

Ds/Dt/Dq

$$\begin{aligned}\varepsilon(d_{x^2-y^2}) &= 6Dq + 2Ds - Dt \\ \varepsilon(d_{z^2}) &= 6Dq - 2Ds - 6Dt \\ \varepsilon(d_{xy}) &= -4Dq + 2Ds - Dt \\ \varepsilon(d_{xz}) = \varepsilon(d_{yz}) &= -4Dq - Ds + 4Dt\end{aligned}$$

splitting of the d on-site energies in D_{4h}

Δ

$$= E(d^{n+1}\underline{L}) - E(d^n)$$

cost of moving a ligand electron into the d shell;
 $\approx \varepsilon_d - \varepsilon_L + nU$

DFT 101

Where do the numbers in your Quanty Hamiltonian come from?

Quanty Workshop 2026

U

Screened, effective Coulomb interaction

10Dq

$$\begin{aligned}\varepsilon(eg) &= 6Dq \\ \varepsilon(t2g) &= -4Dq\end{aligned}$$

splitting of the d on-site energies in O_h

$\hat{H}_{\text{bath}}, \hat{H}_{\text{hyb}}, \hat{h}_{\text{loc}}^{1e}$

ROADMAP

1

PART I

Kohn–Sham in a Nutshell

The many-body problem, made tractable

- Many-body Hamiltonian, Born–Oppenheimer
- Hartree–Fock vs. Kohn–Sham
- XC functionals: LDA → hybrids
- Basis sets, and how FPLO works

→ Kohn–Sham bands and DOS, and when to trust them

2

PART II

Shining X-rays on Kohn–Sham

(X-Ray) Spectroscopy from Kohn–Sham states

- Band structure of Na vs ARPES
- K-edge $\sigma(\omega)$ from Fermi’s golden rule
- Core hole + supercell recipe
- Si K-edge in α -quartz
- Limits: Correlated shells, CoO

→ $\sigma(\omega)$ with a core hole, and where it breaks down

3

PART III

Your Turn

Hands-on: FPLO basics

- Structure input with fedit
- Run to self-consistency
- Plot bands and DOS
- Next session: downfolding

→ A converged FPLO run, ready for downfolding

PART I

KOHN–SHAM IN A NUTSHELL

From the many-body Hamiltonian to one-particle equations

Born–Oppenheimer · Hartree–Fock · Kohn–Sham · XC functionals · Basis sets & FPLO



MANY BODY SYSTEM

$$\hat{H}_{\text{system}} = \hat{T}_e + \hat{T}_{\text{nuc}} + \hat{V}_{e\text{-nuc}} + \hat{V}_{e\text{-e}} + \hat{V}_{\text{nuc-nuc}} + \hat{H}_{\text{rel}} + \hat{V}_{\text{ext}}$$

For $N \sim 10 \dots 10^{24+}$ electrons and nuclei

$$\hat{T}_e = -\frac{1}{2} \sum_{i \in e} \nabla_i^2$$

$$\hat{V}_{e\text{-e}} = \frac{1}{2} \sum_{i \neq j \in e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{e\text{-nuc}} = - \sum_{i \in e, I \in \text{nuc}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

$$\hat{T}_{\text{nuc}} = - \sum_{I \in \text{nuc}} \frac{1}{2M_I} \nabla_I^2$$

$$\hat{V}_{\text{nuc-nuc}} = \frac{1}{2} \sum_{I \neq J \in \text{nuc}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{mv}} + \hat{H}_{\text{D}} + \hat{H}_{\text{SO}} + \dots$$

Relativistic corrections etc.

$$\hat{V}_{\text{ext}} = \dots$$

Some external potential

Atomic units: $\hbar = m_e = e = 4\pi\epsilon_0 = 1$
 i, j : electrons ($\mathbf{r}_i, \mathbf{p}_i, s_i$); I, J : nuclei ($\mathbf{R}_I, Z_I, M_I$)

BORN-OPPENHEIMER APPROXIMATION

$$m_e \ll M_{\text{nuc}} \quad \frac{m_p}{m_e} \approx 1836$$

Slower nuclear motion separates from electronic motion

Keep nuclear positions fixed at $\{\mathbf{R}_I\}$ and solve the electronic part

$$\hat{H}_{\text{BO}}^{\{\mathbf{R}_I\}} = \hat{T}_e + \hat{V}_{\text{e-nuc}}^{\{\mathbf{R}_I\}} + \hat{V}_{\text{e-e}}$$

We still have $N_{\text{elec}} \sim 10 \dots 10^{24}$ interacting particles to solve for



SECOND-QUANTIZED HAMILTONIAN

$$\hat{H} = \sum_{ij} t_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} U_{ijkl} a_i^\dagger a_j^\dagger a_l a_k$$

Orthonormal spin-orbitals $\varphi_i(x)$, $x = (r, \sigma)$; a_i removes an electron from φ_i ; $\{a_i, a_j^\dagger\} = \delta_{ij}$

One-body part t_{ij}

$$t_{ij} = \langle \varphi_i | -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + \dots | \varphi_j \rangle$$

Kinetic energy, nuclei at fixed $\{R_i\}$ (Born–Oppenheimer), relativistic one-body terms such as spin–orbit

Two-body part U_{ijkl}

$$U_{ijkl} = \iint \frac{\varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{x}') \varphi_k(\mathbf{x}) \varphi_l(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}'$$

The Coulomb repulsion between two electrons. Restricted to one d or f shell, Quanta writes it with Slater integrals F^k .

Density matrices

$$\rho_{ij} = \langle a_i^\dagger a_j \rangle, \quad \Gamma_{ijkl} = \langle a_i^\dagger a_j^\dagger a_l a_k \rangle$$

$$E = \langle \hat{H} \rangle = \sum_{ij} t_{ij} \rho_{ij} + \frac{1}{2} \sum_{ijkl} U_{ijkl} \Gamma_{ijkl}$$

The one-body energy needs only ρ .

The two-body energy needs the two-body density matrix Γ : this is the hard part of the many-body problem.

DOOR 1

So we must approximate. The question is what.

Door 1

Treat every electron approximately

- Mean field: DFT, Hartree–Fock
- Fantastic for weakly correlated bands
- Misses multiplets, satellites, Mott physics

Door 2

Treat a few electrons exactly, the rest approximately

- Choose a small local subsystem
- Exact many-body physics inside it
- The rest of the crystal as an effective environment

This workshop is about Door 2.

HARTREE–FOCK IN SECOND QUANTIZATION

Remember: $\rho_{ij} = \langle a_i^\dagger a_j \rangle$

Mean-field decoupling: pair a creator with an annihilator, replace the pair by ρ

$$a_i^\dagger a_j^\dagger a_l a_k \longrightarrow \underbrace{\rho_{ik} a_j^\dagger a_l + \rho_{jl} a_i^\dagger a_k}_{\text{Hartree (direct)}} \underbrace{- \rho_{il} a_j^\dagger a_k - \rho_{jk} a_i^\dagger a_l}_{\text{Fock (exchange)}} \underbrace{- \rho_{ik} \rho_{jl} + \rho_{il} \rho_{jk}}_{\text{double counting}}$$

Sign = parity of the pairing.
Dropped: products of fluctuations $\delta(a^\dagger a) \cdot \delta(a^\dagger a)$, i.e. correlation.

makes $\langle \hat{H}_{MF} \rangle = E_{HF}$

In Matrix Form:

$$U_{jl}^{MF}[\rho] = \underbrace{\sum_{ik} U_{ijkl} \rho_{ik}}_{V_{jl}^H: \text{Hartree}} - \underbrace{\sum_{ik} U_{ijlk} \rho_{ik}}_{V_{jl}^X: \text{Fock}}$$

