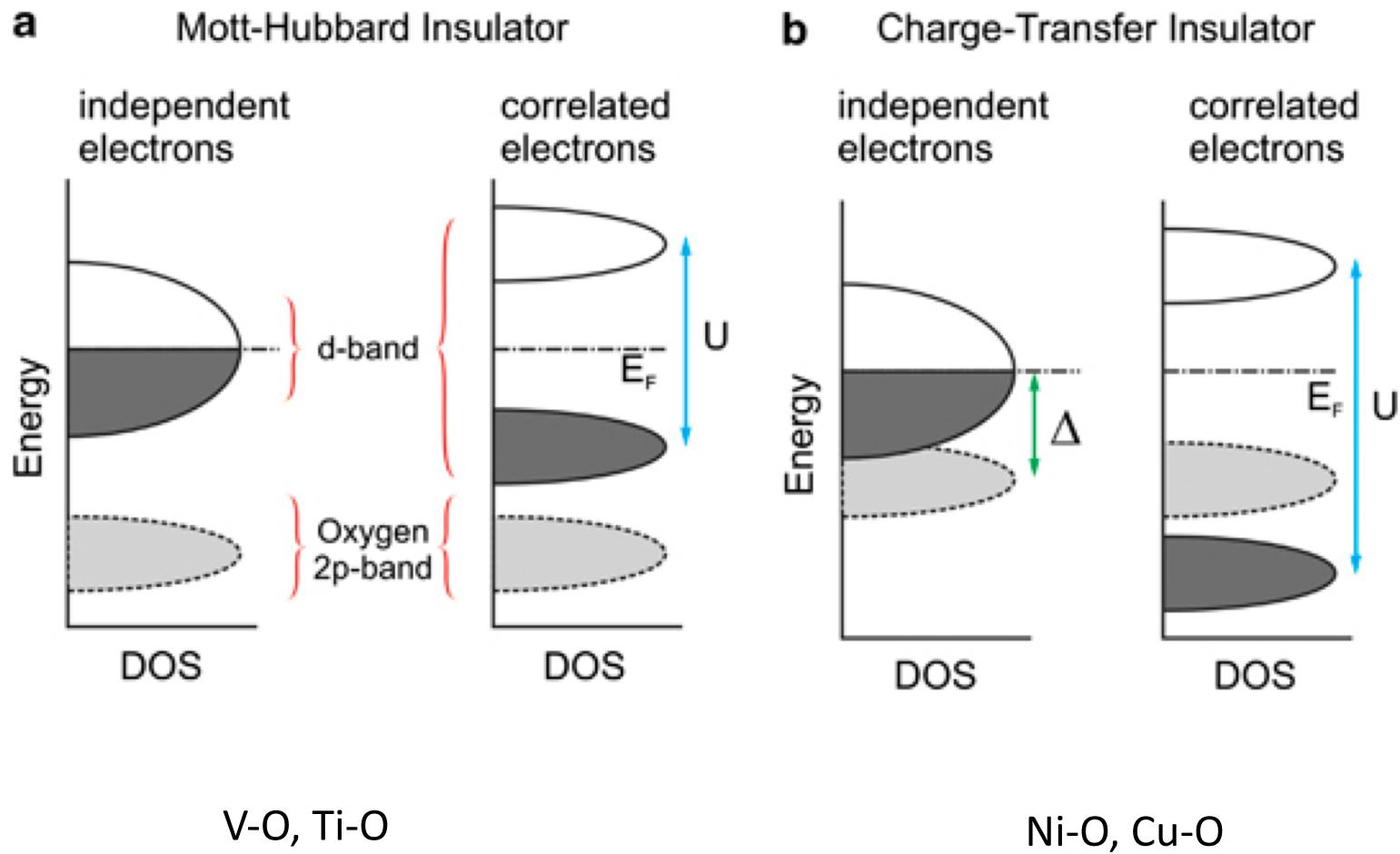
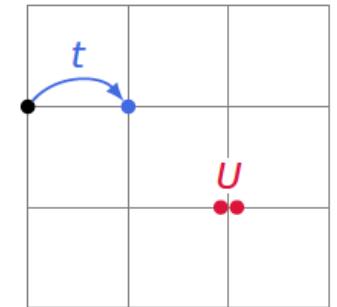


# Strong electron correlation Transition metal oxides



# DFT+U (Hubbard formalism)



Hubbard Hamiltonian

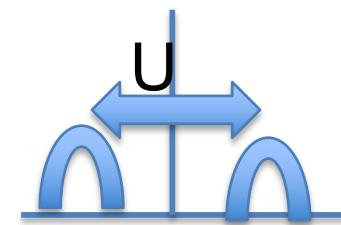
$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma}) + U \sum_{i=1}^N n_{i\uparrow} n_{i\downarrow}$$

Energy functional

$$E = E^{LDA} - U \frac{N(N-1)}{2} + \frac{1}{2} U \sum_{p \neq q} n_p n_q$$

Orbital energy

$$\epsilon_p = \frac{\partial E}{\partial n_p} = \epsilon^{LDA} + U\left(\frac{1}{2} - n_p\right) \quad \begin{array}{l} n_p=1 \rightarrow \epsilon_p=\epsilon_{LDA}-U/2 \\ n_p=0 \rightarrow \epsilon_p=\epsilon_{LDA}+U/2 \end{array}$$



## LDA+U (contd.)

### Generalized LDA+U functional

$$E^{LDA+U}[\rho^\sigma(\mathbf{r}), \{n^\sigma\}] = E^{LSDA}[\rho^\sigma(\mathbf{r})] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}]$$

