

ψ_n: Linear combination of an **infinite number** of Slater determinants

configuration interaction (*"brute force"*)

$$C_{\alpha_{\max}}^N = \frac{\alpha_{\max}!}{N!(\alpha_{\max} - N)!}$$

$N = 5$ α_{max}= 10 ➔ 252 SD

α_{max}= 20 ➔ 15, 504 SD

α_{max}= 50 ➔ 2, 118, 760 SD

$N = 20$ α_{max}= 30 ➔ 3, 004, 015 SD

Mean-field approximation

Non-interacting electrons
Exact solution : SD

Mean-field approximation
Approximative solutions

Interacting electrons
Exact solution : ∞ LC of SD

Exact multilelectronic Hamiltonian

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

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

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

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

Solutions : Slater determinants

Mean-field approximation

Monoelectronic Schrödinger solved **self-consistently** (SCF)

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V^{\text{eff}}_{[\rho]}(\mathbf{r})\right]\phi^{\text{eff}}_i(\mathbf{r}) = \epsilon^{\text{eff}}_i\ \phi^{\text{eff}}_i(\mathbf{r})$$

with $\langle\phi^{\text{eff}}_i|\phi^{\text{eff}}_j\rangle = \delta_{ij}$

electron density $\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi^{\text{eff}}_i(\mathbf{r})|^2$

Mean-field methods: examples

Hartree (H)

Hartree-Fock (HF)

Density Functional Theory (DFT)

Hartree (H) - 1927

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

$$V_{\text{H}}(\mathbf{r}) = e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}'$$

Coulomb interaction between one electron and the electron density

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

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

Hartree multielectronic wave function = **product** of monoelectronic wave functions

→ **exchange not taken into account**

Hartree-Fock (HF) - 1935

- **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 :

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

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

$$H = \underbrace{\sum_i \frac{-\hbar^2 \nabla_i^2}{2m}}_{T} + \underbrace{\sum_i V_{\text{nucl}}(\mathbf{r}_i)}_{V^{\text{ext}}(\mathbf{r})} + \underbrace{\frac{1}{2}\sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V_{\text{e-e}}}$$

$$\left.\begin{aligned} H\ \psi_n &= E_n\ \psi_n \\ \psi_n &\equiv \psi_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N; \mathbf{s}_1, \mathbf{s}_2, ..., \mathbf{s}_N) \end{aligned}\right\} \rightarrow \boxed{\rho(\mathbf{r})}$$

DFT: Hohenberg and Kohn theorems (1964)

The (non-degenerate) ***ground state electron density uniquely*** *determines (to a constant) the* ***external potential*** *(and thus all the properties of the system).*

$$\rho_{\mathrm{gs}}(\mathbf{r}) \longrightarrow V^{\mathrm{ext}}(\mathbf{r})$$

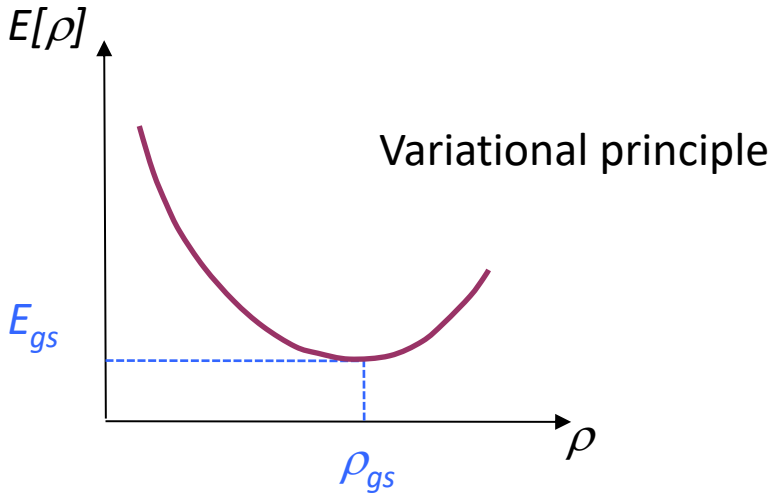
$\rho(\mathbf{r})$ basic variable

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

$$F[\rho] = T[\rho] + V_{\mathrm{e\text{–}e}}[\rho] \quad \text{with} \quad \int \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} = N$$

DFT: Hohenberg and Kohn (1964)

Total energy $$E \equiv E[\rho] = F[\rho] + \int V^{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\ \mathrm{d}\mathbf{r}$$



Exact theory **but**

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

question 1

DFT: Kohn and Sham (1965)

Hohenberg - Kohn theorems valid
for any N-electrons system

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

Kohn – Sham ansatz

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

Exact theory **BUT**

$$V_{\text{KS}}(\mathbf{r}) = ???$$

question 2

DFT: Kohn and Sham (1965)

Kohn-Sham fictitious system:

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

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

Kohn-Sham orbitals solutions of:

$$\left(\frac{-\hbar^2\nabla^2}{2m} + V^{\mathrm{KS}}(\mathbf{r})\right)\phi_\alpha^{\mathrm{KS}}(\mathbf{r}) = \epsilon_\alpha^{\mathrm{KS}}\ \phi_\alpha^{\mathrm{KS}}(\mathbf{r}) \qquad (1)$$

electron density

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

Kinetic energy of the fictitious system

$$T_s[\rho] = \frac{-\hbar^2}{2m}\sum_{i=1}^{N}\int \phi_i^{\mathrm{KS}}(\mathbf{r})^*\nabla^2\phi_i^{\mathrm{KS}}(\mathbf{r})\mathrm{d}\mathbf{r}$$

(indice *s* : « single particle »)

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

DFT: Kohn and Sham (1965)

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

Hartree energy: $$E_{\text{H}}[\rho] = \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$

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

$$= T_s[\rho] + E_{\text{H}}[\rho] + \underbrace{(T[\rho] - T_s[\rho] + V_{\text{e–e}}[\rho] - E_{\text{H}}[\rho])}_{E_{\text{xc}}[\rho]}$$

exchange and correlation energy

we partially answered question 1 !

DFT: Kohn and Sham (1965)

Total energy

$$E[\rho] = T_s[\rho] + V_{\mathrm{H}}[\rho] + V_{\mathrm{xc}}[\rho] + \int V^{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})\ \mathrm{d}\mathbf{r}$$

minimization → Ground state total energy

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

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

$$\left(\frac{-\hbar^2\nabla^2}{2m} + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) + V^{\mathrm{ext}}(\mathbf{r})\right)\phi_\alpha^{\mathrm{KS}}(\mathbf{r}) = \epsilon_\alpha^{\mathrm{KS}}\ \phi_\alpha^{\mathrm{KS}}(\mathbf{r}) \qquad (2)$$

exchange and correlation potential

$$V_{xc} = \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}$$

DFT: Kohn and Sham (1965)

Kohn-Sham equations

$$\left(\frac{-\hbar^2\nabla^2}{2m} + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) + V^{\mathrm{ext}}(\mathbf{r})\right)\phi_\alpha^{\mathrm{KS}}(\mathbf{r}) = \epsilon_\alpha^{\mathrm{KS}}\ \phi_\alpha^{\mathrm{KS}}(\mathbf{r}) \qquad (2)$$

Schrödinger equations of the fictitious system

$$\left(\frac{-\hbar^2\nabla^2}{2m} + V^{\mathrm{KS}}(\mathbf{r})\right)\phi_\alpha^{\mathrm{KS}}(\mathbf{r}) = \epsilon_\alpha^{\mathrm{KS}}\ \phi_\alpha^{\mathrm{KS}}(\mathbf{r}) \qquad (1)$$

Kohn – Sham potential

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) + V^{\mathrm{ext}}(\mathbf{r})$$

We **partially** answered question 2 !

DFT: Kohn and Sham (1965)

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

$$\left(\frac{-\hbar^2 \nabla^2}{2m} + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) + V^{\mathrm{ext}}(\mathbf{r}) \right) \phi_\alpha^{\mathrm{KS}}(\mathbf{r}) = \epsilon_\alpha^{\mathrm{KS}} \ \phi_\alpha^{\mathrm{KS}}(\mathbf{r})$$

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

DFT: exchange and correlation functionals

The Local Density Approximation (LDA)

the simplest

$$E_{\mathrm{xc}}^{\mathrm{LDA}} \equiv \int \epsilon_{\mathrm{xc}}[\rho(\mathbf{r})]\,\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

$\epsilon_{\mathrm{xc}}[\rho(\mathbf{r})]$: exchange - correlation energy for a particle in a **homogeneous electron gas** (with density ρ)

$$\epsilon_{\mathrm{xc}}[\rho] = \epsilon_{\mathrm{x}}[\rho] + \epsilon_{\mathrm{c}}[\rho]$$

known analytically
(Dirac exchange energy)

calculated
using Ceperley-Alder Monte-Carlo method, or other parametrization
(ex: Hedin-Lundqvist)

*In the LDA, DFT is still **exact** for an homogeneous electron gas.*

DFT: exchange and correlation functionals

Generalized Gardient Approximation (GGA)

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

↳ the density gradient at $\mathbf{r}$ is taken into account

Various parameterizations

example: the **PBE** functional
J.P. **P**erdew, K. **B**urke & M. **E**rnzerhof
« *Generalized Gradient Approximation Made Simple* » *Phys. Rev. Lett.*, 77:3865 (**1996**).

DFT: exchange and correlation functionals

Hybrid functionals (H-GGA)

combine the **exchange** and the **correlation** obtained by using **GGA** methods

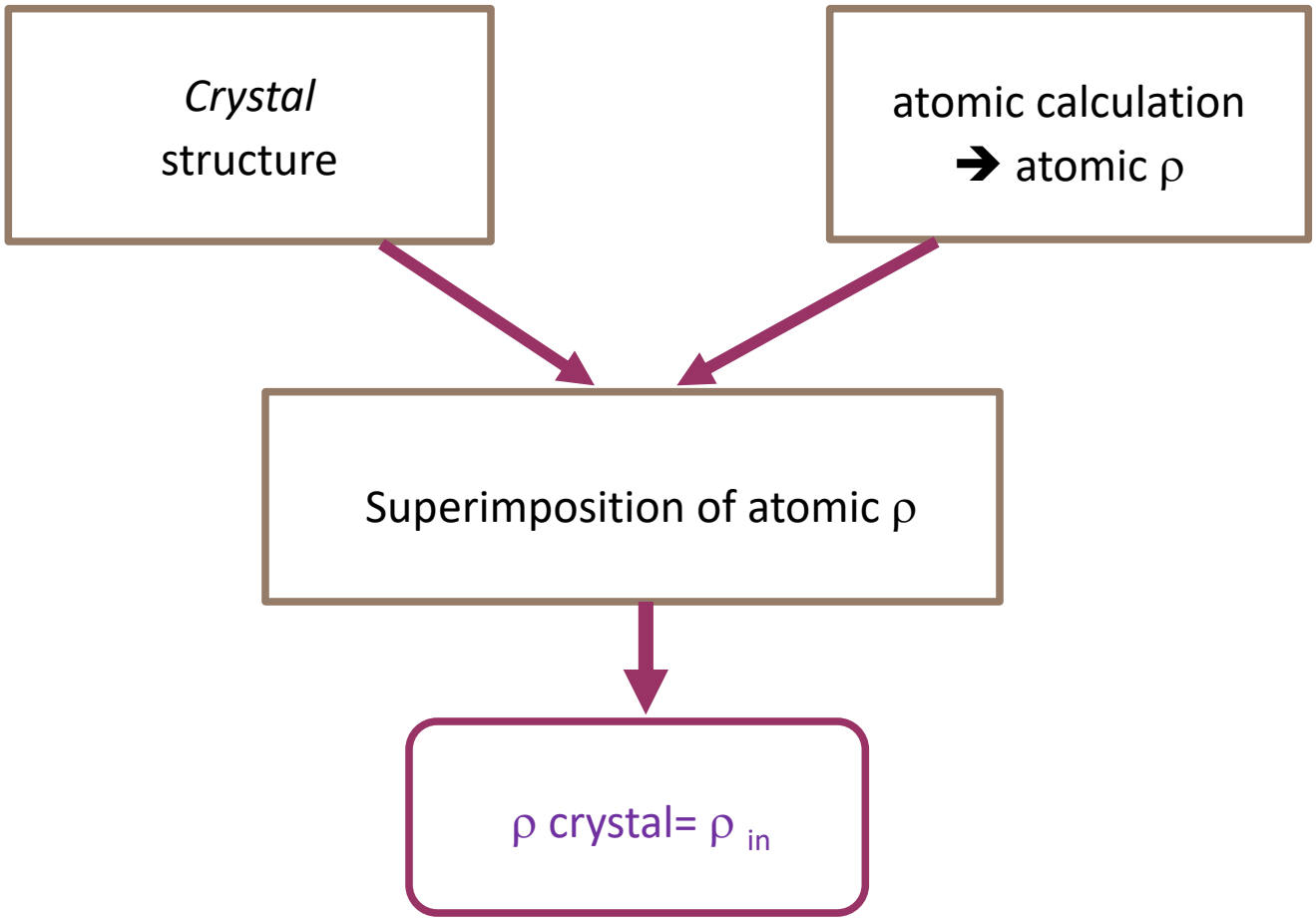
with a given proportion of the **exchange** described by **Hartree-Fock**

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

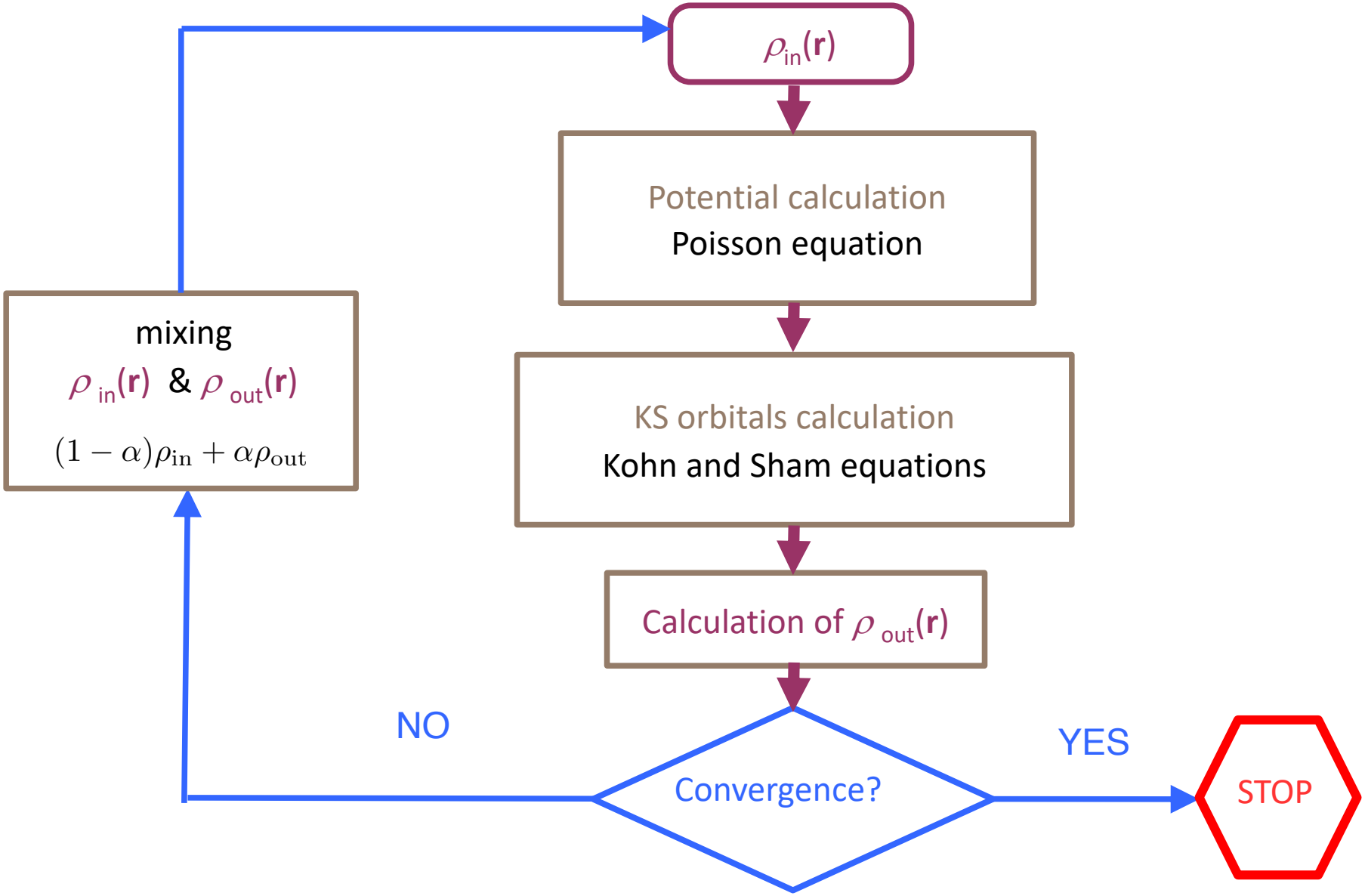
$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = E_{\mathrm{xc}}^{\mathrm{LDA}} + a_0(E_{\mathrm{x}}^{\mathrm{HF}} - E_x^{\mathrm{LDA}}) + a_x(E_{\mathrm{x}}^{\mathrm{GGA}} - E_x^{\mathrm{LDA}}) + a_c(E_{\mathrm{c}}^{\mathrm{GGA}} - E_{\mathrm{c}}^{\mathrm{LDA}})$$

DFT: SCF cycle

1st step



DFT: SCF cycle



DFT: softwares

Solid state physics and quantum chemistry

Abinit
ADF
AIMPRO
Augmented Spherical Wave
Atomistix Toolkit
CADPAC
CASTEP
CP2K
CPMD
CRYSTAL
DACAPO
DALTON
deMon2K
DFT++
DMol3
EXCITING
Fireball
FLEUR
GAMESS (UK)
GAMESS (US)
GAUSSIAN
GPAW
JAGUAR
MOLCAS
MOLPRO
MPQC
NWChem
OpenMX
ORCA
ParaGauss
PARATEC
PARSEC
PC GAMESS
PLATO
Parallel Quantum Solutions
PWscf (Quantum Espresso)
Q-Chem
SIESTA
Socorro
Spartan
SPR-KKR
TURBOMOLE
VASP
WIEN2k

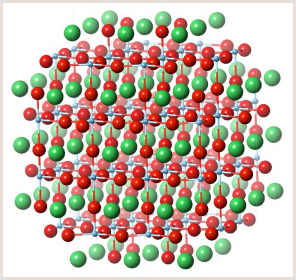
non-exhaustive list

DFT: softwares

the main differences between them

real space

cluster

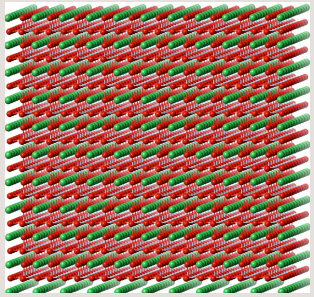


no periodicity constraint
(amorphous and crystalline materials)

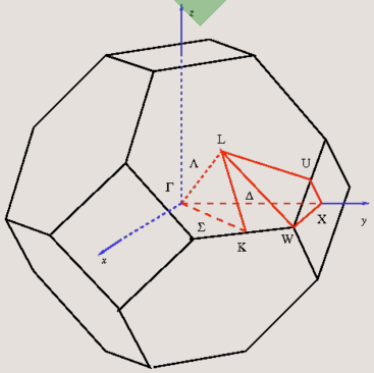
suited to molecules

or

periodic boundary conditions



infinite number of atoms



1st Brillouin zone

suited to cristals
supercell

DFT: sofwares

the main differences between them

Basis to expand the Kohn-Sham orbitals

$$\phi_i^{\mathrm{KS}}(\mathbf{r}) = \sum_n c_n^i \, \varphi_n(\mathbf{r})$$

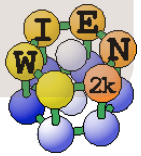
Plane waves
Pseudopotentials

QUANTUMESPRESSO

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

Abinit
ADF
AIMPRO
Augmented Spherical Wave
Atomistix Toolkit
CADPAC
CASTEP
CP2K
CPMD
CRYSTAL
DACAPO
DALTON
deMon2K
DFT++
DMol3
EXCITING
Fireball
FLEUR
GAMESS (UK)
GAMESS (US)
GAUSSIAN
GPAW
JAGUAR
MOLCAS
MOLPRO
MPQC
NWChem
OpenMX
ORCA
ParaGauss
PARATEC
PARSEC
PC GAMESS
PLATO
Parallel Quantum Solutions
PWscf (Quantum Espresso)
Q-Chem
SIESTA
Socorro
Spartan
SPR-KKR
TURBOMOLE
VASP
WIEN2k

non-exhaustive list

http://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

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

X-ray **A**bsorption **N**ear-Edge **S**tructure

Near-**E**dge **X**-ray **A**bsorption **F**ine **S**tructure

XANES modeling

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
ex : $L_{2,3}$ edges of 3*d* elements

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

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
$\hat{\varepsilon}$: polarization direction

$$\mathcal{O} = \sum_i \hat{\varepsilon}\cdot\mathbf{r}_i + \frac{i}{2}\sum_i \hat{\varepsilon}\cdot\mathbf{r}_i \; \mathbf{k}\cdot\mathbf{r}_i$$

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*d* transition elements

Interaction operator between x-rays and electrons

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

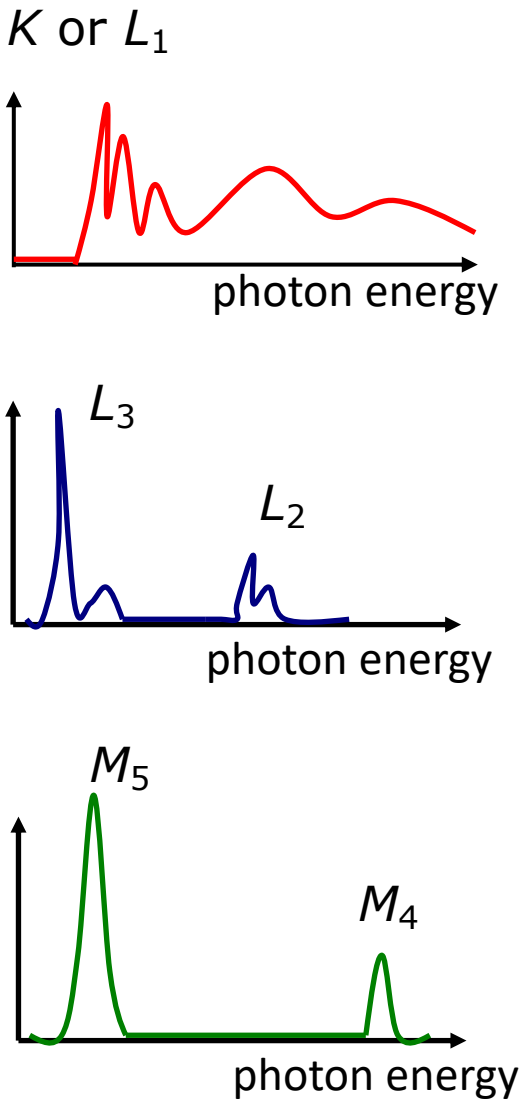
Initial State quantum numbers		Edge	final state symmetry
n	ℓ		
1	0	*K*	*p*
2	0	L_1	*p*
2	1	$L_{2,3}$	*s+d*
3	0	M_1	*p*
3	1	$M_{2,3}$	*s+d*
3	2	$M_{4,5}$	*p+f*

delocalised final state (weak electron repulsion) : ***p***

↳ **monoelectronic** theories (DFT)

localized final state (strong electron repulsion) : ***3d, 4f***

↳ **multielectronic** theories (multiplets)



XANES and DFT

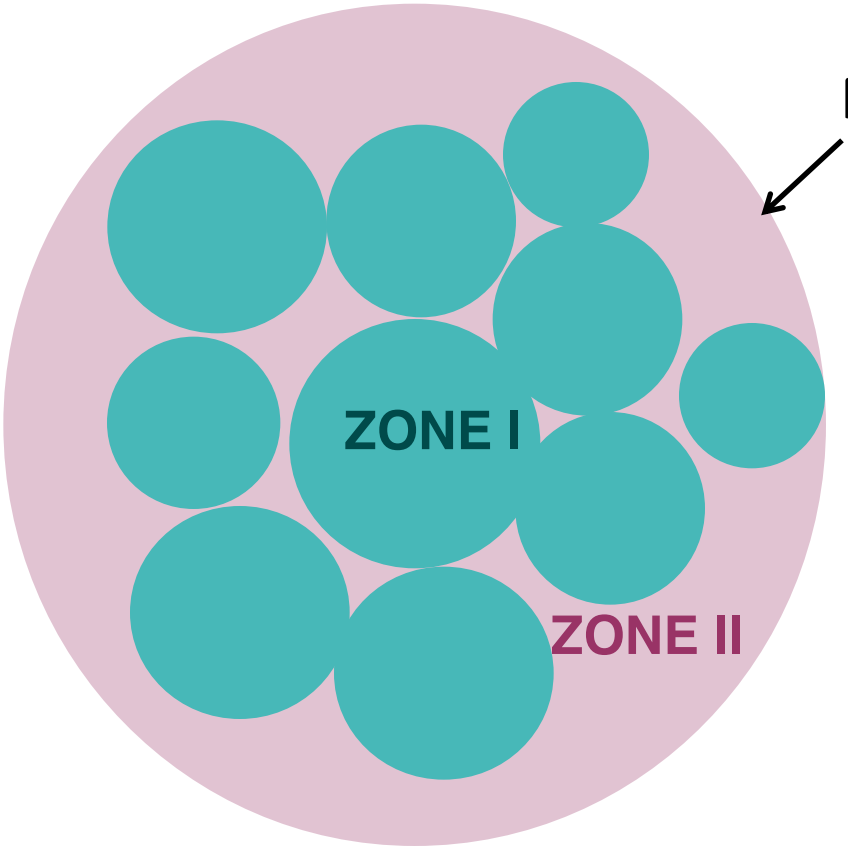
For *K* edges:

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

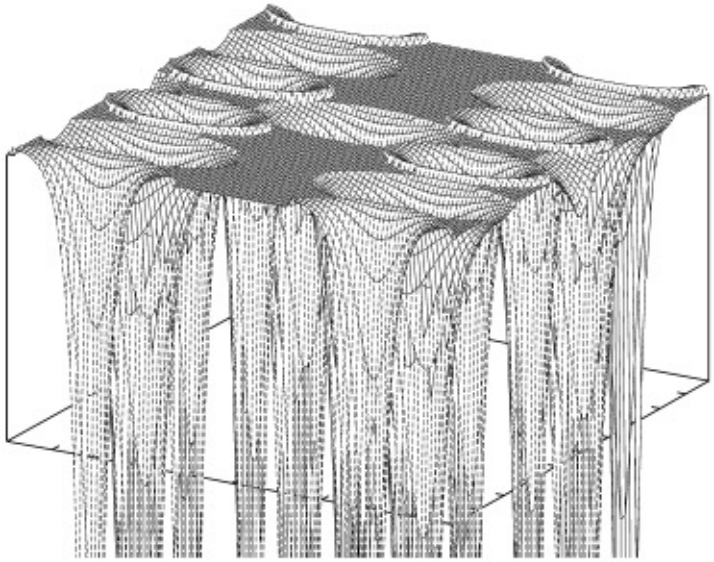
monoelectronic empty state (KS) calculated with a **1*s* core-hole** in the electronic configuration of the absorbing atom

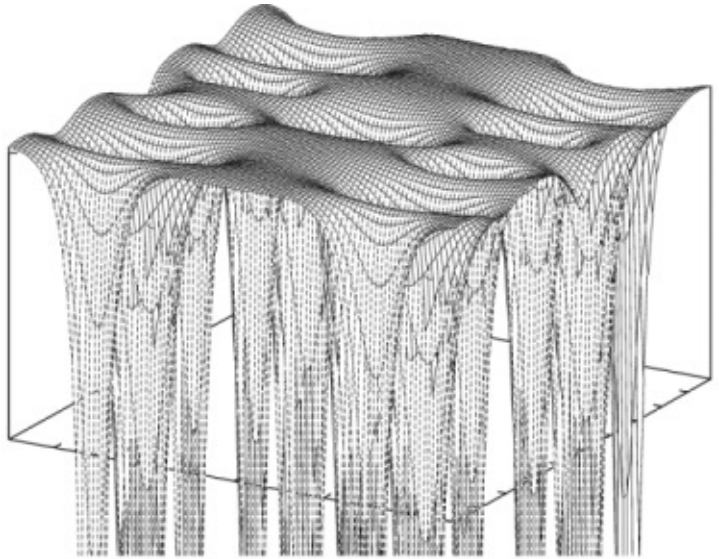
1*s* atomic orbital

Note: *muffin-tin (MT)* potential



MT





Full Potential

ZONE I: atomic spheres
spherical symmetry potentials

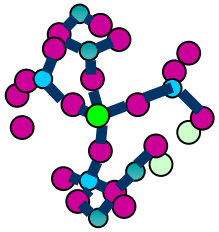
ZONE II: interstitial region
constant potential

XANES and DFT: the calculation codes

2 types

1- Those written to calculate core-level spectra

cluster, real space



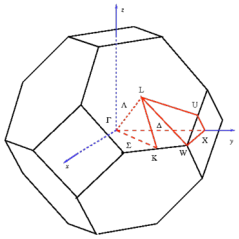
at the beginning: multiple scattering (no self-consistency, *muffin-tin* potential)

continuum, feff, icxanes,....

at the end of the 90's: finite differences method with fdmnes

currently: fdmnes, feff

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

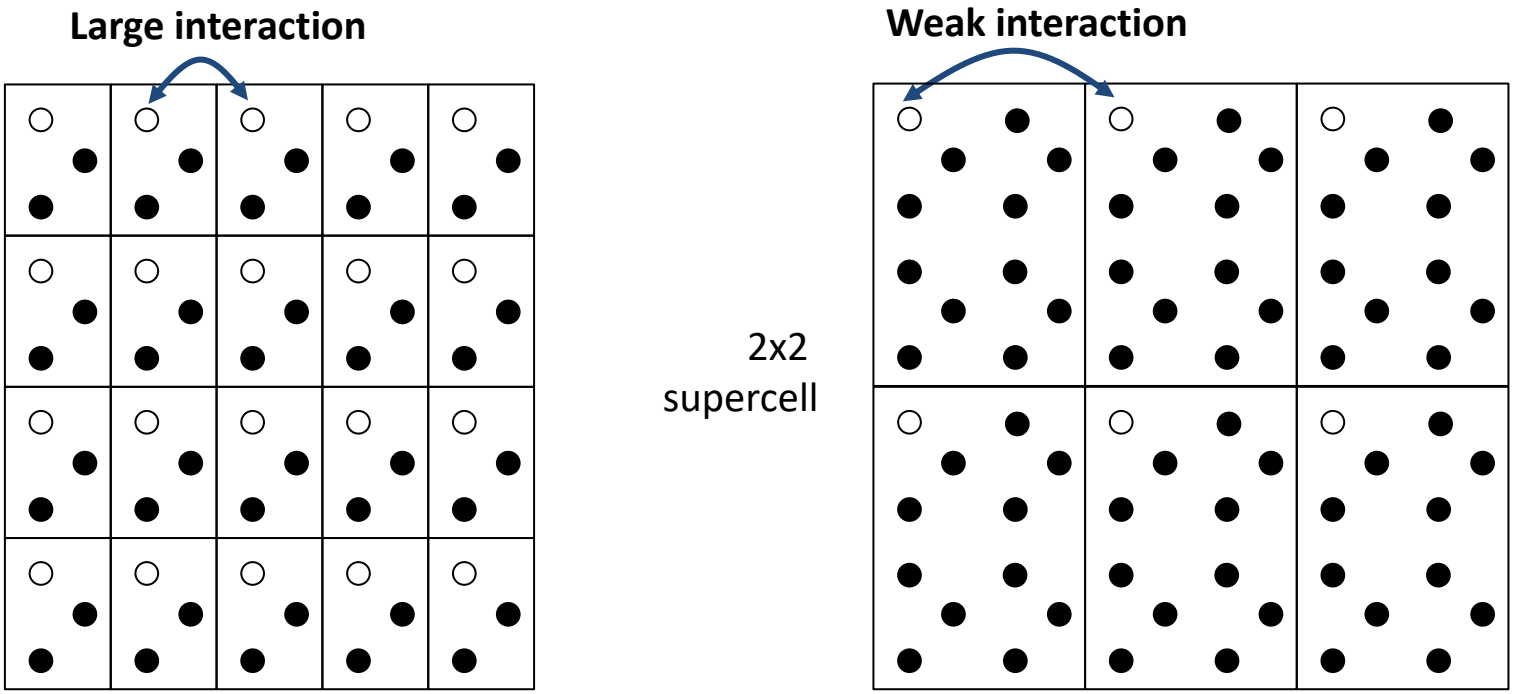


periodic boundary conditions, reciprocal space

Wien2k, CASTEP, Quantum-Espresso (XSpectra), ...

XANES and DFT: periodic boundary conditions and core hole

With codes using periodic boundary conditions (for crystals), we have to avoid **spurious interaction of the excited atom with its periodically repeated images**.



○ atom with a core-hole

● atom without a core-hole

To restore neutrality :

(i) Negative background charge

(ii) Excited electron in conduction band

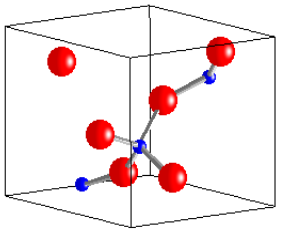
XANES and DFT: periodic boundary conditions and core hole

Si *K* edge in α-quartz

unit cell

a = 4.91Å, *c* = 5.40Å

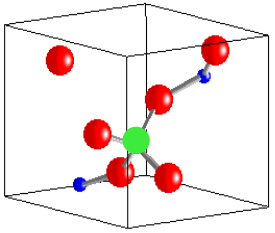
3 Si 6 O



1×1×1 supercell

= unit cell with 1 core-hole

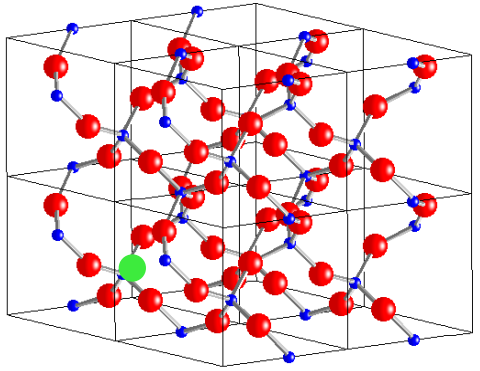
1 Si* 2 Si 6 O



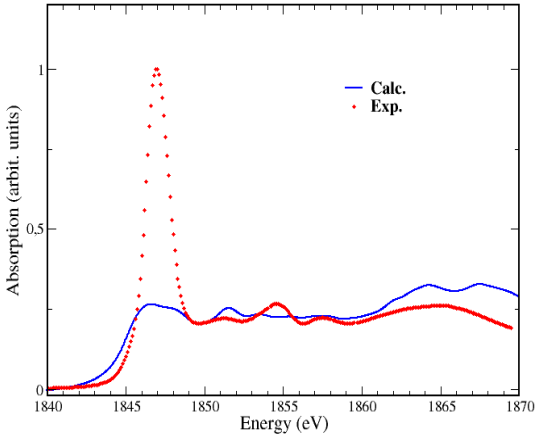
2×2×2 supercell

a = 9.82Å, *c* = 10.80Å

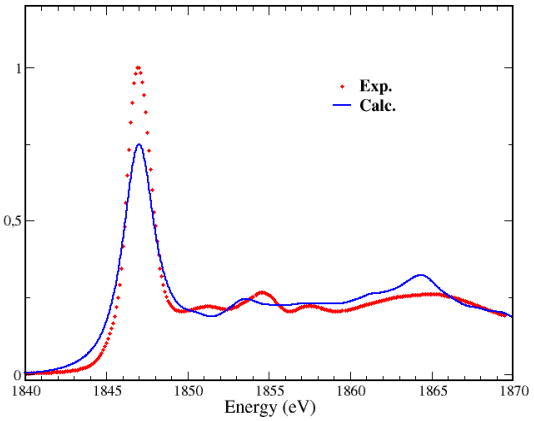
1 Si* 23 Si 48 O



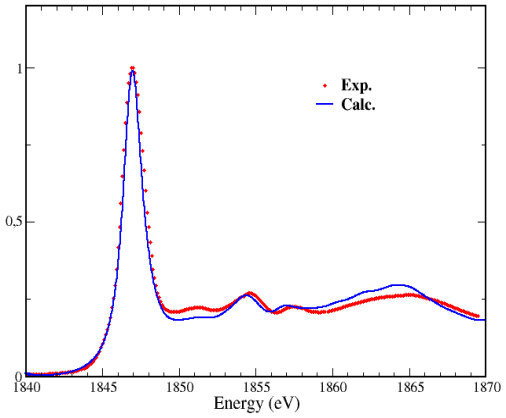
without core-hole



interaction between core-holes



convergence



XANES and DFT: the drawbacks

well identified

- 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

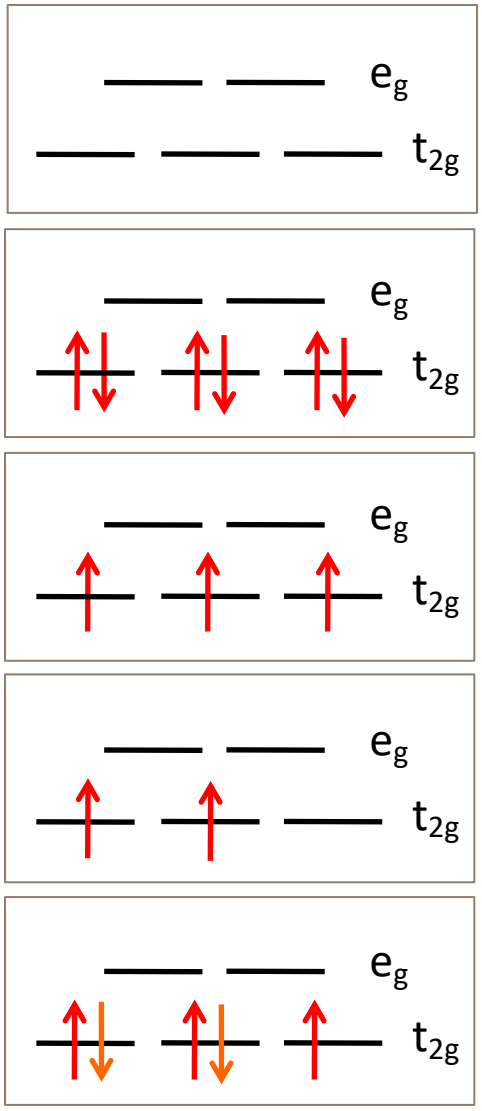
XANES and beyond DFT

- **G*W* + 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, …
- **DMFT**

3*d* elements in *octahedral* site

single-particle picture

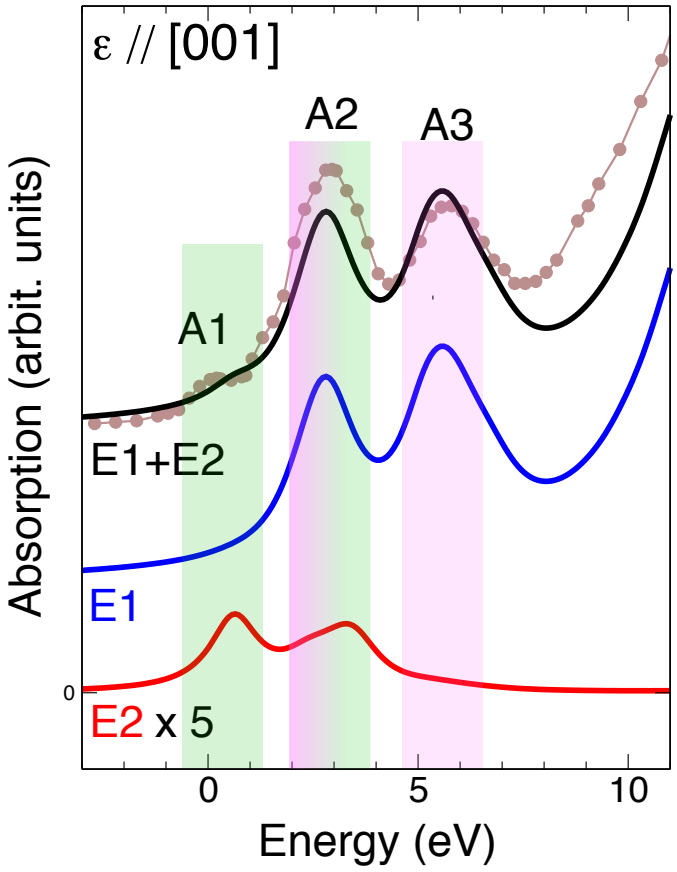
Cabaret *et al*. PCCP (2010)



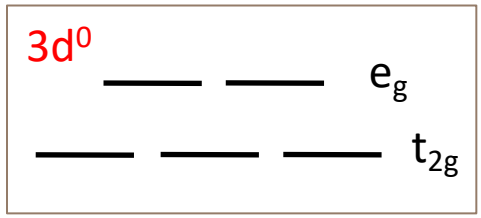
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

↳ pre-edge : E2 + *non local* E1



single-particle picture



peak A1

local E2 transition 1*s* ⟶ 3*d* t_{2g}

peak A2

local E2 transition 1*s* ⟶ 3*d* e_g

+

non-local E1 transition 1*s* ⟶ *p* hybrid. 3*d* t_{2g} (neighb.)

peak A3

non-local E1 transition 1*s* ⟶ *p* hybrid. 3*d* e_g (neighb.)

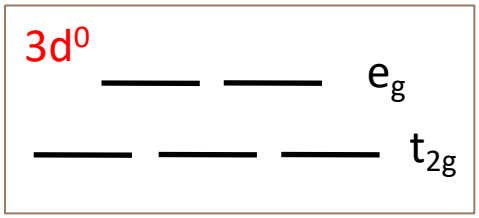
Cabaret *et al.* Phys. Chem. Chem. Phys. **12**:5619 (2010)

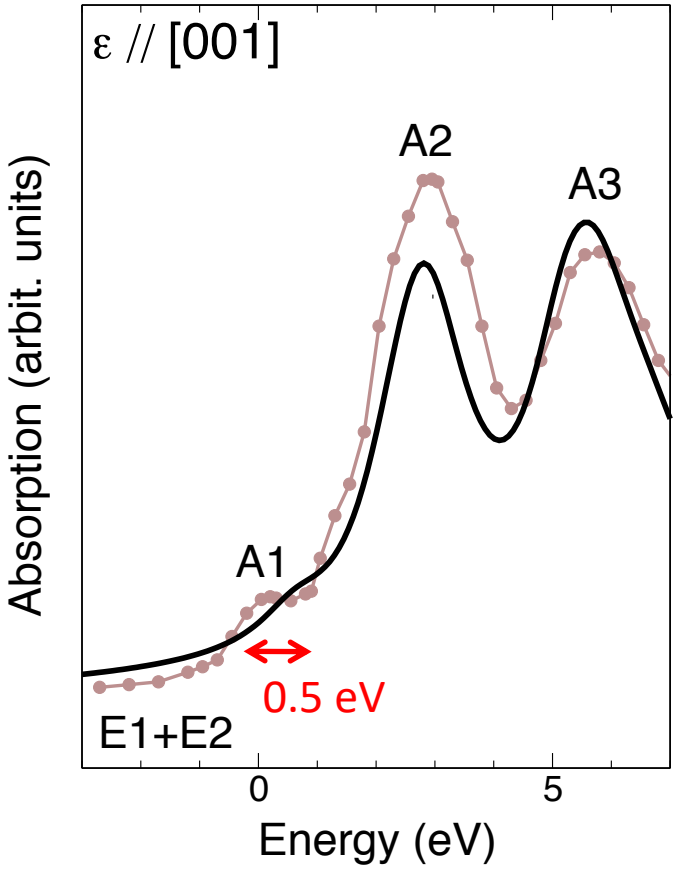
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

↳ pre-edge : E2 + *non local* E1

single-particle picture





➡ A1 calc. at too high energy !

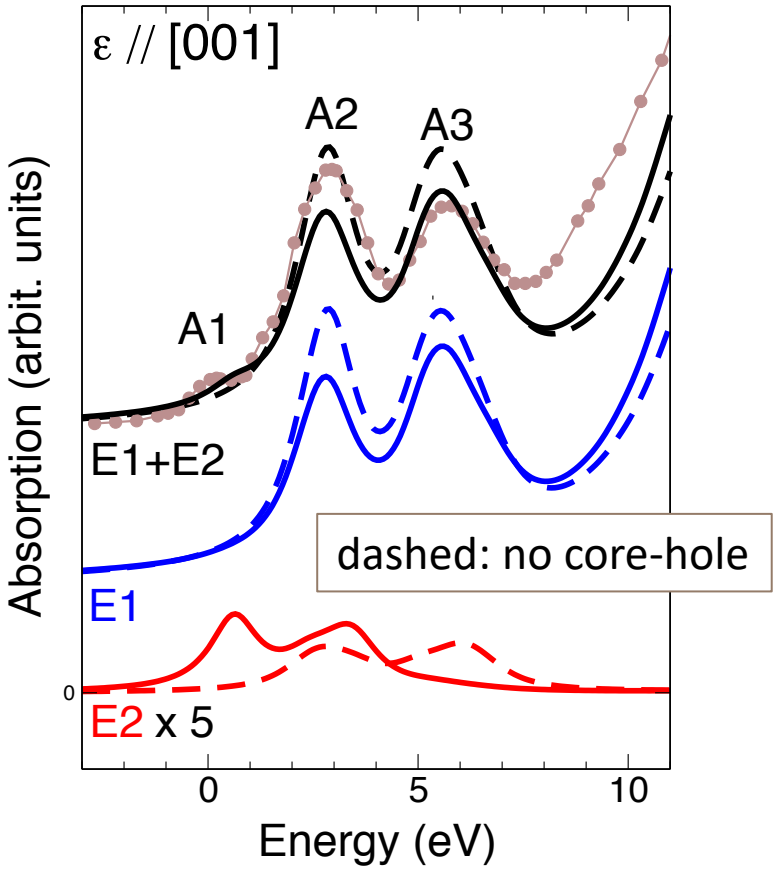
WHY?

Cabaret *et al.* Phys. Chem. Chem. Phys. **12**:5619 (2010)

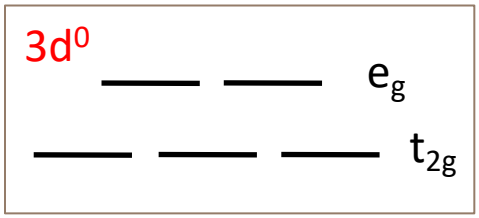
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

↳ pre-edge : E2 + *non local* E1



single-particle picture



➡ A1 calc. at too high energy !

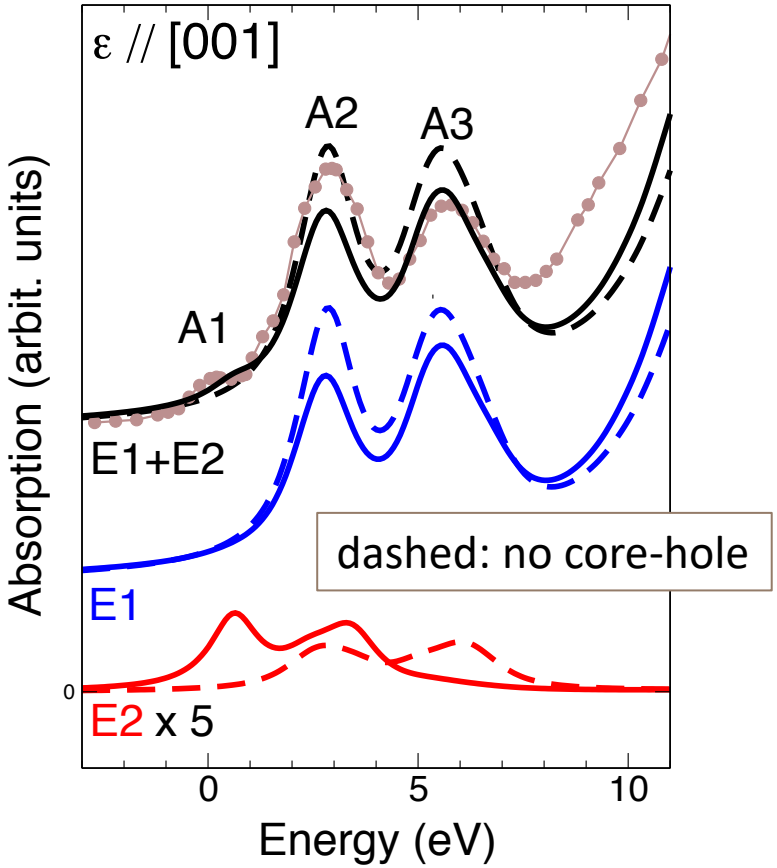
The 1*s* core-hole is not attractive enough…

How to improve ?

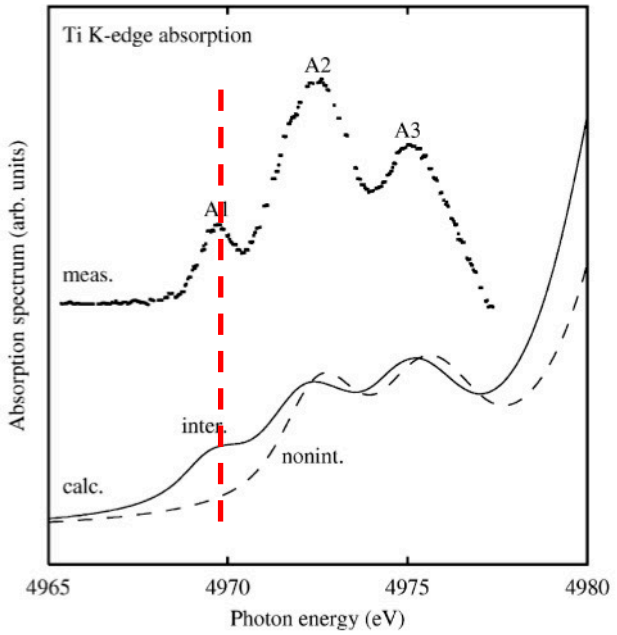
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

↳ pre-edge : E2 + *non local* E1



Bethe-Salpeter equation

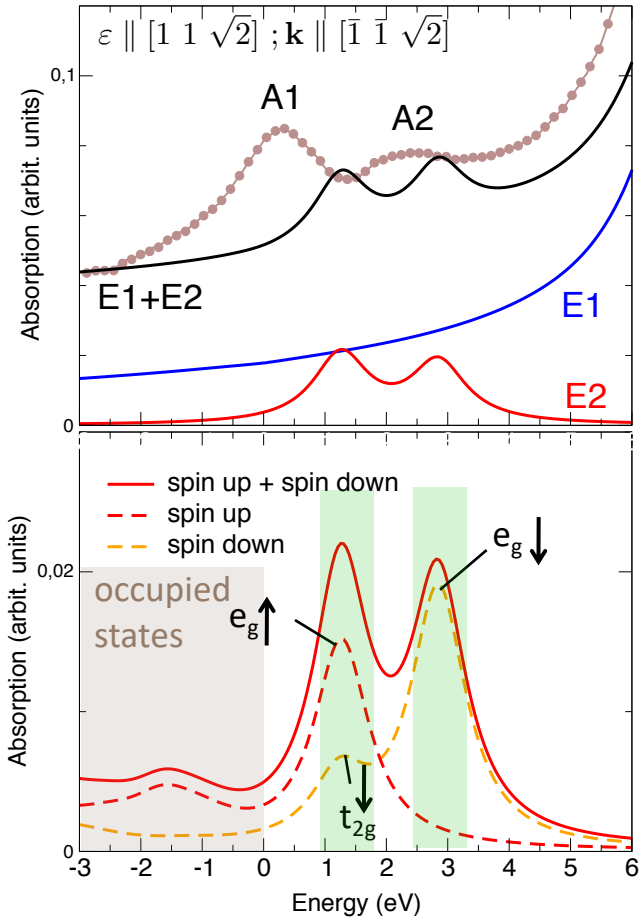


Shirley, J. Electr. Spectr. Rel. Phenom. **136**:77 (2004)

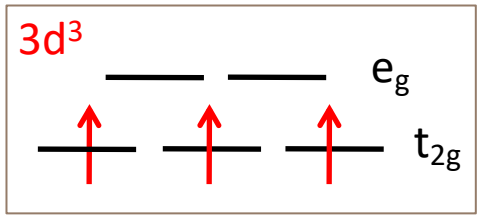
Cr^{3+} in *octahedral* site

$MgAl_2O_4:Cr^{3+}$, Cr site: centrosymmetric

↳ pre-edge : E2

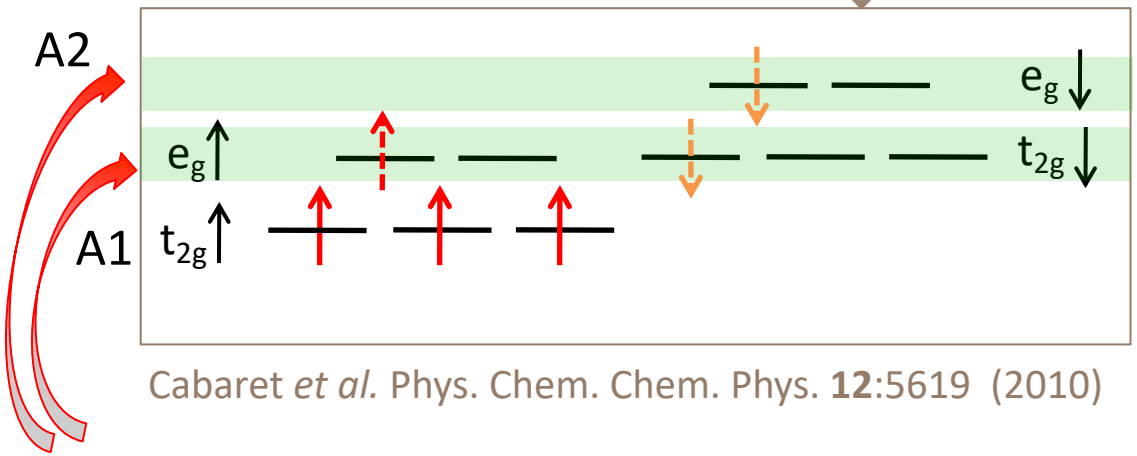


single-particle picture



two E2 peaks *(at too high energy…)*

Origin?

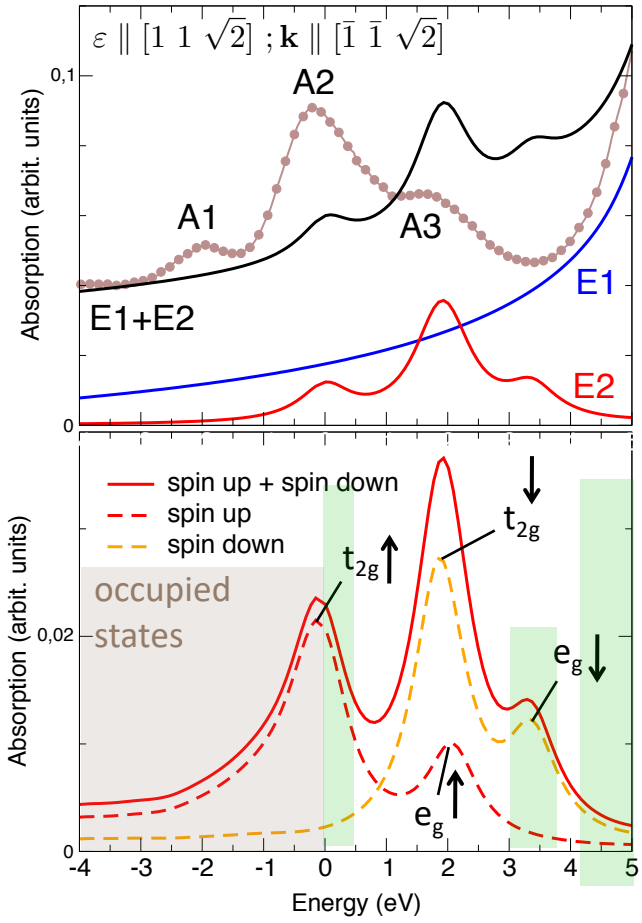


Cabaret *et al.* Phys. Chem. Chem. Phys. **12**:5619 (2010)

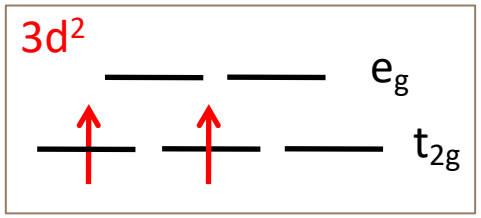
V^{3+} in *octahedral* site

$Ca_3Al_2(SiO_4)_3:V^{3+}$, V site: centrosymmetric

↳ pre-edge : E2

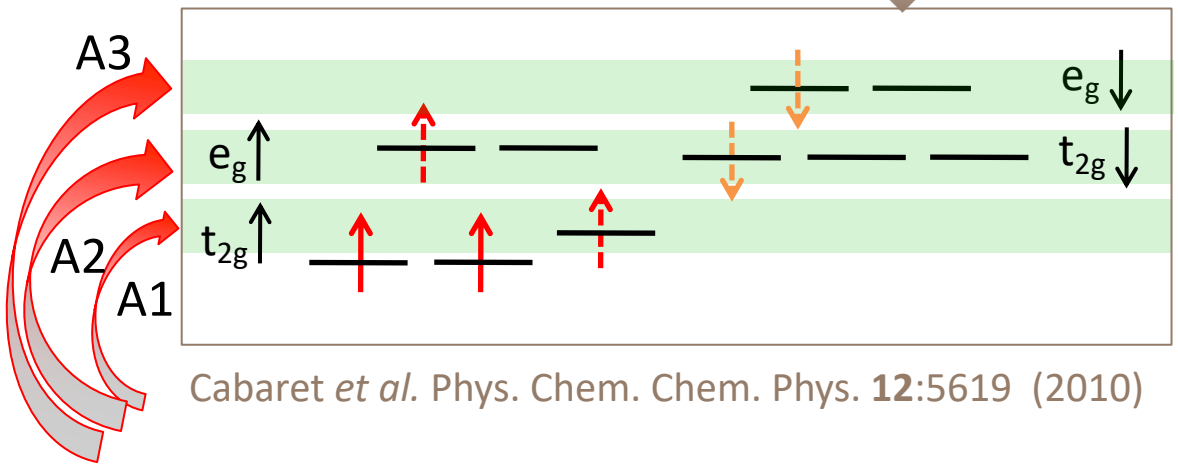


single-particle picture



Three E2 peaks *(at 2eV too high energy…)*

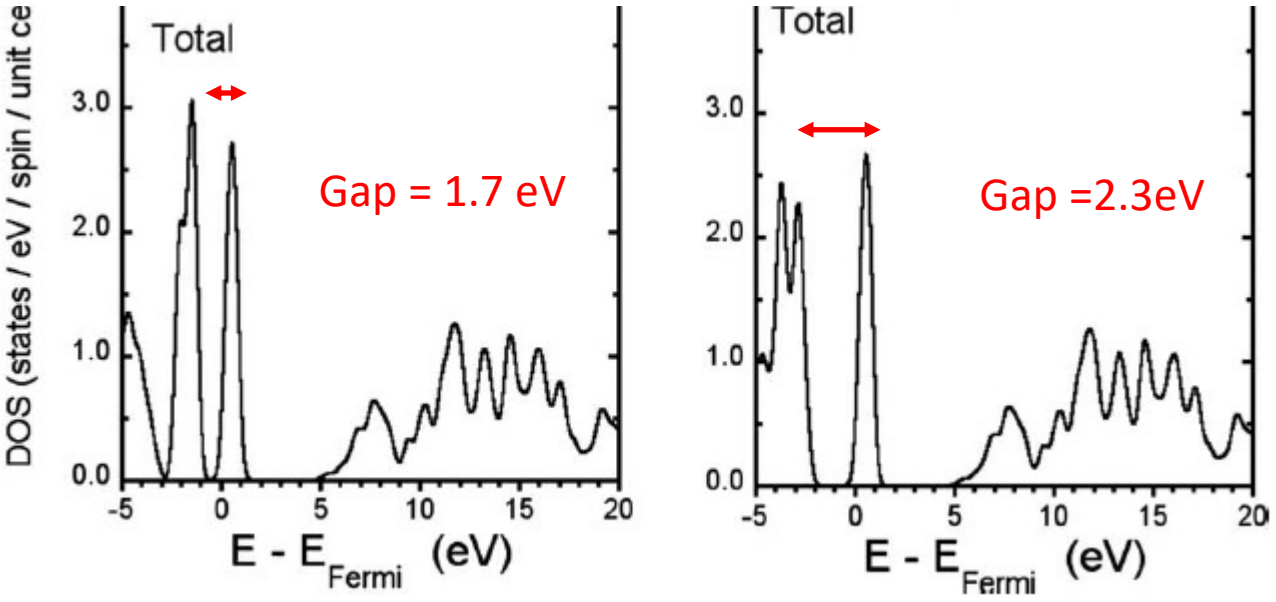
Origin?



Cabaret *et al.* Phys. Chem. Chem. Phys. **12**:5619 (2010)

Angular dependence of core hole screening in $LiCoO_2$

DFT-GGA ⟹ DFT-GGA +U



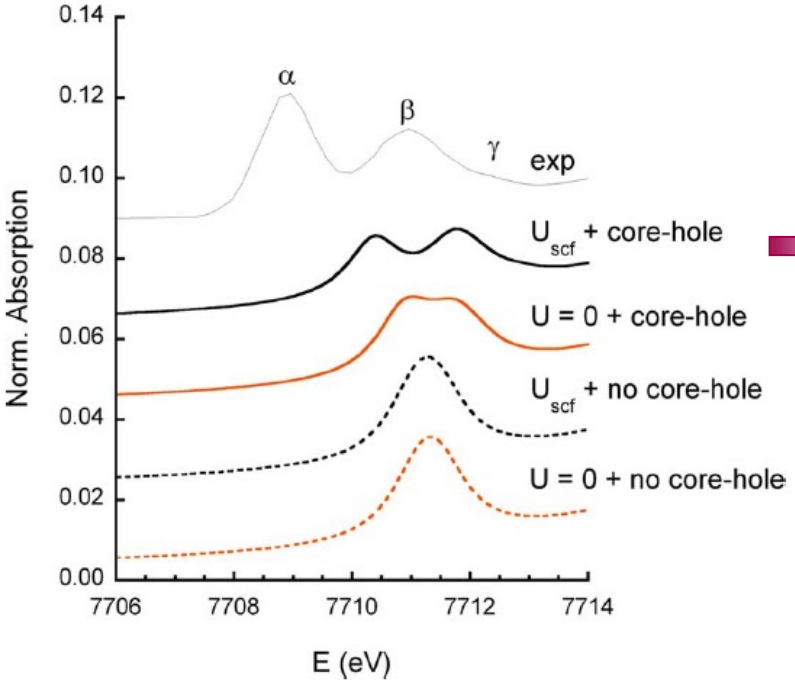
Electronic structure poorly described in GGA

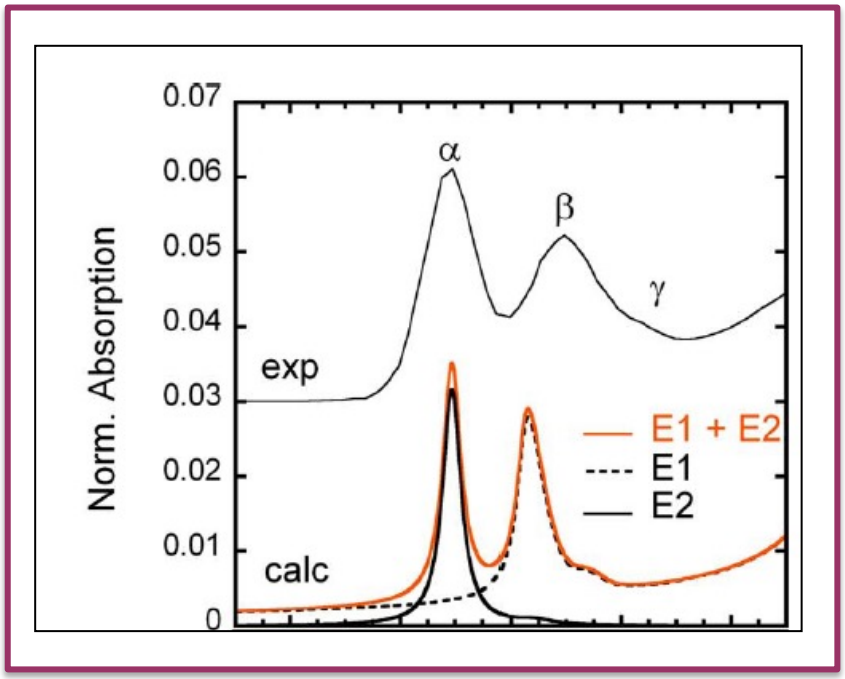
Better described using Hubbard parameter (U) on Co 3d states

Juhin *et al*. PRB 81 (2010)

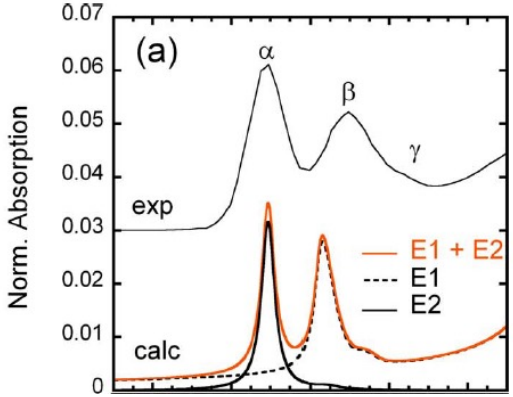
$LiCoO_2$: the Co *K* pre-edge

Best agreement is obtained when including U and the 1s core hole

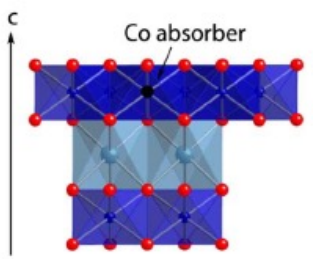


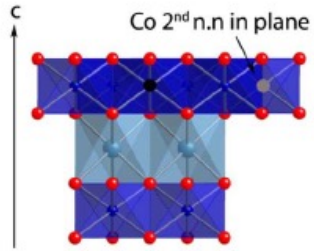


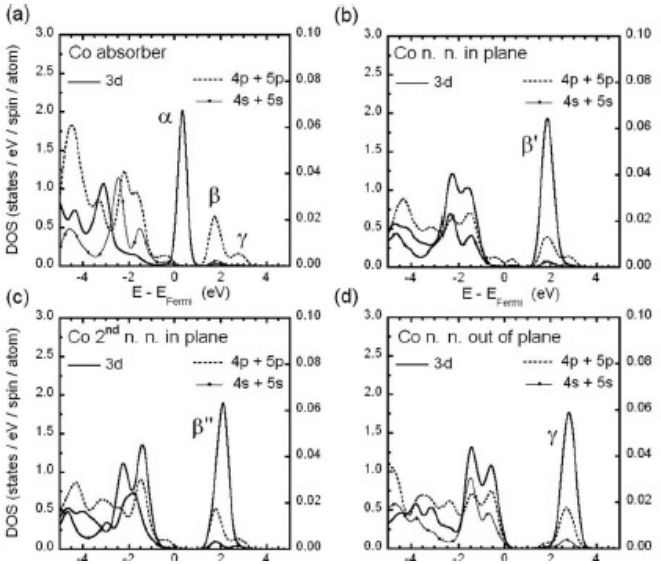
$LiCoO_2$: the Co *K* pre-edge

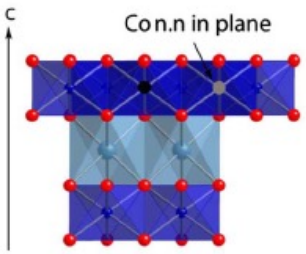


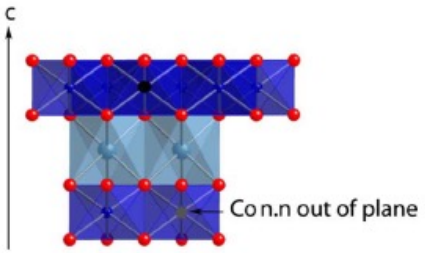
pre-edge : E2 + nonlocal E1











Peak α : 1s→3d (Co*)

Peak β : 1s→4p + O(2p) + Co (3d) n.n. in plane

Peak γ : 1s→4p + O(2p) + Li (2p)+Co (3d) n.n. out of plane

Summary

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

- electronic repulsion modeling
- core hole-electron interaction modeling

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

$3d^0$ (TiO_2) ~ **0.5 eV** *reduced to 0 using BSE of E. Shirley*

$3d^6$ LS (MbCO, FeS_2) ~ **0.8 eV**

$3d^3$ (Cr-spinel, emerald) **1 ~eV**

$3d^5$ LS (MbCN) ~ **1.7 eV**

$3d^3$ (ruby) and $3d^2$ (V-grossular) **2 ~eV**

GGA+*U* reduces **2 eV** ⟶ **1 eV** for $3d^8$ (NiO) Gougoussis *et al.* PRB **79**:045118 (2008)

2.4 eV ⟶ **1.7 eV** for $3d^6$ LS ($LiCoO_2$) Juhin *et al*. PRB **81**:115115 (2010)

*TDDFT+hybrid functionals in Fe complexes : DeBeer et al. J.Phys.Chem.A **112**:12936 (2008)*

Summary

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

- electronic repulsion modeling
- core hole-electron interaction modeling

→ E2 and E1 transitions toward 3*d* (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, $LiCoO_2$, …)

Thank you for your attention.

Thanks to Delphine Cabaret for slide courtesy