In Operator Form:

$$\hat{U}_{MF} = \sum_{jl} U_{jl}^{MF} a_j^\dagger a_l - E_{dc}[\rho]$$

In Real Space:

$$\gamma(x, x') = \sum_{ij} \rho_{ij} \varphi_j(x) \varphi_i^*(x')$$

$$V^H(x) = \int \frac{\gamma(x', x')}{|x - x'|} dx' = \int \frac{n(x')}{|x - x'|} dx' \quad \left. \vphantom{\int} \right\} \text{Local}$$

$$\hat{H}^H \varphi_i(x) = V^H(x) \varphi_i(x)$$

$$V^X(x, x') = -\frac{\gamma(x, x')}{|x - x'|}$$

$$\hat{H}^X \varphi_i(x) = \int V^X(x, x') \varphi_i(x') dx' \quad \left. \vphantom{\int} \right\} \text{Non-Local}$$

HARTREE-FOCK

Fock matrix

$$F_{jl}[\rho] = t_{jl} + \underbrace{\sum_{ik} U_{ijkl} \rho_{ik}}_{V_{jj}^H: \text{Hartree}} - \underbrace{\sum_{ik} U_{ijlk} \rho_{ik}}_{V_{jj}^X: \text{Fock}}$$

$$\hat{H}_{\text{HF}} = \sum_{jl} F_{jl}[\rho] a_j^\dagger a_l - E_{\text{dc}}[\rho]$$

- $\hat{H}_{\text{HF}}$ only contains single-particle operators
- Solutions will be single Slater determinants

$$\Psi_{\text{HF}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det[\varphi_i(\mathbf{x}_j)]$$

$$\Leftrightarrow \rho^2 = \rho$$

Applying the variational principle yields Hartree-Fock

$$E_{\text{HF}} = \min_{\Phi \in \text{SD}} \langle \Phi | \hat{H} | \Phi \rangle = \min_{\rho^2 = \rho, \text{Tr } \rho = N} E_{\text{HF}}[\rho]$$

$$E_{\text{HF}}[\rho] = \sum_{ij} t_{ij} \rho_{ij} + \frac{1}{2} \sum_{ijkl} (U_{ijkl} - U_{ijlk}) \rho_{ik} \rho_{jl}$$

$$\delta E_{\text{HF}} = 0 \Rightarrow F \mathbf{c}_n = \varepsilon_n \mathbf{c}_n$$

$$E_{\text{exact}} = \sum_{ij} t_{ij} \rho_{ij} + \frac{1}{2} \sum_{ijkl} U_{ijkl} \Gamma_{ijkl}$$

HF gives the single Slater determinant with lowest energy w.r.t. the original Hamiltonian!

Remember: $n(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x})$

FROM HARTREE–FOCK TO KOHN–SHAM DFT

1 Hohenberg–Kohn I

The ground-state density fixes the external potential (up to a constant).

$$n_0(\mathbf{r}) \mapsto v_{\text{ext}}(\mathbf{r}) \mapsto \hat{H} \mapsto \Psi_0[n_0]$$

⇒ every ground-state property is a functional of n

2 Hohenberg–Kohn II

The energy functional is minimal at the true ground-state density.

$$E_v[n] = F[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \geq E_0$$

$F[n] = \langle \Psi[n] | T + V_{\text{ee}} | \Psi[n] \rangle$ is universal: the same for every material

P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Same mean-field Hamiltonian, one block swapped

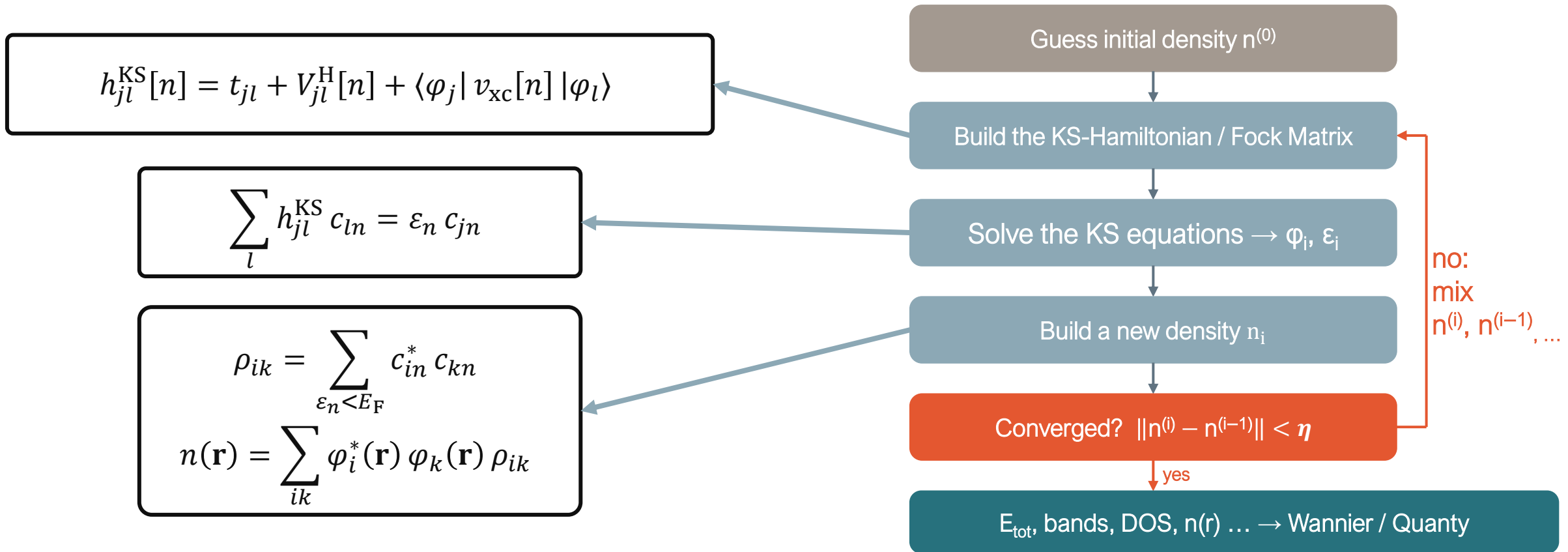
$$\begin{aligned} \hat{H}_{\text{HF}} &= \sum_{jl} \left(\boxed{t_{jl}} + \boxed{V_{jl}^{\text{H}}[n]} + \boxed{V_{jl}^{\text{X}}[\gamma]} \right) a_j^\dagger a_l \\ &\quad \downarrow \qquad \qquad \qquad = \qquad \qquad \qquad = \text{swap} \\ \hat{H}_{\text{KS}} &= \sum_{jl} \left(\boxed{t_{jl}} + \boxed{V_{jl}^{\text{H}}[n]} + \boxed{V_{jl}^{\text{xc}}[n]} \right) a_j^\dagger a_l \end{aligned}$$

$$V_{jl}^{\text{X}}[\rho] = - \sum_{ik} U_{ijkl} \rho_{ik} \qquad (\text{non-local, from } \gamma)$$

$$V_{jl}^{\text{xc}}[n] = \langle \varphi_j | v_{\text{xc}}[n] | \varphi_l \rangle, \quad v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad (\text{local, only from } n)$$

- Both are one-body Hamiltonians: diagonalize, occupy, rebuild ρ and n , iterate
- **Same** general structure
- **HF**: $V^{\text{X}}[\rho]$ is exact exchange, but there is no correlation
- **KS**: $v_{\text{xc}}[n]$ is chosen such that the determinant has the **exact** n_0 (HK I); E_0 then follows from HK II
- $E_{\text{xc}}[n]$ is unknown → approximations (next slides); KS orbitals are auxiliary