### Matrix elements of screened Coulomb interactions

$$\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_k a_k(m, m', m'', m''') F^k$$

$0 \leq k \leq 2l$   $F^k$ : Slater integrals

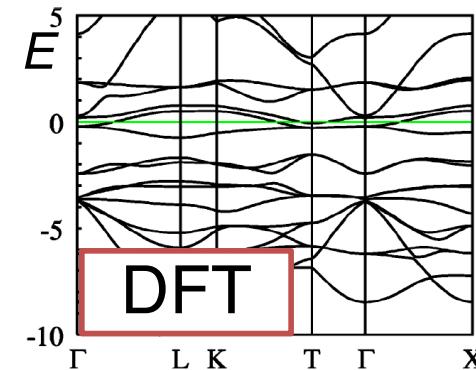
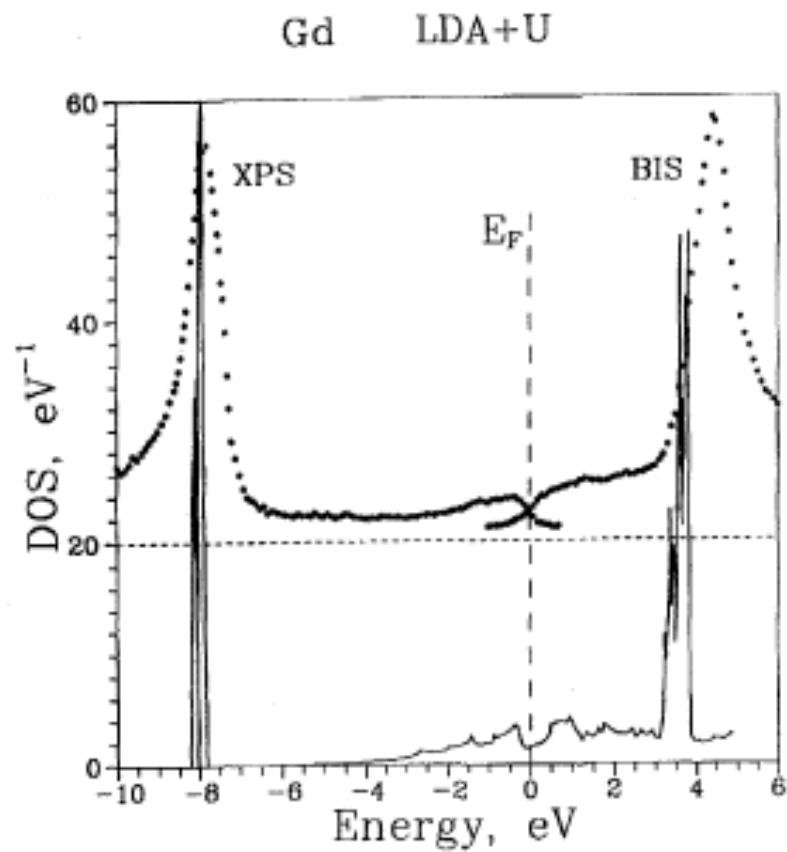
$$a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle$$

$$U = F^0, J = (F^2 + F^4)/14$$

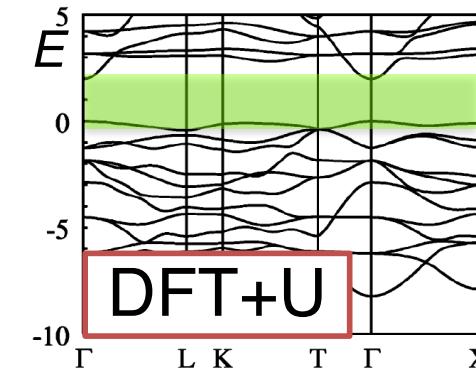
$$F^2/F^4 \sim 0.625 \quad \text{for 3d electrons}$$

$$J = (286F^2 + 195F^4 + 250F^6)/6435 \quad \text{for f electrons}$$

# Hubbard U (electronic structure)



metal



insulator

**Figure 1.** The density of states for ferromagnetic Gd metal from LDA+*U* calculation and results of BIS (bremsstrahlung isochromat spectroscopy) and XPS (x-ray photoemission spectroscopy) experiments.

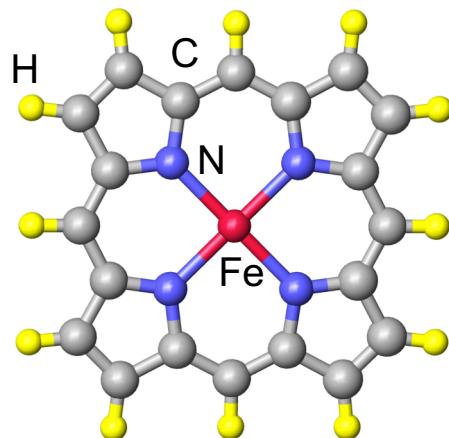
V.I. Anisimov, J. Zaanen and O.K. Andersen. *Phys. Rev. B*, (1991).  
M. Cococcioni and S. de Gironcoli. *Phys. Rev. B*, (2005).

TABLE II. Experimental (expt) and calculated (LDA +  $U$ ) spin moments ( $m$ , in  $\mu_B$ ) and energy gaps ( $E$ , in eV) of the late- $3d$ -transition-metal monoxides. For comparison, we also show these quantities as calculated from LSDA (Ref. 1).

	$E_{\text{LSD}}$	$E_{\text{LSD}+U}$	$E_{\text{expt}}$	$m_{\text{LSD}}$	$m_{\text{LSD}+U}$	$m_{\text{expt}}$
CaCuO <sub>2</sub>	0.0	2.1	1.5 <sup>a</sup>	0.0	0.66	0.51 <sup>b</sup>
CuO	0.0	1.9	1.4 <sup>c</sup>	0.0	0.74	0.65 <sup>d</sup>
NiO	0.2	3.1	4.3, <sup>e</sup> 4.0 <sup>f</sup>	1.0	1.59	1.77, <sup>g</sup> 1.64, <sup>h</sup> 1.90 <sup>i</sup>
CoO	0.0	3.2	2.4 <sup>j,k</sup>	2.3	2.63 (3.60)	3.35, <sup>l</sup> 3.8 <sup>m</sup>
FeO	0.0	3.2	2.4 <sup>n</sup>	3.4	3.62 (4.59)	3.32 <sup>m</sup>
MnO	0.8	3.5	3.6–3.8 <sup>o</sup>	4.4	4.61	4.79, <sup>g</sup> 4.58 <sup>i</sup>

# Organometallics

# Iron porphyrin (FeP)

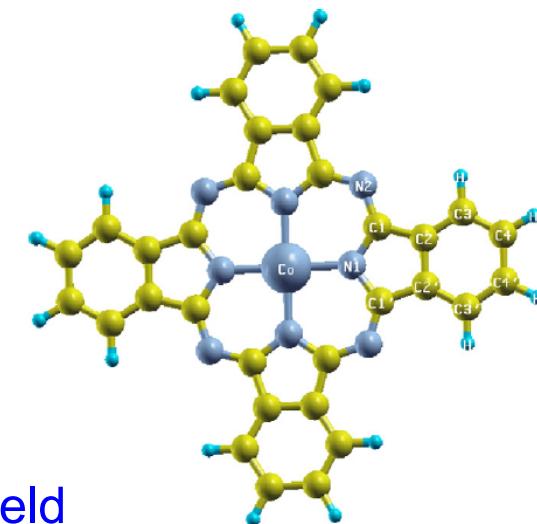


$\text{Fe}^{3+}$  ( $d^5$ )  
 $S=1/2, 3/2, 5/2$

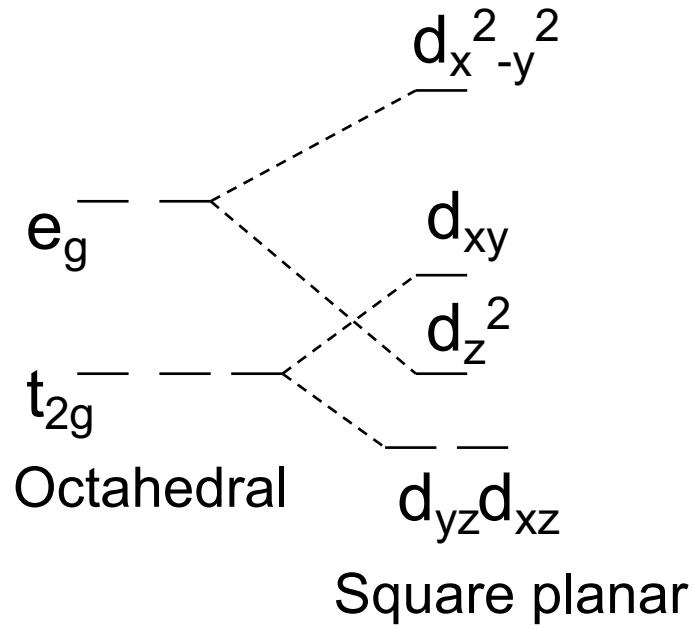
$\text{Fe}^{2+}$  ( $d^6$ )  
 $S=0, 1, 2$

- Spin crossover molecule:  
Light, temperature, electric field

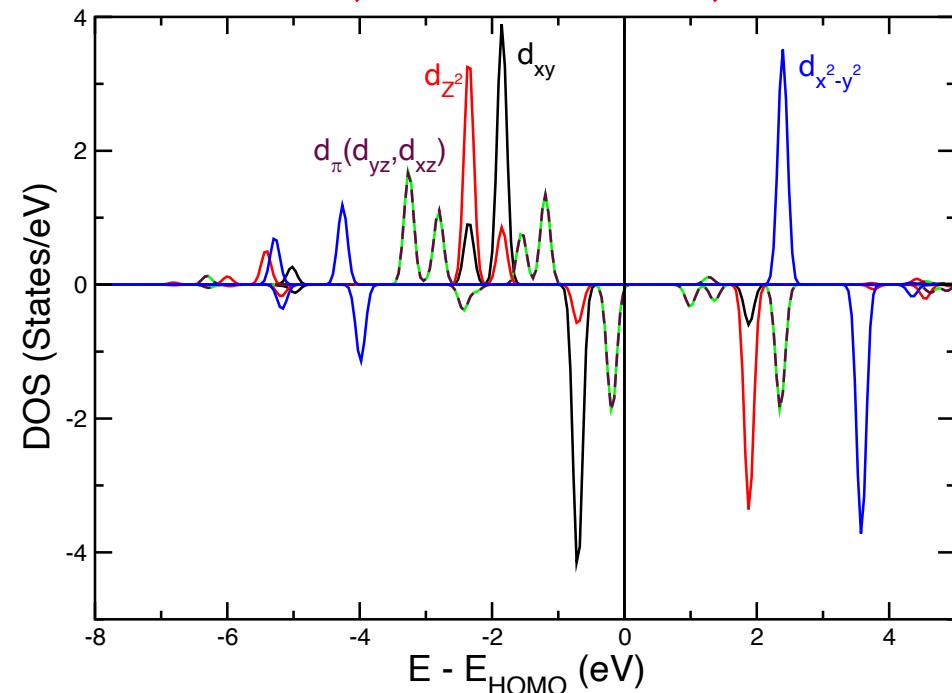
## Iron phthalocyanine (FePc)



# Crystal field splitting

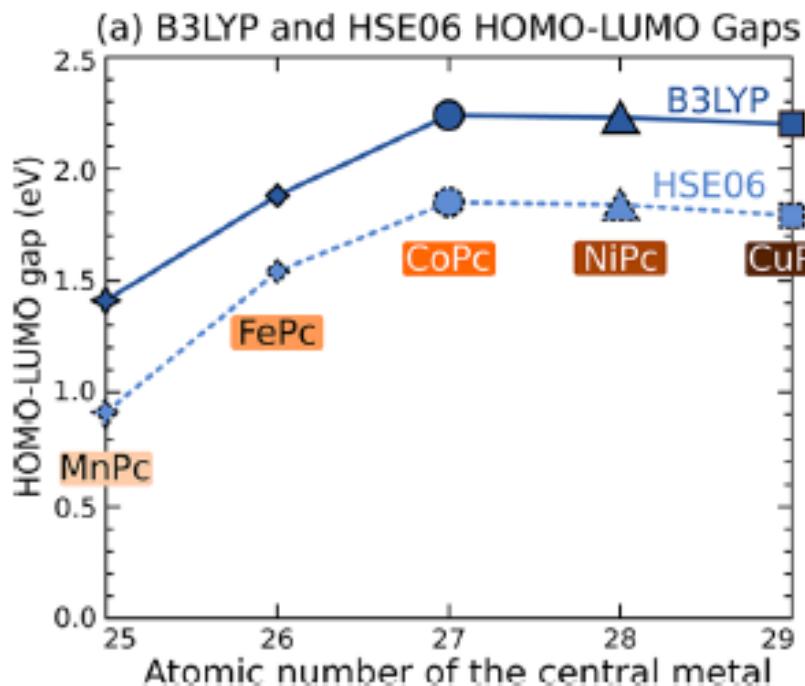


## FeP, LDA+U=4 eV, J= 1 eV

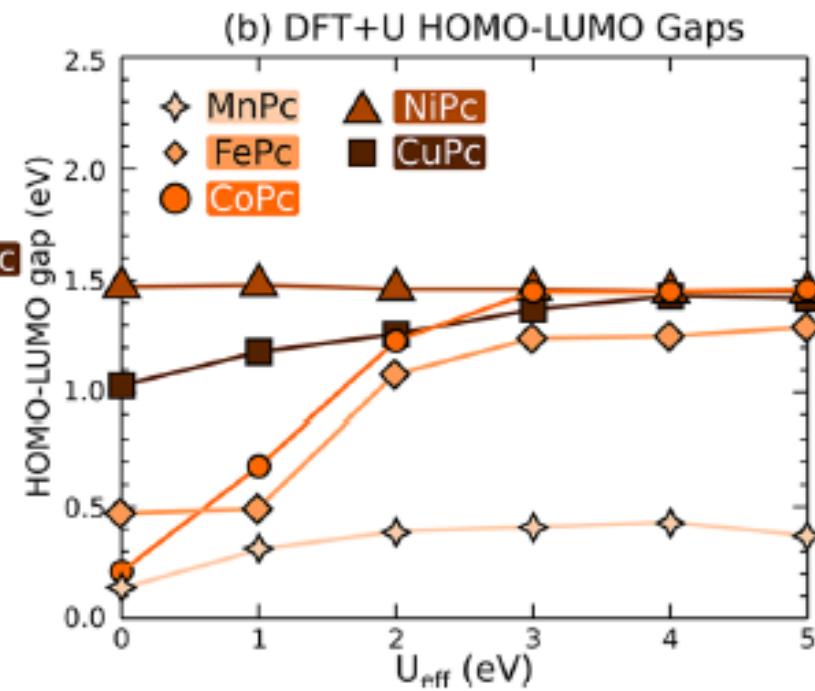


# A meaningful estimation of Hubbard U in DFT+U

B3LYP & HSE06: Hybrid functionals



Effective U ( $U_{\text{eff}}$ ) =  $U - J$



Metal moments ( $\mu_B$ )

Molecule	DFT+U	B3LYP	HSE06
MnPc	3.42( $U_{\text{eff}}=3$ ) 3.54( $U_{\text{eff}}=4$ )	3.43	3.57
FePc	2.03 ( $U_{\text{eff}}=5$ )	2.10	2.12
CoPc	1.06 ( $U_{\text{eff}}=5$ )	1.09	1.1
NiPc	0	0	0
CuPc	0.57 ( $U_{\text{eff}}=2$ ) 0.59 ( $U_{\text{eff}}=3$ )	0.57	0.59

# Calculations of U from linear response

$$E_{Hub} - E_{dc} = \sum_{I,\sigma} \frac{U_{eff}}{2} Tr[n^{I\sigma}(1 - n^{I\sigma})]$$

$$U = \frac{d^2(E^{DFT})}{d(n^I)^2}$$

$$U = \chi_0^{-1} - \chi^{-1}$$

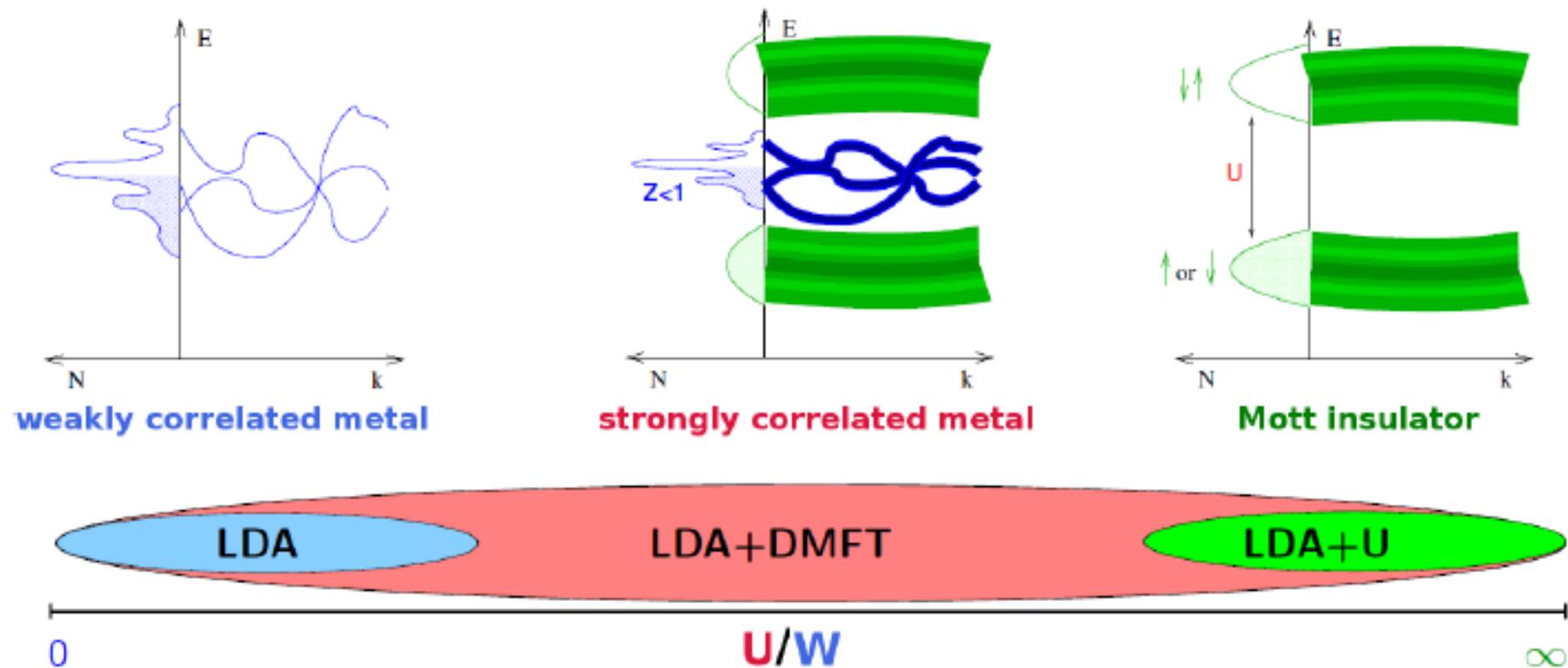
Difference in response  
matrices due to perturbation  
in occupation

## Calculated values of U (eV)

molecule	$U_0$ (eV)	$U_0^{sf}$ (eV)	$U^{\parallel}$ (eV)	$U_{eff}^{PES}$ (eV)	$ U_0 - U^{\parallel} $ (eV)
MnPc	6.2	6.3	6.1	4	0.1
FePc	4.4	4.4	4.4	4–5	0.0
CoPc	6.1	6.1	6.0	4–6	0.1
NiPc	8.2	8.2	8.4	5–7	0.2
CuPc	3.7	3.6	4.0	4–5	0.3

MnPc, FePc & CoPc: calculated U values produce good agreement with experimental spectroscopy

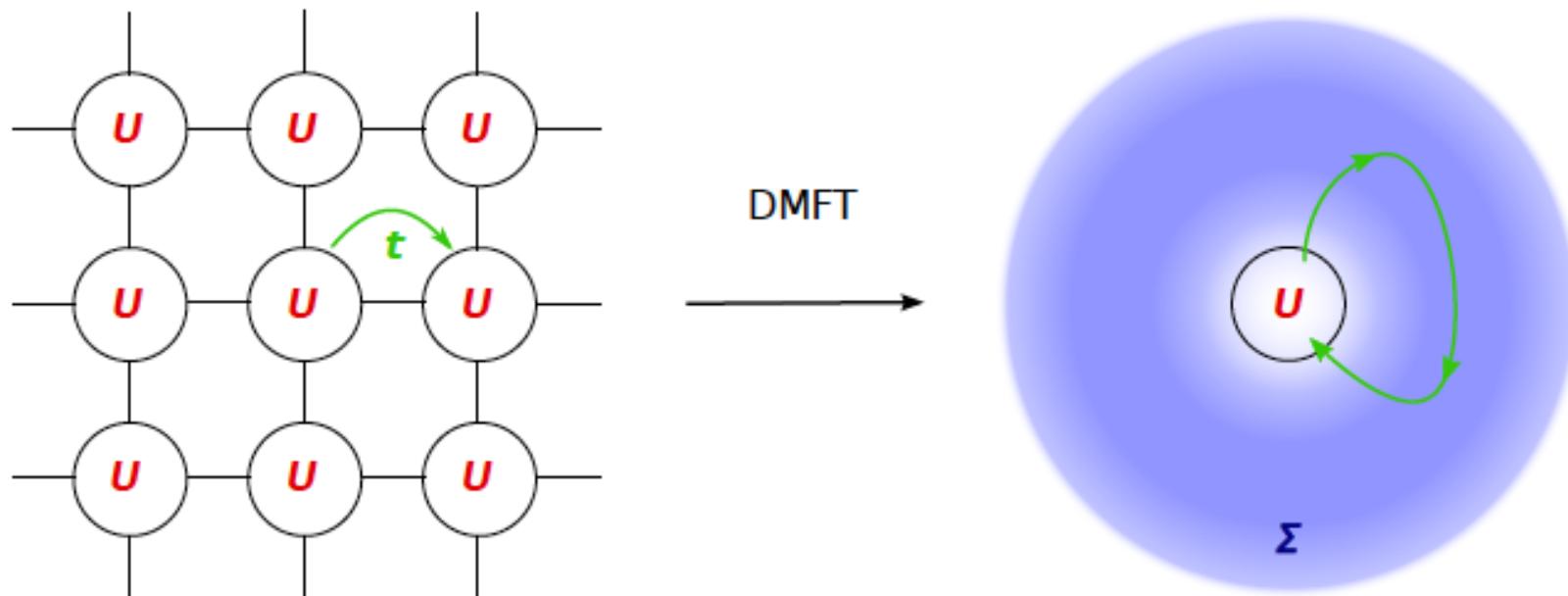
# Correlation Regimes



$U$ : screened local interaction

$W$ : bandwidth,  $\sim t$

# From lattice models to DMFT



## lattice model

- $e^-$  hop between sites
- local repulsion (screened)

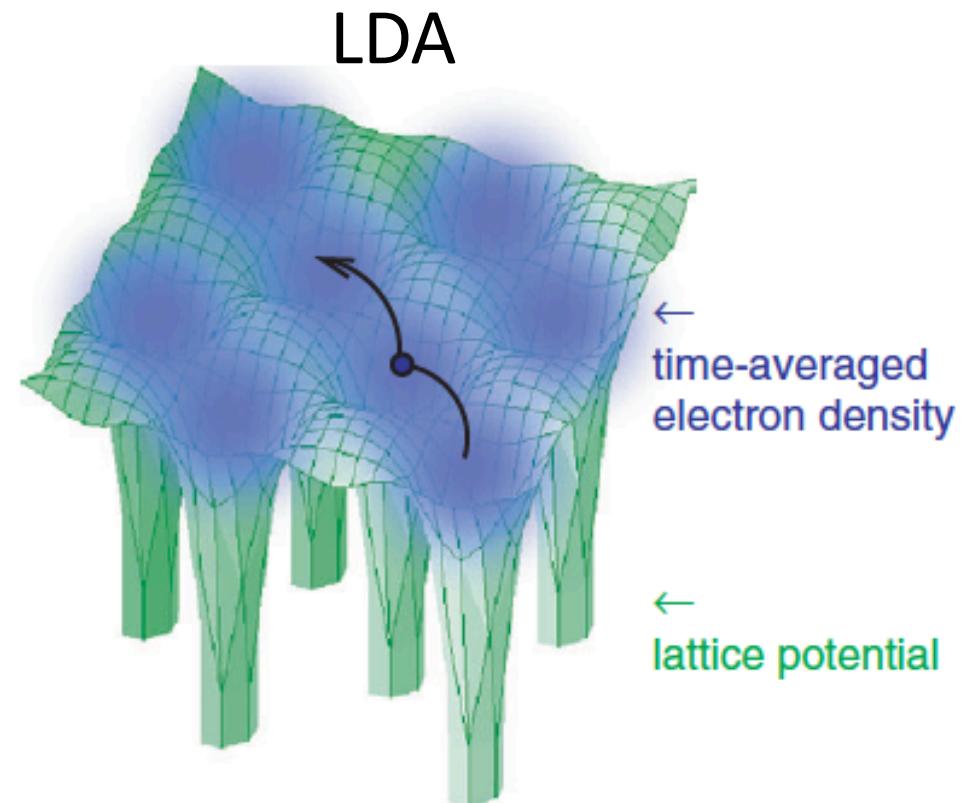
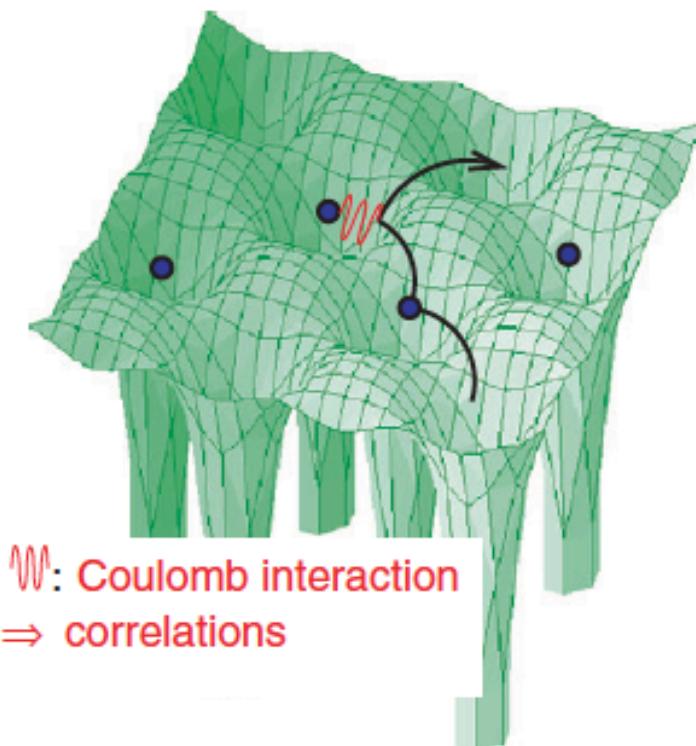
## impurity model

- one interacting site
- non-interacting “bath”

## dynamical mean-field theory

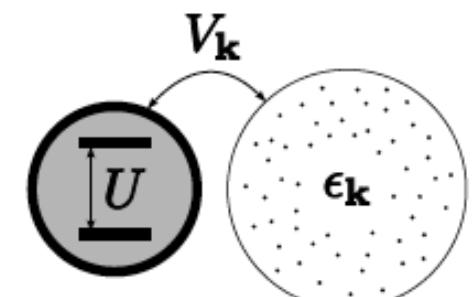
- lattice model  $\rightarrow$  impurity model
- self-energy  $\Sigma(\omega)$

Georges et al., RMP 1996,  
Kotliar & Vollhardt, Phys. Today 2004

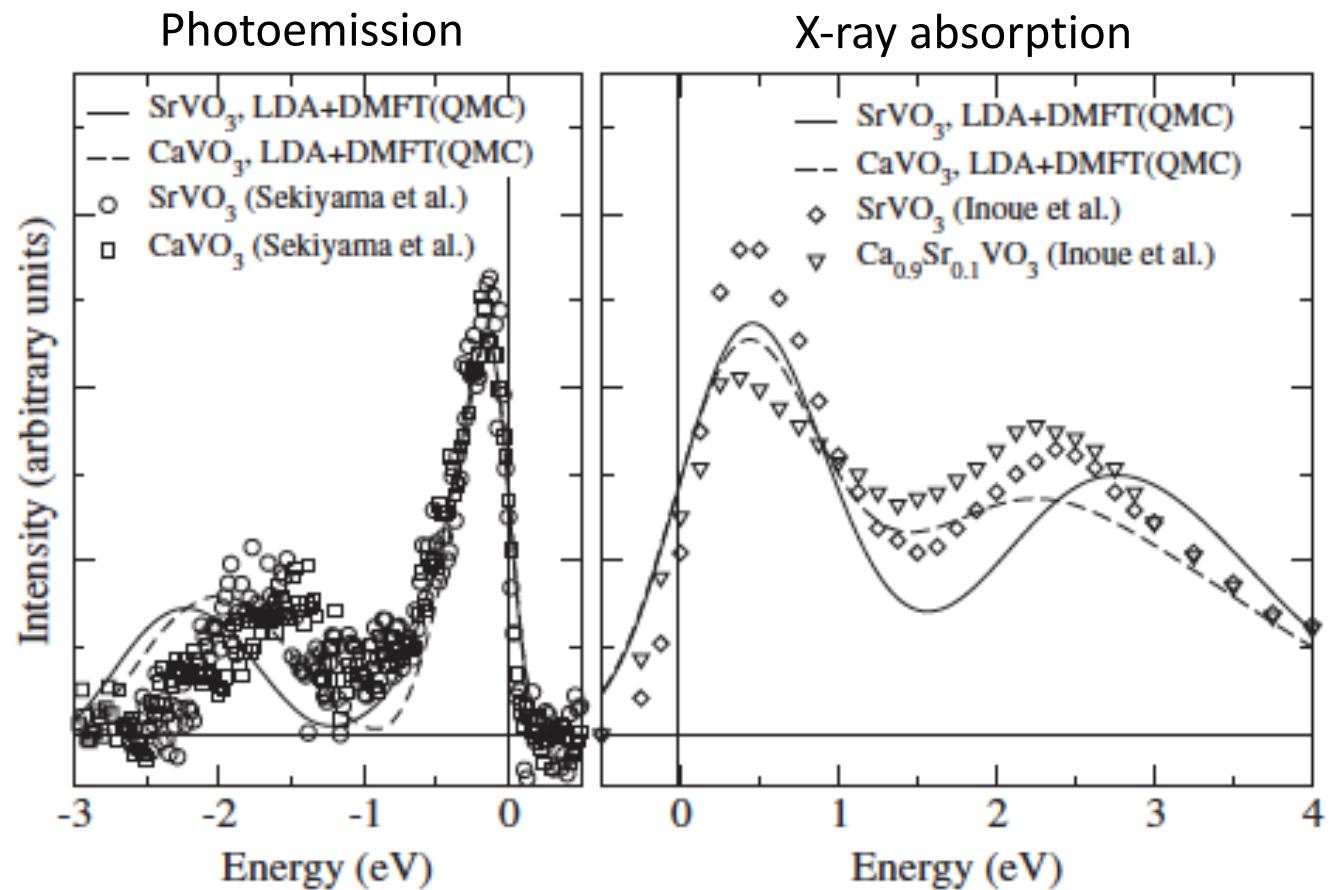
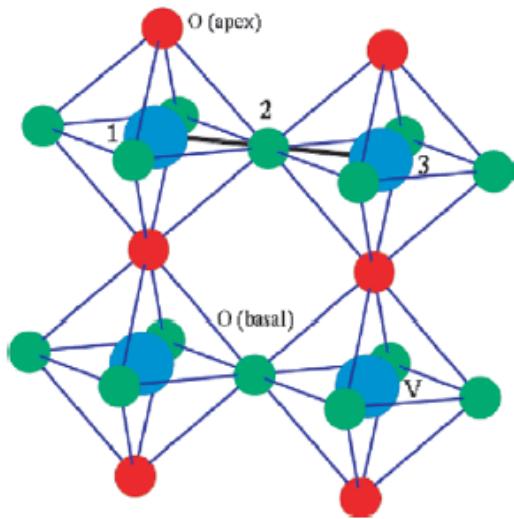


