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Soutenance de stage d'option

Spin and exchange effects in NiO

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Outline

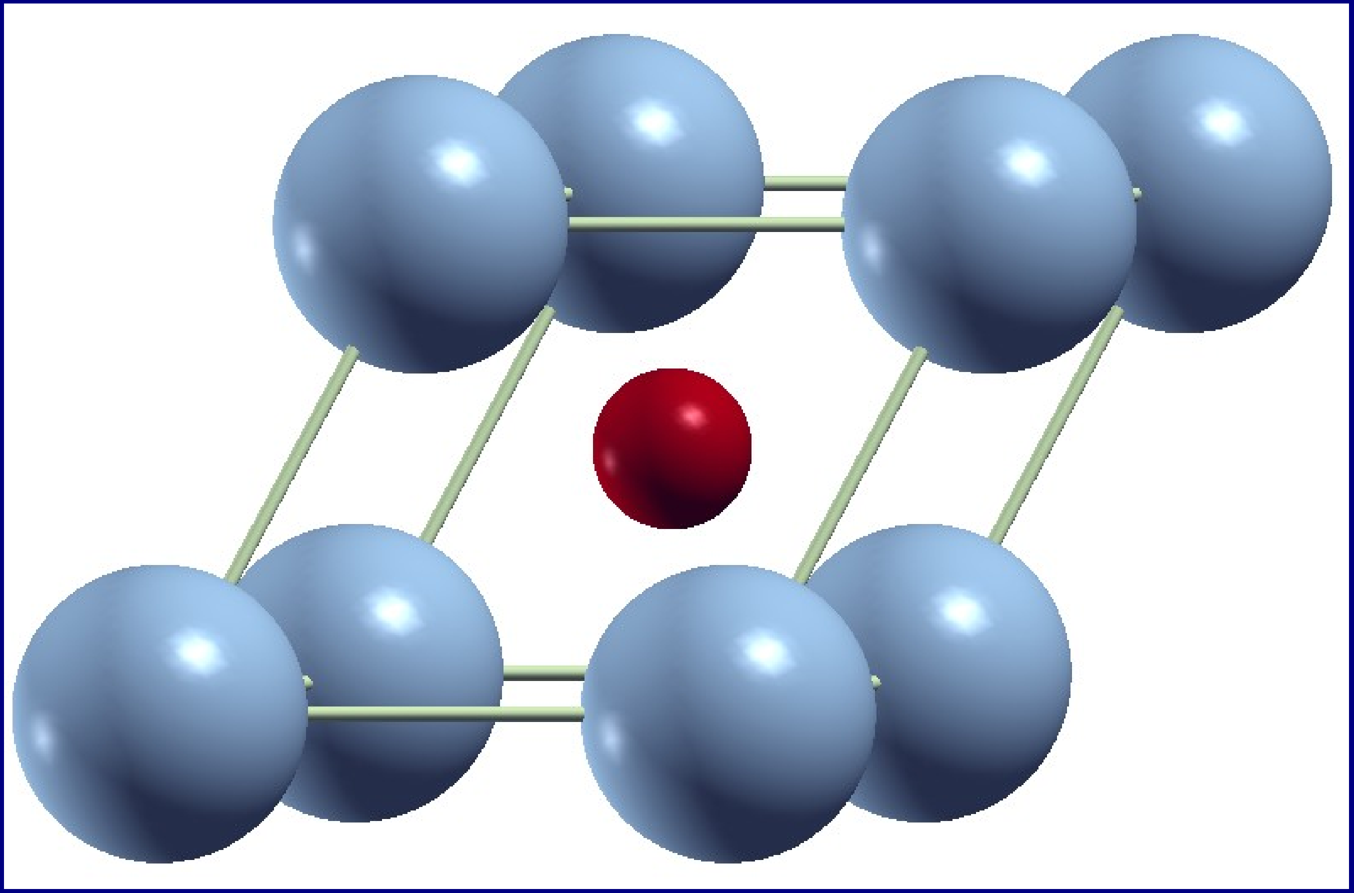
- NiO – General features
- The theoretical issue: strong correlation
- Band structure: experiment and theory
- Density-Functional Theory (DFT) and LDA
- Green's functions theory and GW approximation
- GW and Hartree-Fock (HF) approximation
- NiO by means of LDA and HF – The role of spin and exchange
- Conclusion and further perspective

Nickel oxide - Properties

- Transitional metal compound.
- Insulator – E_G=4.3 eV.
- Anti-ferromagnetic – Paramagnetic transition (Néel's temperature T_N=525°C).
- Rhombohedral – Rocksalt (Na-Cl-like) structure transition at T_N.

Anti-ferromagnetic structure

- Exp. values:
  - acell: 2.9490 Å
  - angle: 60.087
- Ions positions:
  - Ni: (0,0,0)
  - O: (0.5,0.5,0.5)

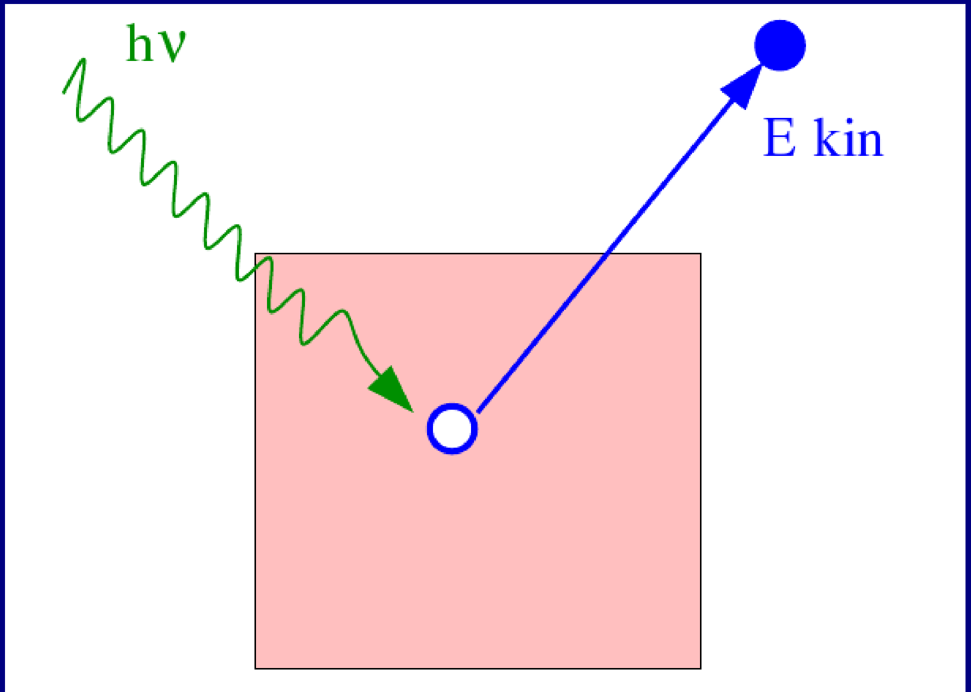


What's the problem with NiO?

- Problem raised by Mott for the paramagnetic phase:
  - Bloch LCAO description gives a metal.
  - Strong correlation (strong d-electrons localization and repulsion) causes gap opening (Hubbard insulator).
  - Strong correlation prevents a band structure description (independent electrons approximation).
- To study paramagnetic we must first understand anti-ferromagnetic.

How band structure is determined?

- By experiments:
  - Direct and inverse photoemission. It gives electron addition and removal energies.



$$h\nu - E_{kin} = E_{N-1,i} - E_{N,0} \hat{=} -\epsilon_i$$

- By theory:
  - Kohn-Sham structure from DFT is the most commonly used and the most computationally affordable tool. An example of a “mean field” theory.

Density Functional Theory

- Ground-state (GS) theory based on the density n_0.
- Direct relation between GS n_0 and GS observables (Hohenberg-Kohn theorem).
- Kohn-Sham scheme permits practical application. -> $V_{xc}[n]$
- Exact density functional is unknown. Approximation necessary --> LDA.

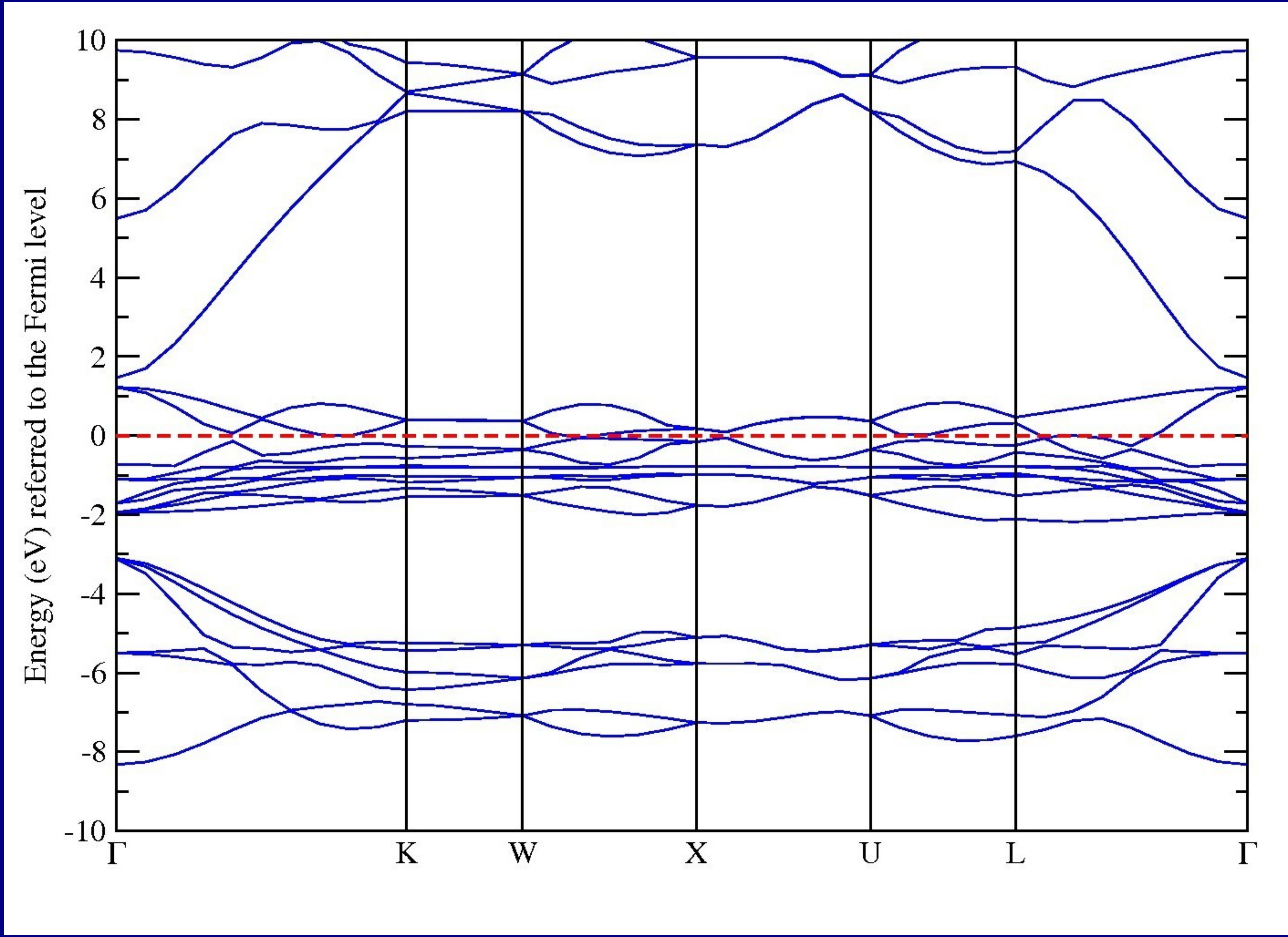
DFT on NiO

- KS equation:

$$\left(-\frac{\nabla^2}{2} + v_{KS}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

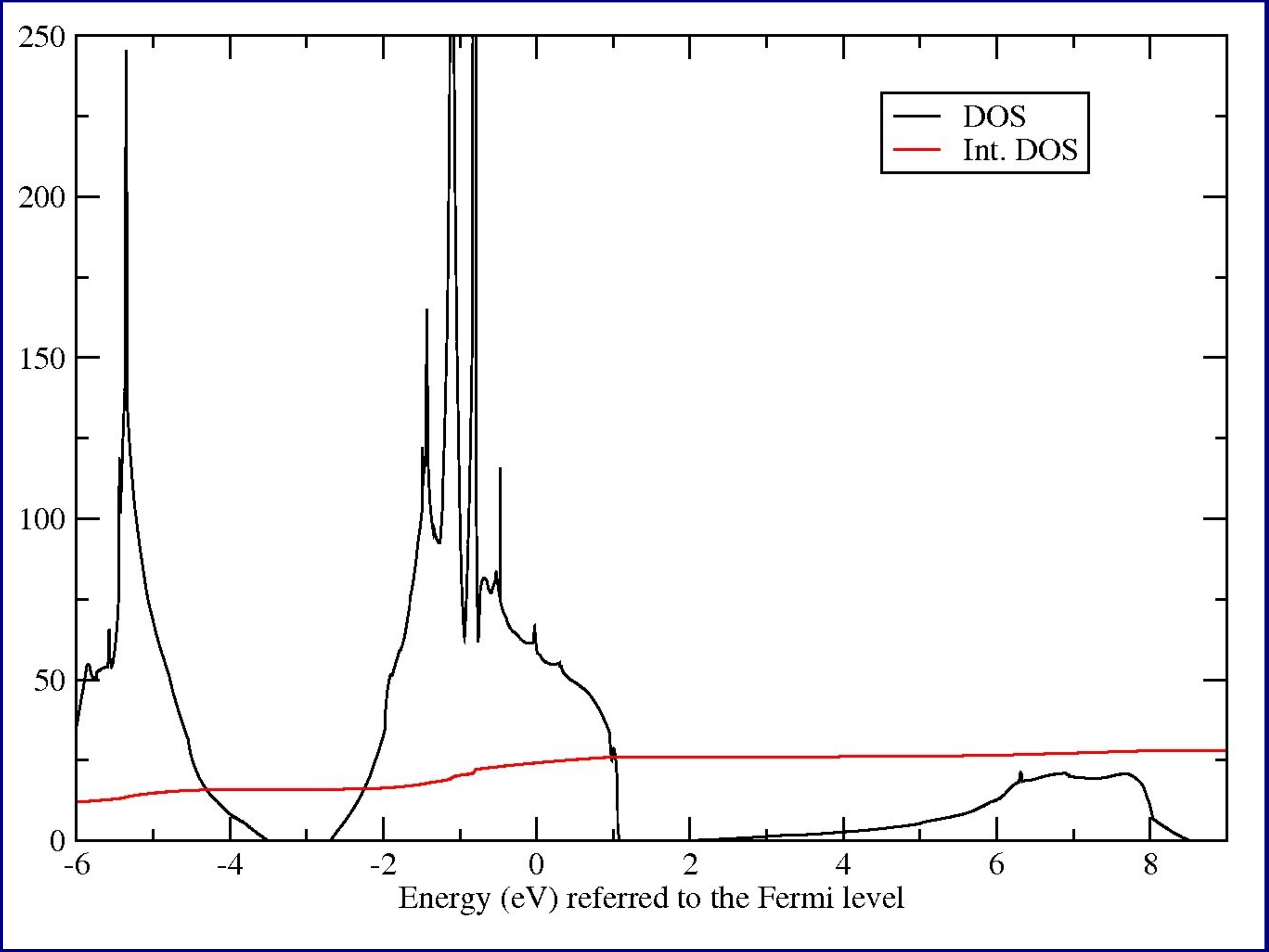
- ABINIT software package
  - LDA exchange-correlation functional
  - Planewaves expansion of KS orbitals
  - Norm-conserving pseudopotentials

LDA on NiO – Band structure



LDA on NiO – Density Of States

Undoubtedly a metal!



Band structure = excited states

- LDA is not supposed to give us excited state properties. KS orbitals are not even real!
- By definition LDA cannot give us the correct band structure.
- We need a proper theoretical tool:
  - Green's functions theory.

One-particle Green's function

$$iG(1,2) = \langle N | \mathcal{T} \left[\hat{\psi}(1) \hat{\psi}^{\dagger}(2) \right] | N \rangle$$

- Propagation of an electron (hole) from 2 to 1. It gives:

$$1 \longrightarrow (\mathbf{r}_1, t_1, \sigma_1)$$

  - Any single-particle GS observable.
  - GS energy.
  - Single-particle excitation spectrum, i.e. addition and removal energies (Photoemission spectrum).

How to find G?

- With G's equation of motion:

$$\left[i\frac{\partial}{\partial t_1} - h(\mathbf{r}_1)\right] G(1,2) + i\int d3 v(1,3) G_2(1,3^+;2,3^{++}) = \delta(1,2)$$

but G depends on G_2 (and G_2 depends on G_3...) which is not easier to find...

- We need to get rid of G_2... with Σ!

$$i\int d3 v(1,3) G_2(1,3^+;2,3^{++}) = -\int d3 \Sigma(1,3) G(3,2)$$

The self energy Σ

- Σ can be written as a function of G only (thanks to U)!

$$\Sigma(1,2) = -i \int d345 G(1,4) \frac{\delta G^{-1}(4,2)}{\delta U(3)} v(1^+,3)$$

The Dyson equation relates through Σ the non-interacting system (G_0) to the interacting one:

$$G = G_0 + G_0 \Sigma G$$

Σ includes all many-body exchange and correlation interactions.