KOHN–SHAM EQUATIONS

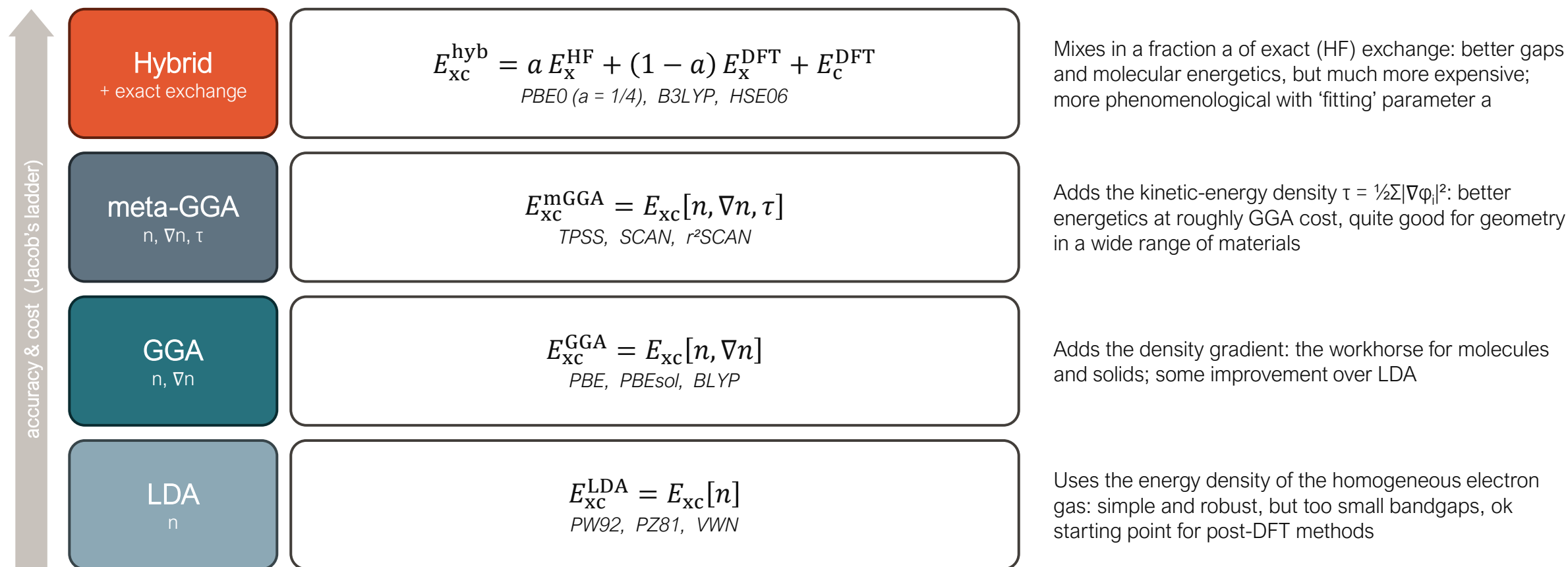


- Same structure as Hartree–Fock, but $v_{\text{xc}}(\mathbf{r})$ is local and contains correlation
- Exact in principle; in practice only as good as the approximate $E_{\text{xc}}[n]$ (next slide)

XC-FUNCTIONAL ZOO

Sadly, the exact XC functional is unknown $E_{xc}[n]$.

However: there is a ginormous Zoo of approximated E_{xc} out there



LDA: PW92, PRB 45, 13244 (1992); PZ81, PRB 23, 5048 (1981); VWN, Can. J. Phys. 58, 1200 (1980). GGA: PBE, PRL 77, 3865 (1996); PBEsol, PRL 100, 136406 (2008); BLYP, PRA 38, 3098 (1988) + PRB 37, 785 (1988). meta-GGA: TPSS, PRL 91, 146401 (2003); SCAN, PRL 115, 036402 (2015); r^2 SCAN, J. Phys. Chem. Lett. 11, 8208 (2020). Hybrids: PBE0, J. Chem. Phys. 110, 6158 (1999); B3LYP, J. Chem. Phys. 98, 5648 (1993); HSE06, J. Chem. Phys. 118, 8207 (2003), 125, 224106 (2006). Jacob's ladder: J. P. Perdew and K. Schmidt, AIP Conf. Proc. 577, 1 (2001).

DFT CODES AND BASIS SETS

Plane waves

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

VASP, Quantum ESPRESSO, ABINIT, CASTEP

Muffin-tin (LAPW, LMTO)

$$\begin{array}{l} \text{sphere: } \sum_{lm} [A_{lm} u_l(r) + B_{lm} \dot{u}_l(r)] Y_{lm}(\hat{\mathbf{r}}) \\ \text{interstitial: } e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \end{array}$$

WIEN2k, FLEUR, Elk; RSPt, Questaal

Numerical atomic orbitals

$$\chi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\hat{\mathbf{r}}), \quad R_{nl}(r > r_c) = 0$$

FPLO, FHI-aims, SIESTA, OpenMX

Gaussian-type orbitals

$$\chi(\mathbf{r}) = x^a y^b z^c e^{-\alpha r^2}$$

Gaussian, ORCA, CRYSTAL, CP2K, PySCF

Real-space grids / wavelets

$$\varphi_i(\mathbf{r}_{jkl}) \text{ on a grid, spacing } h$$

GPAW, Octopus, BigDFT

And for Quantity?

The choice of basis mostly matters for accuracy and cost of the DFT step.

Local orbitals (NAO, LMTO) or Wannier functions (e.g. Wannier90, from any basis) give a local d/f-shell picture:

crystal field, hybridisation and hopping parameters, the input for a Quantity model Hamiltonian.

FPLO: FULL-POTENTIAL LOCAL-ORBITAL METHOD

1

Compact basis of atom-like local orbitals

Core, semicore, valence and polarisation orbitals from a DFT atom in a confining potential; zero beyond the compact-support radius ρ

$$\Phi_{nlm}(\mathbf{r}) = \varphi_{nl}(r) Y_{lm}(\hat{\mathbf{r}}) \chi_s, \quad V_{nl}^{\text{conf}}(r) = \left(\frac{r}{P P_{nl} \rho} \right)^N, \quad N = 14$$

2

Full potential, all electrons

No shape approximation to matrix elements: no muffin tin like separations of space
No Pseudopotentials / ECPs

3

Bloch sums and a small eigenproblem

Non-orthogonal basis gives a generalised eigenproblem; the compact basis keeps the matrices small, so many $\mathbf{k}$ points are cheap

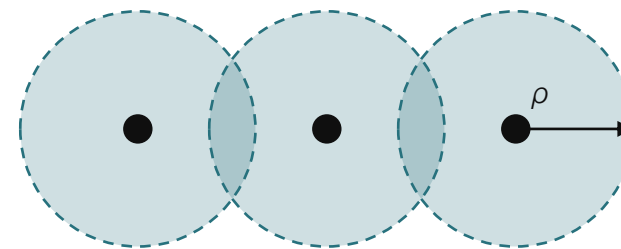
$$\phi_{\mathbf{k}L}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi_L(\mathbf{r} - \mathbf{R} - \mathbf{s}), \quad H c = \varepsilon S c$$

4

Relativity and extras

Scalar-relativistic (default) or full-relativistic with four-spinor orbitals and spin-orbit coupling; LSDA+U, CPA, fixed spin moment, mBJ potential

Compressed atom-like orbitals on every site



Orbitals overlap, but each is localised on its site: a natural tight-binding picture

In the tutorial

FPLO: self-consistent DFT (LSDA/GGA, SOC)



FPLO Wannier functions $\rightarrow$ d/f tight-binding H



Quantity (e.g. DFT+DMFT)

PART II

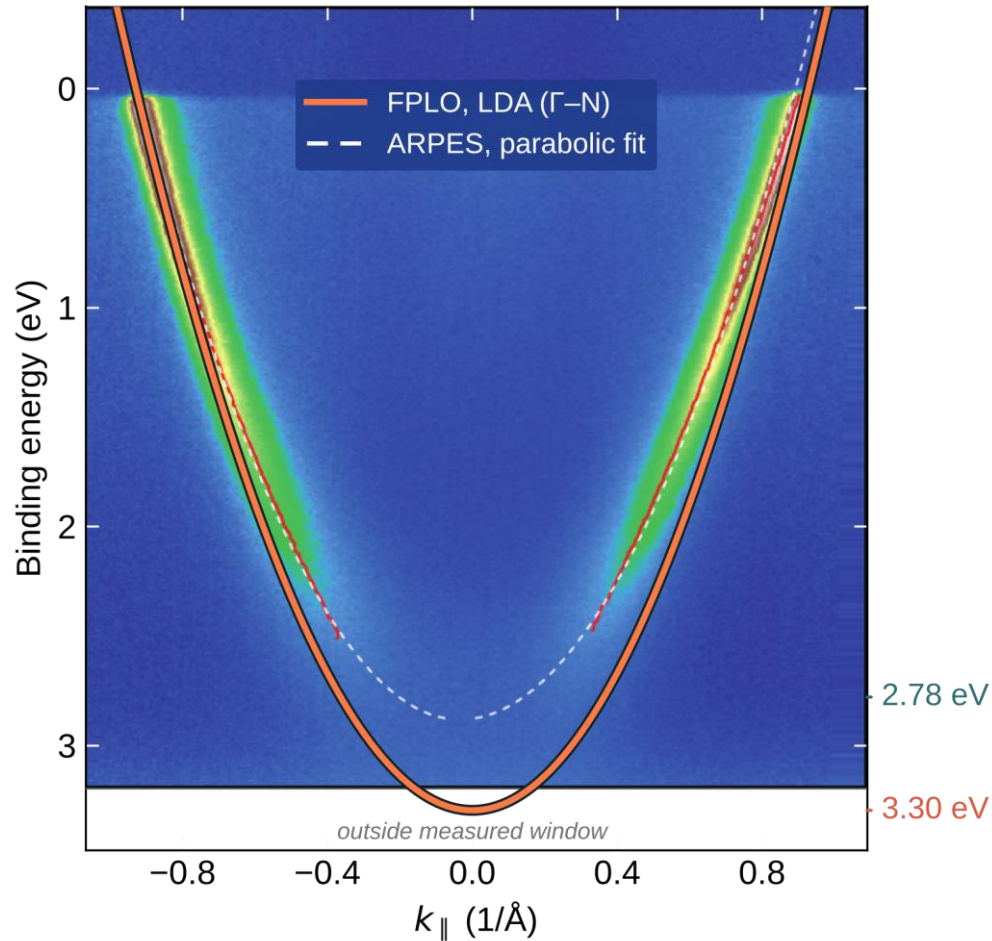
SHINING X-RAYS ON Kohn–SHAM

II

What DFT can, and cannot, tell us about spectroscopy

ARPES on Na · Fermi's golden rule · Core hole & supercell · Si K-edge in α -quartz · CoO

SODIUM: ARPES VS. LDA



Nearly-free-electron metal

bcc Na, one 3s electron per atom. If LDA works anywhere, it is here.

	ARPES	FPLO (LDA)
Occupied bandwidth W	2.78 eV	3.30 eV
Fermi wave vector k_F	0.91 $\text{\AA}^{-1}$	0.93 $\text{\AA}^{-1}$

$$m^*/m = W_{\text{LDA}} / W_{\text{exp}} \approx 1.19$$



Fermi surface is right

k_F agrees to 2 %: the Fermi volume is fixed by the electron count, and DFT gets the density right.



Band is ~0.5 eV too wide

Kohn–Sham eigenvalues are missing dynamic screening effects. The missing self-energy $\Sigma(k, \omega)$ narrows the occupied band.



Beyond DFT

GW-type self-energies give $W \approx 2.5\text{--}3.0$ eV, depending on vertex corrections and on how Σ is evaluated.

M. Cazzaniga, PRB 86, 035120 (2012); J. Lischner et al., PRB 89, 081108(R) (2014);

A. L. Kutepov, PRB 94, 155101 (2016)

ARPES: D. V. Potorochin et al., *Phys. Rev. B* 106, 125138 (2022),
 Fig. 1, Table I ($h\nu = 70$ eV, 20 K; W from the quartic fit). FPLO: LDA, bcc $a = 4.235$ $\text{\AA}$, Γ -N.

X-RAY ABSORPTION FROM DFT (K-EDGE)

Fermi's golden rule

$$\sigma(\omega) = 4\pi^2\alpha_0 \hbar\omega \sum_f |M_{i \rightarrow f}|^2 \delta(E_f - E_i - \hbar\omega)$$

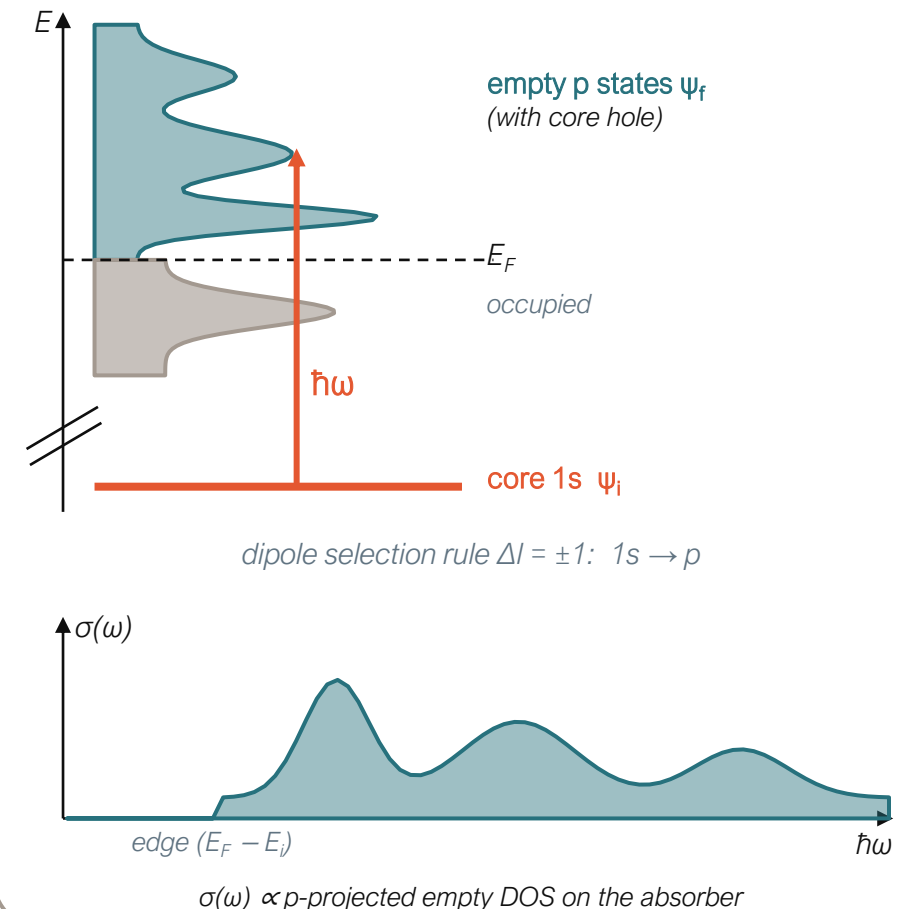
Transition amplitude

$$M_{i \rightarrow f} = \langle \psi_f | \hat{O} | \psi_i \rangle, \quad \hat{O} = \hat{\varepsilon} \cdot \mathbf{r} \left[1 + \frac{i}{2} \mathbf{k} \cdot \mathbf{r} \right]$$

- **Initial state** ψ_i : core state (e.g. 1s) of the absorbing atom from an all-electron atomic calculation (frozen core)
- **Final states** ψ_f , E_f : empty Kohn–Sham states computed with a core hole on the absorber (impurity model)
- **Operator** $\hat{O}$: electric dipole $\hat{\varepsilon} \cdot \mathbf{r}$ (selection rule $\Delta l = \pm 1$) plus the quadrupole correction $(i/2)(\hat{\varepsilon} \cdot \mathbf{r})(\mathbf{k} \cdot \mathbf{r})$

M. Taillefumier, D. Cabaret, A.-M. Flank, F. Mauri, Phys. Rev. B 66, 195107 (2002), Eqs. (1)–(2)

One-electron picture of a K edge



ADDING A CORE HOLE IN DFT

1

Single out one absorber

Give it its own species / Wyckoff site: this breaks the lattice symmetry

2

Remove one 1s electron

Pseudopotential generated for the $1s^1$ configuration (as in the paper); all-electron codes set the absorber's core occupation directly

3

Build a supercell

Repeat the cell $n \times n \times n$ so the hole is isolated from its images (for example: α -quartz: $2 \times 2 \times 2 = 72$ atoms is sufficient)

4

Run to self-consistency

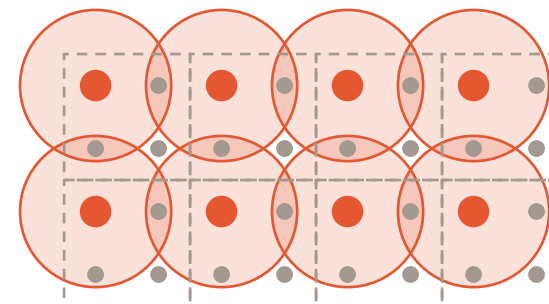
The valence electrons relax and screen the hole (at all orders, within DFT)

5

Compute $\sigma(\omega)$ and converge

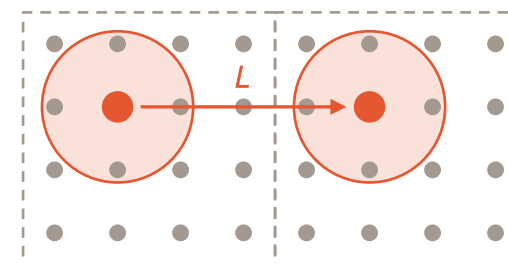
Empty states in this potential give $\sigma(\omega)$; enlarge the cell until the spectrum stops changing

Small cell: the hole sees its own images



screening clouds of neighbouring core holes overlap: a spurious hole-hole interaction distorts $\sigma(\omega)$

Supercell: an isolated impurity



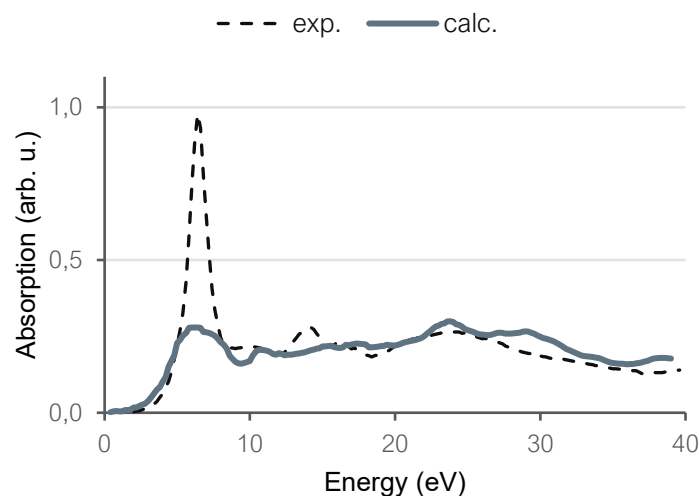
one hole per large cell: images a distance L apart no longer interact; converge L

Recipe as in M. Taillefumier et al., Phys. Rev. B 66, 195107 (2002)

LDA, Troullier-Martins pseudopotentials, supercell enlarged until neighboring excited potentials no longer interact.

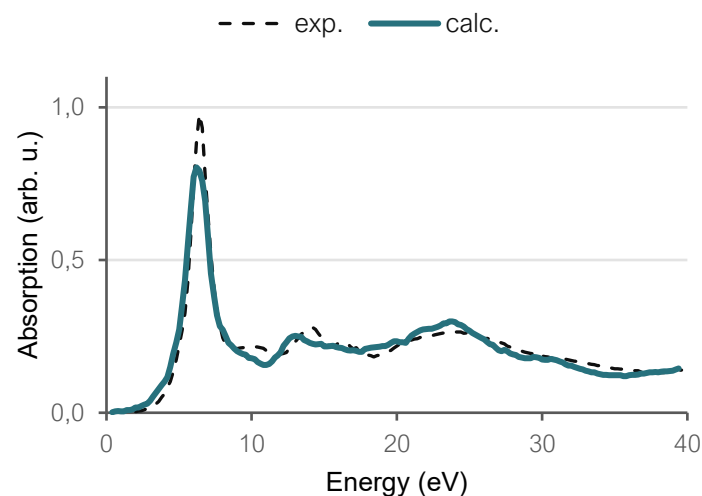
CORE-HOLE EFFECTS AT THE SI K-EDGE IN α -QUARTZ

1 No core hole
ground state, primitive cell (9 atoms)



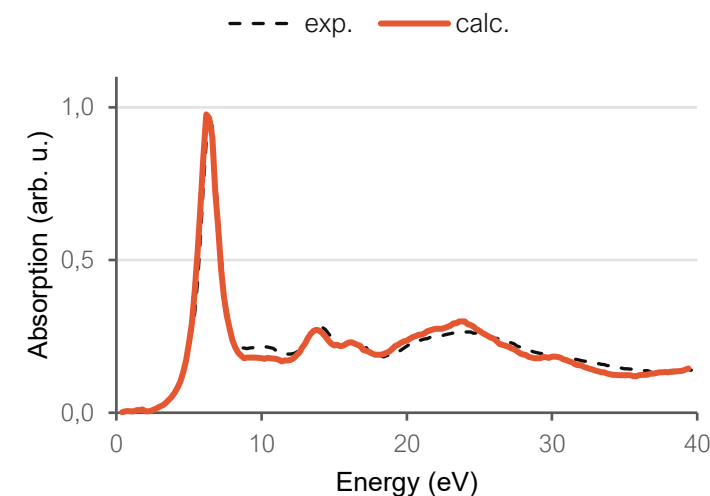
The intense white line is missing

2 1s core hole
primitive cell (9 atoms)



White line appears, but the core hole is close to its periodic images

3 1s core hole
2×2×2 supercell (72 atoms): converged



Changes at 8–18 eV: medium-range order around the absorber

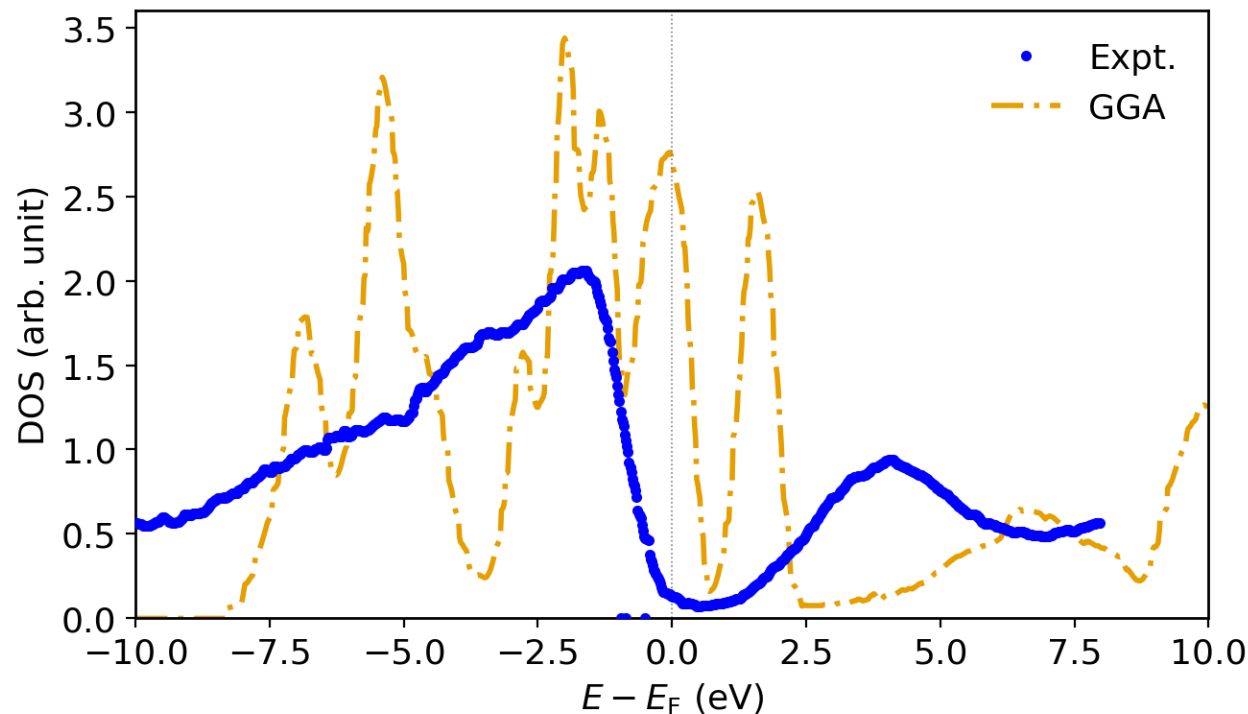
Why a core hole?

The excited electron feels the attraction of the 1s hole (final-state effect): spectral weight is pulled towards the edge and forms the white line.

Why a supercell?

The core-hole atom is an impurity. Its periodic images must be far apart: converge the cell size like any other finite-size effect.

GGA SAYS METAL. EXPERIMENT SAYS INSULATOR.



Does the method open a gap at E_F ?

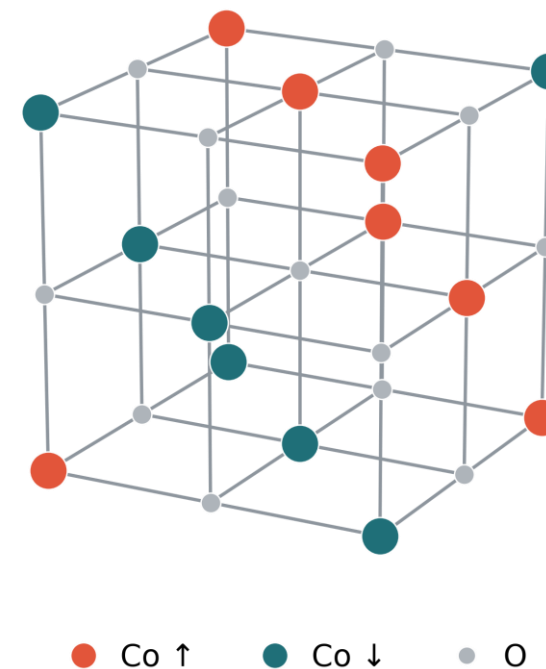
GGA
X metal

mBJ
?

B3LYP
?

GGA+U
?

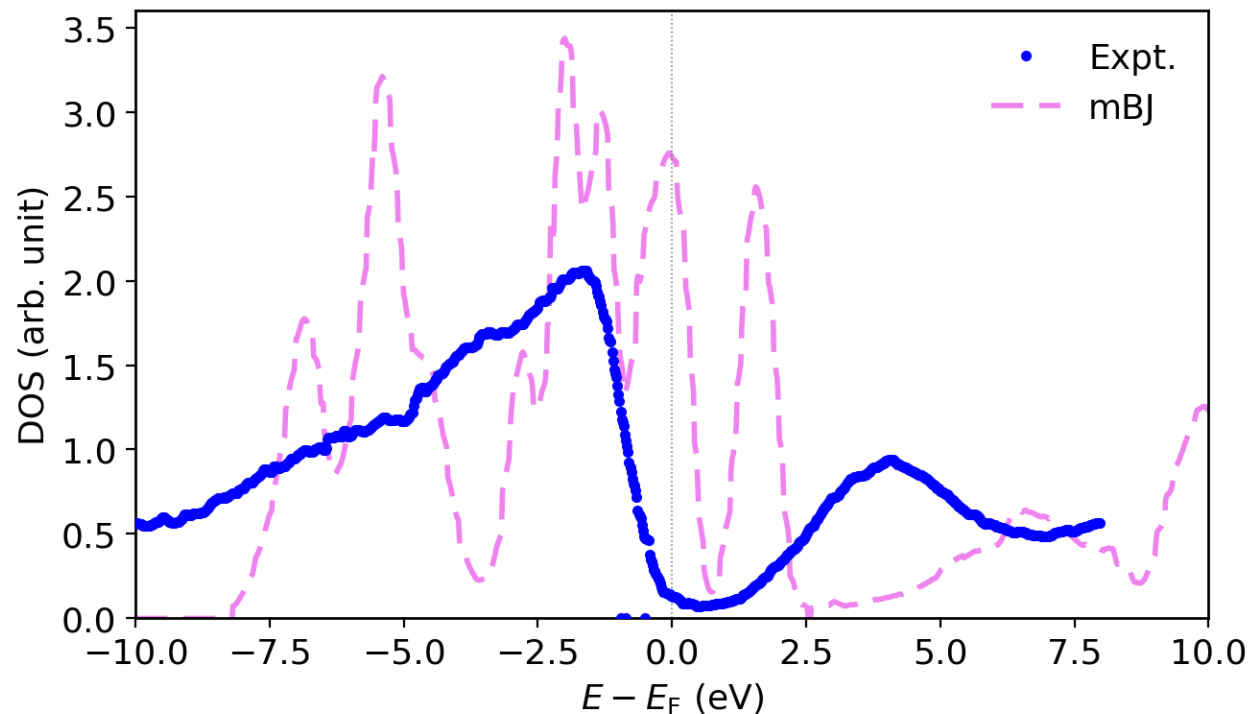
eDMFT
?



Cobalt(II) oxide
rocksalt structure
antiferromagnetic (AFM II) below 289 K

Data digitized from Fig. 1d of S. Mandal, K. Haule, K. M. Rabe, D. Vanderbilt, *npj Comput. Mater.* 5, 115 (2019), CC BY 4.0: DOS of AFM CoO, dots: PES/IPES. Structure: rocksalt, $a = 4.254 \text{ \AA}$, AFM II.

GGA SAYS METAL. EXPERIMENT SAYS INSULATOR.



Does the method open a gap at E_F ?

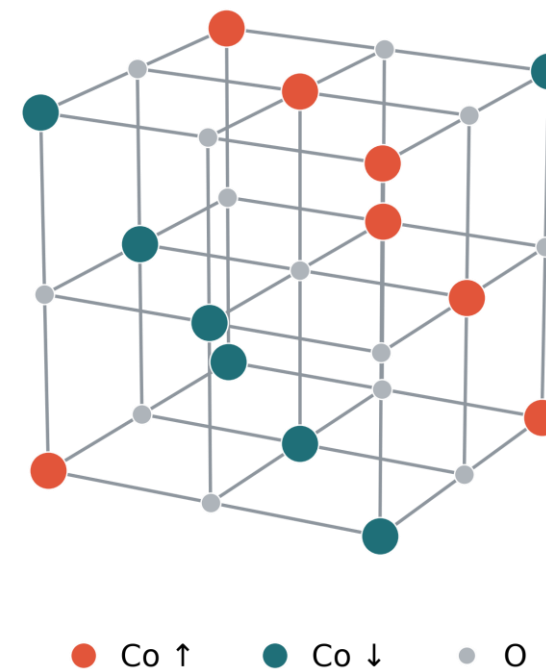
GGA
X metal

mBJ
X metal

B3LYP
?

GGA+U
?

