LDA + U calculations using pwscf

LDA + U:

- What is it ?
- When is it useful ?
- How to use it ?

→ Examples on NiO and FeO

LDA + U

- LDA + U energy functional:

$$\begin{aligned} E^{\mathrm{LDA+U}}[\rho^\sigma, n_\lambda^{I,\sigma}] &= E^{\mathrm{LDA}}[\rho^\sigma] + E_U^{\mathrm{Hub}}[n_\lambda^{I,\sigma}] - E_U^{\mathrm{dc}}[n^{I,\sigma}] \\ &= E^{\mathrm{LDA}}[\rho^\sigma] + \frac{U}{2} \sum_{I,\lambda,\sigma} n_\lambda^{I,\sigma} \left(1 - n_\lambda^{I,\sigma}\right) \end{aligned}$$

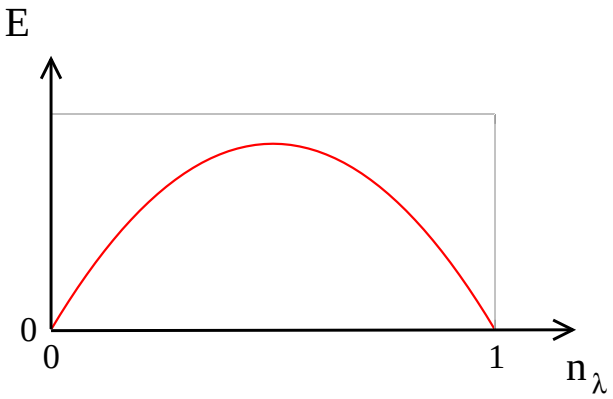
- $n_\lambda^{I,\sigma}$: occupation numbers of the localized (d or f) orbitals, obtained by diagonalizing atomic occupation matrices:

$$n_{m,m'}^{I,\sigma} = \sum_{\mathbf{k},\mathbf{i}} f_{\mathbf{k},\mathbf{i}}^\sigma \langle \varphi_m^{I,\sigma} | \psi_{\mathbf{k},\mathbf{i}}^\sigma \rangle \langle \psi_{\mathbf{k},\mathbf{i}}^\sigma | \varphi_{m'}^{I,\sigma} \rangle,$$

where $\varphi_m^{I,\sigma}(\mathbf{r})$ are localized (d or f) atomic orbitals

Note on onsite correction:

$$\frac{U}{2} \sum_{I,\lambda,\sigma} n_\lambda^{I,\sigma} \left(1 - n_\lambda^{I,\sigma}\right)$$



→ **penalty for partial occupation of the localized orbitals**

Helps for Mott insulators, where LDA does not give a proper description.

Ex.: CoO and FeO LDA fails to predict a gap;
NiO, MnO: gap too small

For LDA + U calculations:

with pwscf:

Two modes:

- LDA + U scf calculations (U input)

  → use variable Hubbard_U(ityp)
  starting_ns_eigenvalue(m,ispin,I)

- Calculate U (by LDA linear-response type of calculations with onsite perturbation U_α)

  → use variable Hubbard_alpha(ityp)

  See Cococcioni and de Gironcoli,
  cond-mat/0405160 and Phys. Rev. B 71, 035105 (2005)

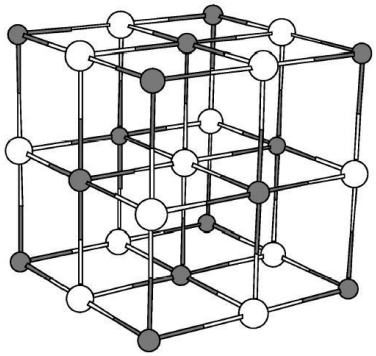
References

(also in INPUT_PW)

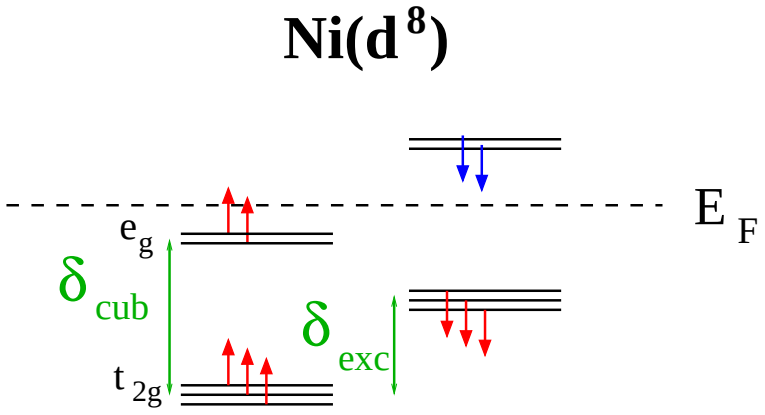
- Anisimov, Zaanen, and Andersen, PRB 44, 943 (1991)
- Anisimov et al., PRB 48, 16929 (1993)
- Liechtenstein, Anisimov, and Zaanen, PRB 52, R5467 (1994);
- Cococcioni and de Gironcoli, PRB 71, 035105 (2005) ⇐