## Anderson impurity Hamiltonian

$$\begin{aligned}
 H = & \sum_{i,j} \epsilon_{ij}^d d_i^\dagger d_j + \frac{1}{2} \sum_{i,j,k,l} U_{ijkl} d_i^\dagger d_j^\dagger d_k d_l \\
 & + \sum_{ik} (V_{ik} c_k^\dagger d_i + H.c..) + \sum_k \epsilon_k c_k^\dagger c_k
 \end{aligned}$$



# DMFT: theory vs. experiment



K. Held, Advances in Physics, 56, 829 (2007)

# Multiferroic BiFeO<sub>3</sub>

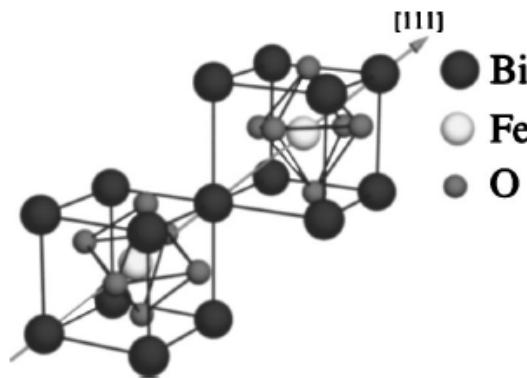


FIG. 1. Structure of  $R3c$  BiFeO<sub>3</sub>. Notice the position of the oxygen octahedra relative to the Bi framework; in the ideal cubic perovskite structure the oxygen ions would occupy the face-centered sites.

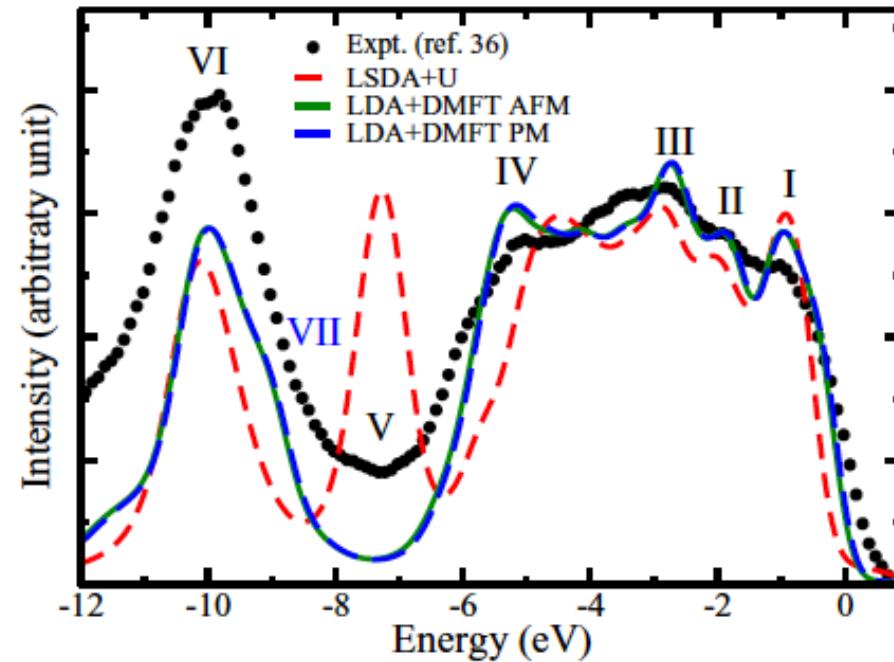


FIG. 5. A comparison between the HAXPES spectra [36] and theoretical spectra of BiFeO<sub>3</sub> computed using the LSDA+ $U$  and LDA+DMFT methods. The LDA+DMFT spectra are shown for the PM and AFM phases. The theoretical calculations are performed using  $U = 6$  eV and  $J = 0.9$  eV. The experimental data are shifted to align with the calculated valence-band edge (see text).

# Hybrid functionals

Exchange-correlation energy in DFT Kohn-Sham scheme is obtained through the coupling strength integrated exchange-correlation hole.

**Adiabatic connection formula:**  $E_{XC} = \int_0^1 d\lambda E_{ncl}^\lambda$

- $E_{ncl}^{\lambda=0}$  Exchange contribution of a Slater determinant (no correlation)
- $E_{ncl}^{\lambda=1}$  Exchange and correlation for a fully interacting system

## Hybrid functionals: combination of Hartree Fock and DFT

**B3LYP** (Becke, 3-parameter, Lee-Yang-Parr)

$$E_{XC}^{B3LYP} = E_X^{LDA} + a_0(E_X^{HF} - E_X^{LDA}) + a_x(E_X^{GGA} - E_X^{LDA}) + E_C^{LDA} + a_C(E_C^{GGA} - E_C^{LDA})$$

$a_0=0.20, a_x=0.72, a_C=0.81$

**PBEO**

$$E_{XC}^{PBE0} = \frac{1}{4}E_X^{HF} + \frac{3}{4}E_X^{PBE} + E_C^{PBE}$$

**HSE** (Heyd-Scuseria-Ernzerhof)  $a=0.25, \omega=0.2$  (HSE06)

$$E_{XC}^{HSE} = aE_X^{HF,SR}(\omega) + (1-a)E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$

(controls range of interaction)

Long ranged (LR)  $v(r) = \frac{1}{r} = \frac{\operatorname{erf}(\omega r)}{r} + \frac{\operatorname{erfc}(\omega r)}{r}$  Short ranged (SR)

# Band gaps: Theory & Experiment