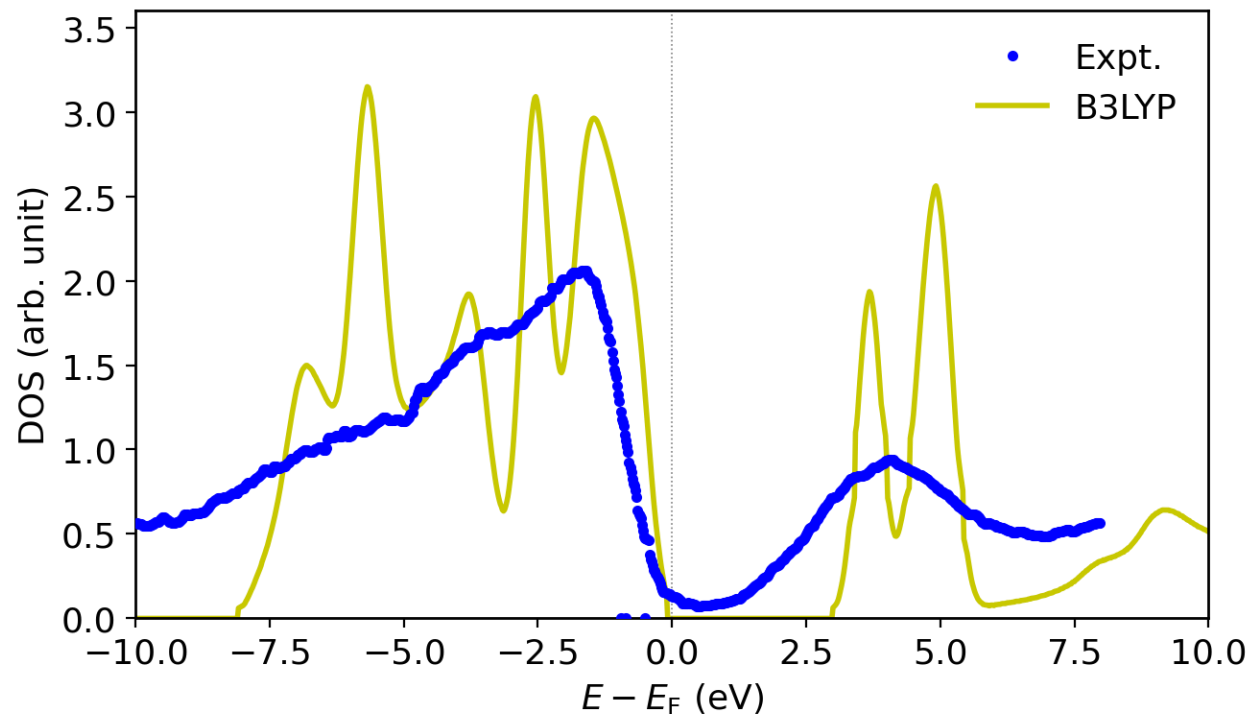
eDMFT
?



Cobalt(II) oxide
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Data digitized from Fig. 1d of S. Mandal, K. Haule, K. M. Rabe, D. Vanderbilt, *npj Comput. Mater.* 5, 115 (2019), CC BY 4.0: DOS of AFM CoO, dots: PES/IPES. Structure: rocksalt, $a = 4.254 \text{ \AA}$, AFM II.

GGA SAYS METAL. EXPERIMENT SAYS INSULATOR.



Does the method open a gap at E_F ?

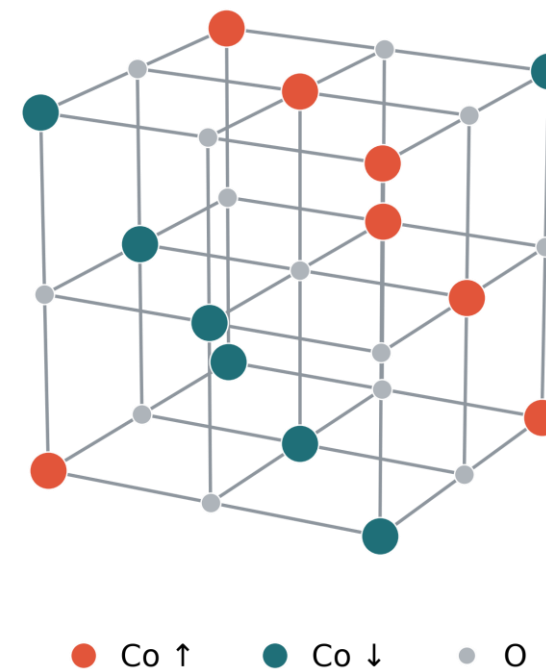
GGA
X metal

mBJ
X metal

B3LYP
✓ gap

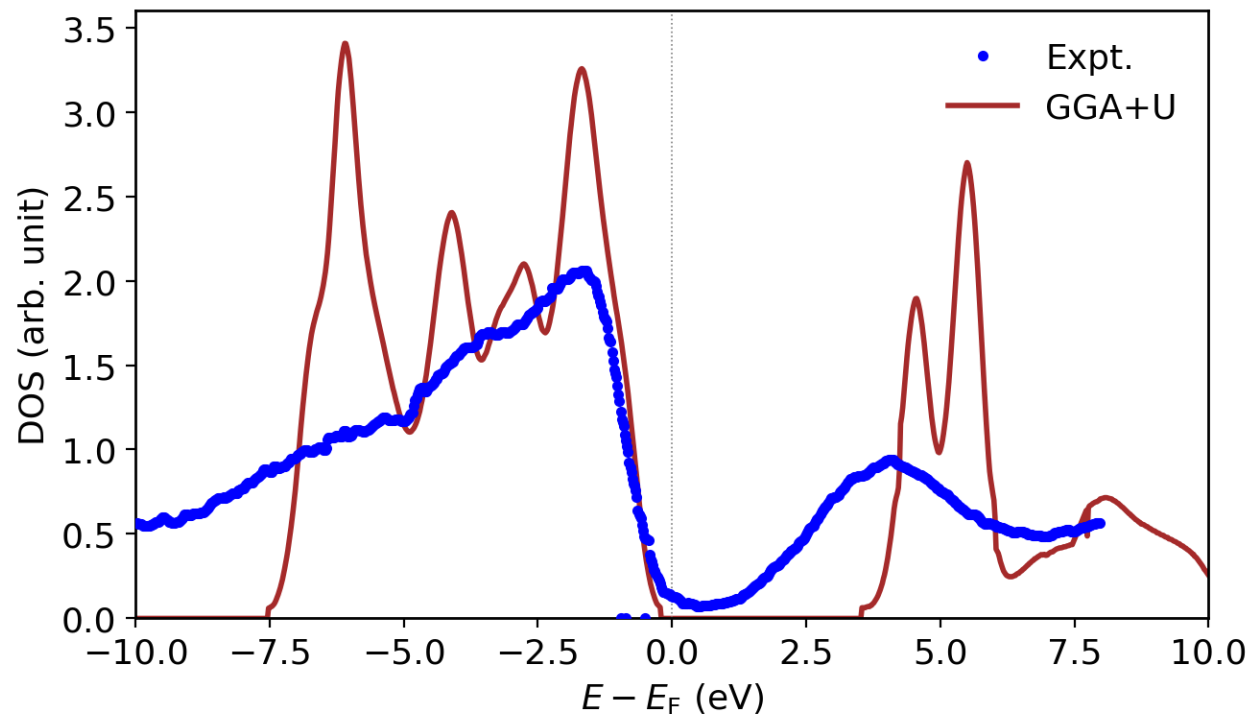
GGA+U
?

eDMFT
?



Cobalt(II) oxide
rocksalt structure
antiferromagnetic (AFM II) below 289 K

GGA SAYS METAL. EXPERIMENT SAYS INSULATOR.



Does the method open a gap at E_F ?

