Localized and Itinerant States in a Unified Picture beyond Density Functional Theory

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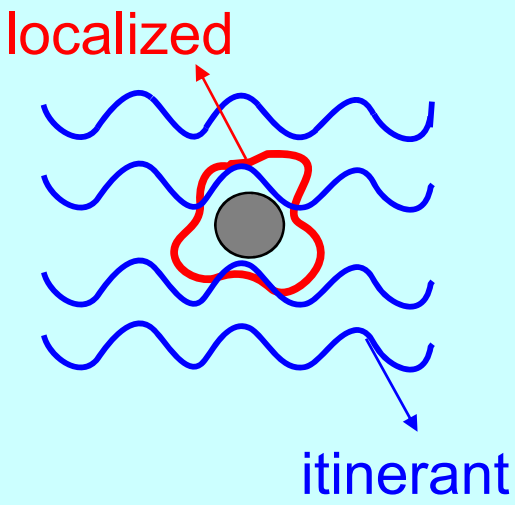
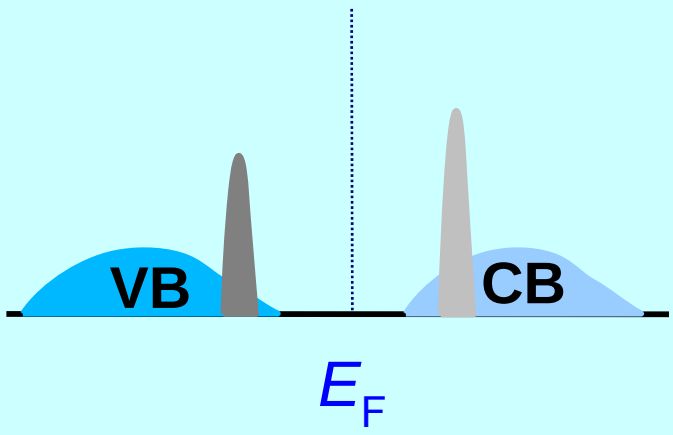
Outline

- Motivation: Why is it important to describe localized and itinerant states in an unified picture?
- Failure of LDA/GGA and its extensions
- What *GW* can do? *GW*@LDA+*U* and others
- Mott insulator from the *GW* perspective
- Concluding remarks

To localize or delocalize:

