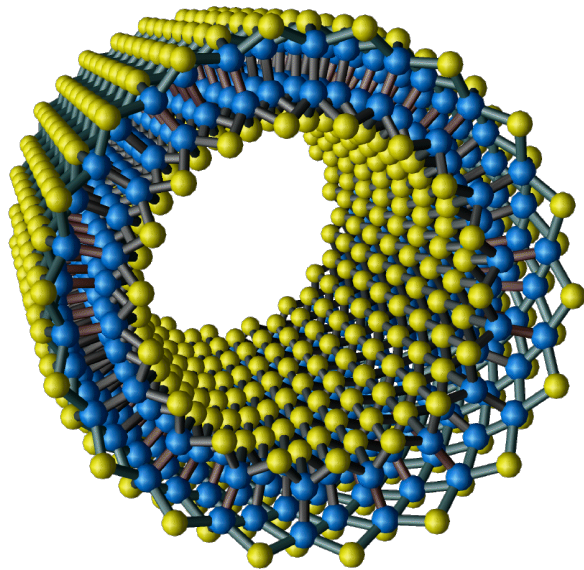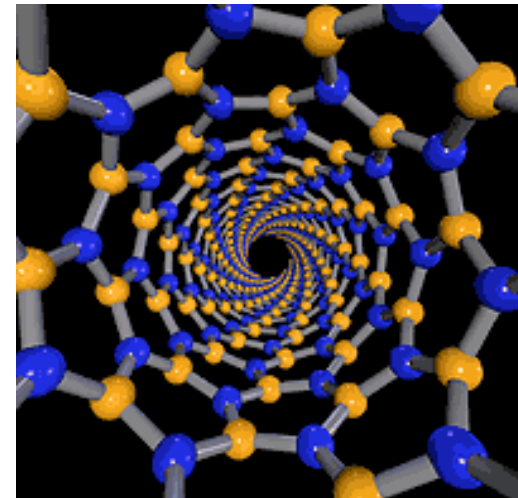# Introduction to DFT+U

by Michel Côté
Physics Department
Université de Montréal

Success of DFT

BN nanotubes:

- Simulated:

  Rubio, Corkill and Cohen,PRB 49, 5081 (1994)

- Realised:

  Chopra et. al., Science 269, 966 (1995)

GaSe nanotubes:

- Simulated:

  MC et al,PRB 58, R4277 (1998)

- Realised:

  Gautam et al., J Am Chem Soc, 127, pp. 3658 (2005)

Success of DFT

- Can predict structure: bond lengths, stability, ...
- Give good structure properties
  - Lattice constants
  - Phonon spectrum
  - Formation energies
- Give good electronic properties
  - Band structure (band gap problem)
  - Ionization potentials
  - Superconducting properties (phonon)
  - Excitation energies (TDDFT)
- ...

Electron system

$$\hat{H} = \hat{H}_o + \hat{V}_{ee} \qquad \hat{H}_o = \int d^3r\, a_\sigma^\dagger(\mathbf{r}) \left[\frac{\hat{\mathbf{p}}^2}{2m} + V_{\text{ext}}(\mathbf{r}) \right] a_\sigma(\mathbf{r})$$

$$\hat{V}_{ee} = \frac{1}{2} \int d^3r\, d^3r'\, V_{ee}(\mathbf{r} - \mathbf{r}') a_\sigma^\dagger(\mathbf{r}) a_{\sigma'}^\dagger(\mathbf{r}') a_{\sigma'}(\mathbf{r}') a_\sigma(\mathbf{r})$$

Let us use a basis of localized states:

$$a_\sigma^\dagger(\mathbf{r}) = \sum_i \psi_{\mathbf{R}_i}^*(\mathbf{r}) a_{i\sigma}^\dagger \qquad a_\sigma(\mathbf{r}) = \sum_i \psi_{\mathbf{R}_i}(\mathbf{r}) a_{i\sigma}$$

The electronic system can be written:

$$\hat{H} = \sum_{ii'} a_{i\sigma}^\dagger t_{ii'} a_{i'\sigma} + \sum_{ii'jj'} U_{ii'jj'} a_{i\sigma}^\dagger a_{i'\sigma'}^\dagger a_{j'\sigma'} a_{j\sigma}$$

$$t_{ii'} = \int d^3r\, \psi_{\mathbf{R}_i}^*(\mathbf{r}) \left[\frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) \right] \psi_{\mathbf{R}_{i'}}(\mathbf{r})$$

$$U_{ii'jj'} = \frac{1}{2} \int d^3r\, d^3r'\, \psi_{\mathbf{R}_i}^*(\mathbf{r}) \psi_{\mathbf{R}_j}(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') \psi_{\mathbf{R}_{i'}}^*(\mathbf{r}') \psi_{\mathbf{R}_{j'}}(\mathbf{r}')$$

Simplified Hubbard Model

$$U_{ii'jj'} = \frac{1}{2} \int d^3r \, d^3r' \, \psi^*_{\mathbf{R}_i}(\mathbf{r}) \psi_{\mathbf{R}_j}(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') \psi^*_{\mathbf{R}_{i'}}(\mathbf{r}') \psi_{\mathbf{R}_{j'}}(\mathbf{r}')$$

The $U_{ii'jj'}$ matrix elements are largest when $i=j$ and $i'=j'$.

$$\hat{H} = \sum_{ii'} a^\dagger_{i\sigma} t_{ii'} a_{i'\sigma} + \sum_{ii'} U_{ii'ii'} a^\dagger_{i\sigma} a^\dagger_{i'\sigma'} a_{i'\sigma'} a_{i\sigma}$$

If we also consider that only when i=i' is most important, then we must have that $\sigma \neq \sigma'$.

$$
\begin{aligned}
\hat{H} = \quad & \sum_{ii'} a^\dagger_{i\sigma} t_{ii'} a_{i'\sigma} + U \sum_i a^\dagger_{i\sigma} a^\dagger_{i,-\sigma} a_{i,-\sigma} a_{i\sigma} \\
= \quad & \sum_{ii'} a^\dagger_{i\sigma} t_{ii'} a_{i'\sigma} + U \sum_i a^\dagger_{i\sigma} a_{i\sigma} a^\dagger_{i,-\sigma} a_{i,-\sigma} \\
= \quad & \sum_{ii'} a^\dagger_{i\sigma} t_{ii'} a_{i'\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}
\end{aligned}
$$

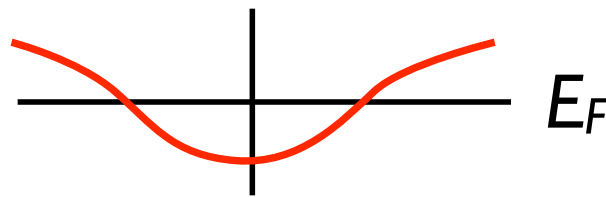# Hubbard Model

$$\hat{H}_o = -t \sum_{<ij>} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

$t \gg U$

The total energy is minimized by making the kinetic term as small as possible through delocalization of the wave functions (Bloch states).

It is possible to define a Fermi energy which divide occupied and unoccupied states.

E_F

$t \ll U$

The total energy is minimized by making the Coulomb term as small as possible by avoiding double occupancy of each site. Localized state are preferable (Wannier) which are made by a linear combination of all *k*-states.

At half-filling, each site is occupied by one electrons and we have a insulator: Mott insulator

Mott insulator and DFT

The Kohn-Sham equation:

$$\hat{H}_{\mathrm{DFT}} = \frac{-\hbar^2}{2m}\nabla^2 + V_{\mathrm{ext}}(r) + V_{\mathrm{Hartree}}(r) + V_{\mathrm{xc}}(r) \to \sum_{ij} h_{ij} a_i^\dagger a_j$$

where $V_{\mathrm{xc}}(r) = \dfrac{\partial E_{\mathrm{xc}}[n]}{\partial n(r)}$ is obtained from LDA or GGA is like a mean-field solution.

Note that the potential is the same for both occupied and unoccupied states.

Conclusion: LDA or GGA will not be able to reproduce a Mott insulator.

- LDA/GGA functionals tend to over-delocalize electrons
- On-site U repulsion is not well accounted for
- The electrons see their own potential, self-interaction
- Because the solution is mean-field, there is no correlation among the electrons.

NiO
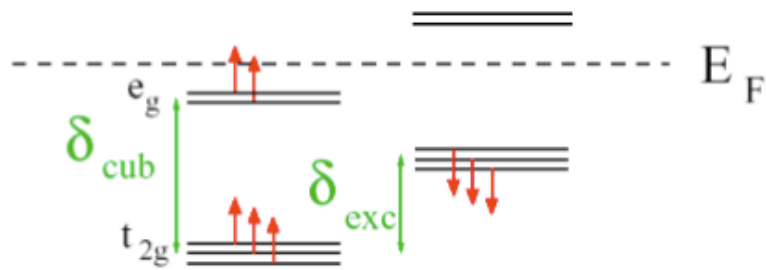
With LSDA we have:
- the correct ground state (antiferromagnetic)
- the correct structure (cubic)
- crystal field splitting
- but energy gap is too small
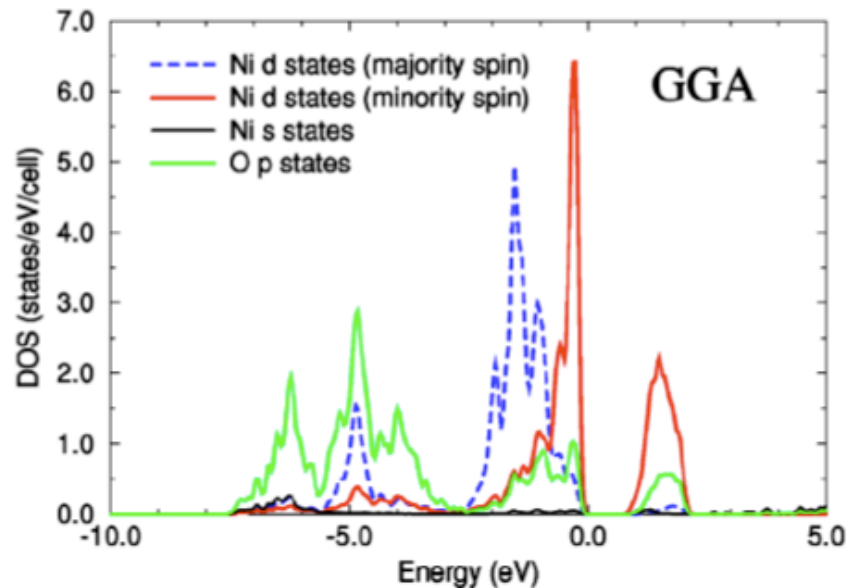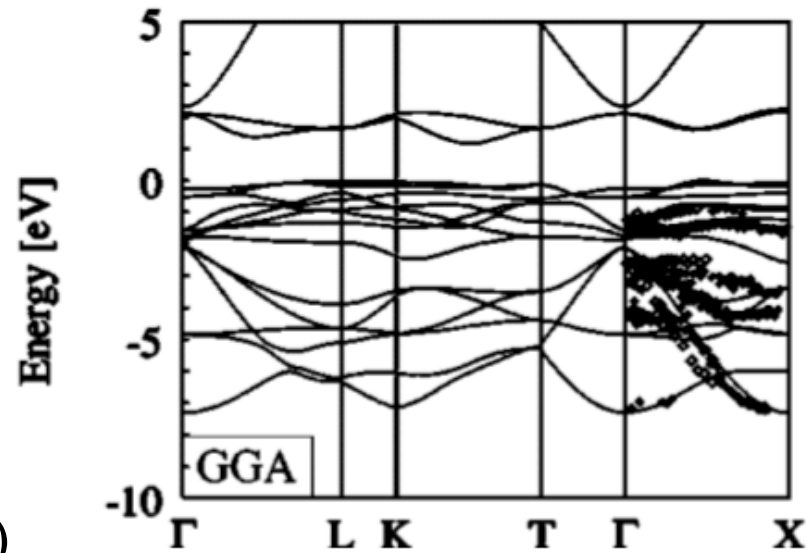
Main idea of LDA+U

To separate electrons into two subsystems: localized d of f electrons for which the Coulomb d-d interaction should be taken into account by a term:

$$\sum_{ii'} U_{ii'ii'} a_{i\sigma}^{\dagger} a_{i'\sigma'}^{\dagger} a_{i'\sigma'} a_{i\sigma} \longrightarrow \frac{1}{2} U \sum_{i \neq j} n_i n_j$$

in a model Hamiltonian and delocalized s and p electrons which could be described by using an orbital-independent one-electron potential (LDA).

LDA+U

The new functional is:

$$E^{\mathrm{LDA+U}}[n] = E^{\mathrm{LDA}}[n] + E^{U}[n_i^{\sigma}] - E^{\mathrm{dc}}[n_i^{\sigma}]$$

The $E^{\mathrm{dc}}[n_i^{\sigma}]$ is called the "double counting" term. Because we add explicitly the Hubbard term, we have to remove the energy contribution of these orbitals included in the LDA functional in order to not count twice their contributions.

It is found that even if LDA/GGA functionals describe poorly the electronic properties of these localized orbitals, the total energy of the system that they give is quite good, i.e. the structural properties are adequately reproduced.

The $E^{\mathrm{dc}}[n_i^{\sigma}]$ is approximated as mean-field value of the Hubbard term as in the DFT spirit. With $\frac{1}{2}U\sum_{i\neq j} n_i n_j$, the double counting term is $UN(N-1)/2$ where $N = \sum_{i} n_i$.

Therefore:

$$E^{\mathrm{LDA+U}}[n] = E^{\mathrm{LDA}}[n] + \frac{U}{2}\sum_{i\neq j} n_i n_j - UN(N-1)/2$$

LDA+U (2)

We can obtain the orbital eigenvalue by taking the derivative of the total energy with respect to the occupation number of that orbital. For LDA+U, we get:

$$
\begin{aligned}
\epsilon_i = \frac{\partial E^{\mathrm{LDA+U}}}{\partial n_i} &= \epsilon_i^{\mathrm{LDA}} + U \sum_{j \neq i} n_j - U(N-1)/2 - UN/2 \\
&= \epsilon_i^{\mathrm{LDA}} + U(N - n_i) - UN + U/2 \\
&= \epsilon_i^{\mathrm{LDA}} + U\left(\frac{1}{2} - n_i\right)
\end{aligned}
$$

This last expression shows that is the state is occupied, its energy is shifted - *U/2* and if it is not occupied, its energy is raised by *U/2*.

The LDA+U potential would be: $V^{\mathrm{LDA+U}}(r) = V^{\mathrm{LDA}} + U\left(\frac{1}{2} - n_i\right) P_i$

The operator P_i is the projection operator on the localized orbital.

From this formulation of the potential we can see that if the state *i* is initially less than half occupied, the Hubbard potential is positive and tend to repulse electrons. On the other hand, if the occupation is more than half filled, the potential is attractive and encourage electrons to localized on this particular site.

Hubbard model and _d_ and _f_ electrons

$$\hat{H} = \sum_{ii'} a_{i\sigma}^{\dagger} t_{ii'} a_{i'\sigma} + \sum_{ii'jj'} U_{ii'jj'} a_{i\sigma}^{\dagger} a_{i'\sigma'}^{\dagger} a_{j'\sigma'} a_{j\sigma}$$

Let the indices _i,i',j_ and _j'_ represent the different _m_ orbitals of a give _l_ subspace.

$$\hat{H}_U = \sum_{I,mm'm''m'''} U_{mm''m'm'''} a_{m\sigma}^{\dagger} a_{m''\sigma'}^{\dagger} a_{m'''\sigma'} a_{m'\sigma}$$

If $\sigma \neq \sigma'$, then

$$a_{m\sigma}^{\dagger} a_{m''-\sigma}^{\dagger} a_{m'''-\sigma} a_{m'\sigma} = a_{m\sigma}^{\dagger} a_{m'\sigma} a_{m''-\sigma}^{\dagger} a_{m'''-\sigma} = n_{mm'}^{\sigma} n_{m''m'''}^{-\sigma}$$

And the matrix element associated is:

$$U_{mm''m'm'''} = \frac{1}{2} \int d^3r d^3r' \psi_m^*(\mathbf{r}) \psi_{m'}(\mathbf{r}) V(\mathbf{r}-\mathbf{r}') \psi_{m''}^*(\mathbf{r}') \psi_{m'''}(\mathbf{r}')$$

$$= \frac{1}{2} <m, m''|V_{\text{ee}}|m'm'''>$$

Hubbard model and d and f electrons (2)

If $\sigma' = \sigma$, then we have two possibilities:

$$a_{m\sigma}^{\dagger} a_{m''\sigma}^{\dagger} a_{m'''\sigma} a_{m'\sigma} = a_{m\sigma}^{\dagger} a_{m'\sigma} a_{m''\sigma}^{\dagger} a_{m'''\sigma} = n_{mm'}^{\sigma} n_{m''m'''}^{\sigma}$$

and

$$a_{m\sigma}^{\dagger} a_{m''\sigma}^{\dagger} a_{m'''\sigma} a_{m'\sigma} = -a_{m\sigma}^{\dagger} a_{m'''\sigma} a_{m''\sigma}^{\dagger} a_{m'\sigma} = -n_{mm'''}^{\sigma} n_{m''m'}^{\sigma}$$

On the second term, let's interchange m' and m''', such that the density operators are the same but then the matrix element will be: $< m, m''|V_{\text{ee}}|m'''m' >$

Together the Hubbard part is:

$$
\begin{aligned}
\hat{H}_U \quad = \quad & \frac{1}{2} \sum_{\{m\},\sigma} \{ < m, m''|V_{\text{ee}}|m'm''' > n_{mm'}^{\sigma} n_{m''m'''}^{-\sigma} \\
+ \quad & (< m, m''|V_{\text{ee}}|m'm''' > - < m, m''|V_{\text{ee}}|m'''m' >) \, n_{mm'}^{\sigma} n_{m''m'''}^{\sigma} \}
\end{aligned}
$$

This is a rotational invariant formulation (rotation over the m subspace). The previous formulation was not. Also, this formulation includes exchange contribution, see the second term above.

Relation between U, J and <Vee>

$$< m, m''|V_{\text{ee}}|m', m''' > = \int d^3r d^3r' R^*_{lm}(r)Y^*_{lm}R_{lm'}(r)Y^*_{lm'}V(r-r')R^*_{lm''}(r')Y^*_{lm''}R_{lm'''}(r')Y^*_{lm'''}$$

Using the expansion representation for the Coulomb interaction:

$$V(r-r') = \frac{1}{\epsilon}\frac{1}{|r-r'|} = \frac{1}{\epsilon}\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\frac{r^l_<}{r^{l+1}_>}\sum_{m=-l}^{+l}Y_{lm}(r)Y^*_{lm}(r')$$

We can rewrite:

$$< m, m''|V_{\text{ee}}|m', m''' > = \sum_{l'=0}^{\infty}\frac{4\pi}{2l+1}\sum_{p=-l}^{+l} < lm|Y_{l'n}|lm' >< lm''|Y^*_{l'n}|lm''' > F^l$$

$< lm|Y_{l'n}|lm' >$ Gaunt coefficients; F^l screened Slater's integrals

Because of the properties of the Gaunt coefficients, we only need F^0, F^2 and F^4.

We identify U anf J with average of the Coulomb integral:

$$U = \frac{1}{(2l+1)^2}\sum_{m,m'} < mm'|V_{\text{ee}}|mm' > = F^0$$

$$J = \frac{1}{(2l)(2l+1)}\sum_{m\neq m'} < mm'|V_{\text{ee}}|m'm > = \frac{F^2+F^4}{14}$$

More issues

The static dielectric is not know generally.

In practice, U is obtained from a constrained DFT calculation or used as a variable parameter.

We still need a third relation to assign U, J to the F's. It is commonly to refer to the work of DeGroot et al (PRB 42, 5459 (1990)), who determine that the ratio F4/F2 for transition-metal oxides was between 0.62 and 0.63. Hence, the ratio F4/F2=0.625 is often used.

Double Counting term

Now that we include exchange contribution, the mean-field energy for the double counting term is:

$$E^{dc} = UN(N-1)/2 - J/2(N^{\uparrow}(N^{\uparrow} - 1) + N^{\downarrow}(N^{\downarrow} - 1))$$

This is known as the full localized limit (FLL). Czyzyk and Sawatzky (PRB, 49, 14211 (1994)) proposed an "around mean field" expression for the term which is slightly different. Both implementation are available in Abinit.

PAW pseudopotentials


PAW orbital = Plane wave + All electron spherical part − Pseudized part

- The smooth part of the wave function, outside the core, is represented by plane waves
- Inside the core, the wave functions are atomic like
- Because the information of the atomic wave function is retained, it is suitable to introduce Hubbard-like terms that require localized orbitals.
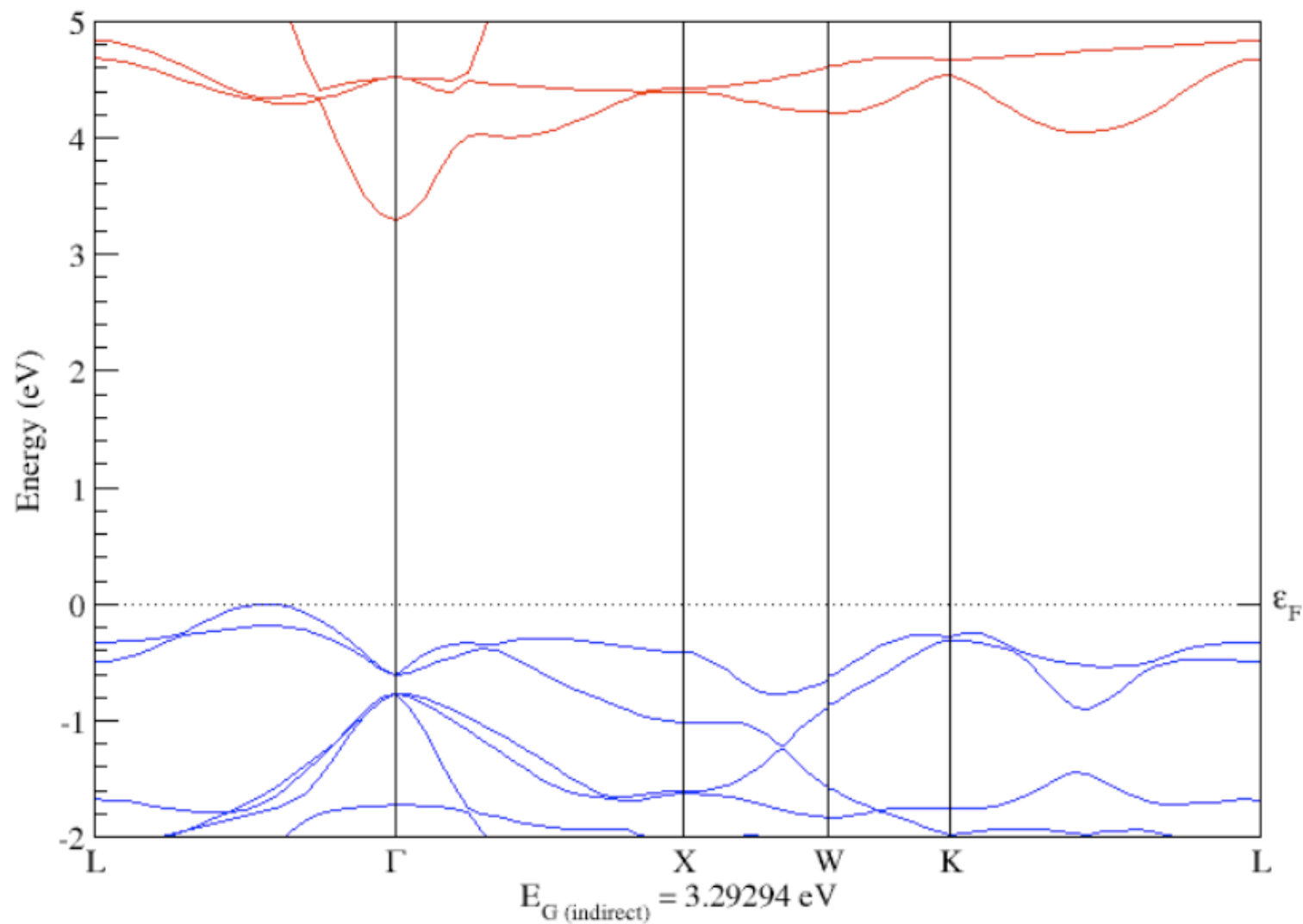
Discontinuity in functional
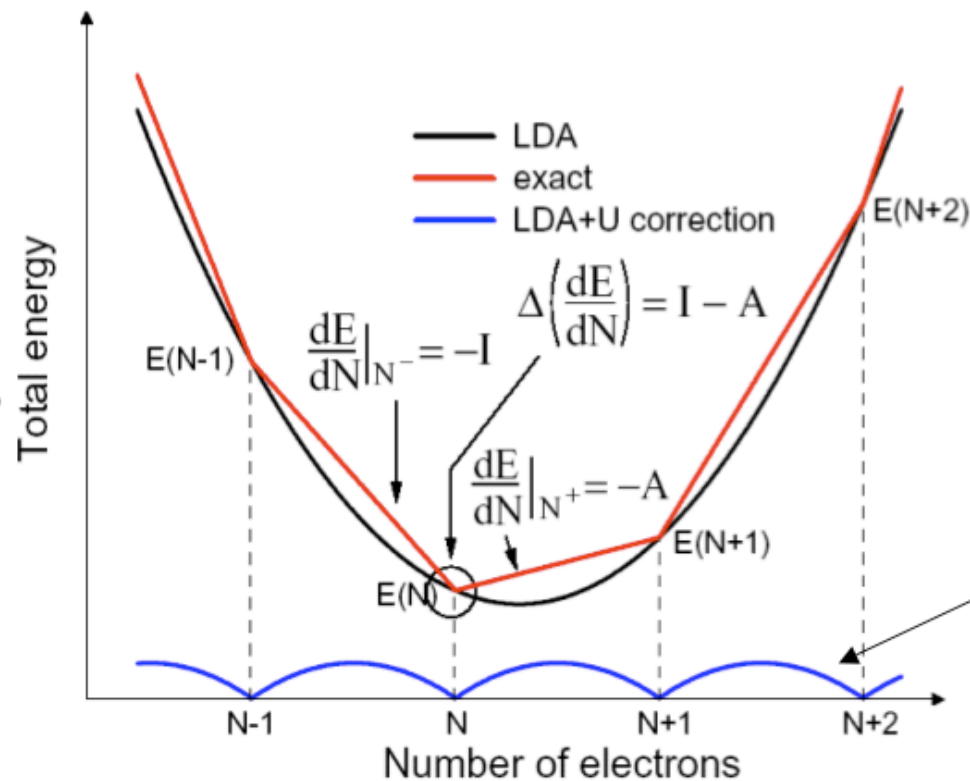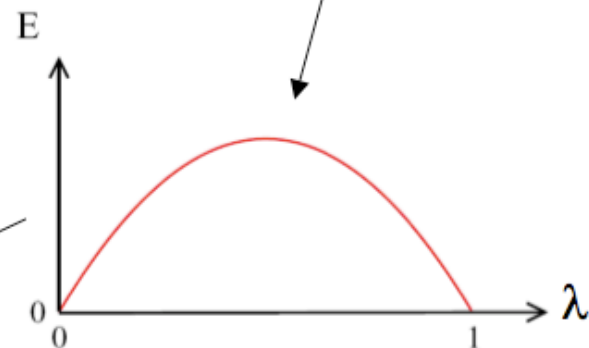
credit: from Matteo Cococcioni's thesis

NiO revisited

U=8 eV

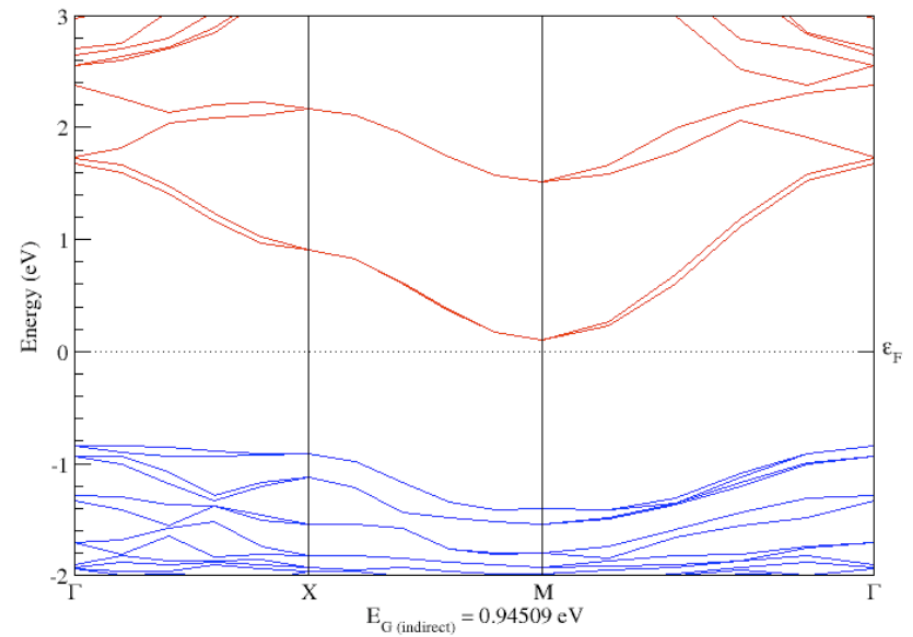$E_{G\ (indirect)} = 3.29294\ eV$

YBa2Cu3O6
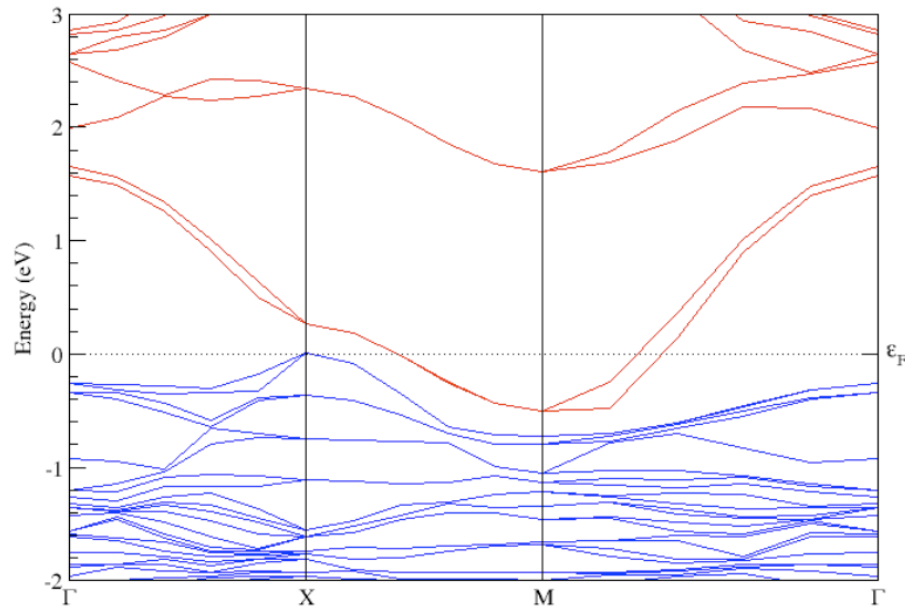
LDA

LDA+U U=8 eV

Other DFT approaches to correlated systems

- GW approximation
  Not strictly a DFT method but a perturbation of Kohn-Sham eigenvalues.
- SIC: Self-Interaction Correction
  Correct for the self-interaction of electrons in DFT, however, it is orbital dependent.
- Hybrid functional
  Functionals that are based on not only based on density but also on orbitals.
- DFT+DMFT, Dynamical Mean Field Theory
  More later in the school

References:

Review articles:

V. I. Anisimov and A. I. Lichtenstein, "LDA+U Method: Screened Coulomb Interaction in the Mean-field Approximation", Chapter 2 in *Strong coulomb correlations in electronic structure calculations: Beyond the local density approximation*, edited by V. I. Anisimov, Gordon and Breach Science Publishers, 2000, ISBN: 90-5699-131-0

V. I. Anisimov, F. Aryasetiawan and A. I. Lichtenstein, "First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA+U method", J. Phys.: Condens. Matter, vol 9, p. 767, 1997, DOI:

Implementation in Abinit

done by Bernard Amadon, CEA Bruyères-le-Châtel, France

ref: B. Amadon, F. Jollet and M. Torrent, PRB 77, 155104 (2008)

see also O. Bengone et al, PRB 62, 16392 (2000) for discussion of implementation in PAW formalism.