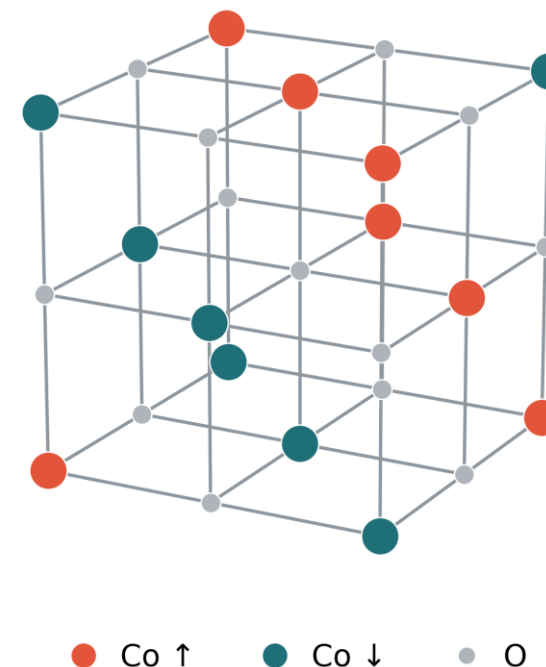
GGA
X metal

mBJ
X metal

B3LYP
✓ gap

GGA+U
✓ gap

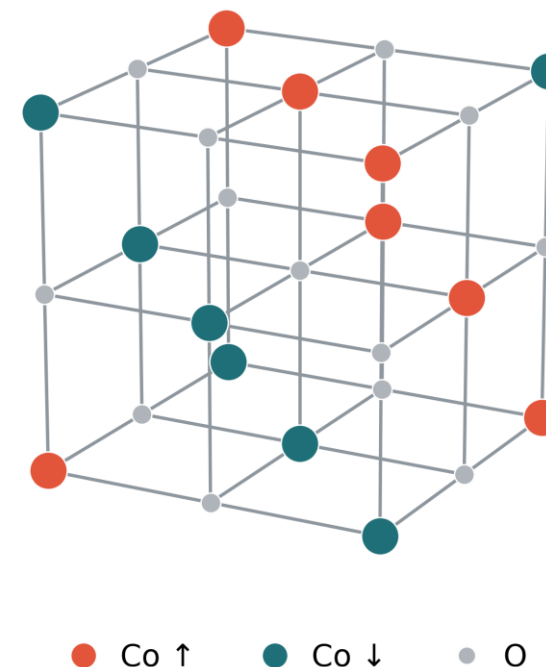
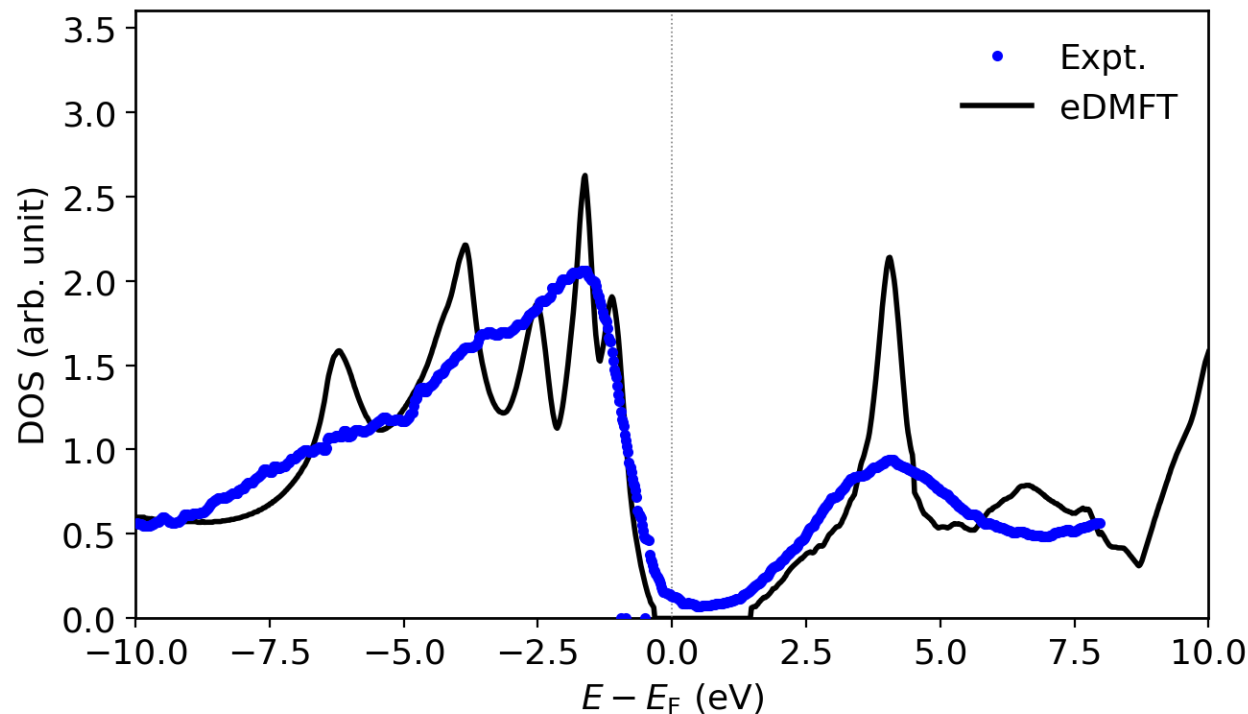
eDMFT
?



Cobalt(II) oxide
rocksalt structure
antiferromagnetic (AFM II) below 289 K

Data digitized from Fig. 1d of S. Mandal, K. Haule, K. M. Rabe, D. Vanderbilt, *npj Comput. Mater.* 5, 115 (2019), CC BY 4.0: DOS of AFM CoO, dots: PES/IPES. Structure: rocksalt, $a = 4.254 \text{ \AA}$, AFM II.

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WHEN IS DFT ENOUGH?

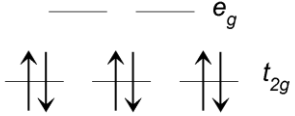
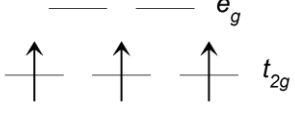
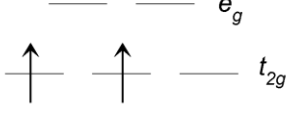
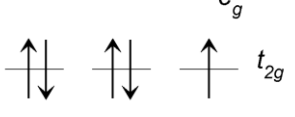
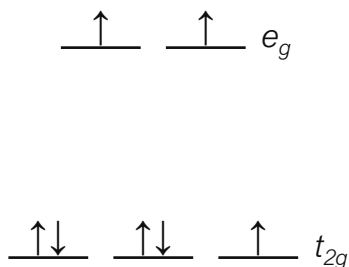
a) Ti^{4+} ($3d^0$) 	Favorable No 3d electrons: nothing for a one-electron picture to miss.
b) Fe^{2+} LS ($3d^6$) 	Acceptable t_{2g} full, only the empty e_g is probed; multiplet effects weak.
c) Cr^{3+} ($3d^3$) 	Acceptable, spin-polarised Spin $\uparrow$ sees only empty e_g, like (b). Spin $\downarrow$ sees an empty shell, like (a).
d) V^{3+} ($3d^2$) 	Critical Spin $\uparrow$ t_{2g} partly filled: occupied and empty t_{2g} not split,
e) Fe^{3+} LS ($3d^5$) 	Critical One t_{2g} hole in spin $\downarrow$: E_F sits inside the Fe 3dxz peak.

Fig. 1 from D. Cabaret, A. Bordage, A. Juhin, M. Arfaoui, E. Gaudry, *Phys. Chem. Chem. Phys.* 12, 5619 (2010): 3d occupation in Oh; comments summarise their §§3–4.

A CRITICAL CASE: COBALT(II) OXIDE

Co²⁺ HS
(3d⁷)



Critical

Spin $\downarrow$: two electrons in three degenerate t_{2g} orbitals, the same situation as V^{3+} (d) and low-spin Fe^{3+} (e) on the previous slide.

A single-particle picture cannot split the occupied from the empty $t_{2g}\downarrow$ states: in GGA the partly filled $t_{2g}\downarrow$ band sits at E_F , so CoO comes out metallic.

From your *homework*:

Coulomb interaction mixes $t_{2g}^5 e_g^2$ and $t_{2g}^4 e_g^3$. The t_{2g} and e_g have non-integer occupations $\Rightarrow N_{t_{2g}} \sim 4.8$ and $N_{e_g} \sim 2.2$. $\Rightarrow$ not single Slater determinant representable

Take-away

A partly filled, localised 3d shell needs more than a one-electron picture: +U, hybrids, DMFT, or a multiplet model built from DFT parameters.

Method	CoO
GGA	metal
mBJ (meta-GGA)	metal
GW ₀ @ LDA	metal
GGA+U (U = 6.88 eV)	insulator
B3LYP (hybrid)	insulator
eDMFT	insulator

Methods and results: S. Mandal, K. Haule, K. M. Rabe, D. Vanderbilt, *npj Comput. Mater.* 5, 115 (2019), Fig. 1d and text. Level scheme after D. Cabaret et al., *Phys. Chem. Chem. Phys.* 12, 5619 (2010), Fig. 1.

PART III

YOUR TURN

Hands-on: FPLO basics

Structure input with fedit · SCF run · Bands & DOS · Next session: downfolding