GW approximation

- Thanks to Hedin's equations and introducing the GW approximation, it is possible to write

$$\Sigma(1,2) = iG(1,2)W(2,1^+)$$

- W is the dynamical screened Coulomb interaction.

$$W(1,2) = \int d3 v(1,3)\varepsilon^{-1}(3,2)$$

Quasi-particle energies

- Self-consistently with quasi-particle equation of motion.

$$\int d\mathbf{r}_3 \left[h(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_3) + \Sigma(\mathbf{r}_1, \mathbf{r}_3, \epsilon_i)\right] f_i(\mathbf{r}_3) = \epsilon_i f_i(\mathbf{r}_1)$$

- Kohn-Sham equations were:

$$\left(-\frac{\nabla^2}{2} + v_{KS}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

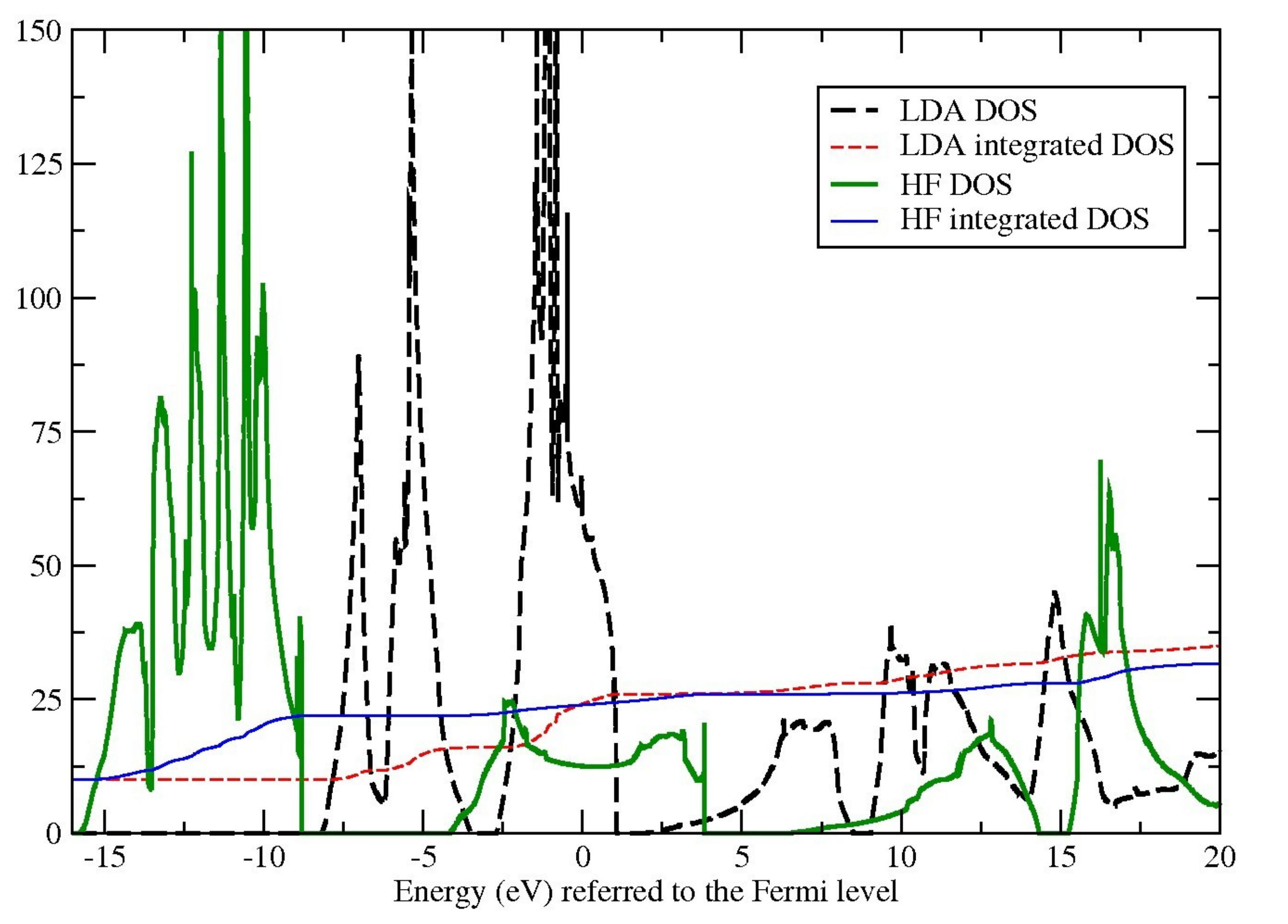
Exchange and correlation

- Correlation = everything beyond Hartree-Fock.
- In GW approximation, correlation is related to the screening ε^{-1}.
- If we put ε^{-1}=1, W -> v, -> Hartree-Fock!

$$\Sigma_x = iv(1^+, 2)G(1,2) = -v(\mathbf{x}_1, \mathbf{x}_2)\gamma(\mathbf{x}_1, \mathbf{x}_2)$$

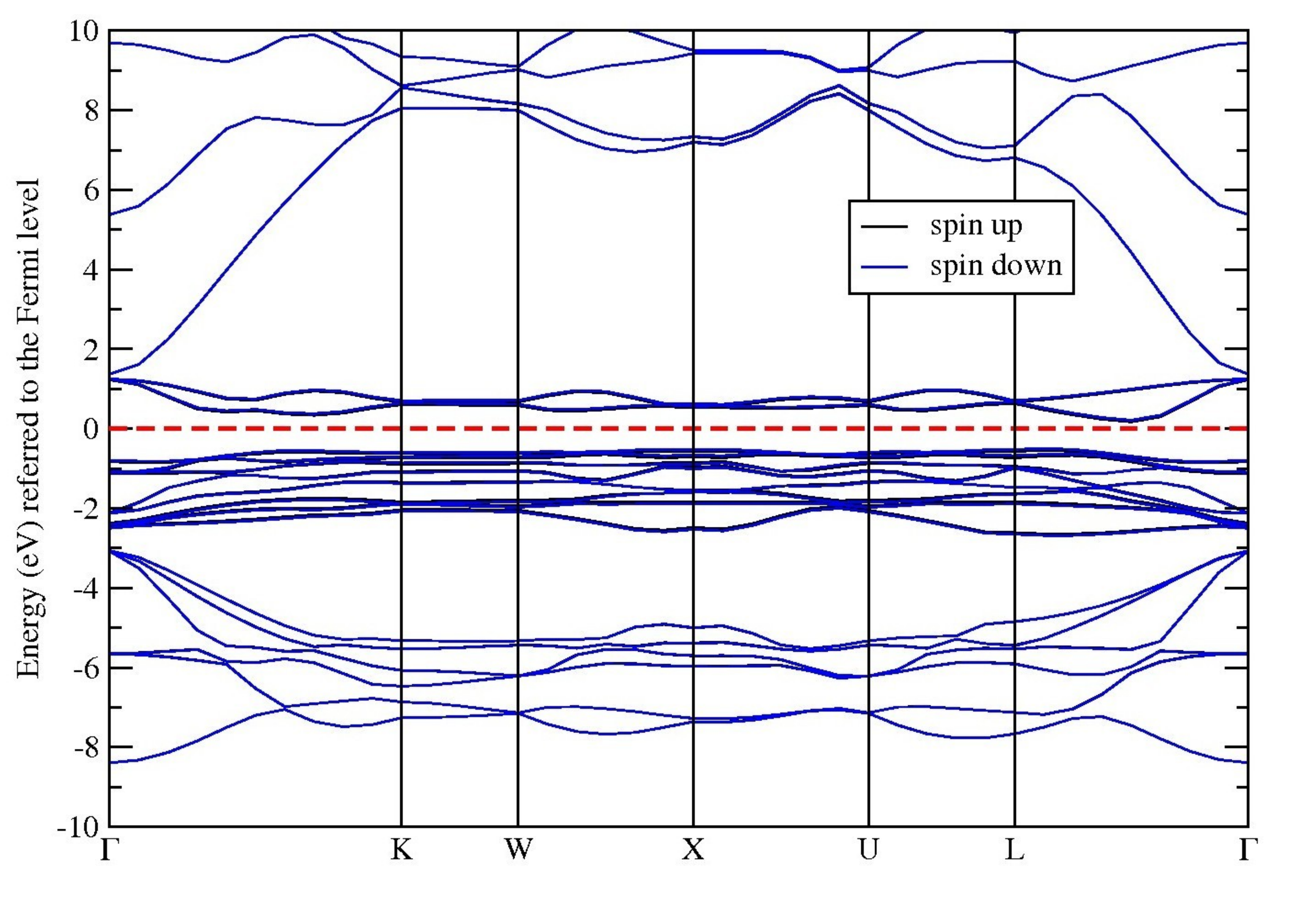
No correlation = No relaxation

HF on NiO



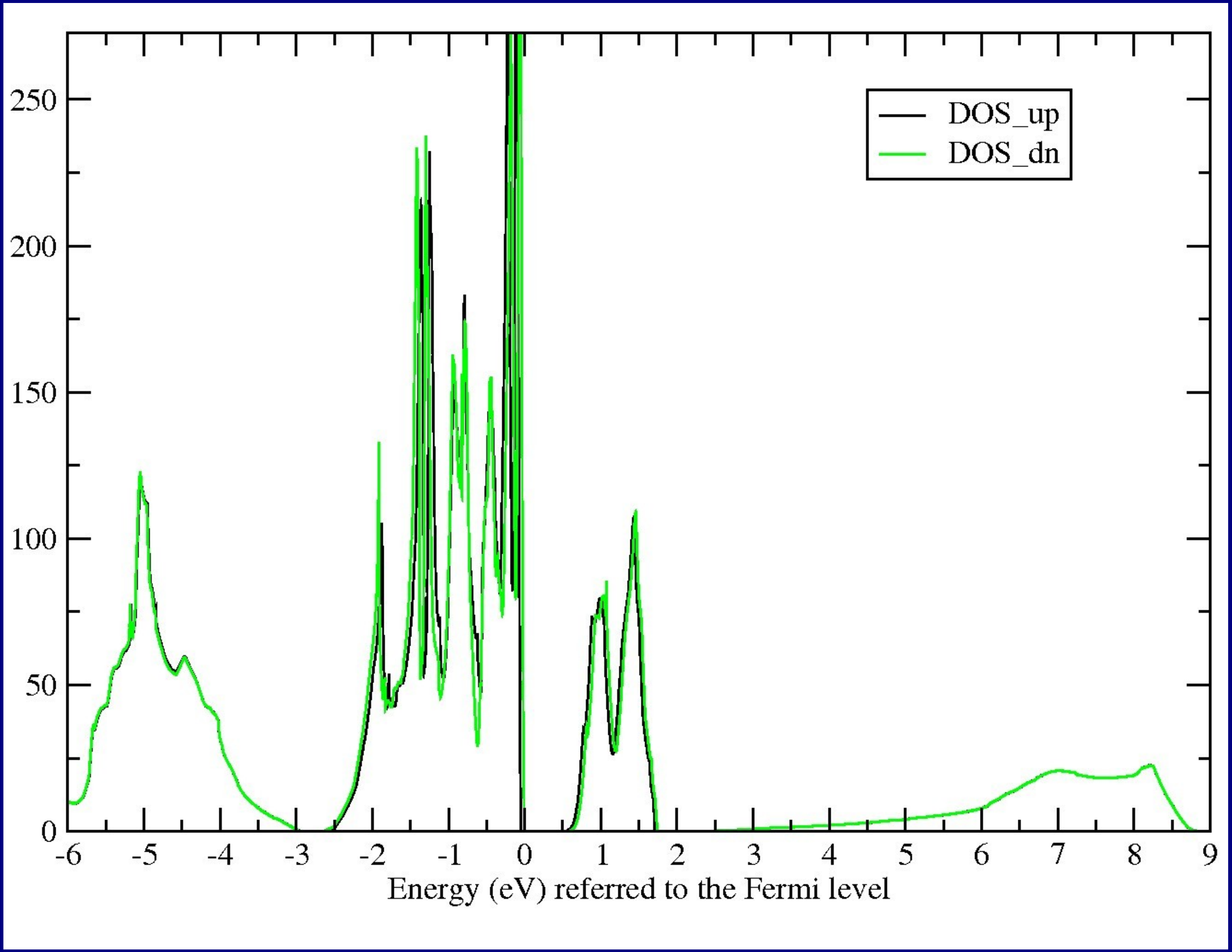
- But we are studying anti-ferromagnetic NiO... we need the spin!

LsDA - Bands



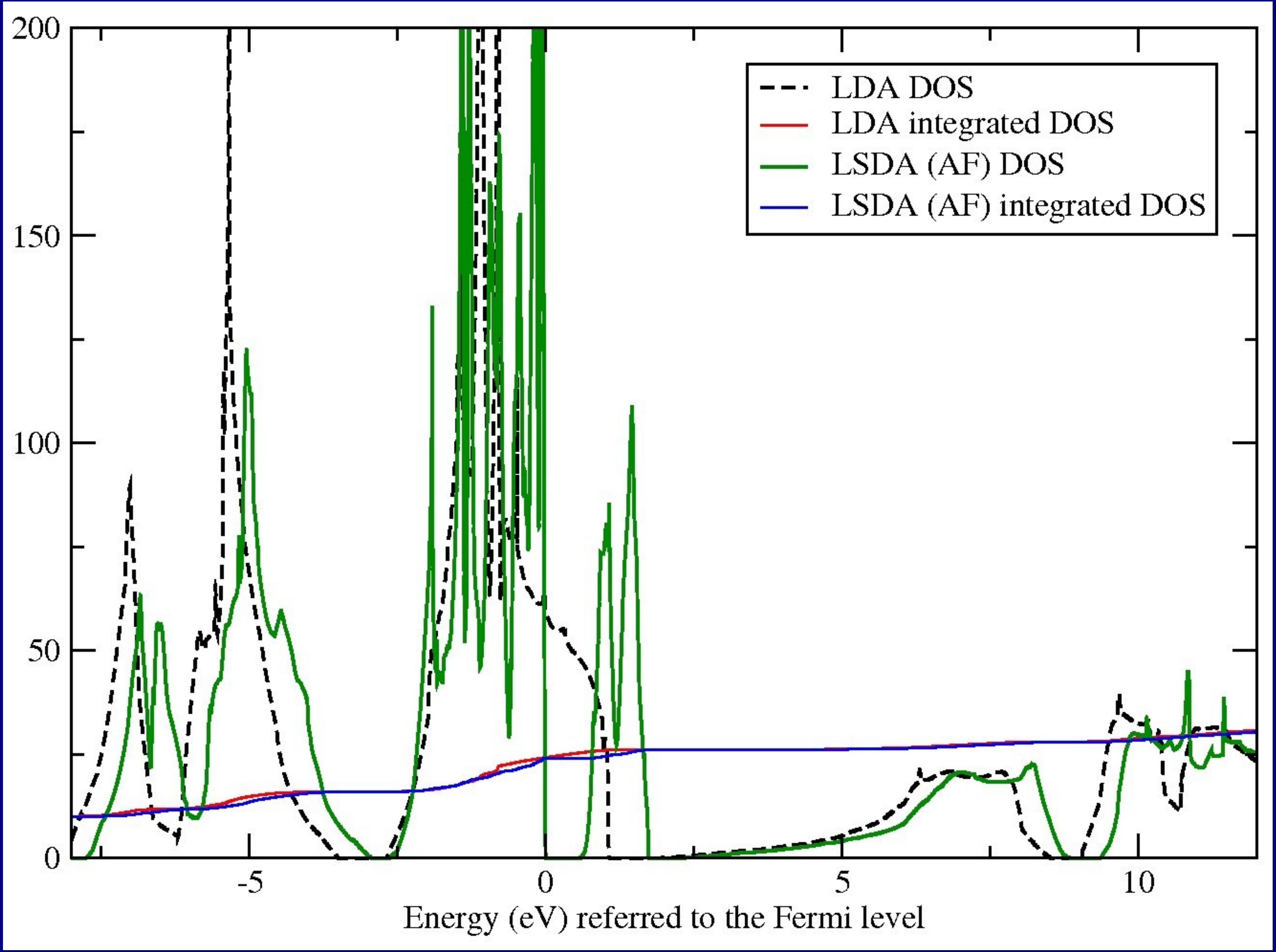
- E_{gap} ~ 0.5 eV

LsDA DOS



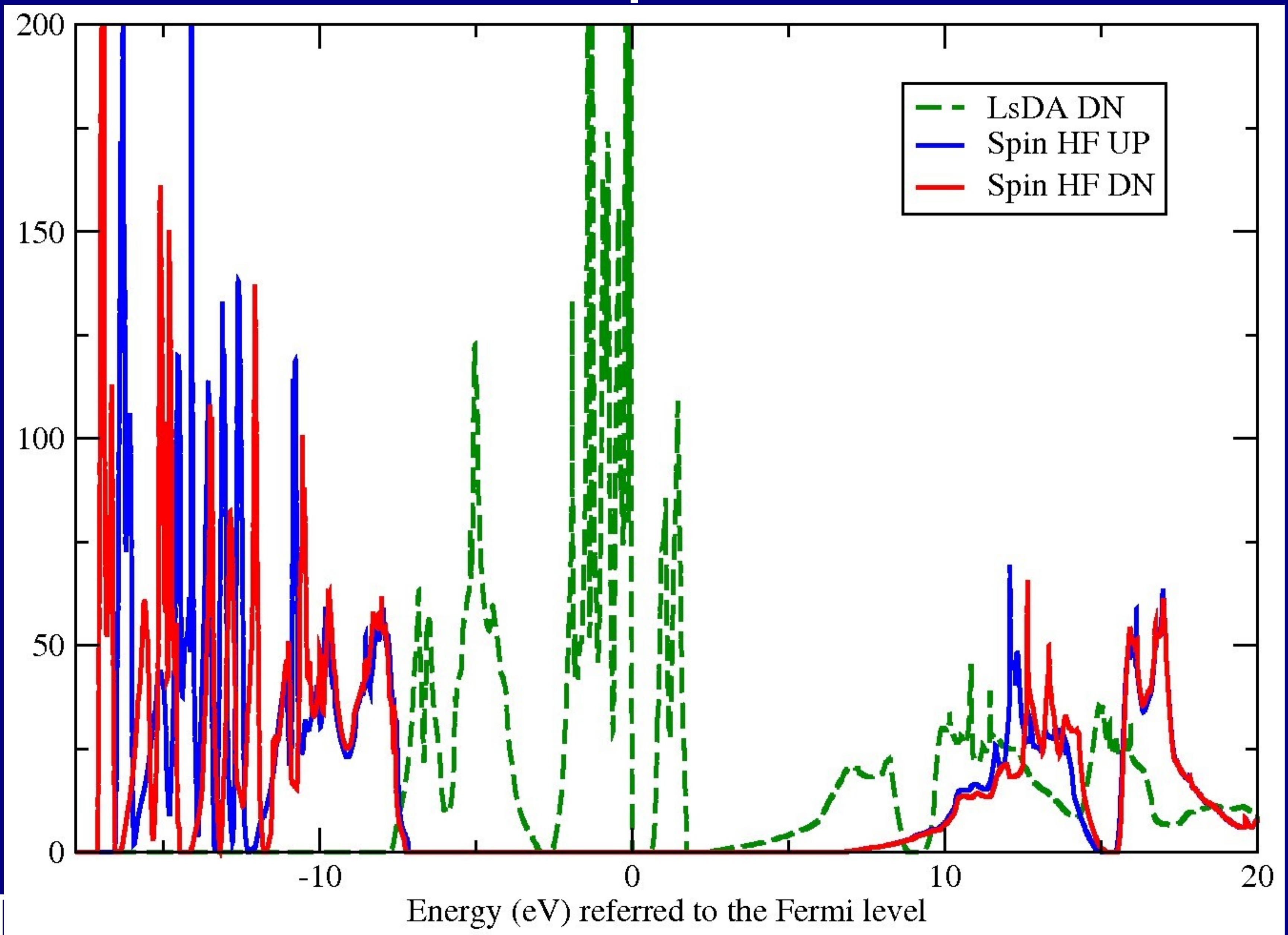
- Spins opens a gap!

LsDA DOS

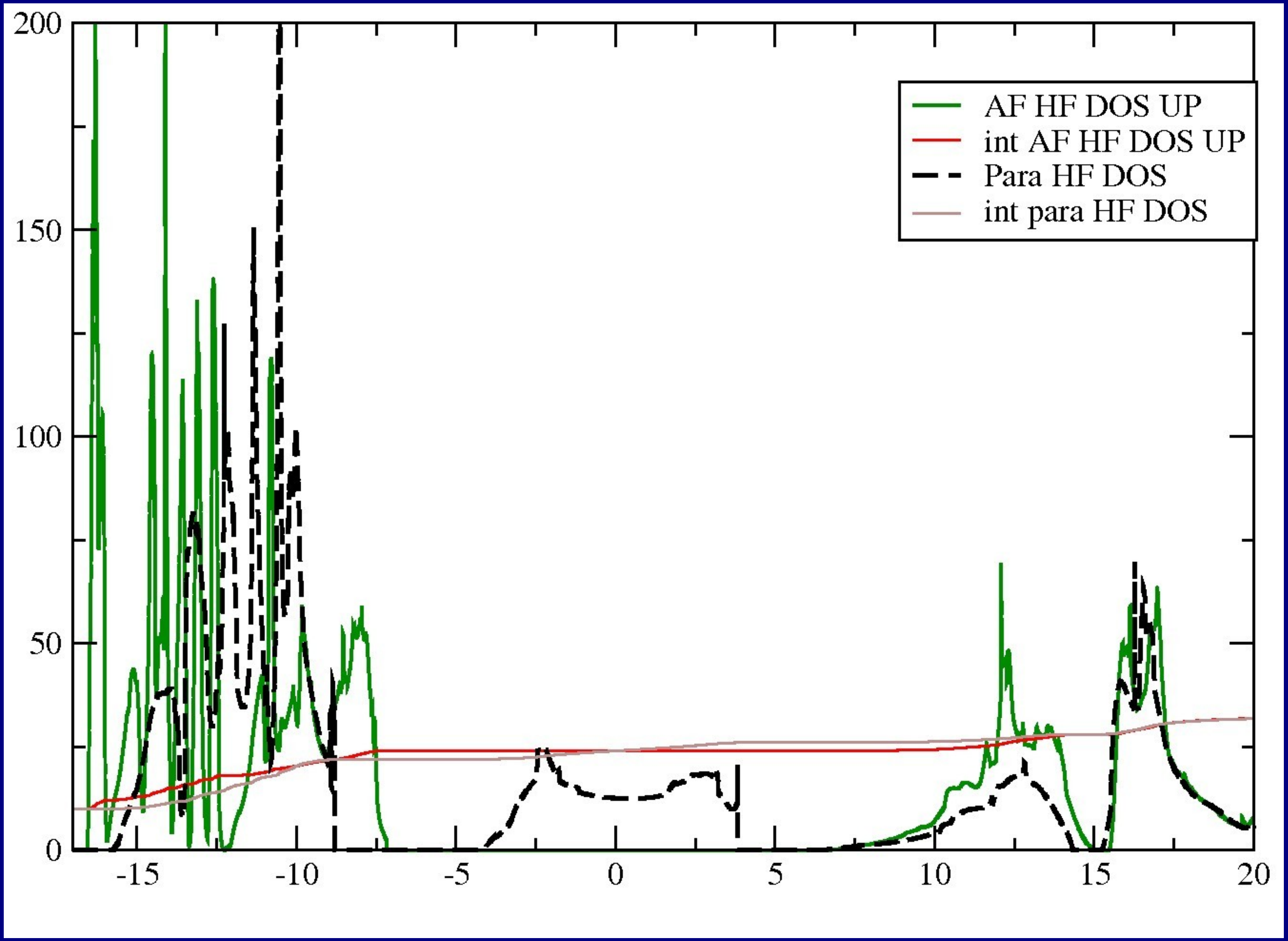


LDA DOS
LDA integrated DOS
LSDA (AF) DOS
LSDA (AF) integrated DOS
200
150
100
50
0
-5
0
5
10
Energy (eV) referred to the Fermi level

HF with spin - DOS



HF with and without spin



- Spin seems necessary to predict a gap.

Conclusion

- KS-LDA cannot give band structure, GW can.
- HF gives a different DOS, but without spin it does not open a gap!
- Spin is crucial in predicting the gap
- Problem: also paramagnetic NiO is an insulator!
  - we did not use the correct structure (rocksalt)

Perspective

- Better converged parameters calculation. (under way)
- Rocksalt paramagnetic structure.
- Include spin in paramagnetic calculation (SUPERCELL).
- GW?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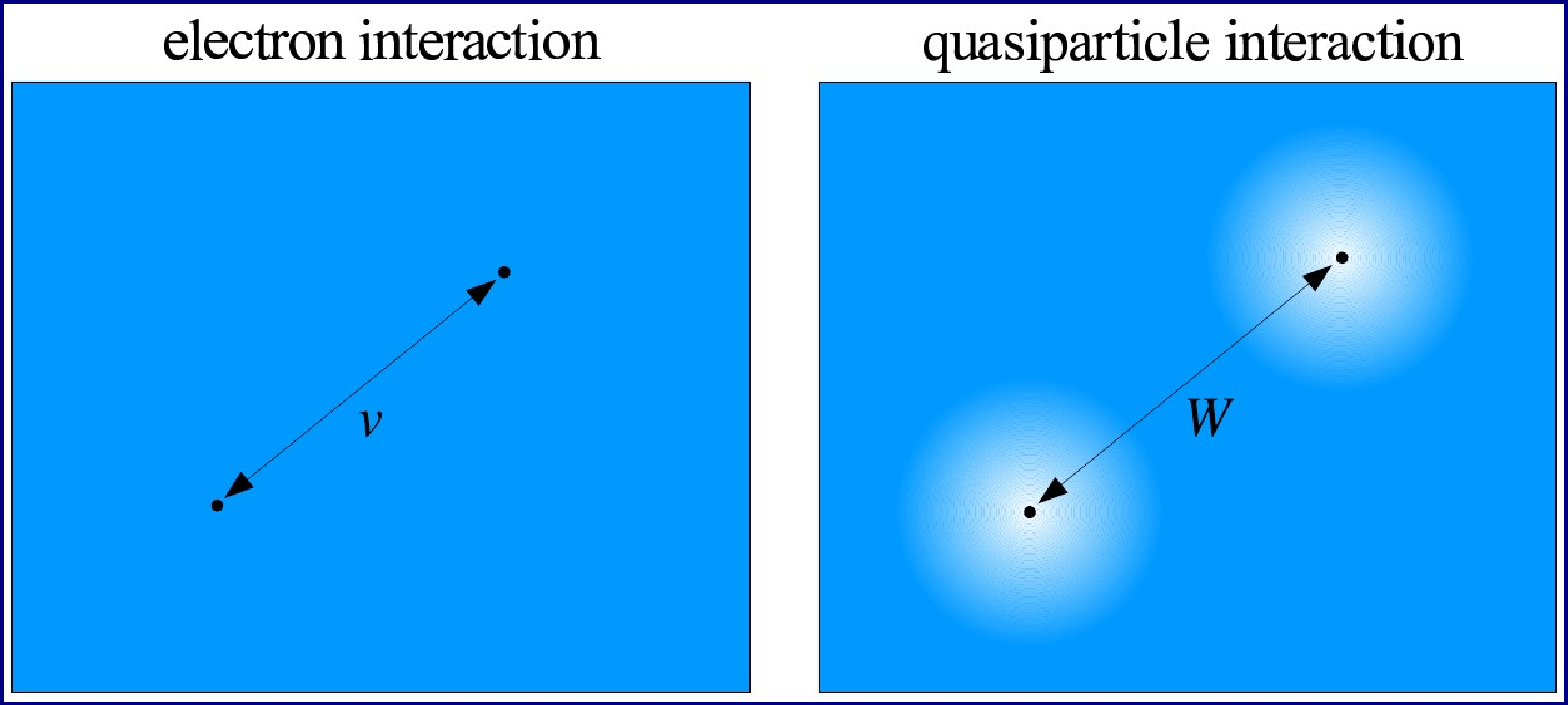
Screened dynamical interaction = Response of the system



The self energy Σ (Backup)

$$\int d\mathbf{r}_3 \left[h(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_3) + \Sigma(\mathbf{r}_1, \mathbf{r}_3, \epsilon_i)\right] f_i(\mathbf{r}_3) = \epsilon_i f_i(\mathbf{r}_1)$$

- Σ includes all many-body interactions in Quasi-particle equation of motion.
- Σ can be written as a function of G only!

$$\Sigma(1,2) = -i \int d345 G(1,4) \frac{\delta G^{-1}(4,2)}{\delta U(3)} v(1^+, 3)$$

- G_0