Example: NiO

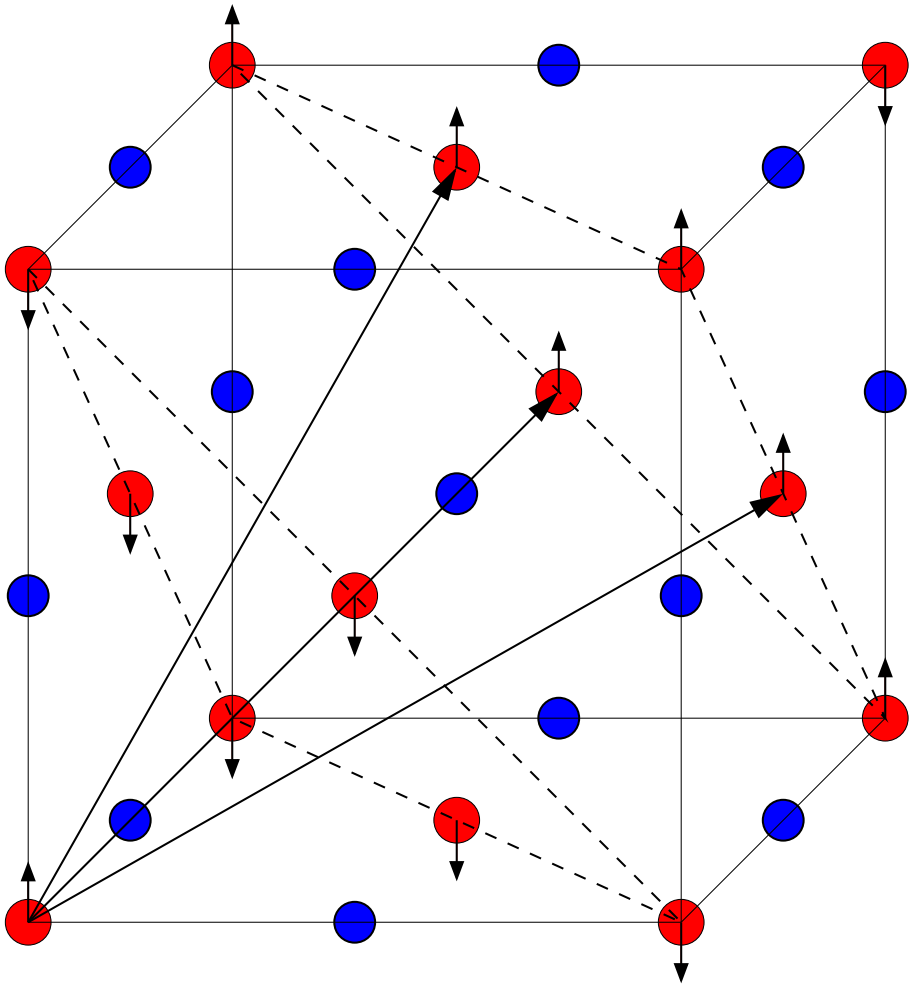
- Antiferromagnetic insulator, $m_s \approx 1.7\mu_B$
- Rocksalt structure, $a = 4.17\mathring{A}$



- Formal charge state: $Ni^{+2} \Rightarrow Ni(d^8)$, with cubic crystal field:

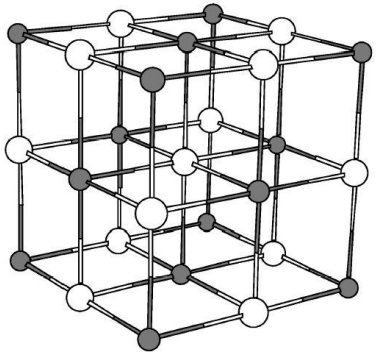


Spin structure:



Example: FeO

- Antiferromagnetic insulator, $m_s \approx 1.7\mu_B$
- Rocksalt structure, $a = 4.43\mathring{A}$



- Formal charge state: $Fe^{+2} \Rightarrow Fe(d^6)$, with cubic crystal field: