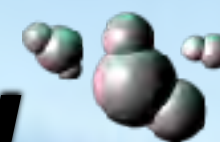


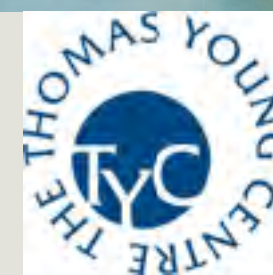
Introduction to DFT+U



Dr Cedric Weber



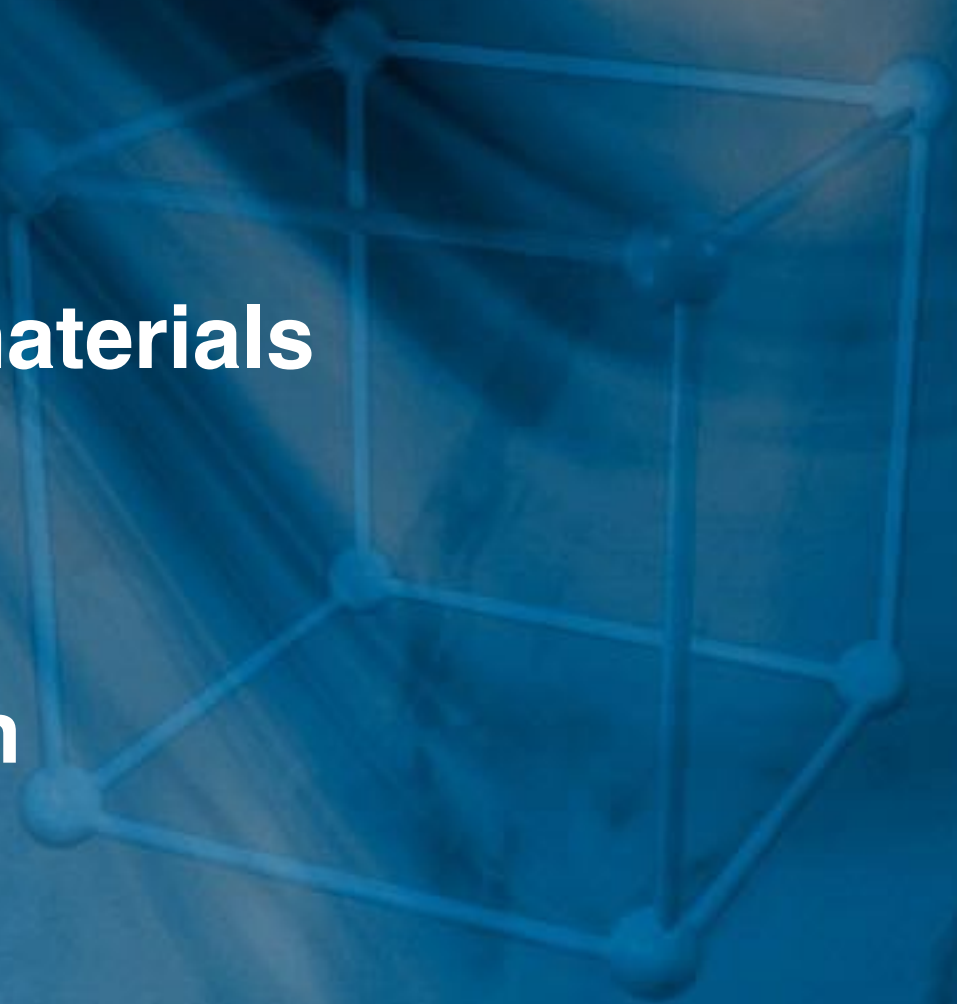
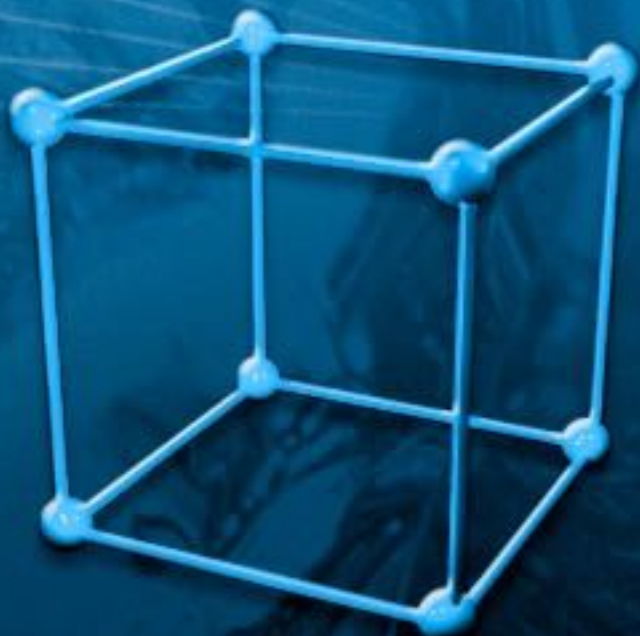
ASESMA 2018, Addis Ababa



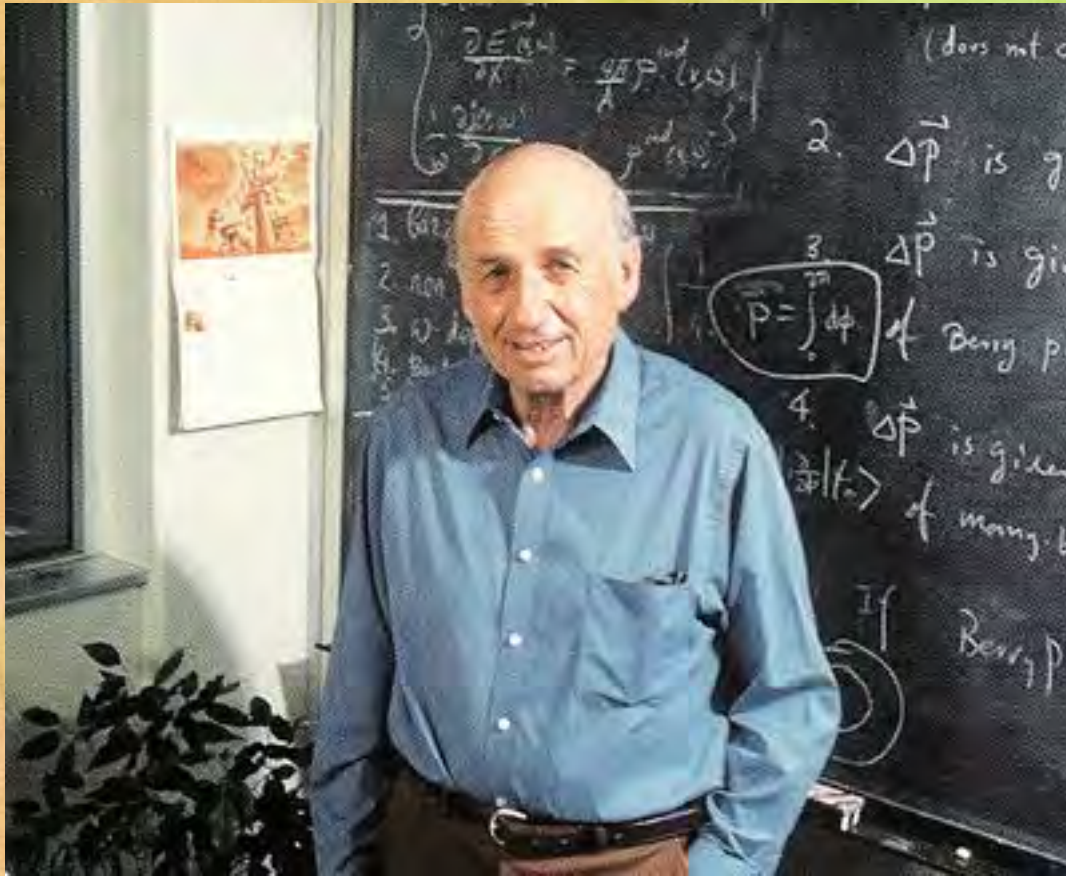
KING'S
College
LONDON

Outlines

- ❑ **Correlated materials**
- ❑ **DFT+U**
- ❑ **Haemoglobin**
- ❑ **Hemocyanin**
- ❑ **Conclusions**



Density functional theory

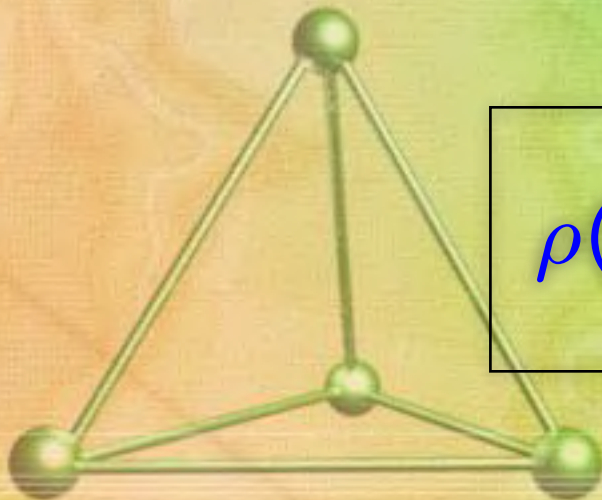


Walter Kohn : Nobel prize 1998

**Simple idea: Transform
a problem of interacting
electrons (N-body problem) to a
problem of individual electron
interacting with a medium**

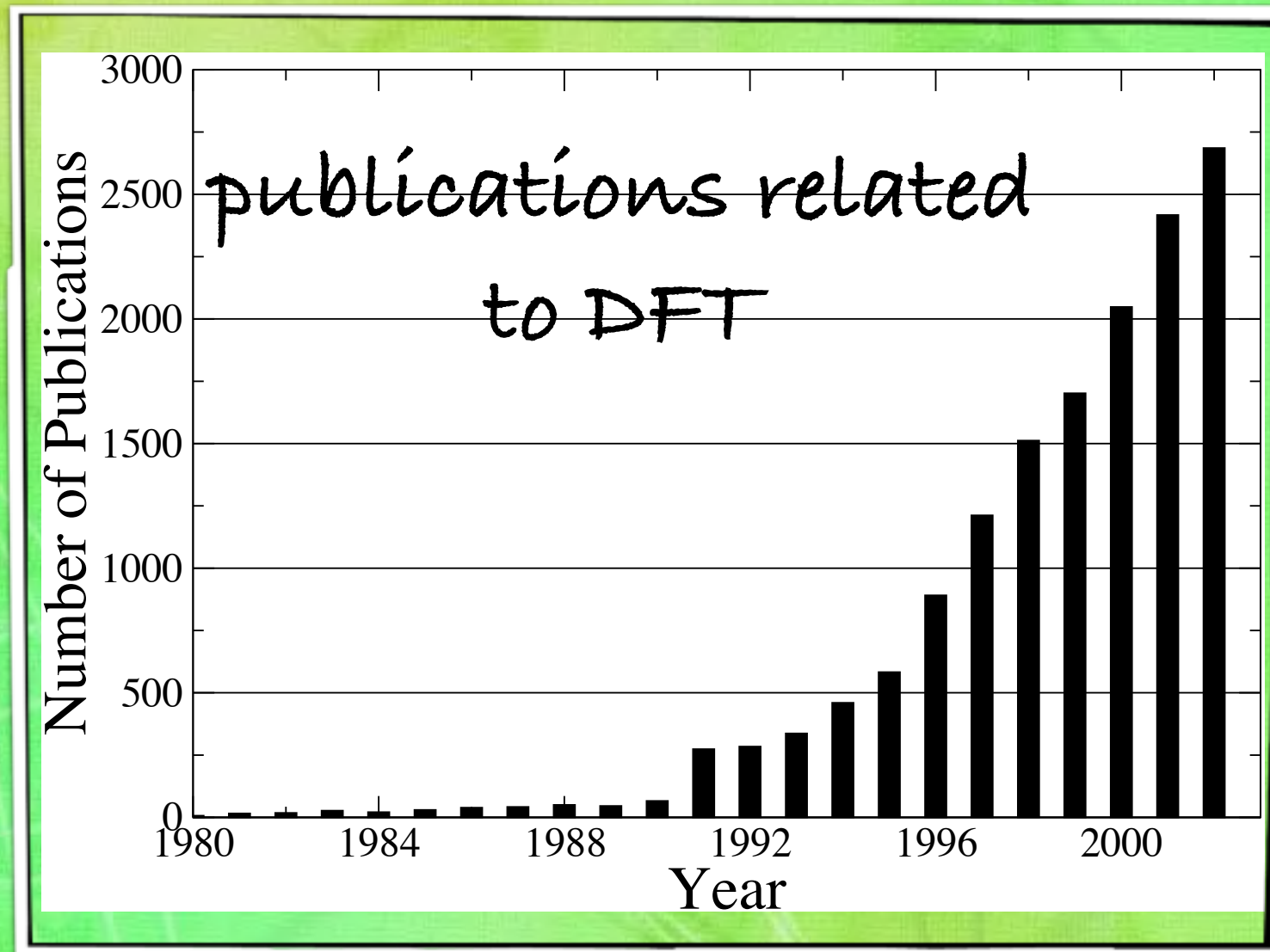
$$\Psi_0 \approx \Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \dots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \dots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \dots & \psi_N(\vec{x}_N) \end{vmatrix}$$

$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N$$



W. Kohn (Nobel Lecture):

“In the intervening decades enormous progress has been made in finding approximate solutions of Shrodinger’s wave equation for systems with several electrons [...]. DFT is an alternative approach to the theory of electronic structure, in which the electron density, rather than the many-body electron wave-function plays a central role.”



Any limiting cases where DFT needs improvement ?

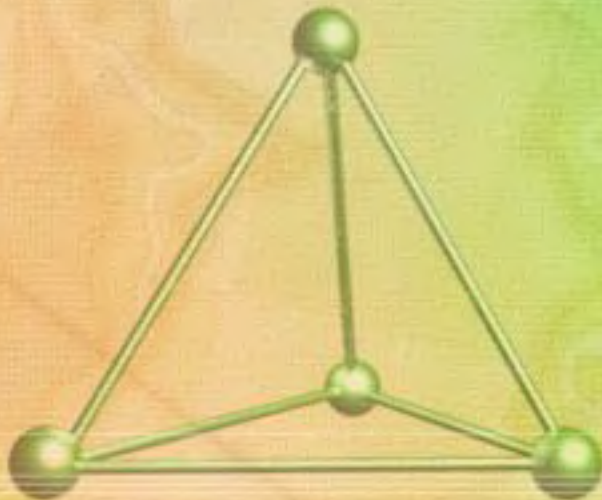
Yes! for localised d- of f- atoms where Coulomb repulsion between electrons is large! Particularly 3d and 4f are close to the nucleus for orthogonality reasons.

Why study d- or f- materials?

2) They raise fundamental questions

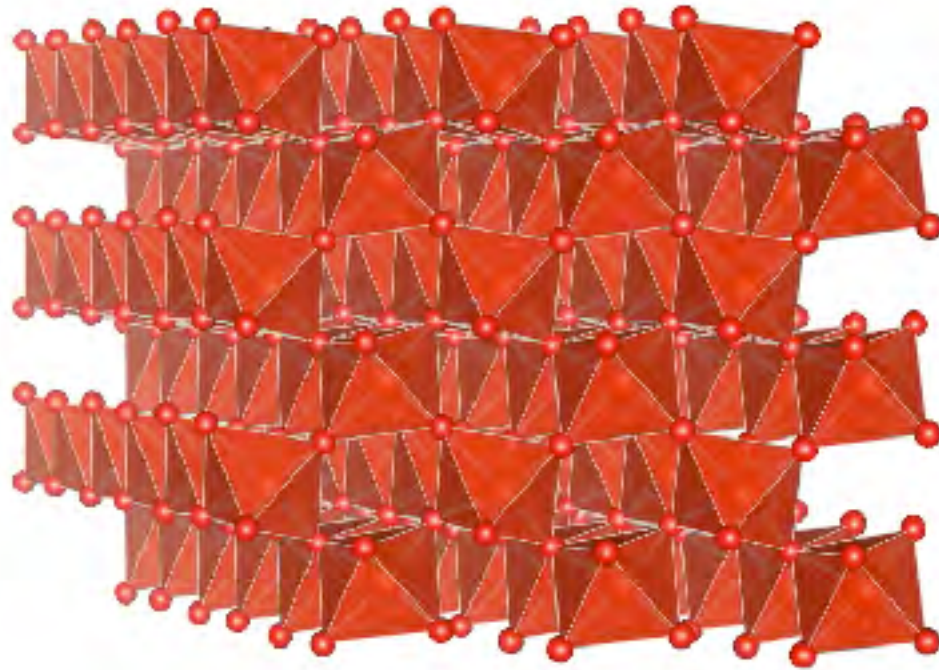
2) Applications

3) They require new formalisms, new ideas



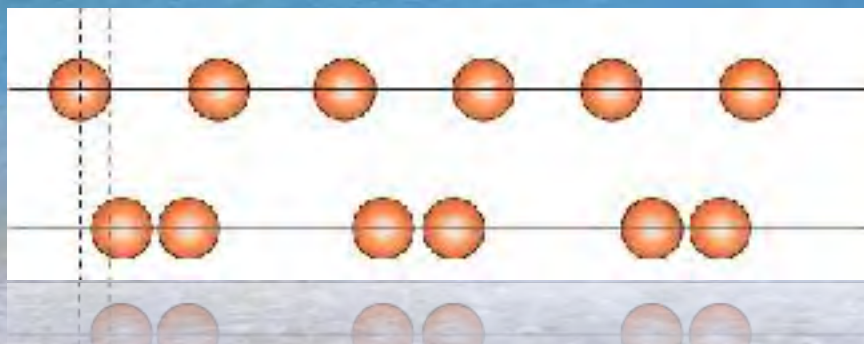
Big thing example: The intelligent window

VO₂

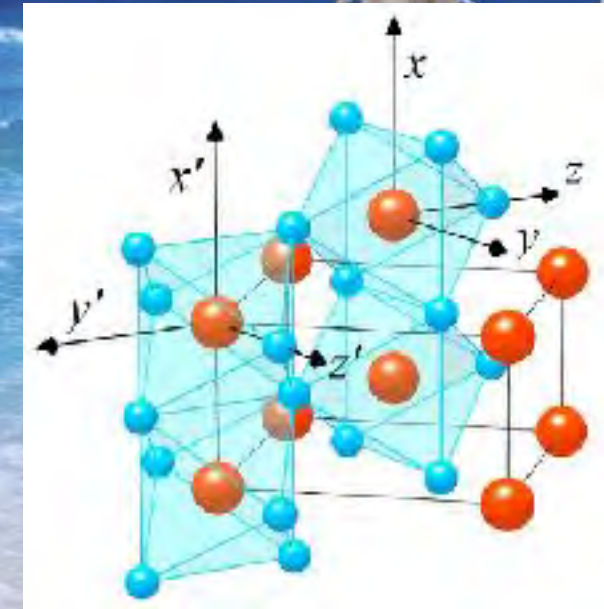


High temperature, rutile phase: ~ Metal, and reflects Infra-red

Low temperature, monoclinic structure: Insulator, and transparent in infra-red



insulator

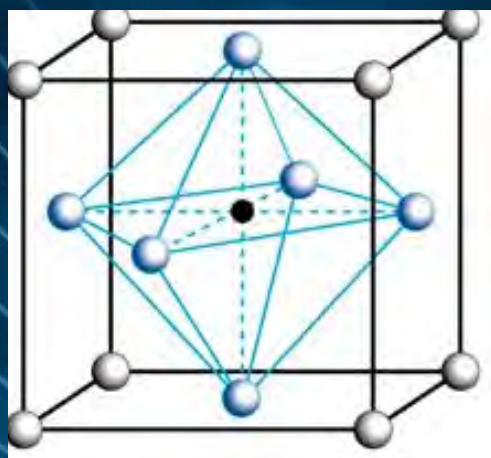


metal

★
T_c=290K

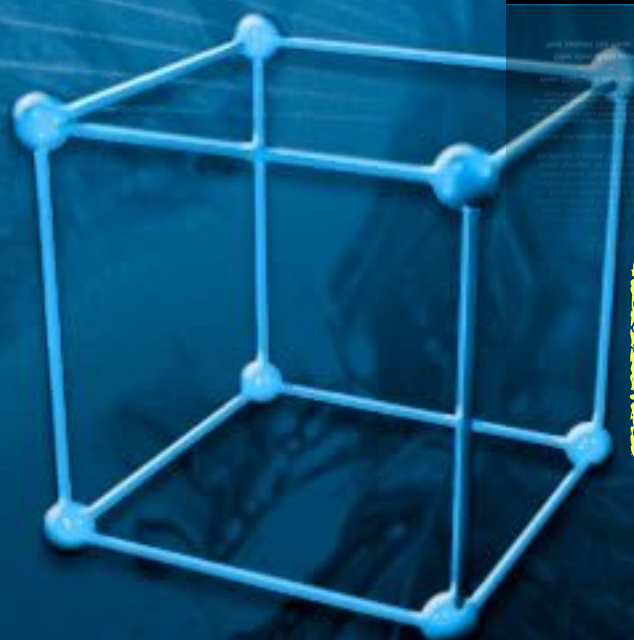
DFT extension required for transition metals

transition
metal ions



ion+oxygen cage
=transition metal
oxide

THE ELEMENTS



VO_2 Room
temperature MIT

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$
Colossal
Magnetoresistance

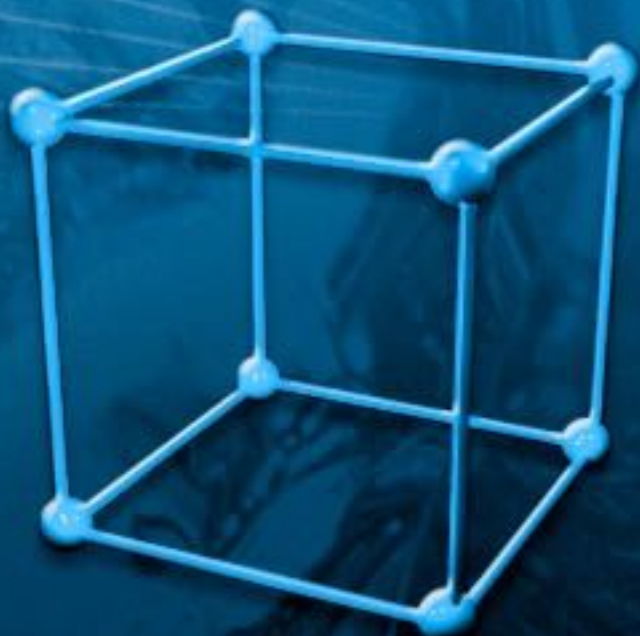
Na_xCoO_2
Thermoelectrics

$\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$
High temperature
superconductor

Extensions of DFT are required

DFT+U

Implementation



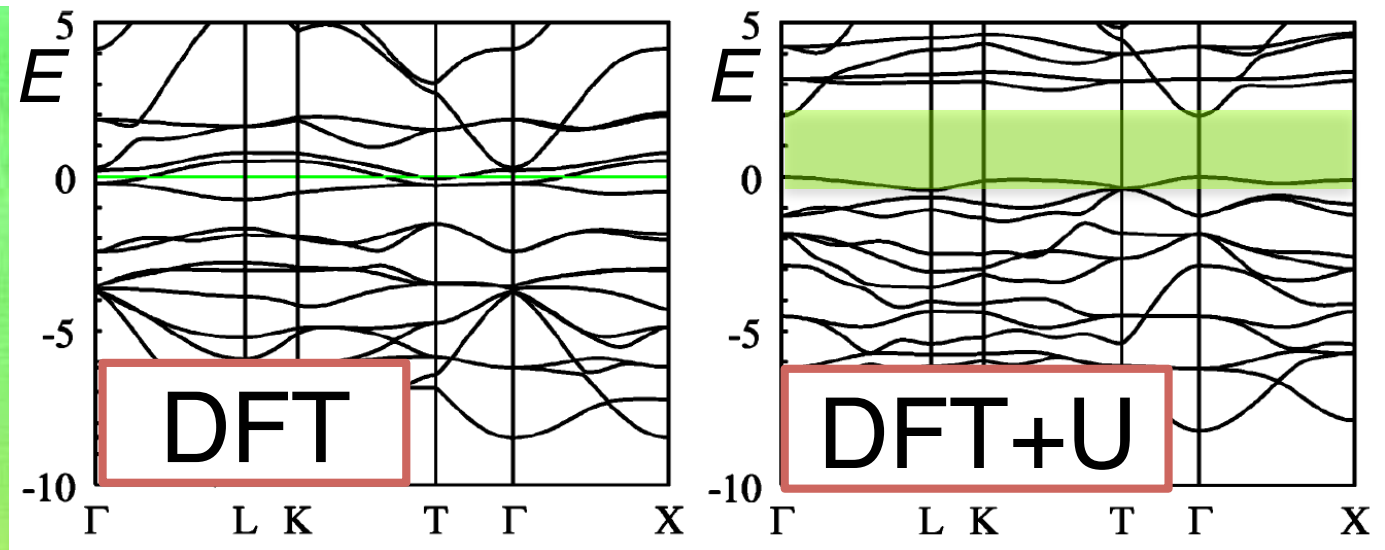
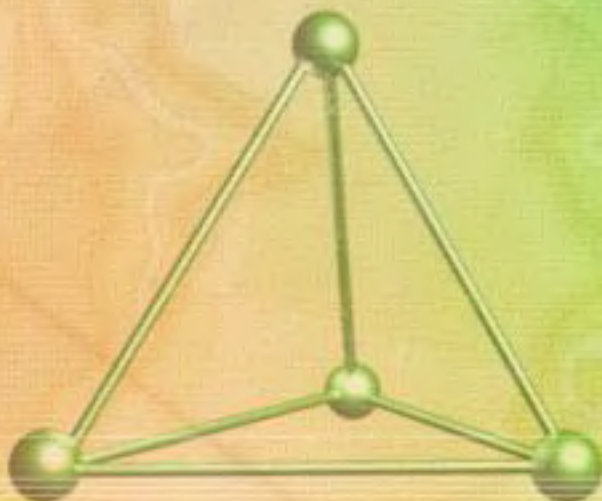
Basic Hubbard model Hamiltonian

$$H_{\text{Hub}} = t \sum_{\langle i, j \rangle, \sigma} (c_{i, \sigma}^{\dagger} c_{j, \sigma} + \text{h.c.}) + U \sum_i n_{i, \uparrow} n_{i, \downarrow}$$

*Conductor to
insulator transition*

$$E_{\text{DFT}+U} = E_{\text{DFT}} + E_U = E_{\text{DFT}} + E_{\text{Hub}} - E_{\text{dc}}$$

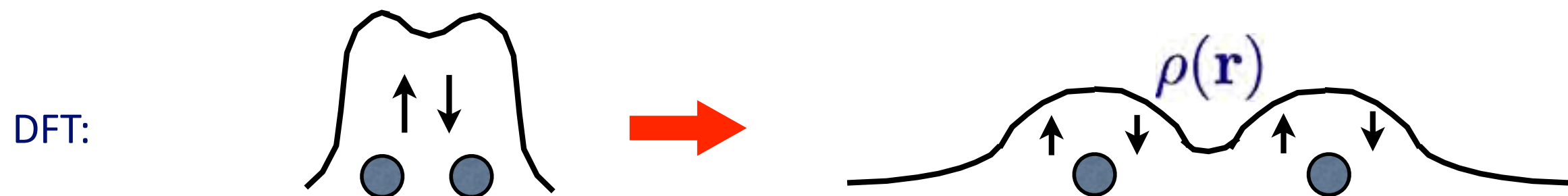
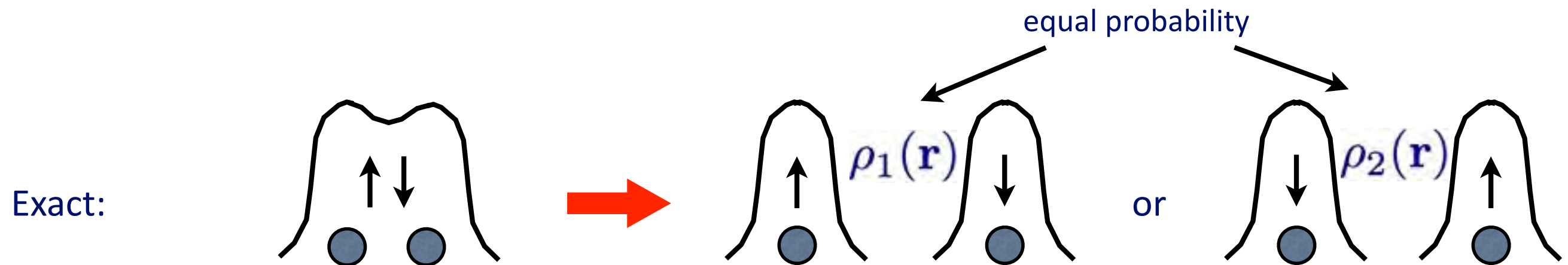
*DFT conductors to
DFT+U insulators*



conductors ↔ insulators

How good is DFT?

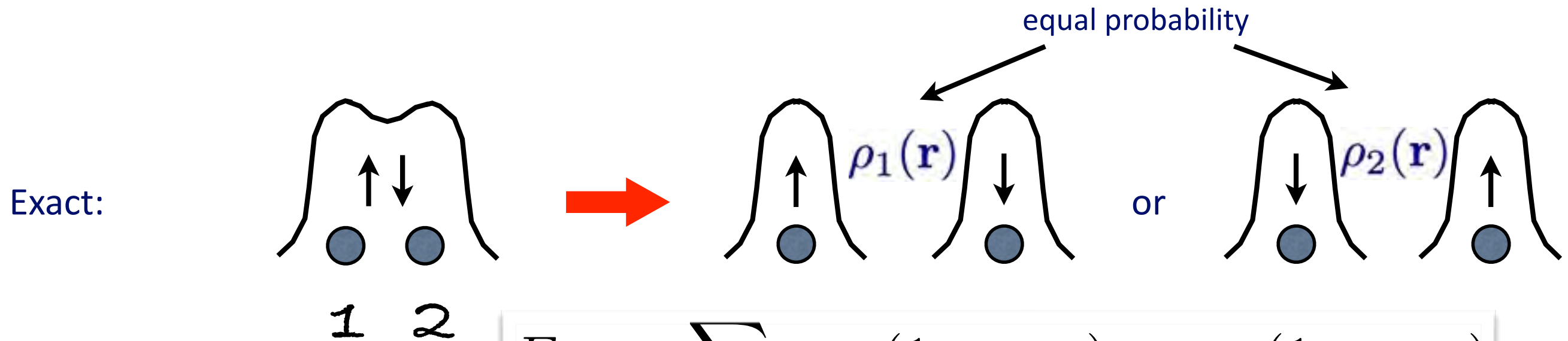
A “simple” case: the dissociation of H_2



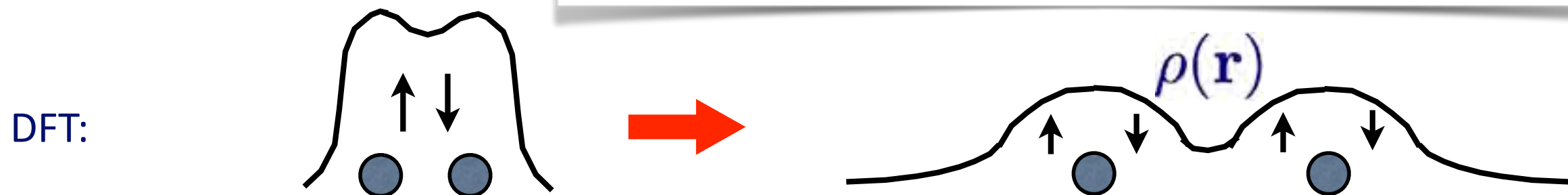
$$\rho(\mathbf{r}) = \frac{1}{2}\rho_1(\mathbf{r}) + \frac{1}{2}\rho_2(\mathbf{r})$$

How good is DFT?

A “simple” case: the dissociation of H₂

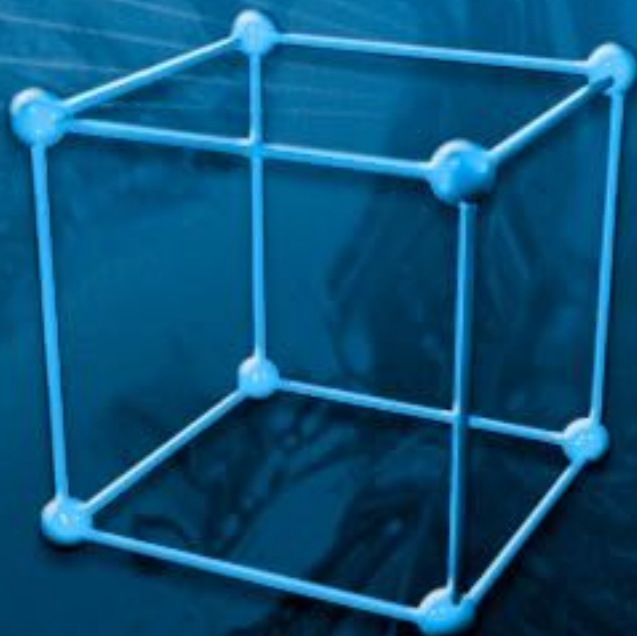
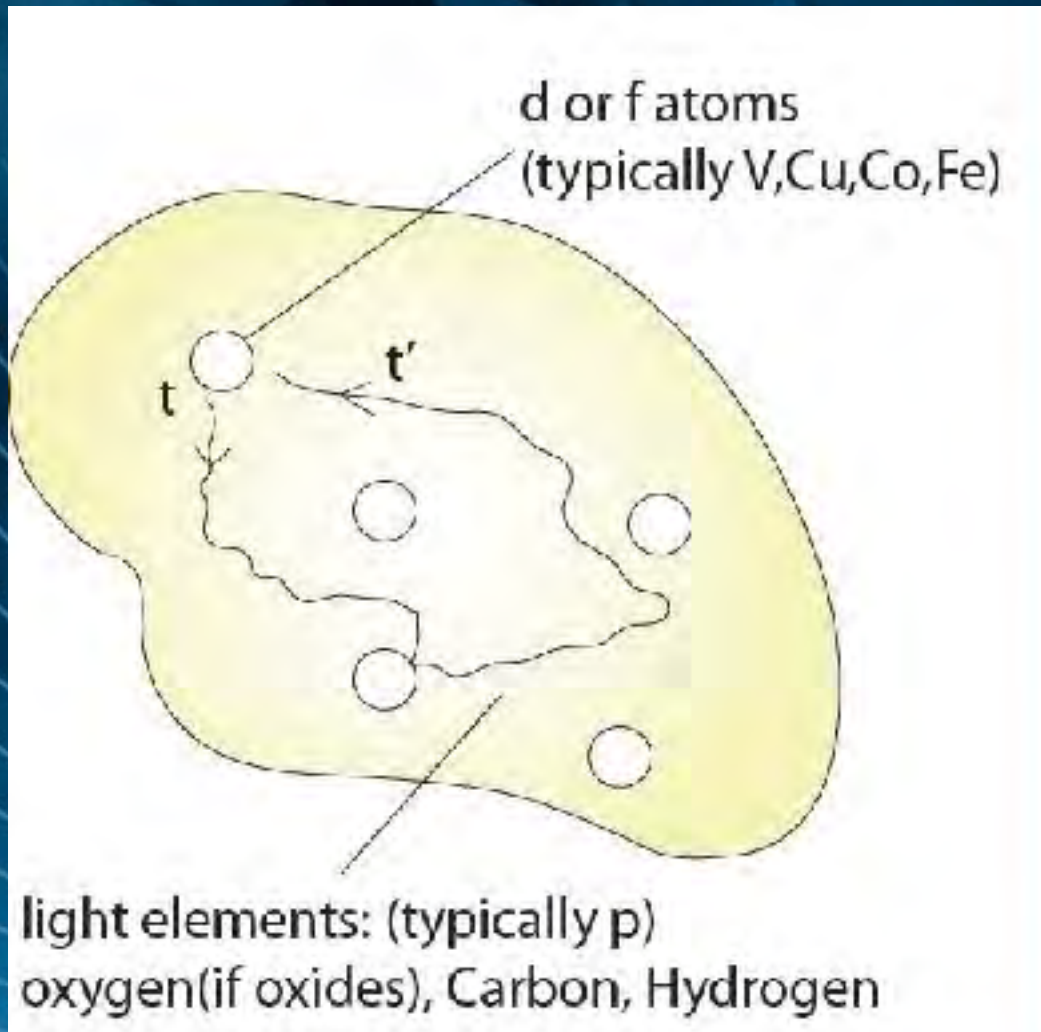


$$E_U = \sum_{I=1,2} n_{I\uparrow}(1 - n_{I\uparrow}) + n_{I\downarrow}(1 - n_{I\downarrow})$$



$$\rho(\mathbf{r}) = \frac{1}{2}\rho_1(\mathbf{r}) + \frac{1}{2}\rho_2(\mathbf{r})$$

DFT+U



12

- 1) we define 'hubbard' atoms (the d or f elements)
- 2) we extract the occupation of the hubbard atoms, by projecting the total density $n(r)$ on the d atomic orbitals, we obtain (α is the d orbital index):

$$n_{\alpha}^I$$

- 3) we add a correction to the DFT energy:

$$E_U = \frac{U}{2} \sum_{I, \alpha \sigma} n_{\alpha \sigma}^I (1 - n_{\alpha \sigma}^I)$$

DFT potentials

We obtain the orbital eigenvalue by taking the derivative of the total energy with respect to the occupation of the orbital:

$$\epsilon_i = \frac{\delta E^{\text{LDA}+U}}{\delta n_i^\sigma}$$

$$\epsilon_i = \frac{\delta E^{\text{LDA}+U}}{\delta n_i^\sigma} = \epsilon_i^{\text{LDA}} + \frac{\delta}{\delta n_i^\sigma} \left(\frac{U}{2} \sum_{j\sigma'} n_j^{\sigma'} (1 - n_j^{\sigma'}) \right)$$

$$\epsilon_i = \frac{\delta E^{\text{LDA}+U}}{\delta n_i^\sigma} = \epsilon_i^{\text{LDA}} + \frac{U}{2} (-n_i^\sigma + (1 - n_i^\sigma))$$

$$\epsilon_i = \frac{\delta E^{\text{LDA}+U}}{\delta n_i^\sigma} = \epsilon_i^{\text{LDA}} + U \left(\frac{1}{2} - n_i^\sigma \right) \begin{cases} \text{occupied:} & -\frac{U}{2} \\ \text{empty:} & +\frac{U}{2} \end{cases}$$

The LDA+U potential would be:

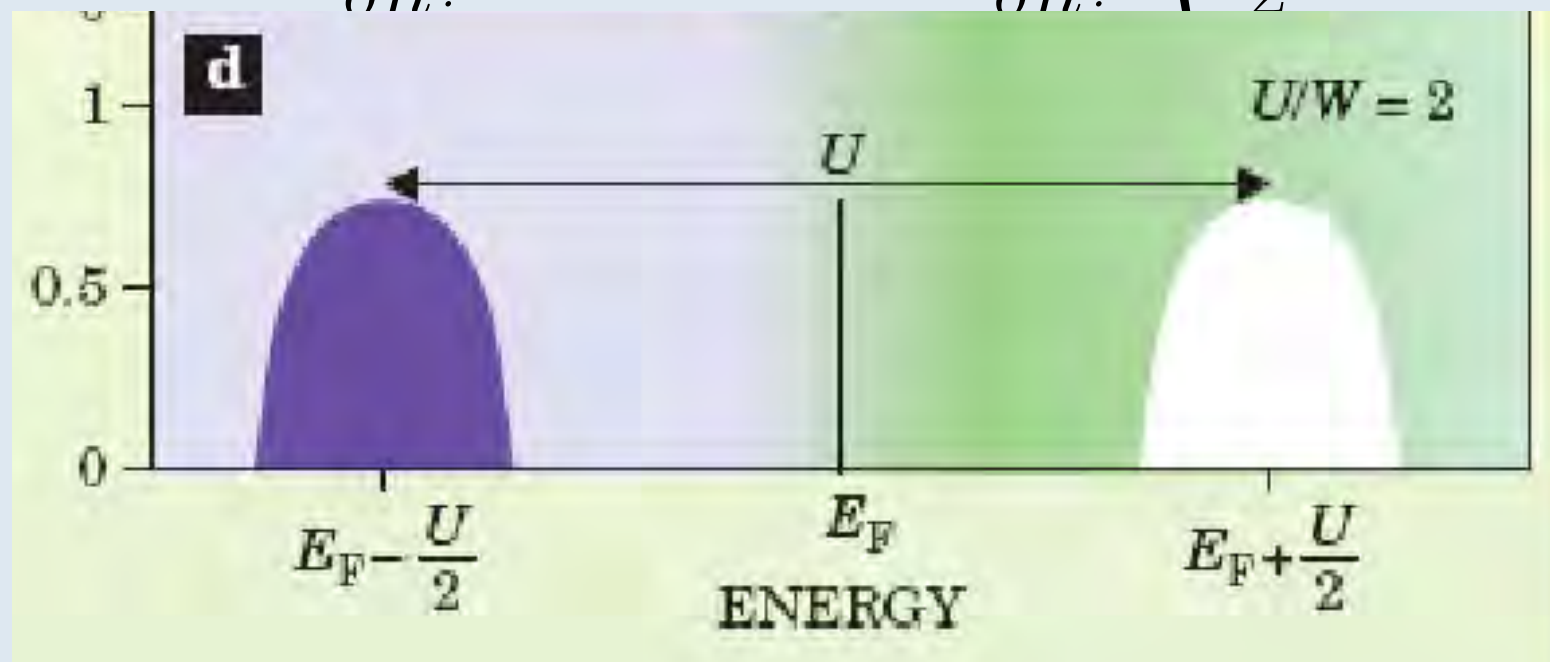
$$V^{\text{LDA}+U}(r) = V_i^{\text{LDA}} + U \left(\frac{1}{2} - n_i^\sigma \right) P_i$$

DFT potentials

We obtain the orbital eigenvalue by taking the derivative of the total energy with respect to the occupation of the orbital:

$$\epsilon_i = \frac{\delta E^{\text{LDA}+U}}{\delta n_i^\sigma}$$

$$\epsilon_i = \frac{\delta E^{\text{LDA}+U}}{\delta n_i^\sigma} = \epsilon_i^{\text{LDA}} + \frac{\delta}{\delta n_i^\sigma} \left(\frac{U}{2} \sum n_j^{\sigma'} (1 - n_j^{\sigma'}) \right)$$



$$- n_i^\sigma))$$

occupied: $-\frac{U}{2}$

empty: $+\frac{U}{2}$

The LDA+U potential would be:

$$V^{\text{LDA}+U}(r) = V_i^{\text{LDA}} + U \left(\frac{1}{2} - n_i^\sigma \right) P_i$$

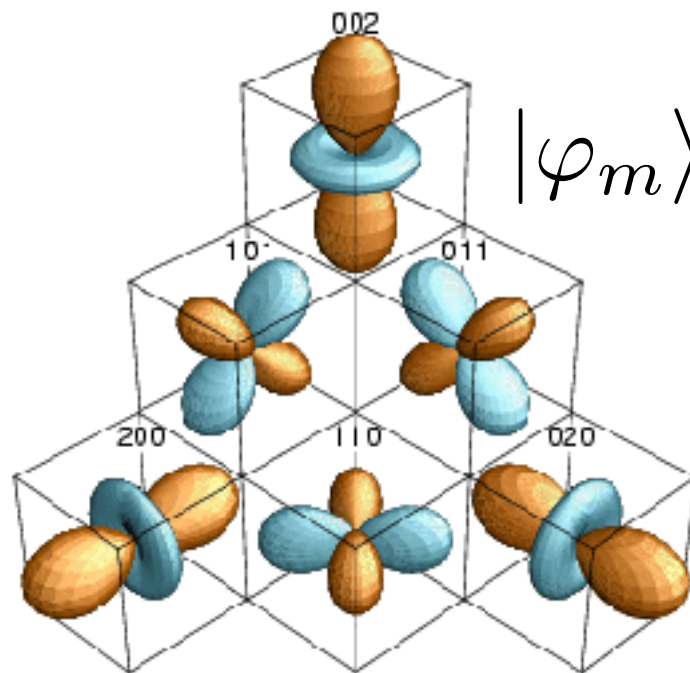
Projectors

eigenstate
occupation

Kohn-Sham
eigenstate

$$n_{mm'}^{I\sigma} = \sum_{\mathbf{k},v} f_{\mathbf{k}v}^{\sigma} \langle \psi_{\mathbf{k}v}^{\sigma} | P_{mm'}^I | \psi_{\mathbf{k}v}^{\sigma} \rangle$$

Hubbard atom
density matrix



projector:

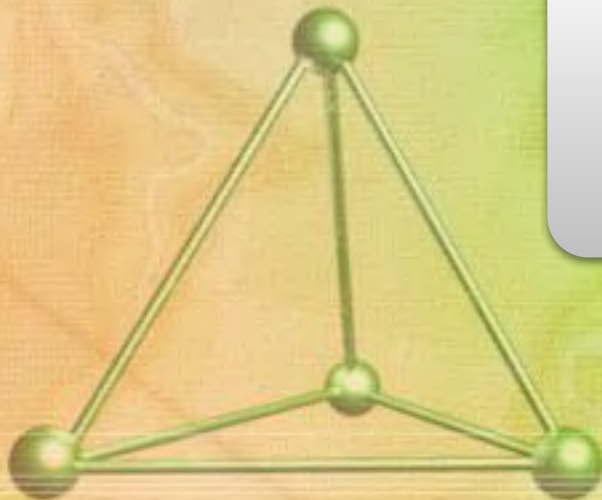
$$P_{mm'}^I = |\varphi_m^I\rangle \langle \varphi_{m'}^I|$$

What about “U”?

What is U? U is the Coulomb repulsion between electron, strong in d orbitals (these orbitals are localized, so the Coulomb repulsion is larger than in s or p orbitals).

Considering the atoms are embedded in a polarizable surrounding, U is the energy required to move an electron from one atom to another.

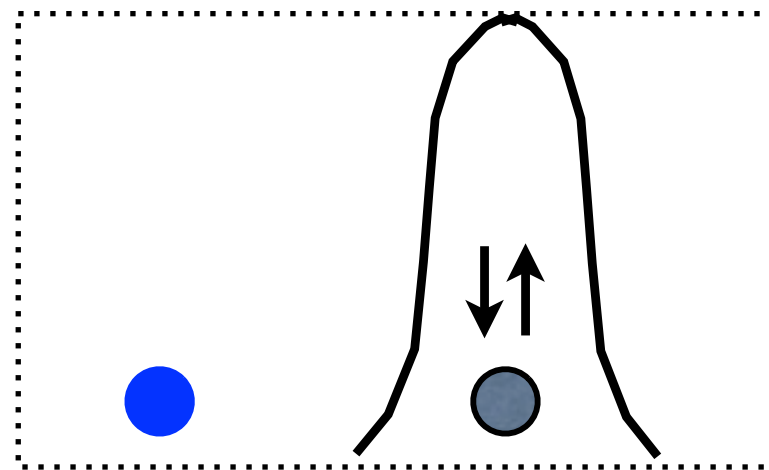
U is equal to the difference of ionization potential and electron affinity of the solid:


$$U = \left(E^{N-1} - E^N \right) - \left(E^N - E^{N+1} \right)$$

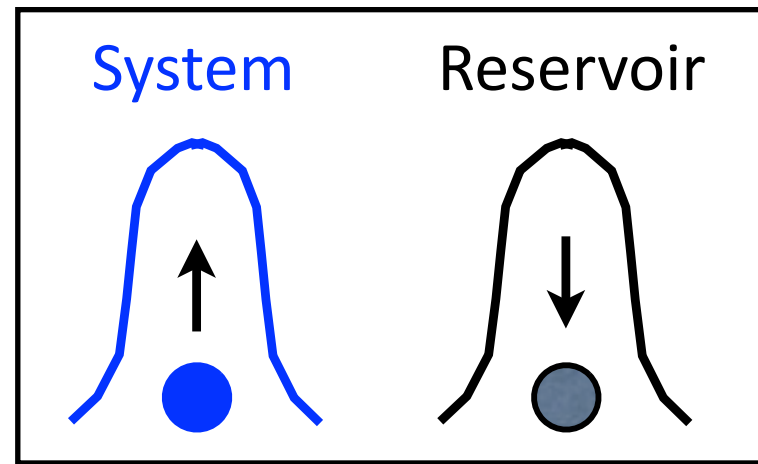
affinity

ionization energy

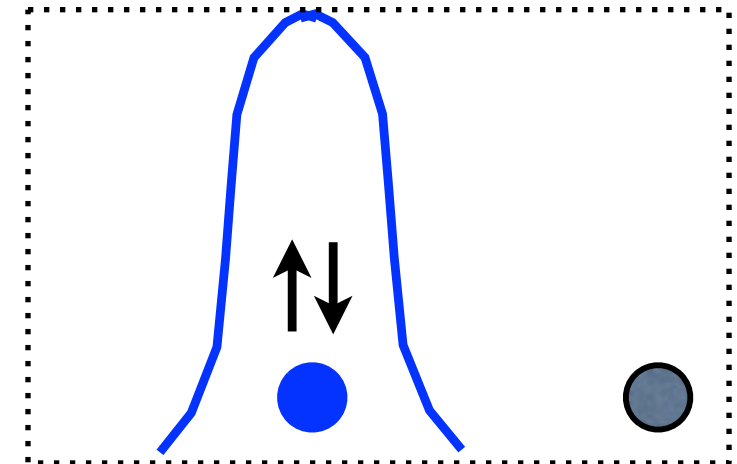
Energy linearity



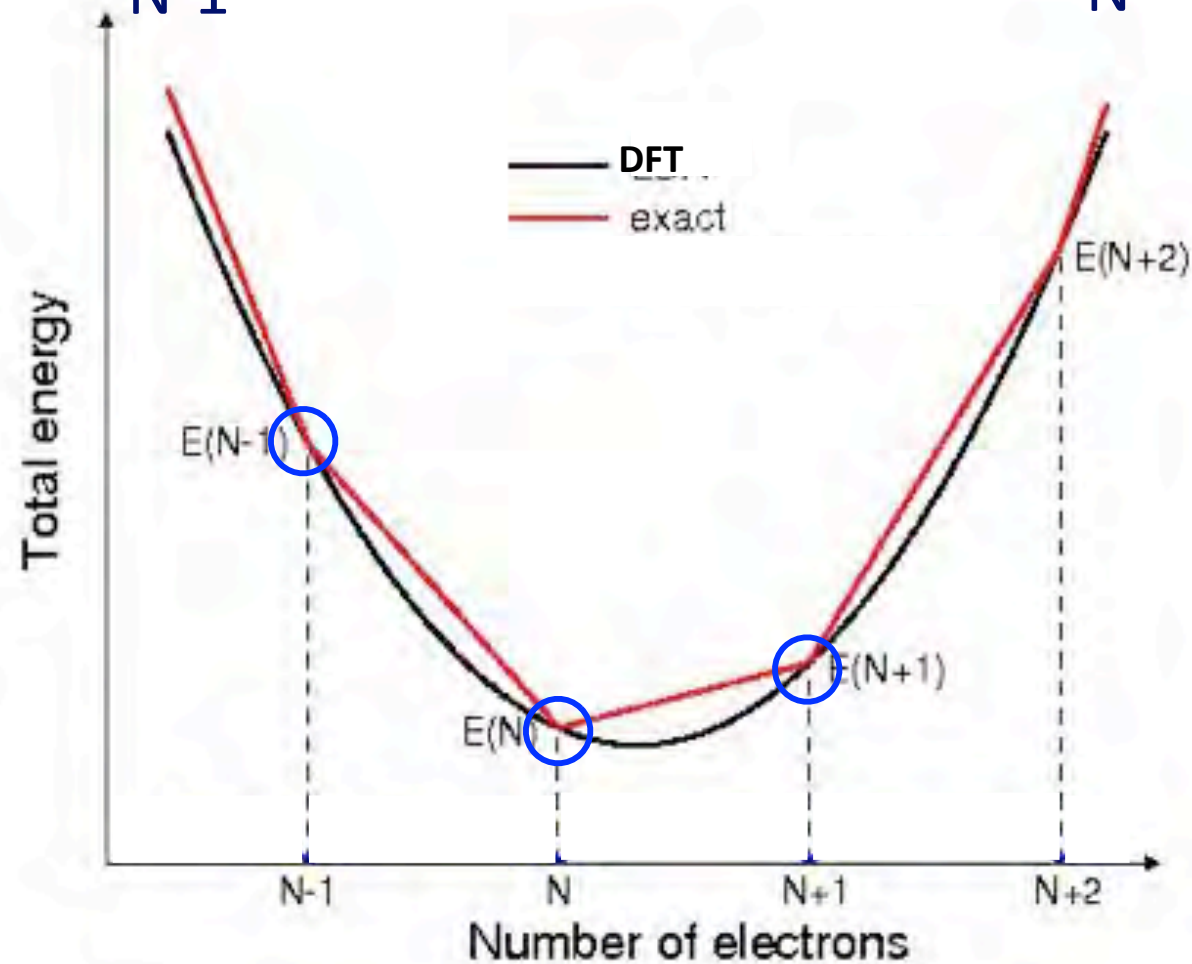
$N-1$



N



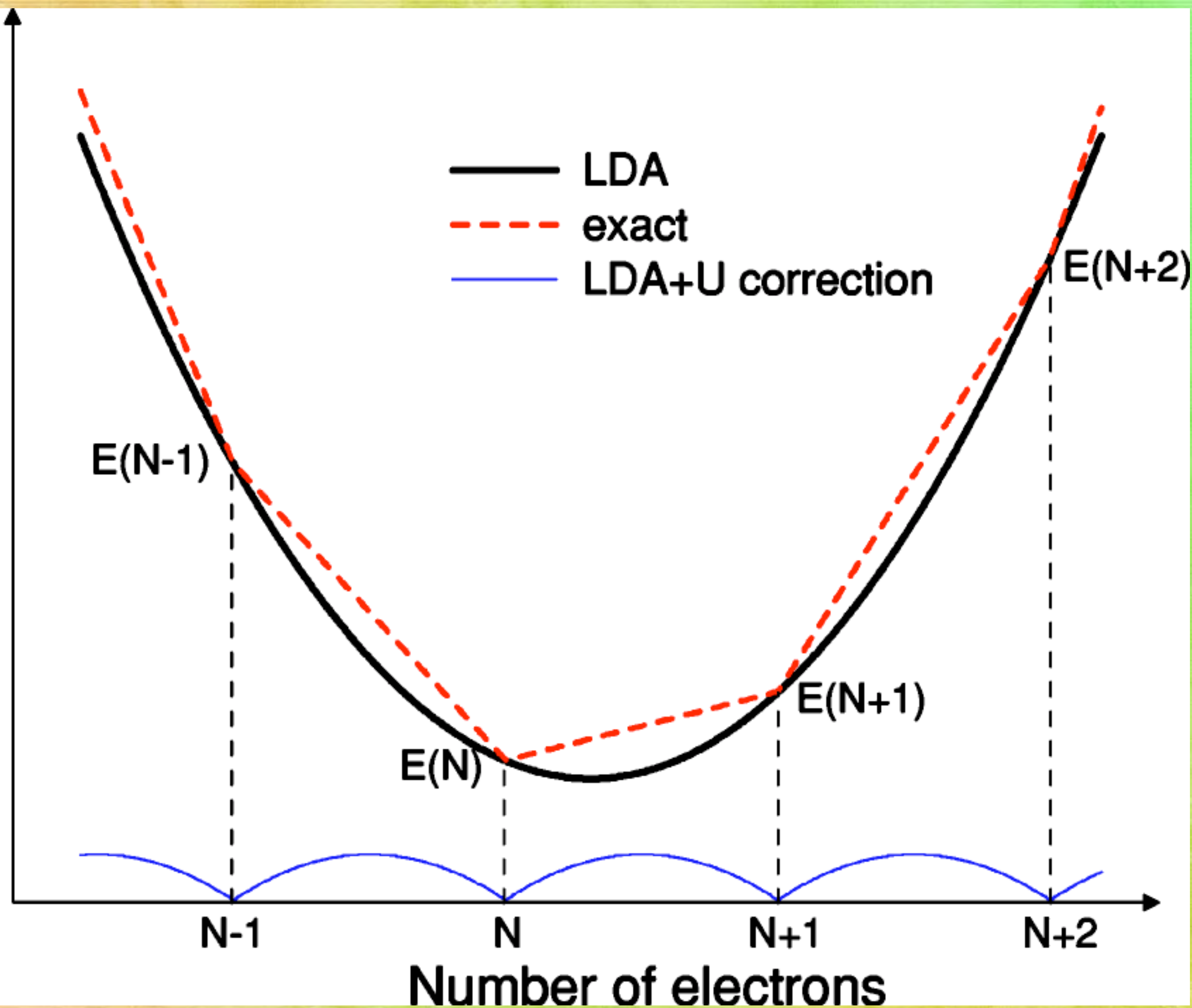
$N+1$



The exact energy is piece-wise linear
(statistical ensemble)

J. Perdew et al., PRL 23, 1691 (1982)

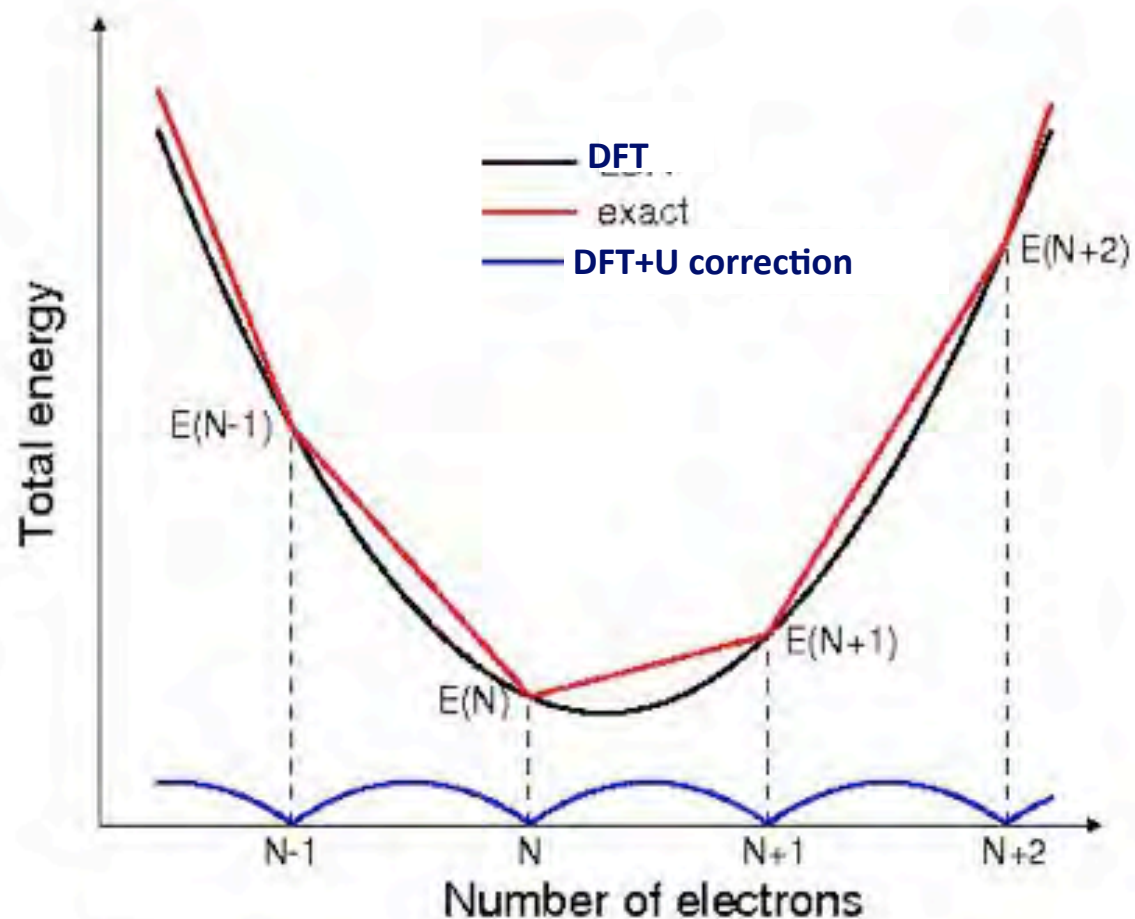
Total energy



Open system in contact with a reservoir

The meaning of U in DFT+U

$$E_{\text{exact}} \approx E_{\text{DFT}} + \sum_I \frac{U^I}{2} \sum_{mm'\sigma} [n_{mm'}^{I\sigma} (\delta_{mm'} - n_{mm'}^{I\sigma})] = E_{\text{DFT+U}}$$



The (approximate) DFT energy has an *unphysical curvature*

The exact solution is *piecewise linear*
+U correction reproduces the exact solution

U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, and coworkers PRB (1995)

LRT U: M. Cococcioni PhD (2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

$$U = \frac{d^2 E_{\text{DFT}}}{dn^2}$$

Linear response in practice

Apply a perturbation to the potential acting on the localized states of each Hubbard atom and compute the response of the occupations

$$V_{tot}|\psi_{kv}^{\sigma}\rangle = V_{KS}|\psi_{kv}^{\sigma}\rangle + \alpha^I \sum_m |\phi_m^I\rangle \langle \phi_m^I | \psi_{kv}^{\sigma}\rangle \Rightarrow \Delta n^I$$

Response matrices:

$$\chi^{IJ} = \frac{dn^I}{d\alpha^J}$$

$$\chi_0^{IJ} = \frac{dn_0^I}{d\alpha^J}$$

$$\chi = \begin{pmatrix} \chi^{11} & \dots & \chi^{18} \\ \dots & \dots & \dots \\ \chi^{81} & \dots & \chi^{88} \end{pmatrix}$$

Effective interactions:

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II}$$

M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)



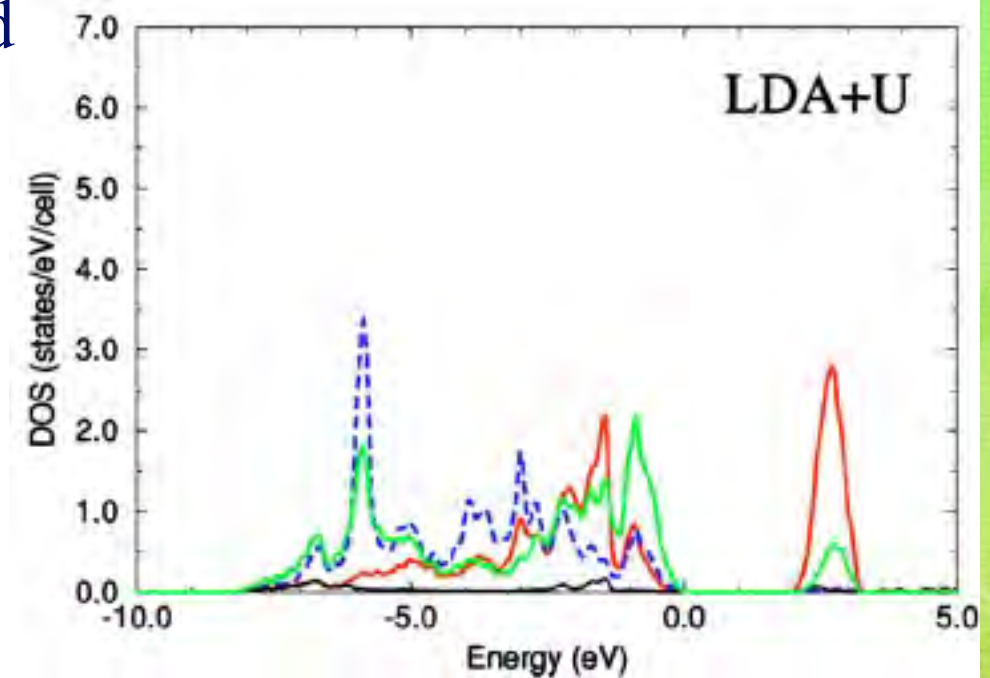
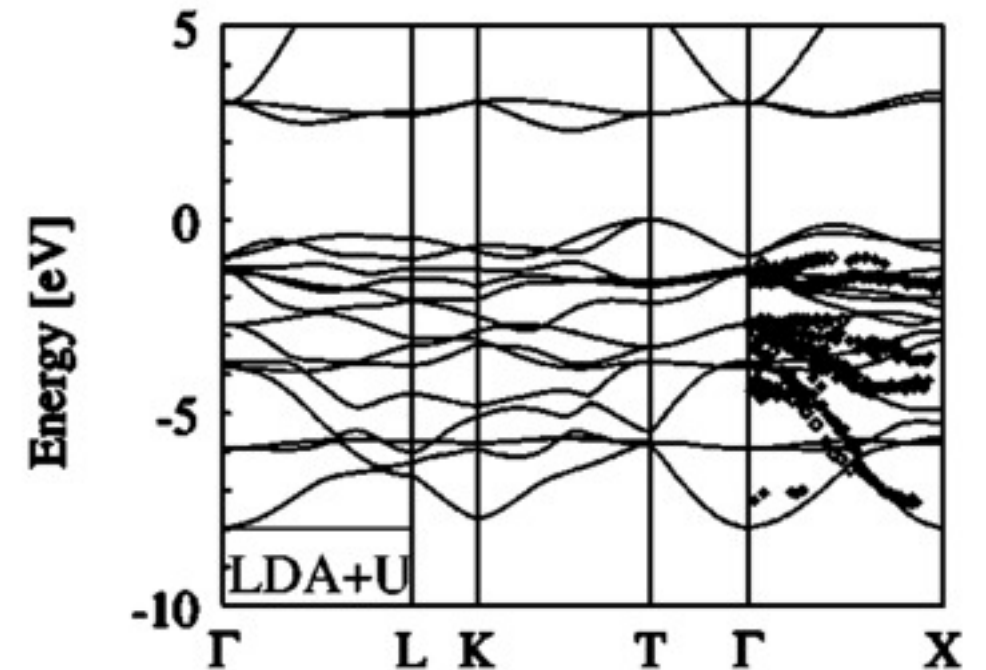
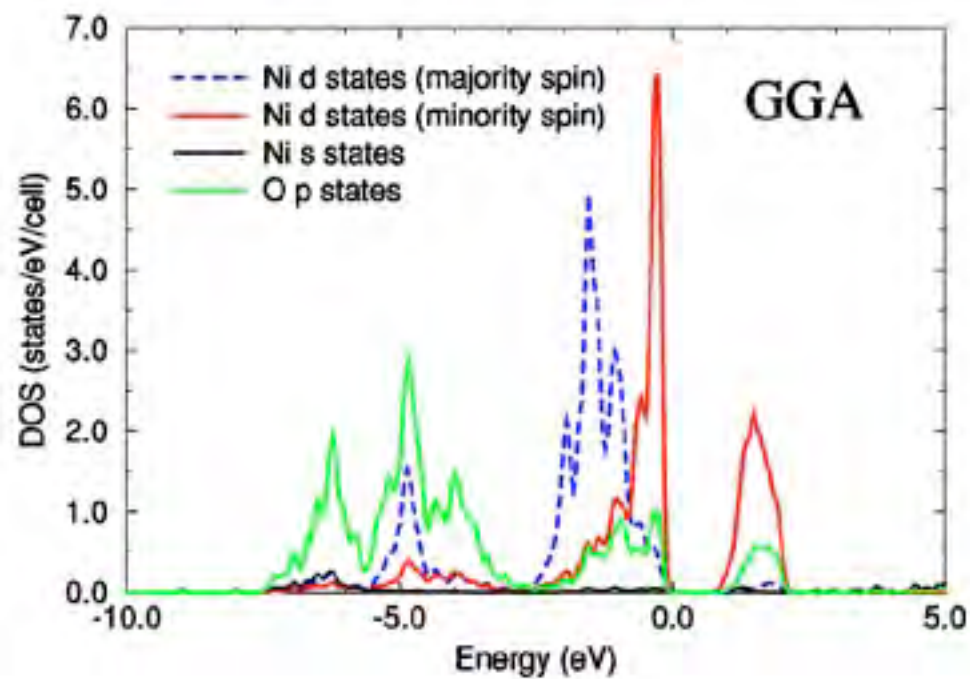
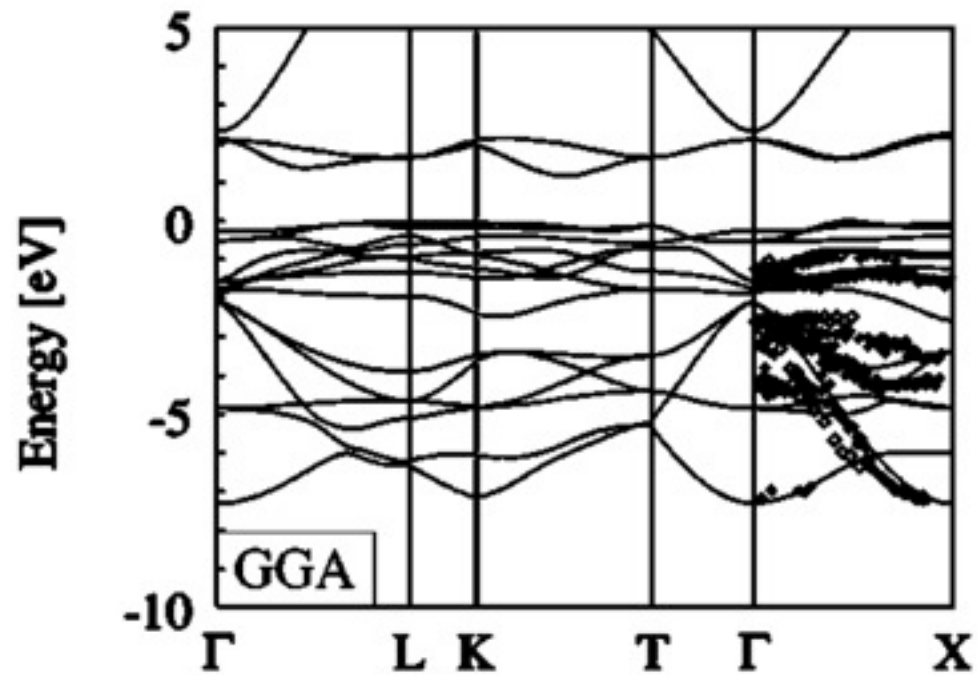
U is a system-dependent property

Compounds	U
CaCuO ₂	7.5 eV (0.550 Ry)
NiO	8.0 eV (0.590 Ry)
CoO	7.8 eV (0.574 Ry)
FeO	6.8 eV (0.500 Ry)
MnO	6.9 eV (0.507 Ry)
VO	6.7 eV (0.493 Ry)
TiO	6.6 eV (0.485 Ry)

Electron configuration
Covalency/ionicity
Spin states/charge states
Element identity
Coordination numbers



LDA+U NiO



✓ Gap improves

✓ O *p* states on top of the valence band

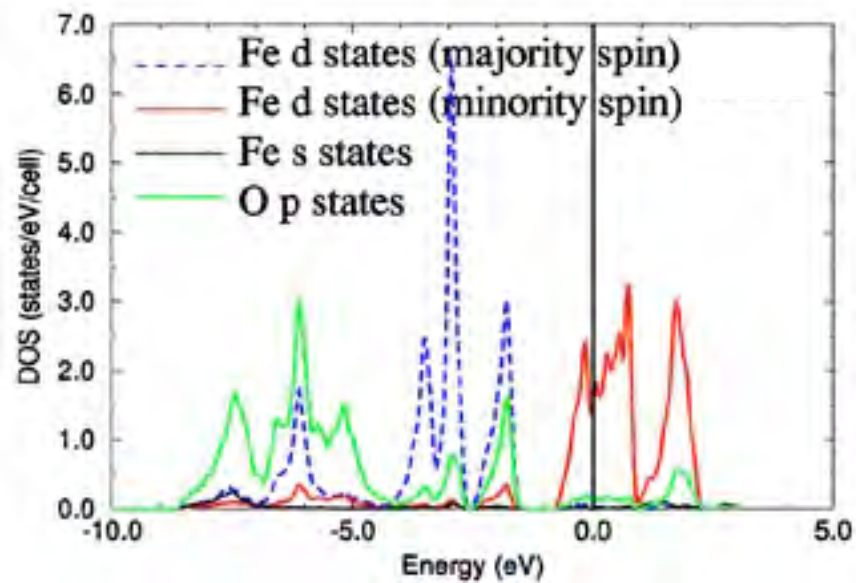
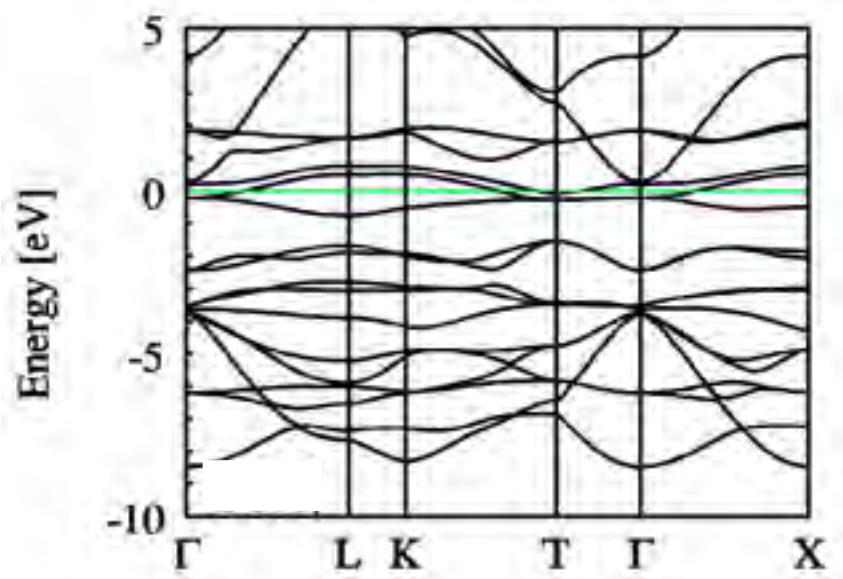


M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

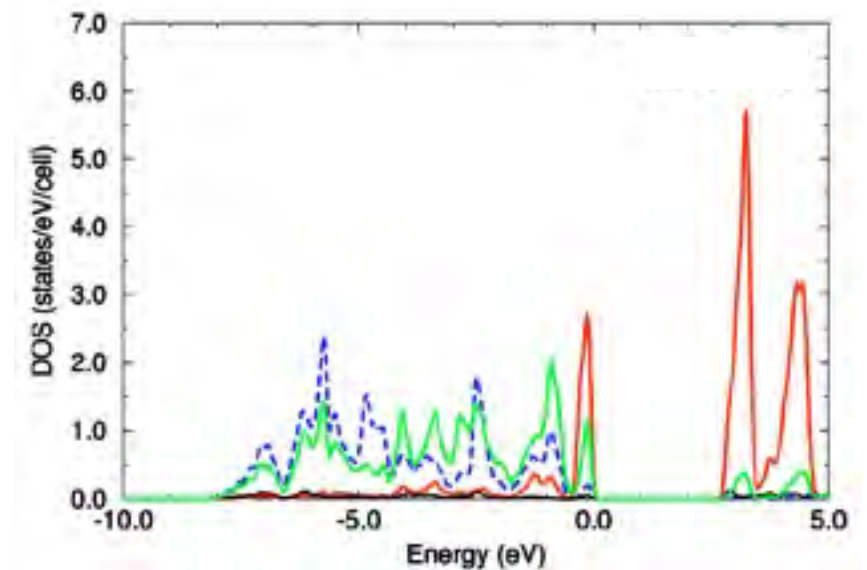
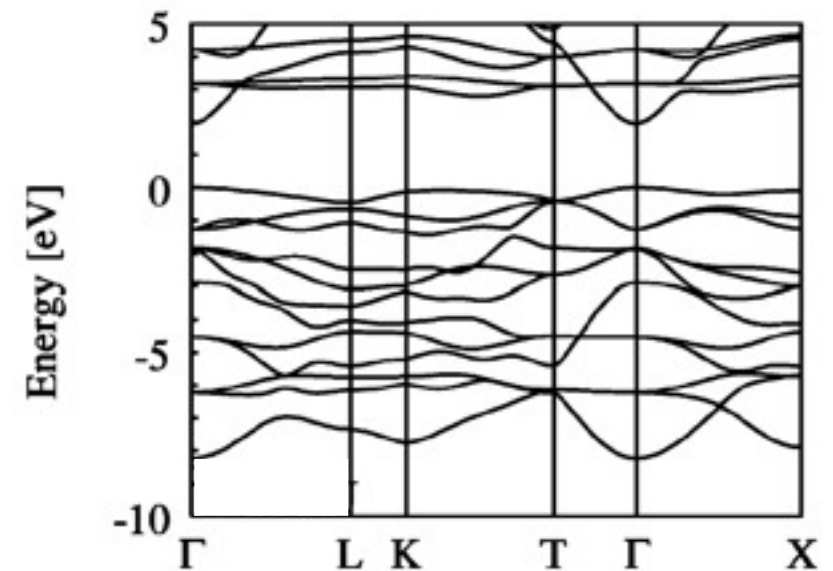


FeO: DFT and DFT+U

DFT



DFT+U



✓ Insulating character
(Gap of right size)

✓ AFM ground state
(AFII)



M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

