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

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

Amélie Juhin

Sorbonne Université-CNRS (Paris)

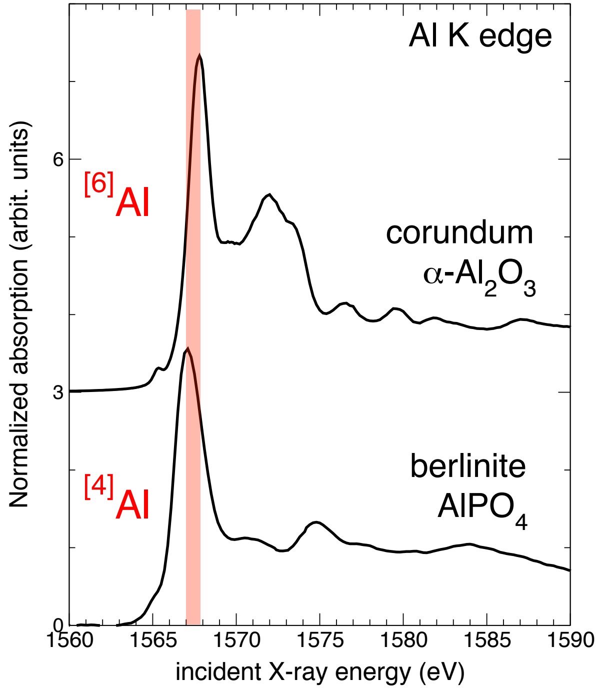
Slide courtesy : Delphine Cabaret

About XANES spectroscopy at the K-edge

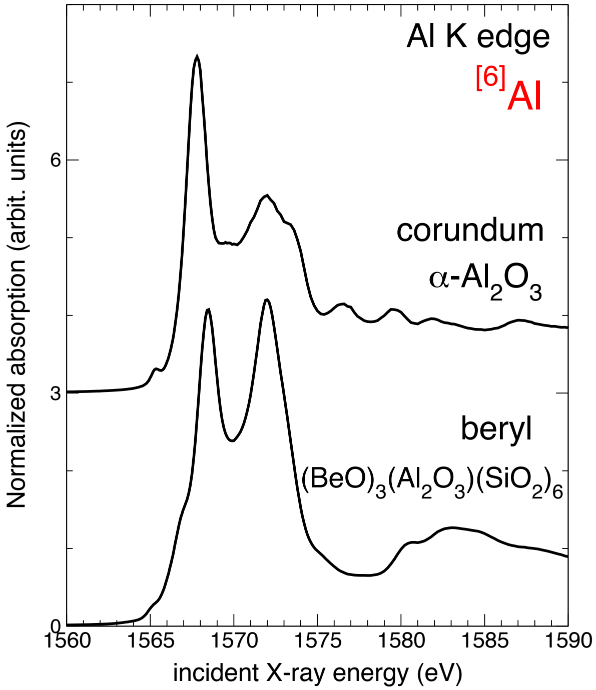
probe of **structural** and electronic **properties** of materials

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

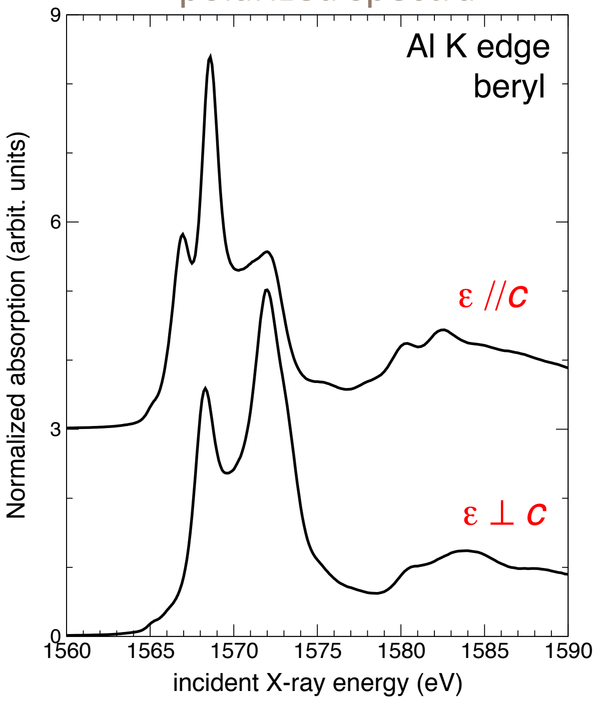
isotropic spectra



isotropic spectra



polarized spectra



1 eV shift

coordination number fingerprint

tremendous amount of information

→ needs for calculations

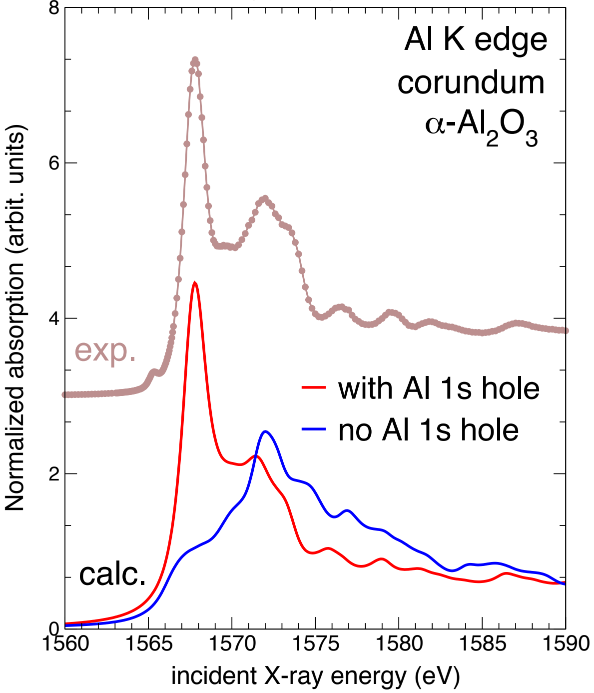
About XANES spectroscopy at the K-edge

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

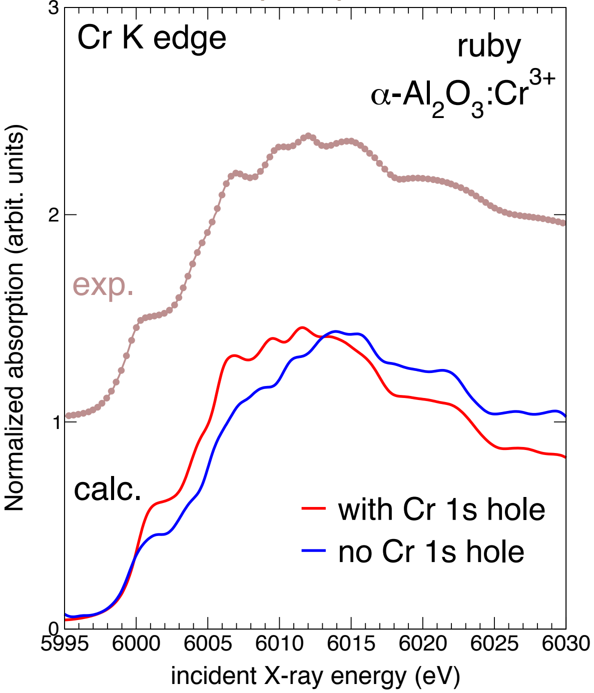
selection rules → **selective** probe of **empty states** localized on the absorber

K edge: 1s → *p* transitions (mainly)

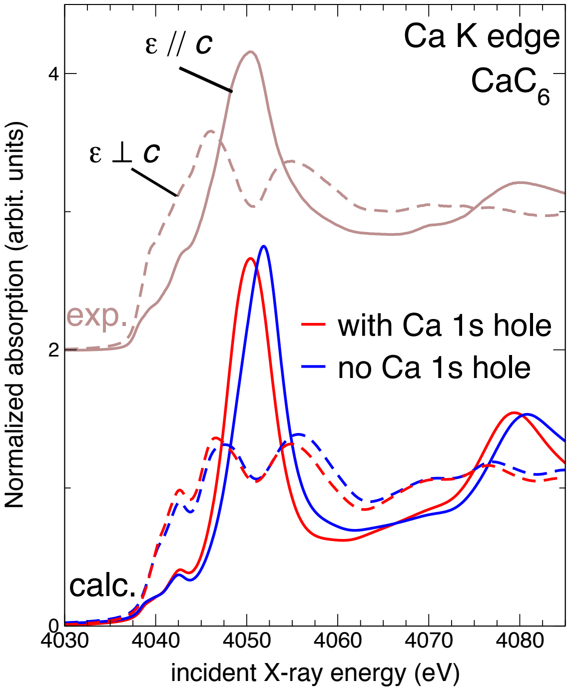
isotropic spectra



isotropic spectra



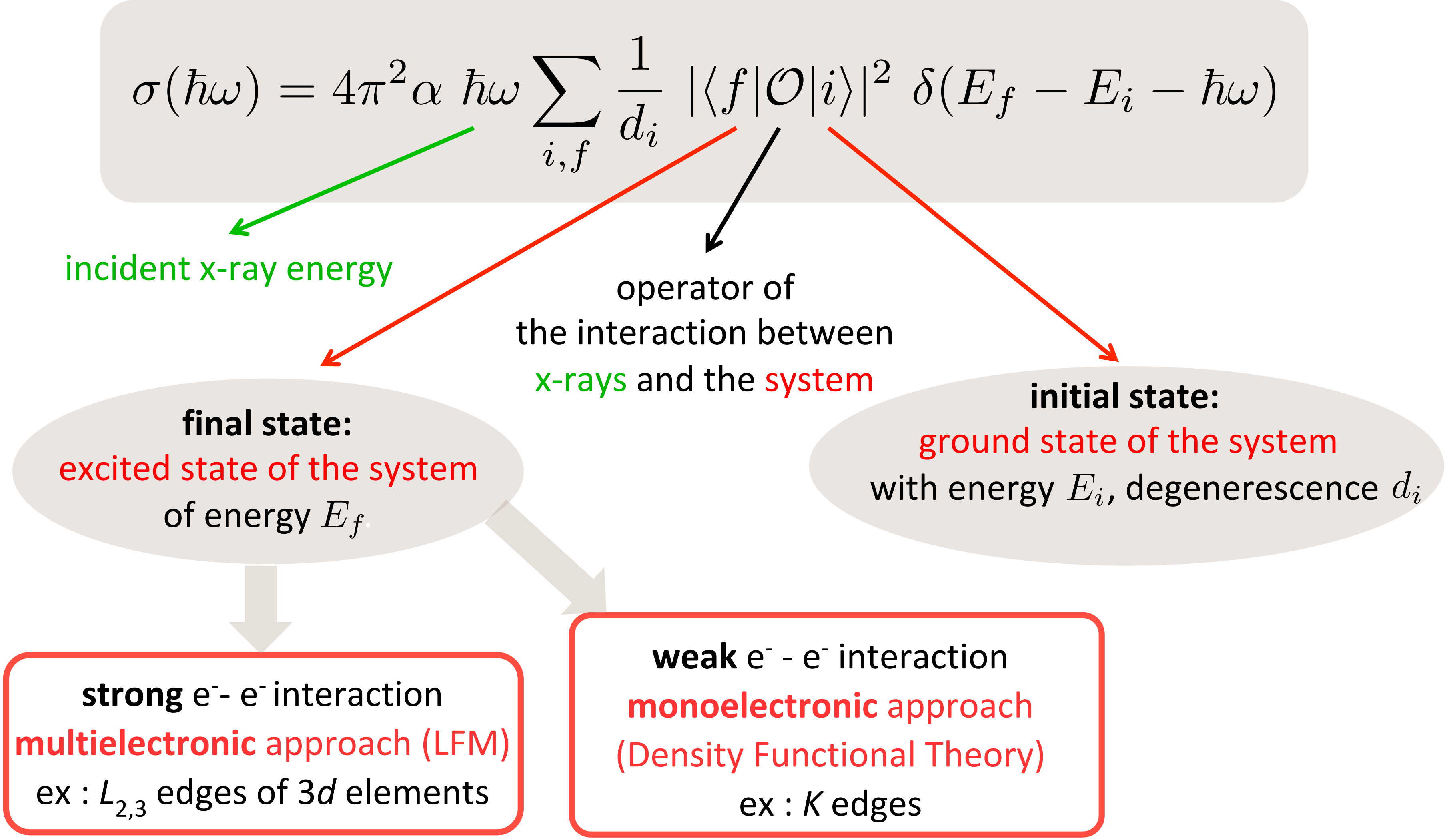
polarized spectra



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

Modeling of XANES spectroscopy

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

Part 1

Introduction to electronic structure calculation using DFT

Basic issue

System composed of N_{at} atoms:

N electrons, mass m, charge $q < 0$, position $\boldsymbol{r}_{\text{i}}$ (i = 1, ..., N)

\+

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

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

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

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

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

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

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

Born-Oppenheimer approximation

$m < M_\mathrm{I}$ (m / m_proton ≈ 1836)

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

Electron : $\frac{1}{2}mv_e^2 = 1\mathrm{Ry}$ ≈ 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 $\boldsymbol{R}_\mathrm{I}$ ➔ **parameter**

Born-Oppenheimer approximation

Electronic Hamiltonian

parameter

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

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

Multielectronic Schrödinger equation

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

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

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

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

↳ 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 !

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

solution

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

↳ spinorbital

ψ_n : Slater determinant (SD) - 1929

build from N spinorbital functions ϕ_α

Slater Determinant

Ground state

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

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

Properties :

- antisymmetric
- Pauli exclusion principle satisfied

Multielectronic Schrödinger equation

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

solution

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

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

The Slater determinants form a **basis** in the N-electrons Hilbert space

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

configuration interaction *("brute force")*

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

$N = 5$
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

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

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

$$\left.\begin{array}{l} H^{\mathrm{eff}} = \displaystyle\sum_{i=1}^{N} H^{\mathrm{eff},(i)}_{\mathrm{mono}} \\ \text{with } H^{\mathrm{eff}}_{\mathrm{mono}} = \dfrac{-\hbar^2\nabla^2}{2m} + V_{\mathrm{nucl}}(\mathbf{r}) + V^{\mathrm{eff}}(\mathbf{r}) \end{array}\right\}$$

Solutions : Slater determinants

Mean-field approximation

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

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

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

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

Mean-field methods: examples

Hartree (H)

Hartree-Fock (HF)

Density Functional Theory (DFT)

Hartree (H) - 1927

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

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

Coulomb interaction between one electron and the electron density

$$\frac{-\hbar^2\nabla^2}{2m}\phi_i^{\mathrm{eff}}(\mathbf{r}) + V_{\mathrm{nucl}}(\mathbf{r})\phi_i^{\mathrm{eff}}(\mathbf{r}) + e^2 \underbrace{\sum_{j=1}^{N} \int \frac{|\phi_j^{\mathrm{eff}}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\mathrm{d}\mathbf{r}'}_{\text{includes a self-interaction term (if } i = j\text{)}} \phi_i^{\mathrm{eff}}(\mathbf{r}) = \epsilon_i^{\mathrm{eff}}\ \phi_i^{\mathrm{eff}}(\mathbf{r})$$

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

Pauli exclusion principle

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 :

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

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

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

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

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).*

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

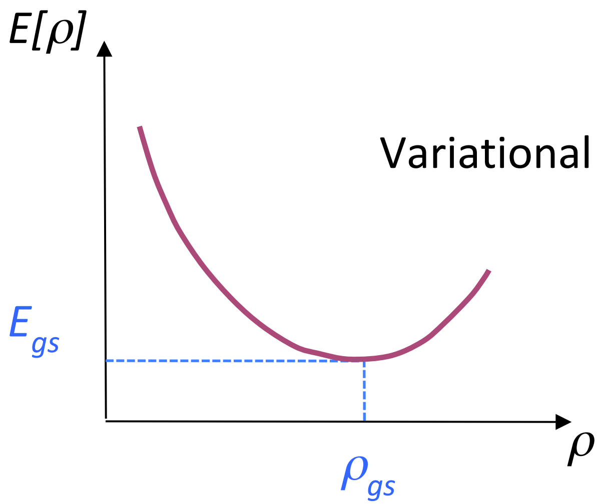
$\rho(\mathbf{r})$ basic variable

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

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

DFT: Hohenberg and Kohn (1964)

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



Variational principle

Exact theory **but**

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

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 »)

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

DFT: Kohn and Sham (1965)

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

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

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

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

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:

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

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

exchange and correlation potential

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

DFT: Kohn and Sham (1965)

Kohn-Sham equations

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

Schrödinger equations of the fictitious system

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

Kohn – Sham potential

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

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

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

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)

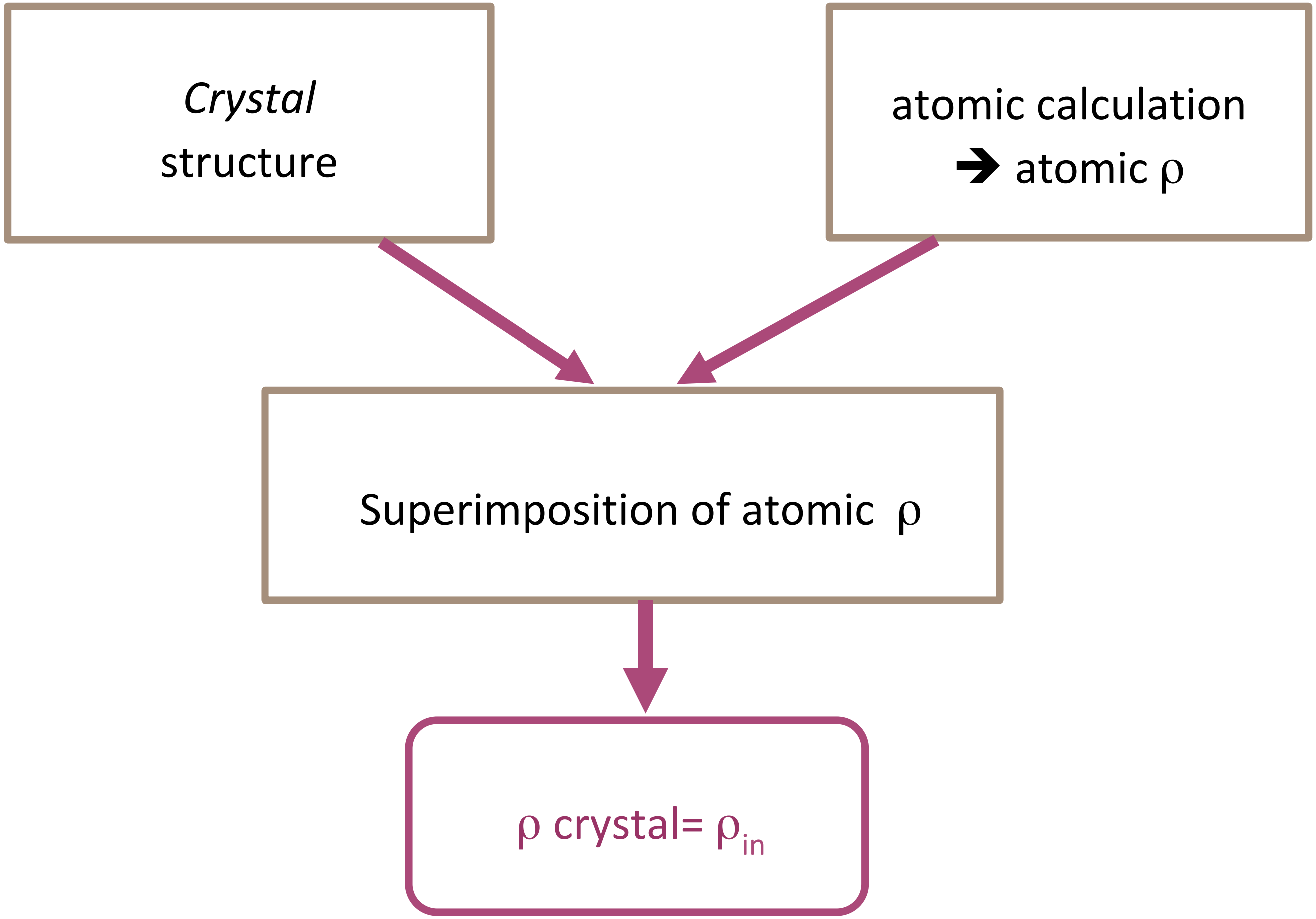
combine the **exchange** **correlation** obtained by using **GGA** methods with a given proportion of the **exchange** described by **Hartree-Fock**

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



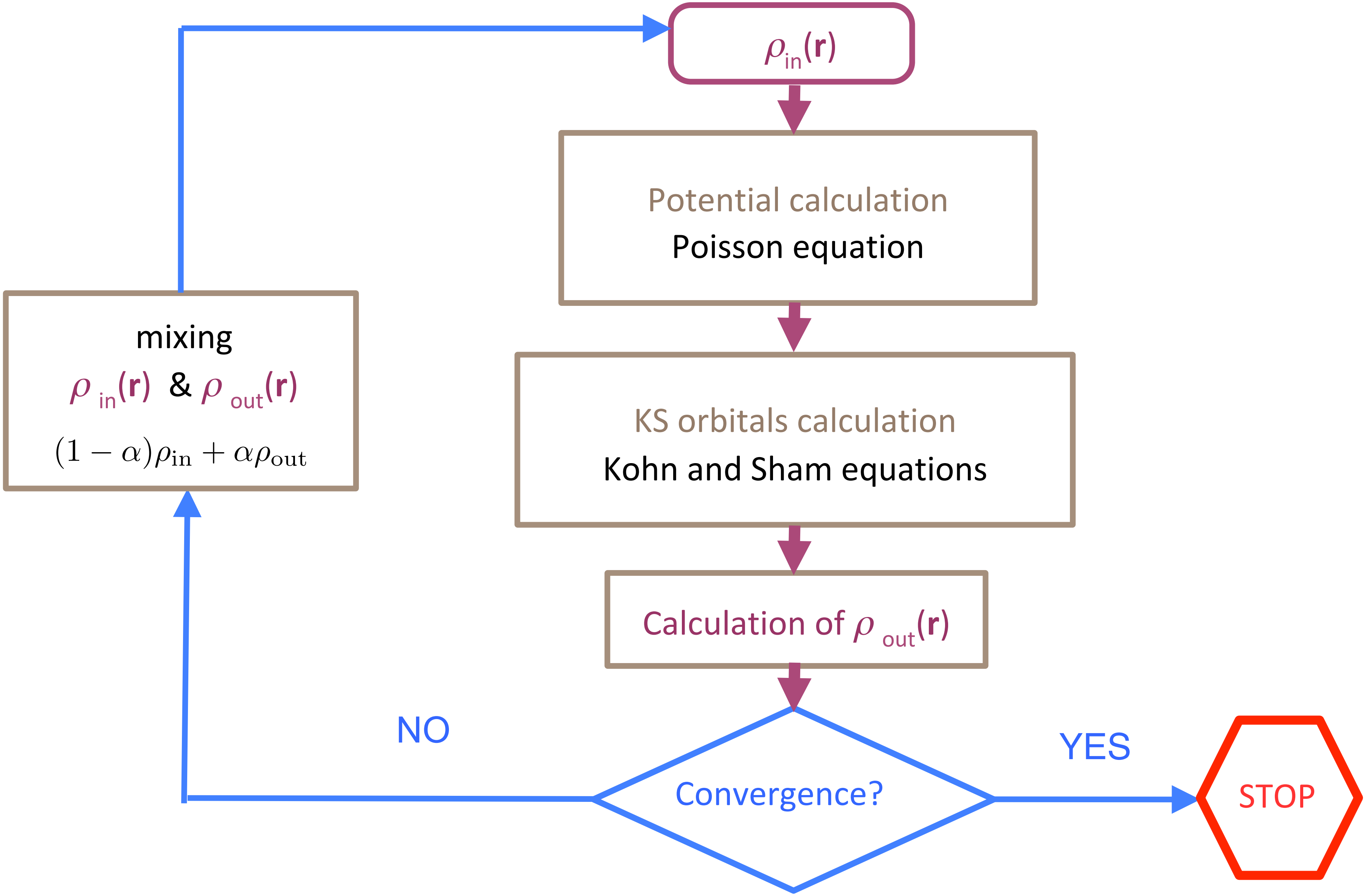
Crystal
structure

atomic calculation
➔ atomic ρ

Superimposition of atomic ρ

ρ crystal= ρ_{in}

DFT: SCF cycle



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

Potential calculation

Poisson equation

KS orbitals calculation

Kohn and Sham equations

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

Convergence?

YES

STOP

NO

mixing

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

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

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

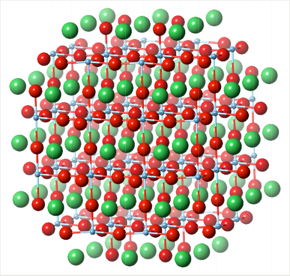
non-exhaustive list

DFT: sofwares

the main differences between them

real space

cluster

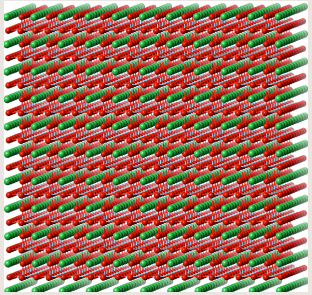


no periodicity constraint (amorphous and crystalline materials)

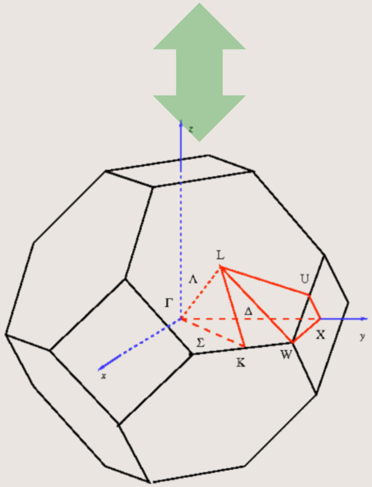
suited to molecules

or

periodic boundary conditions



infinite number of atoms



1^{st} 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

WIEN2k

Muffin-tin orbitals
spherical waves
LMTO,multiple scattering

SPR-KKR

DFT: sofwares

the main differences between them

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

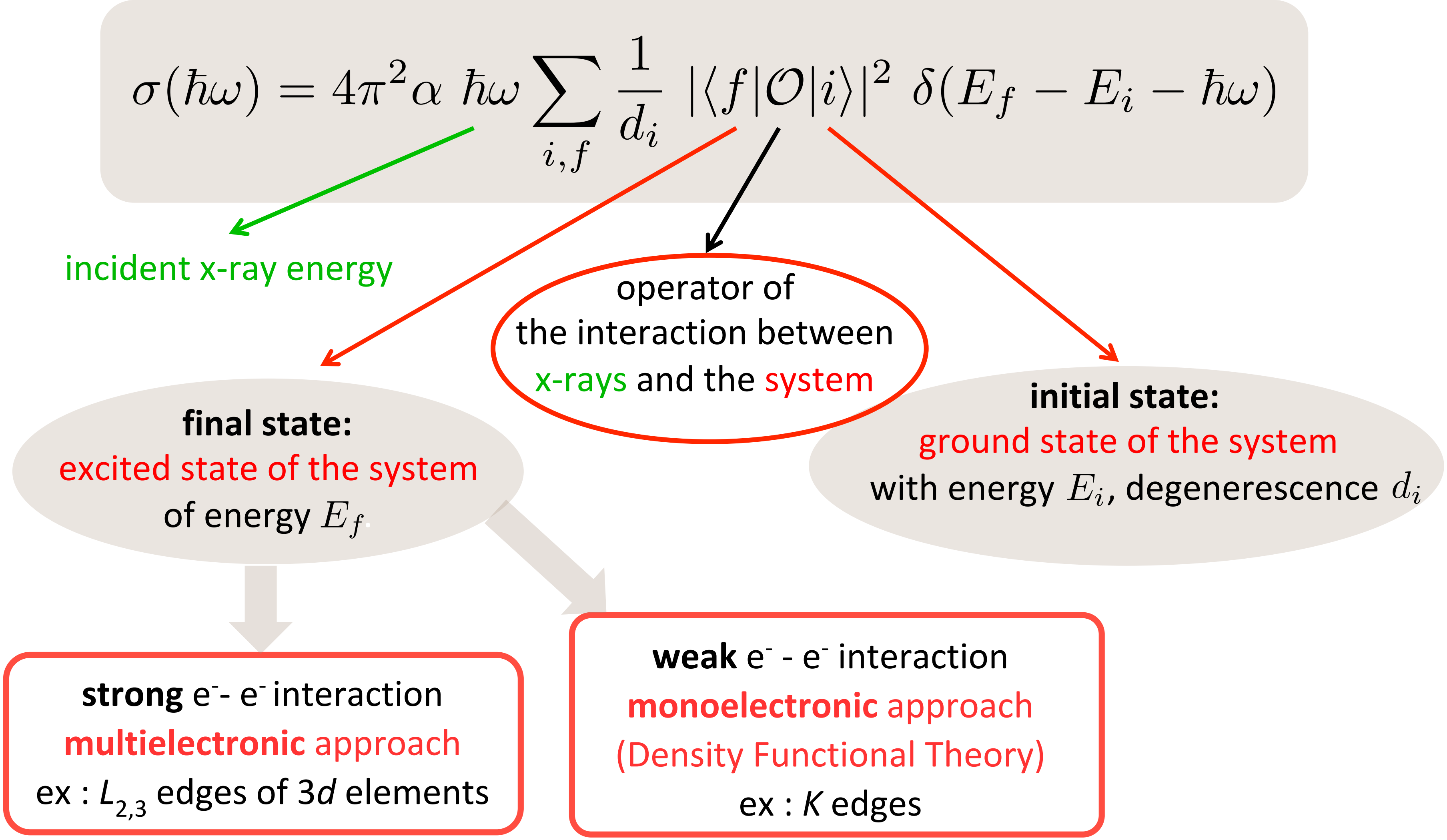
Introduction to the calculation of X-ray absorption spectra

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** $e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$

$\mathbf{k}$: wave vector
$\hat{\varepsilon}$: polarization direction

$$e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} = 1 + \mathrm{i}\mathbf{k}\cdot\mathbf{r} + \ldots$$

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

electric dipole transitions (E1)

$$\Delta\ell = \pm 1$$

majority electronic transitions

electric quadrupole transitions (E2)

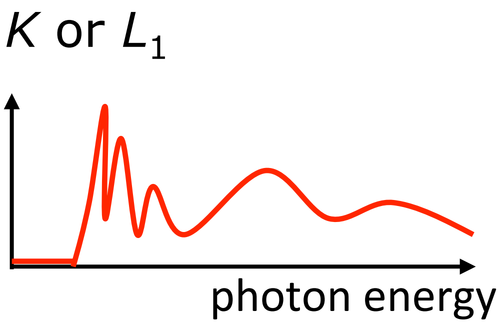
$$\Delta\ell = \pm 2$$

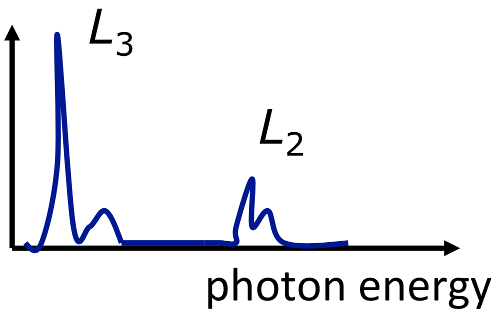
observable in the *K* pre-edge
of 3*d* transition elements

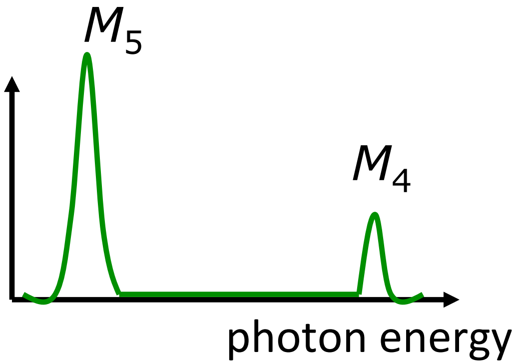
Interaction operator between x-rays and electrons

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) : *3d, 4f*

multielectronic theories (multiplets)

XANES and DFT

For *K* edges:

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

1*s* atomic orbital

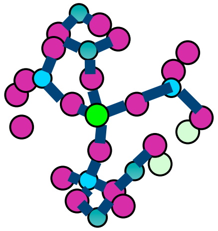
monoelectronic empty state (KS)
calculated with a **1*s* core-hole**
in the electronic configuration
of the absorbing atom

XANES and DFT: the calculation codes

2 types

1- Those written to calculate core-level spectra

cluster, real space

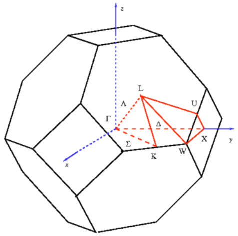


at the beginning: multiple scattering (no self-consistency, *muffin-tin* potential)

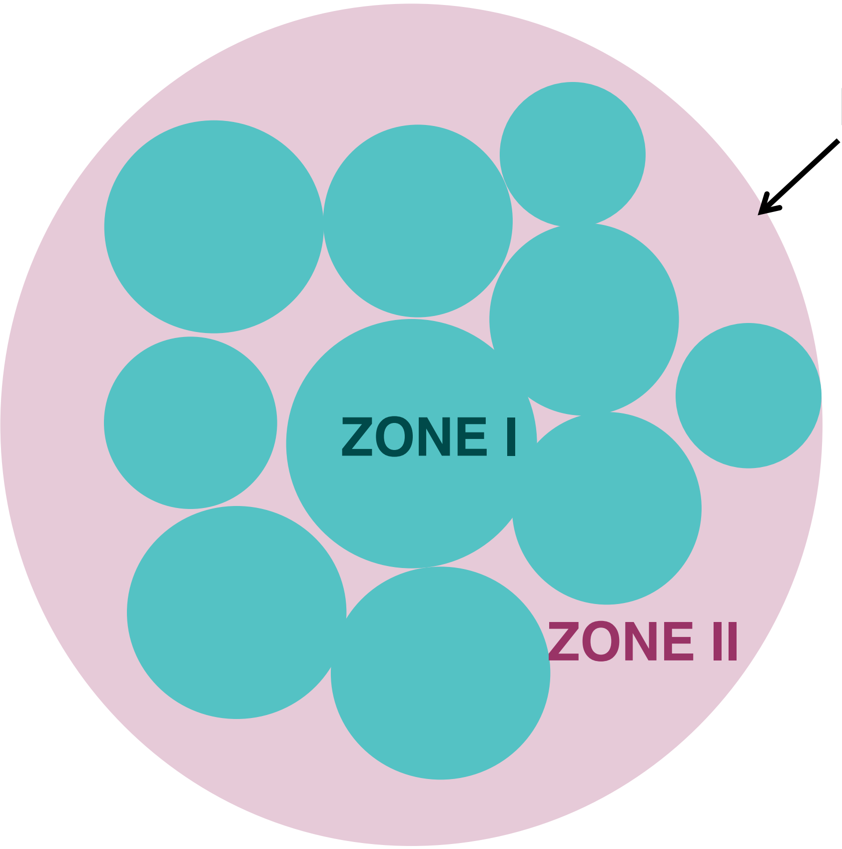
continuum, feff, icxanes,….

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

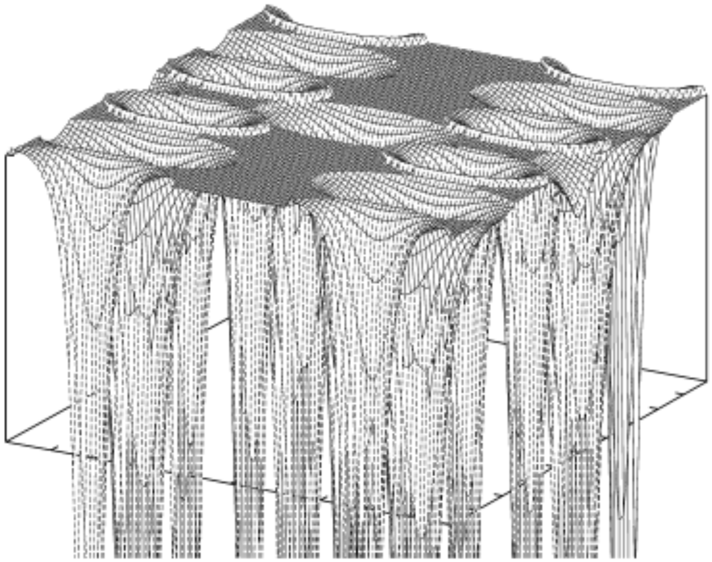
periodic boundary conditions, reciprocal space

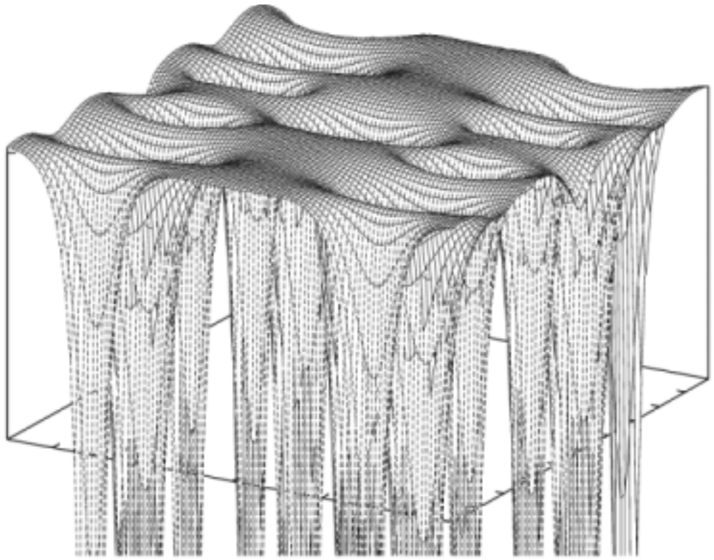


Note: *muffin-tin (MT)* potential



MT





Full Potential

ZONE I: atomic spheres
spherical symmetry potentials

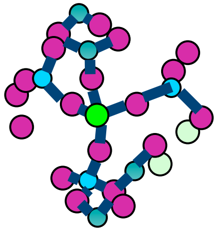
ZONE II: interstitial region
constant potential

XANES and DFT: the calculation codes

2 types

1- Those written to calculate core-level spectra

cluster, real space



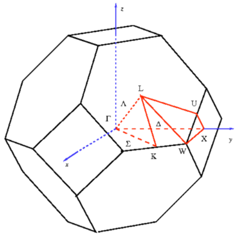
at the beginning: multiple scattering (no self-consistency, *muffin-tin* potential)

continuum, feff, icxanes,….

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

currently: fdmnes, feff9

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

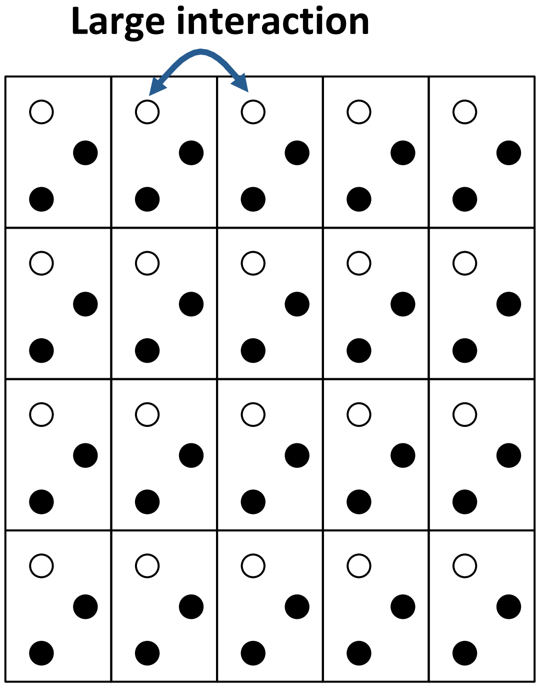


periodic boundary conditions, reciprocal space

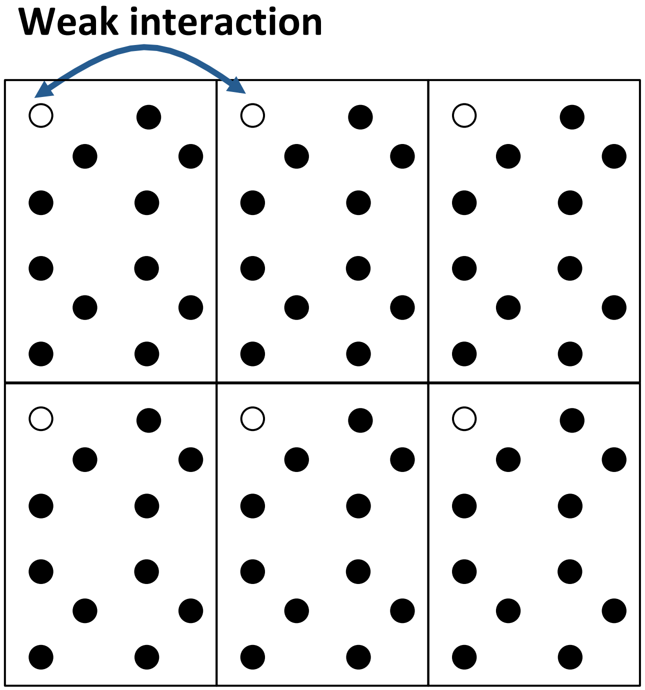
Wien2k, CASTEP, Quantum-Espresso (XSpectra), …

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**.



2x2 supercell



○ atom with a core-hole

● atom without a core-hole

To restore neutrality :

(i) Negative background charge

(ii) Excited electron in conduction band

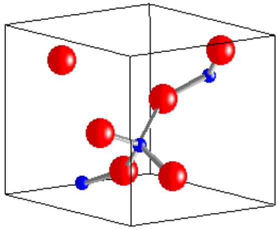
XANES and DFT: periodic boundary conditions and core hole

Si *K* edge in α-quartz

unit cell

a = 4.91Å, *c* = 5.40Å

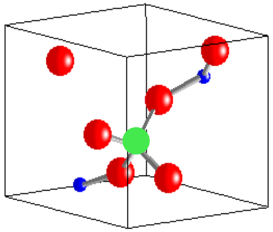
3 Si 6 O



1×1×1 supercell

= unit cell with 1 core-hole

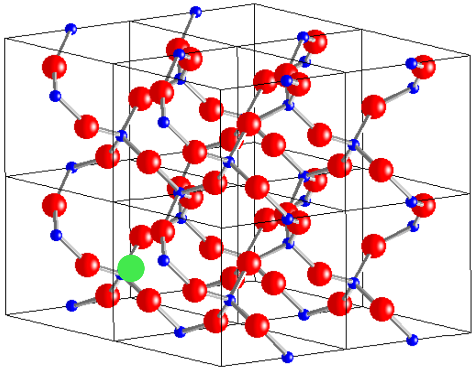
1 Si* 2 Si 6 O



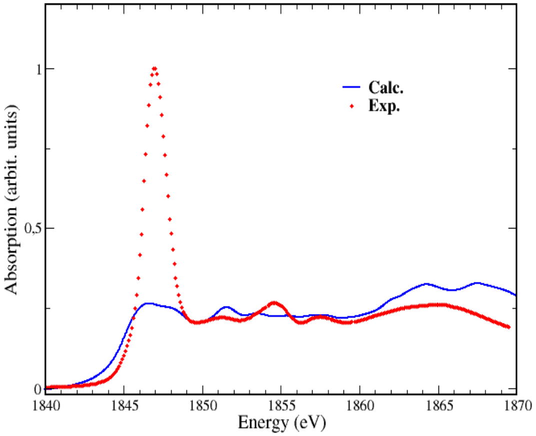
2×2×2 supercell

a = 9.82Å, *c* = 10.80Å

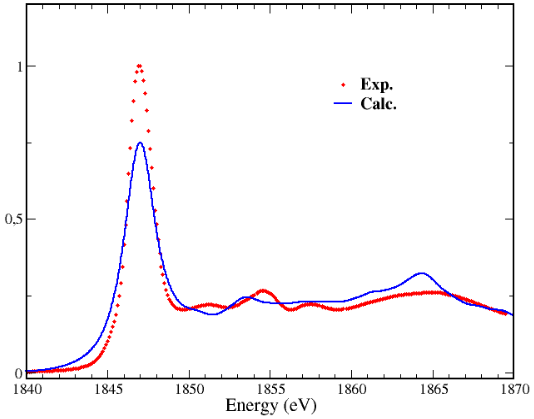
1 Si* 23 Si 48 O



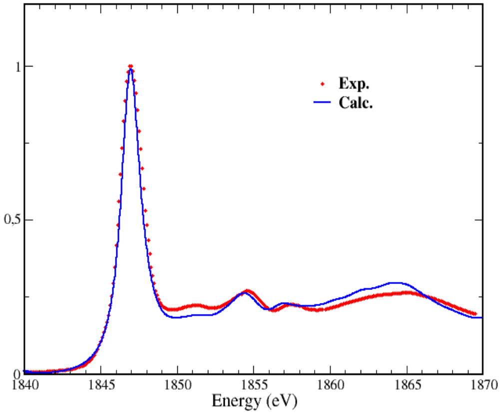
without core-hole



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

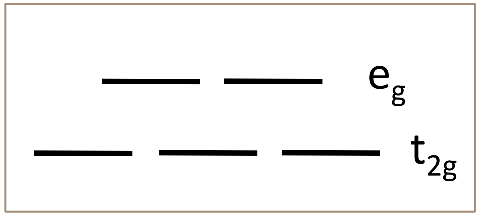
- **TD-DFT** (real-space approaches)
  - ➢ FDMNES
  - ➢ Quantum-Chemistry codes: Orca, ADF, Q-chem, …

$3d$ elements in *octahedral* site

single-particle picture

Cabaret *et al*. PCCP (2010)

$3d^0$

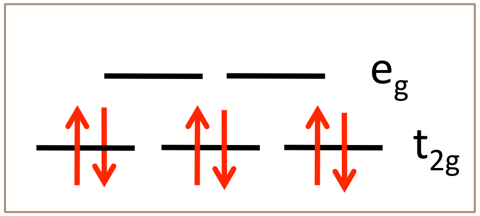


Ti^{4+}

TiO_2 rutile, anatase

t_{2g}, e_g empty ⇒ favorable case

$3d^6$
LS

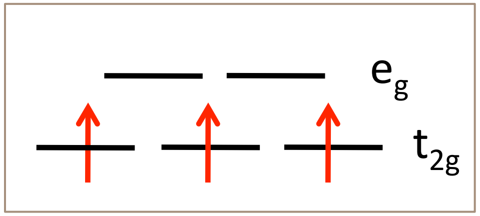


Fe^{2+}

FeS_2 pyrite
MbCO protein

e_g empty ⇒ acceptable case

$3d^3$

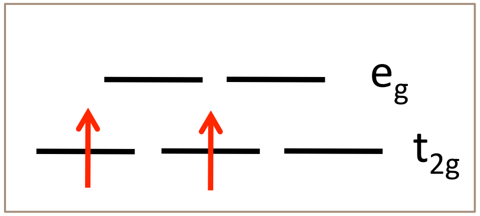


Cr^{3+}

ruby, emerald,
spinel:Cr, pyrope:Cr

e_g ↑ empty
t_{2g}, e_g ↓ empty
⇒ acceptable case

$3d^2$

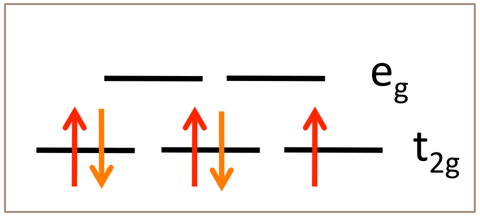


V^{3+}

grossular:V

t_{2g} ↑ partially empty
e_g ↑ empty
t_{2g}, e_g ↓ empty
⇒ critical case

$3d^5$
LS



Fe^{3+}

MbCN protein

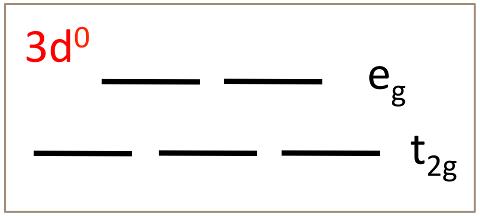
e_g ↑ empty
t_{2g} ↓ partially empty
e_g ↓ empty
⇒ critical case

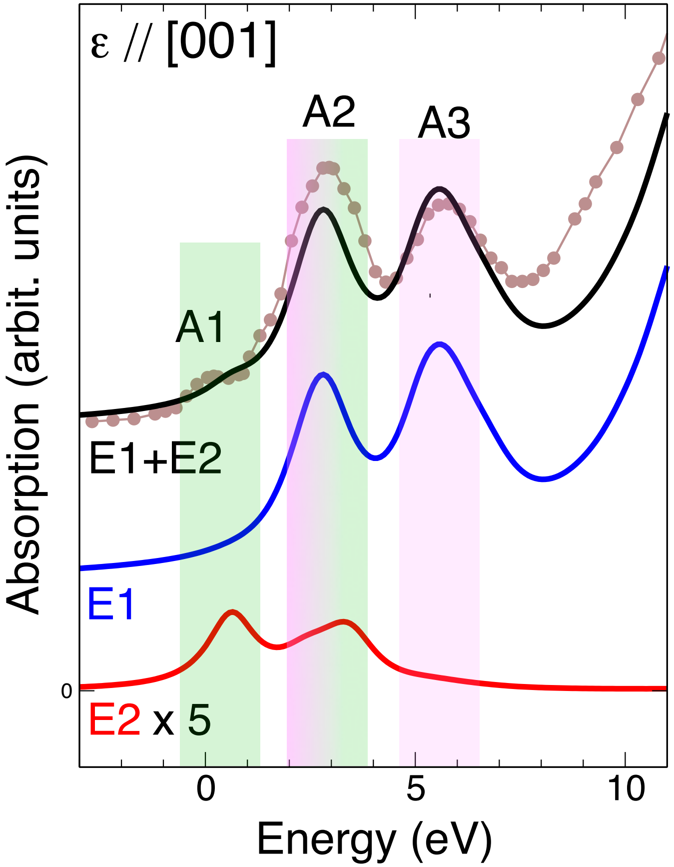
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

pre-edge : E2 + *non local* E1

single-particle picture





peak A1

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

peak A2

local E2 transition 1*s* → *3d* e_g

+

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

peak A3

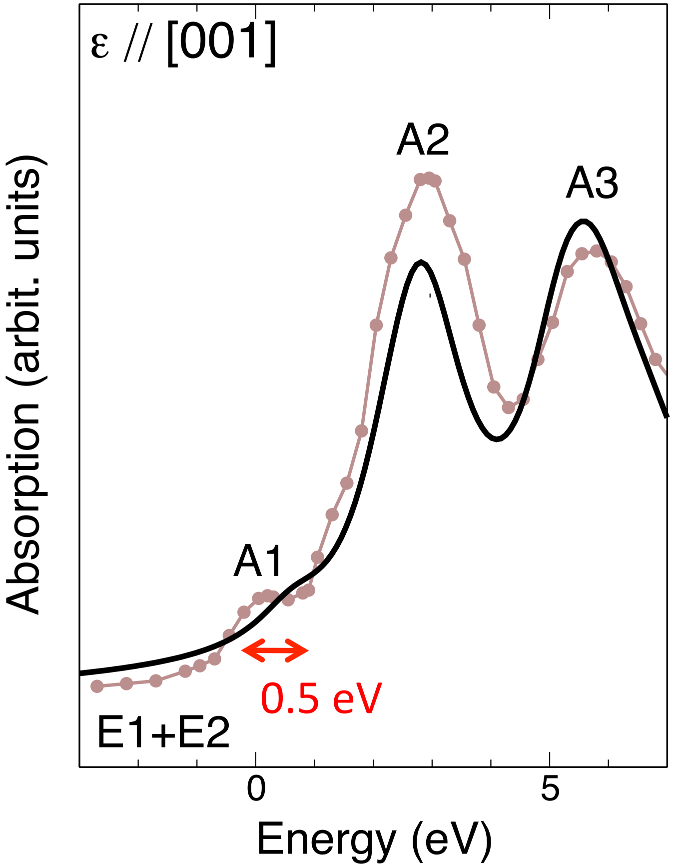
non-local E1 transition 1*s* → *p* hybrid. *3d* e_g (neighb.)

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

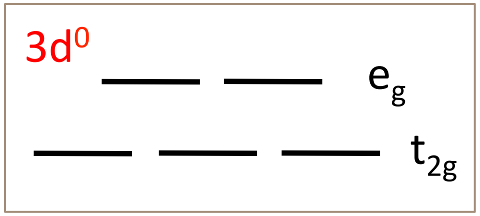
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

pre-edge : E2 + *non local* E1



single-particle picture



A1 calc. at too high energy !

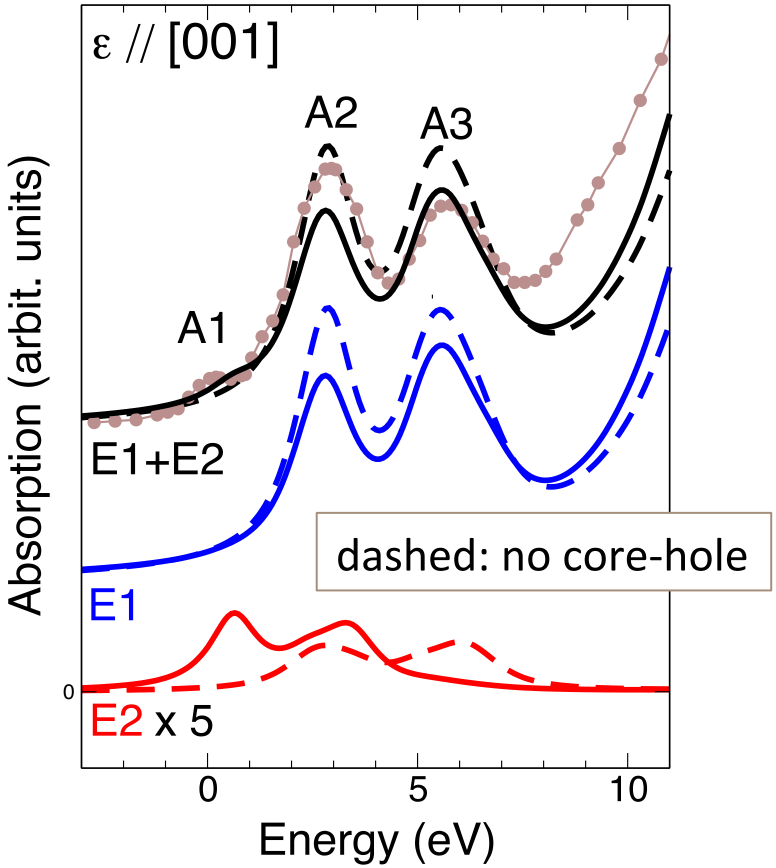
WHY?

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

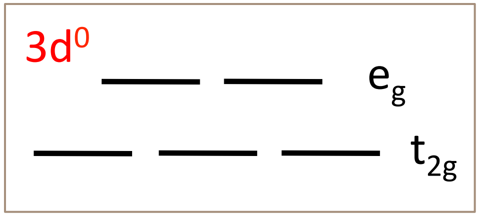
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

pre-edge : E2 + *non local* E1



single-particle picture



A1 calc. at too high energy !

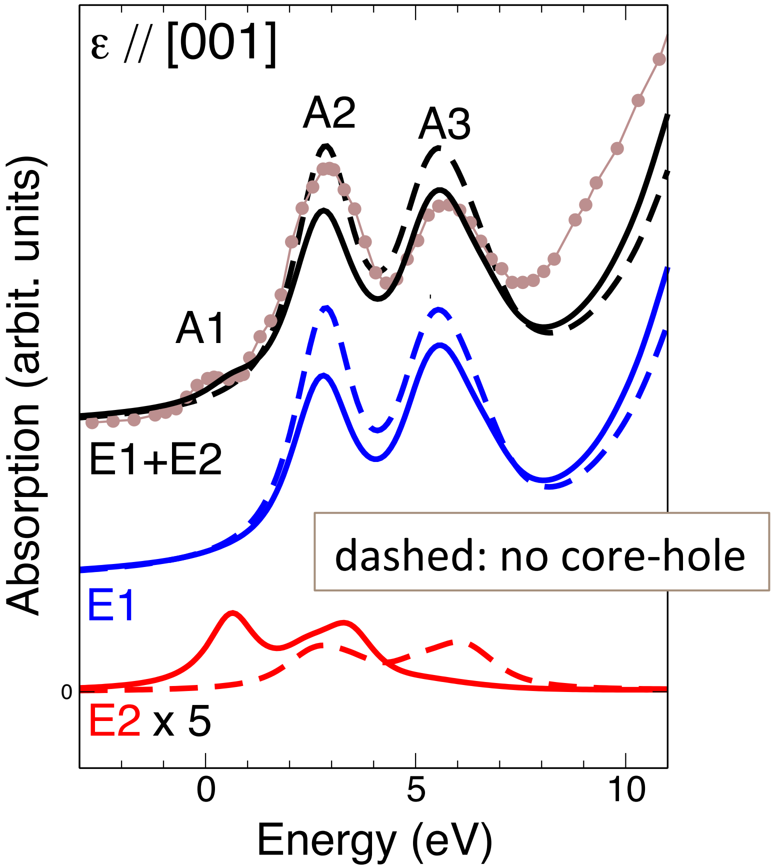
The 1*s* core-hole is not attractive enough…

How to improve ?

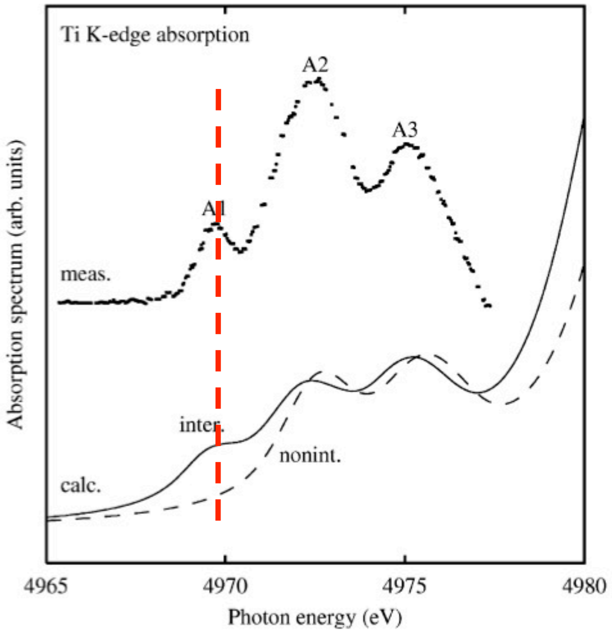
Ti^{4+} in *octahedral* site

TiO_2 rutile, Ti site: centrosymmetric

pre-edge : E2 + *non local* E1



Bethe-Salpeter equation

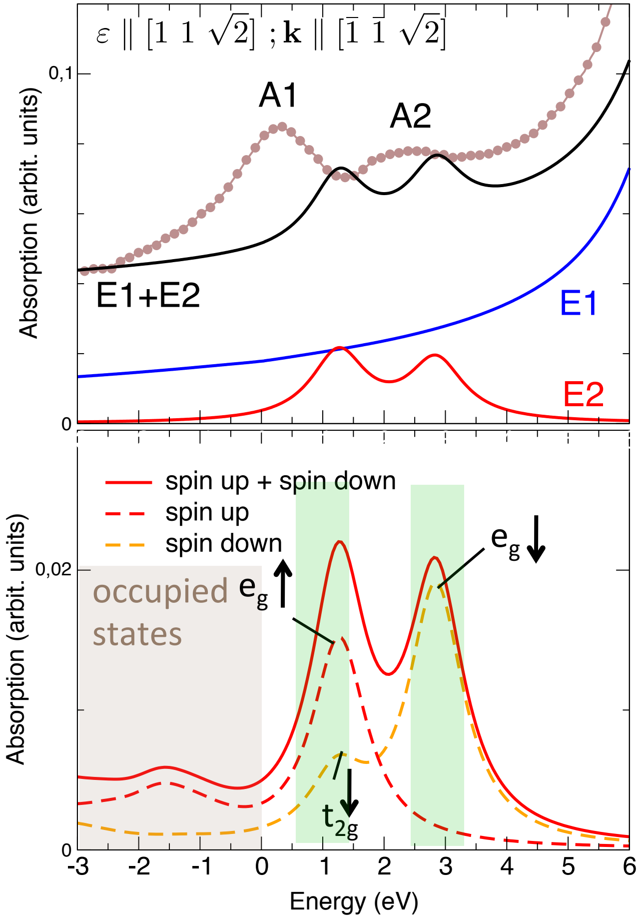


Shirley, J. Electr. Spectr. Rel. Phenom. **136**:77 (2004)

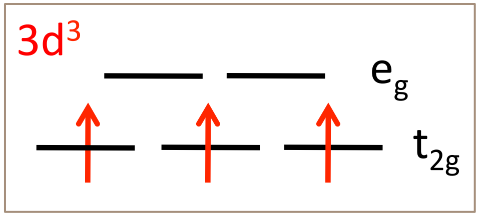
Cr^{3+} in *octahedral* site

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

↳ pre-edge : E2

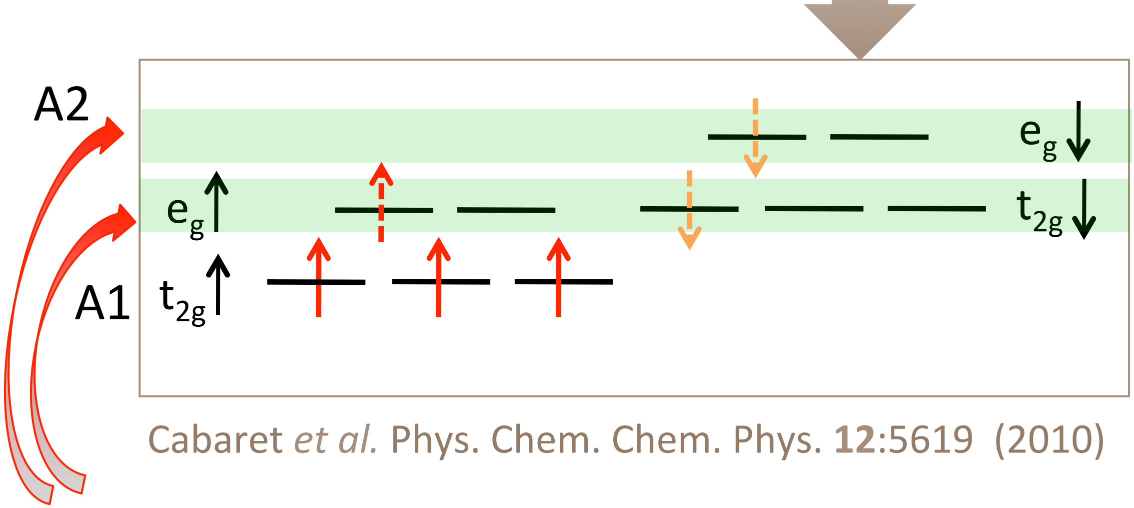


single-particle picture



two E2 peaks *(at too high energy…)*

Origin?



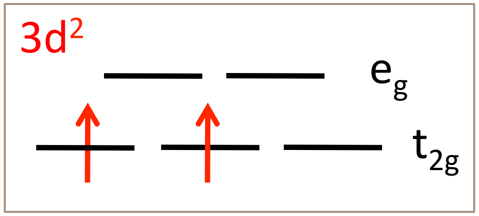
Cabaret *et al.* Phys. Chem. Chem. Phys. **12**:5619 (2010)

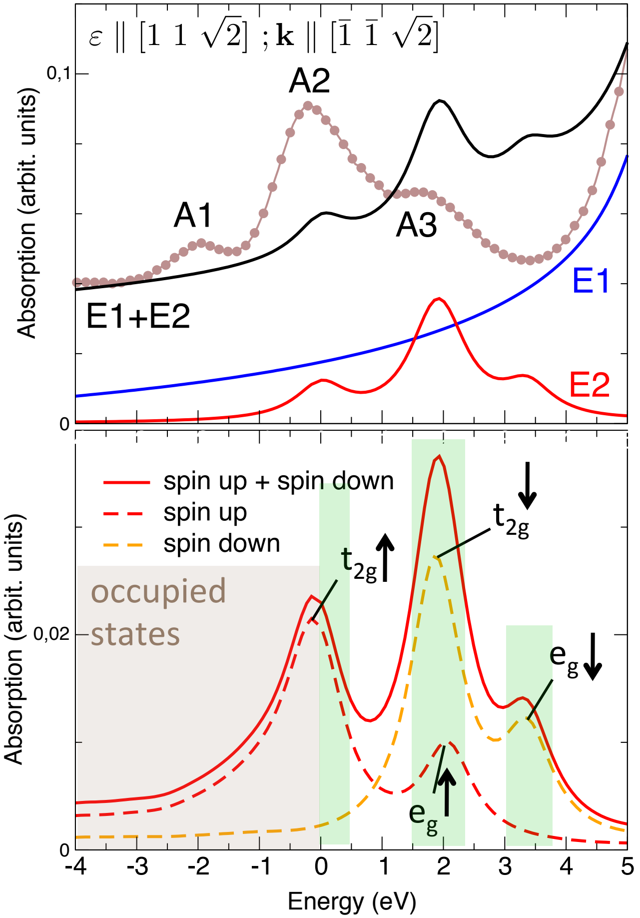
V^{3+} in *octahedral* site

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

pre-edge : E2

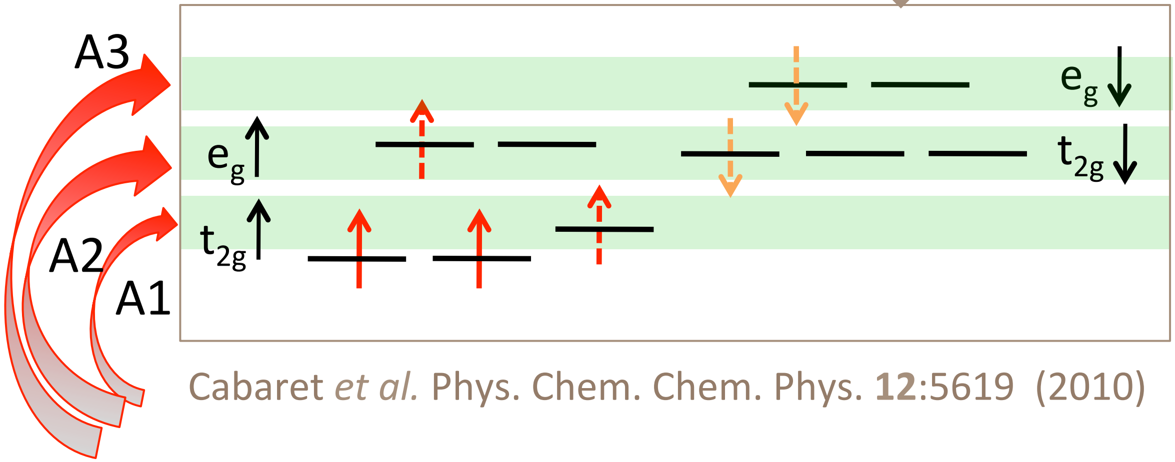
single-particle picture





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

Origin?

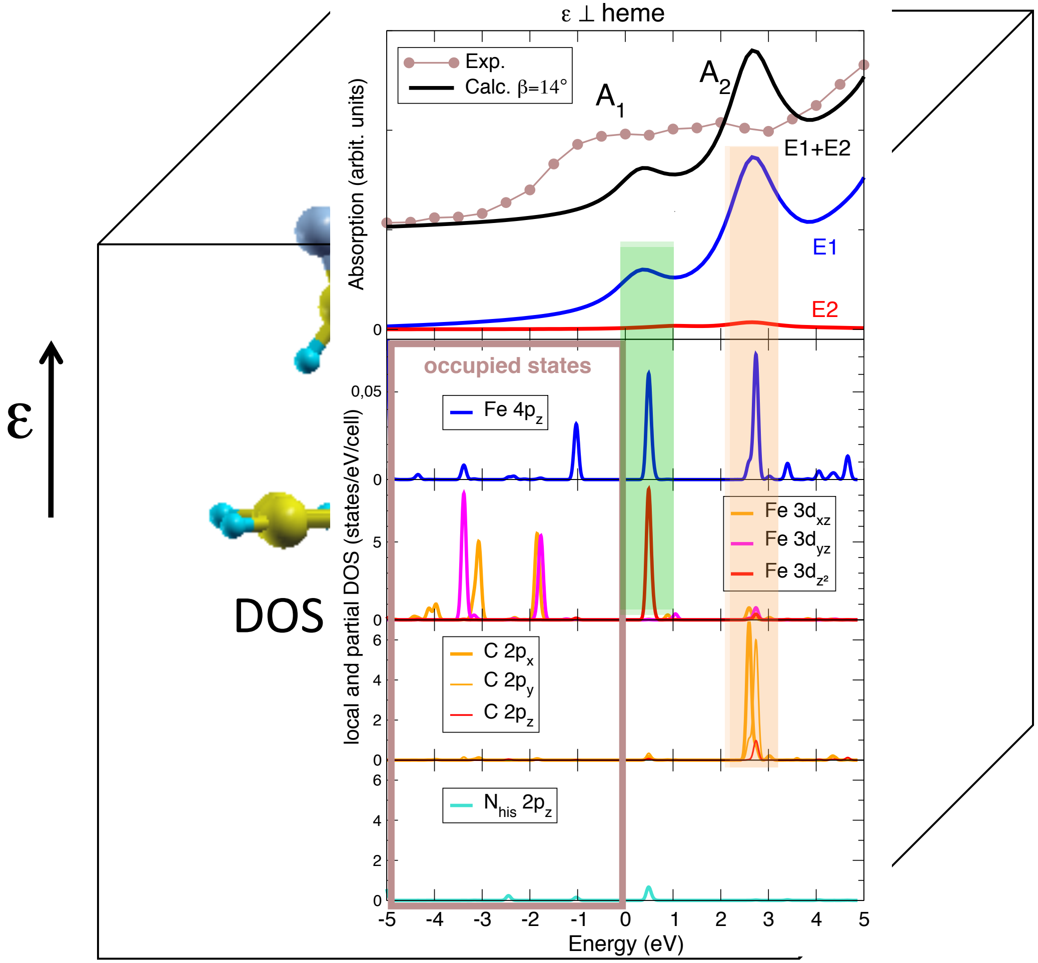


Cabaret *et al.* Phys. Chem. Chem. Phys. **12**:5619 (2010)

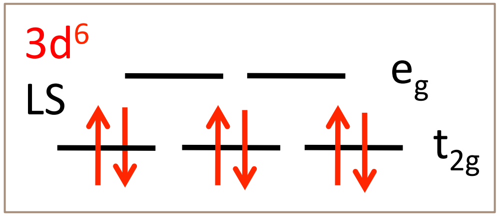
Fe^{2+} in *octahedral* site

MbCO protein, complex Fe site geometry

pre-edge : E2 + *local* E1



single-particle picture



2 peaks essentially E1, but

- at too high energy peak
- A2 too intense

peak A1

$1s \longrightarrow p_z$- $3d_{z^2}$ mixing

local E1

peak A2

$1s \longrightarrow p_z$ weakly mixed with $3d$

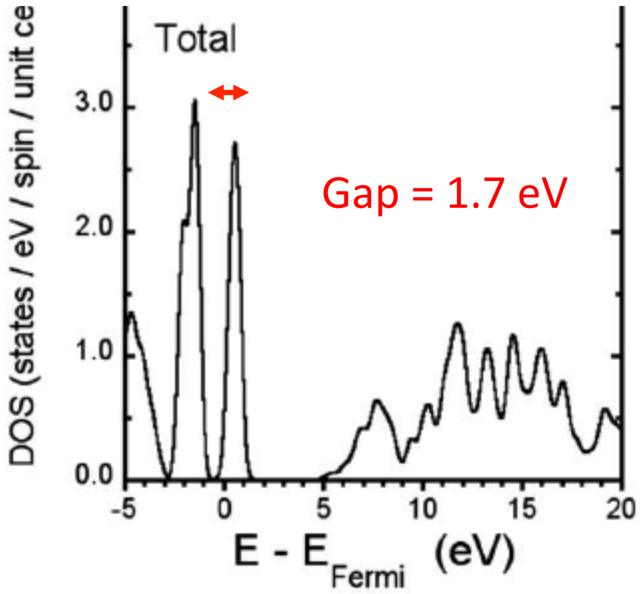
hybridized with π^* of CO

off-site E1

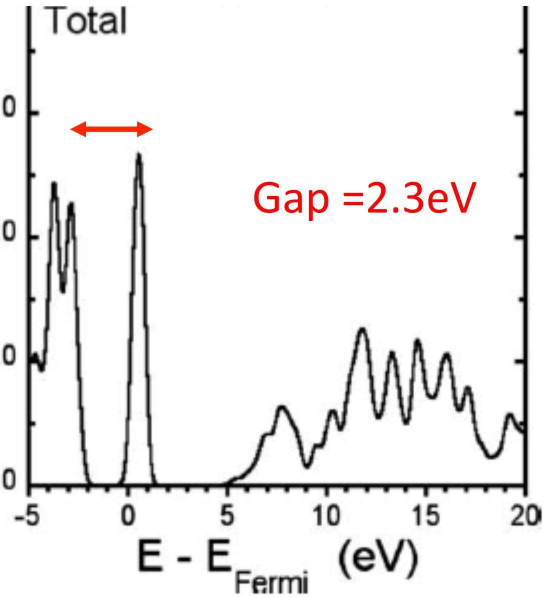
Cabaret *et al*. PCCP (2010)

Angular dependence of core hole screening in $LiCoO_2$

DFT-GGA → DFT-GGA +U



Electronic structure poorly described in GGA

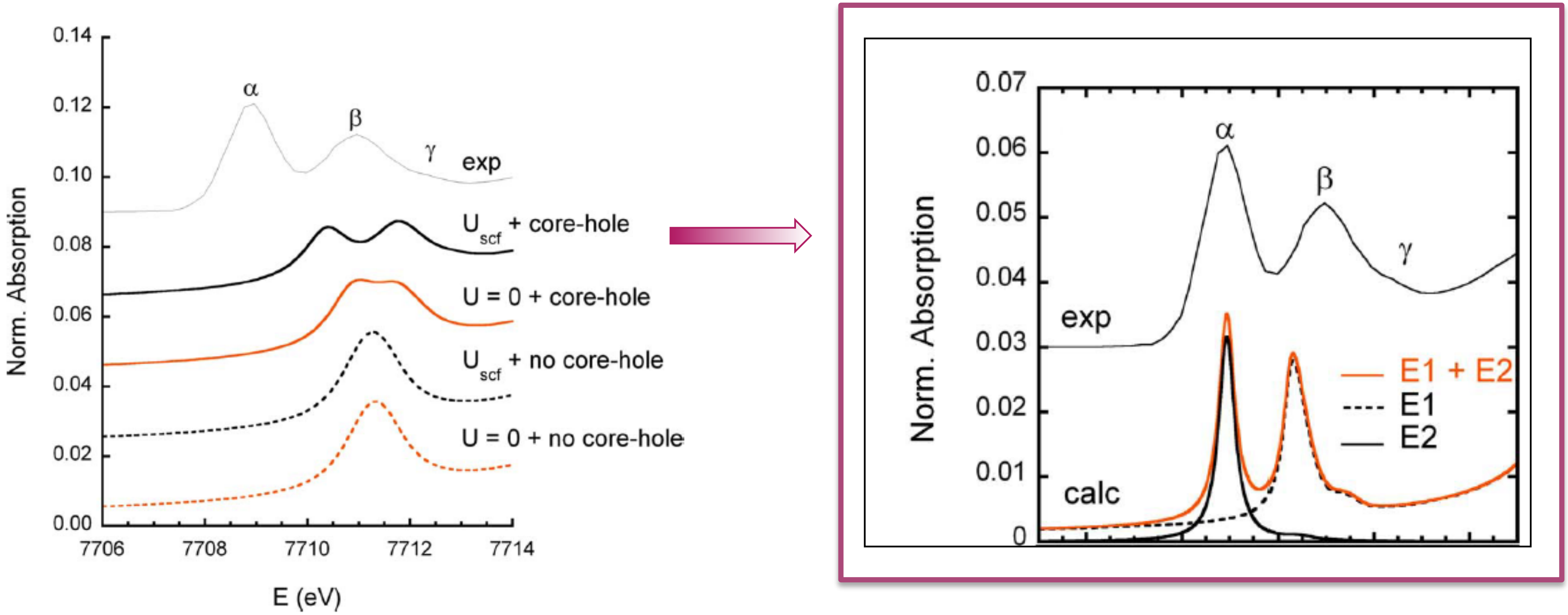


Better described using Hubbard parameter (U) on Co 3d states

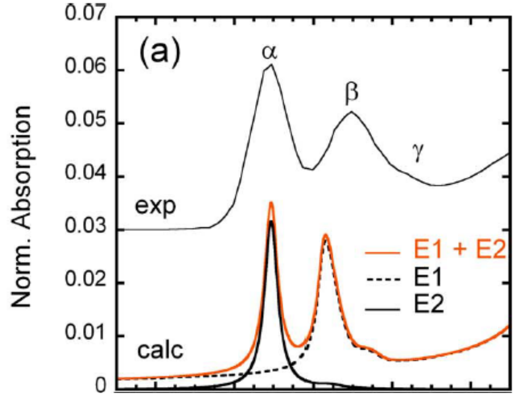
Juhin *et al*. PRB 81 (2010)

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

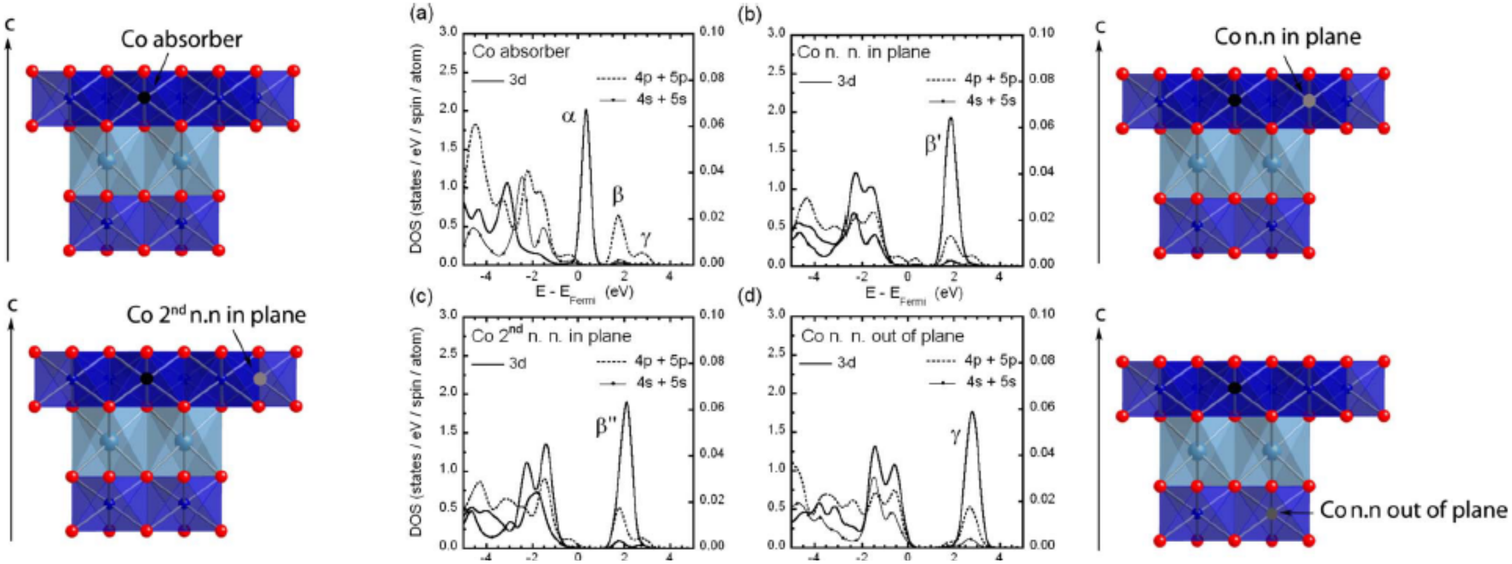
Best agreement is obtained when including U and the 1s core hole



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, $LiCoO_2$, …)