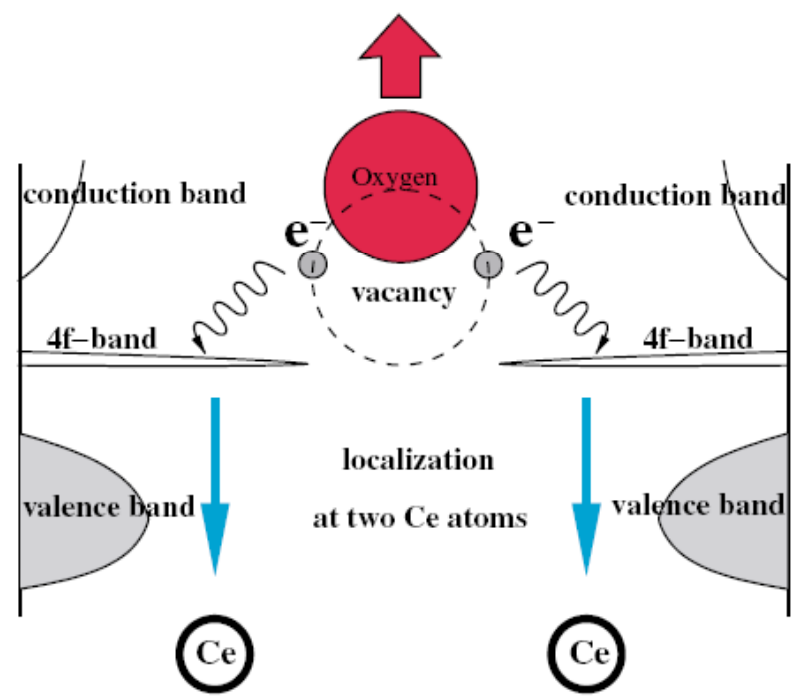
that is the question



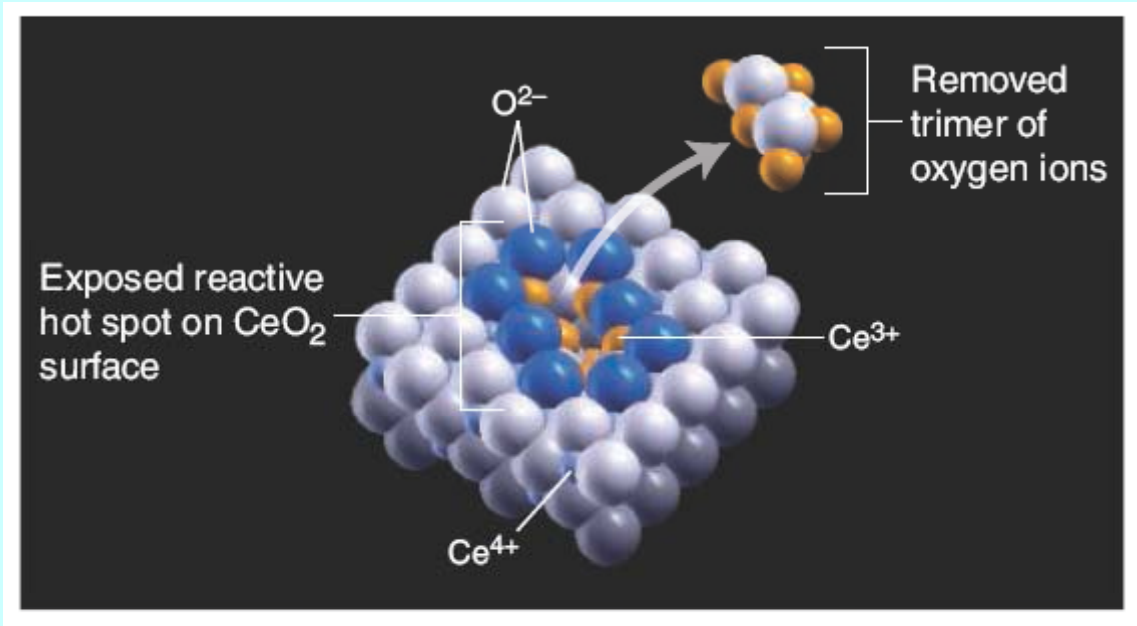


Oxygen vacancy in CeO_2

- The release and storage of oxygen in CeO_2 relies on the localized *f*-states ➔ a unified description of localized and itinerant states is necessary



Skorodumova et. al. PRL 89, 166601 (2002)

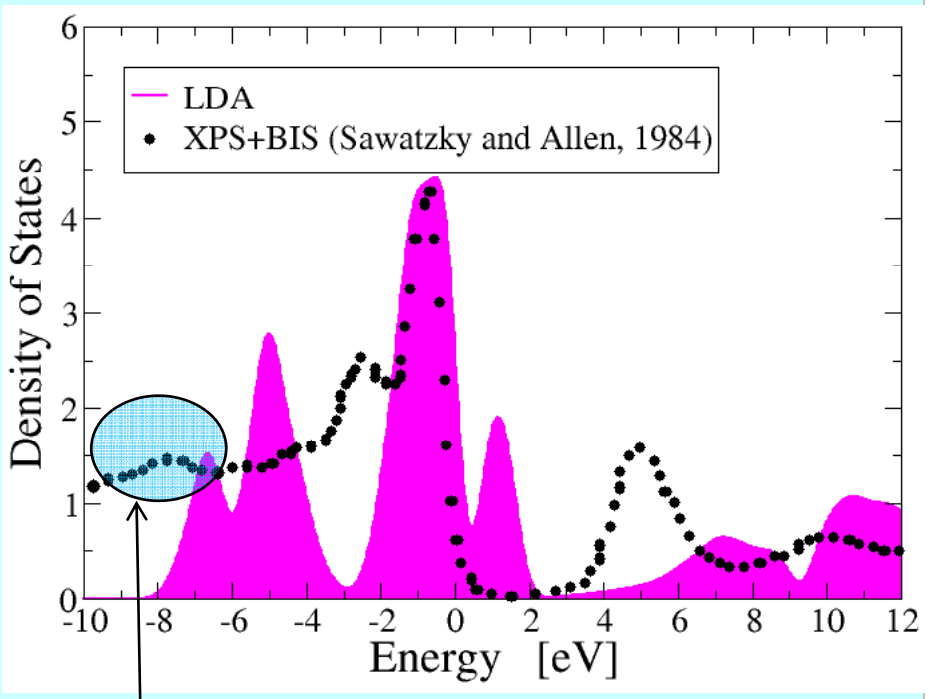


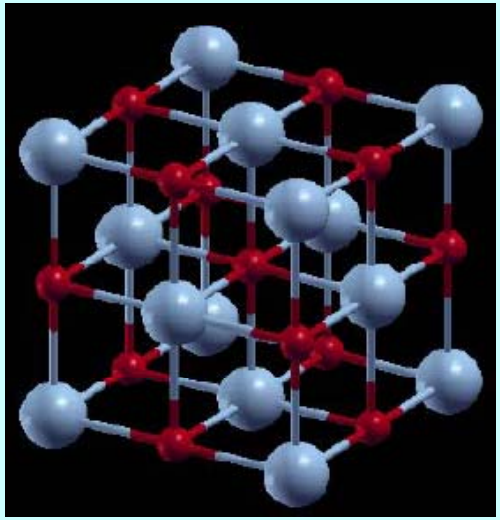
Campbell and Peden, Science 309, 713 (2005)

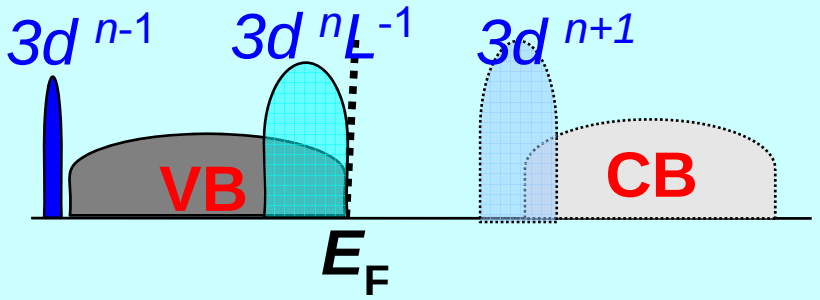
Esch *et al*. Science 309, 752 (2009)

Mott insulator NiO

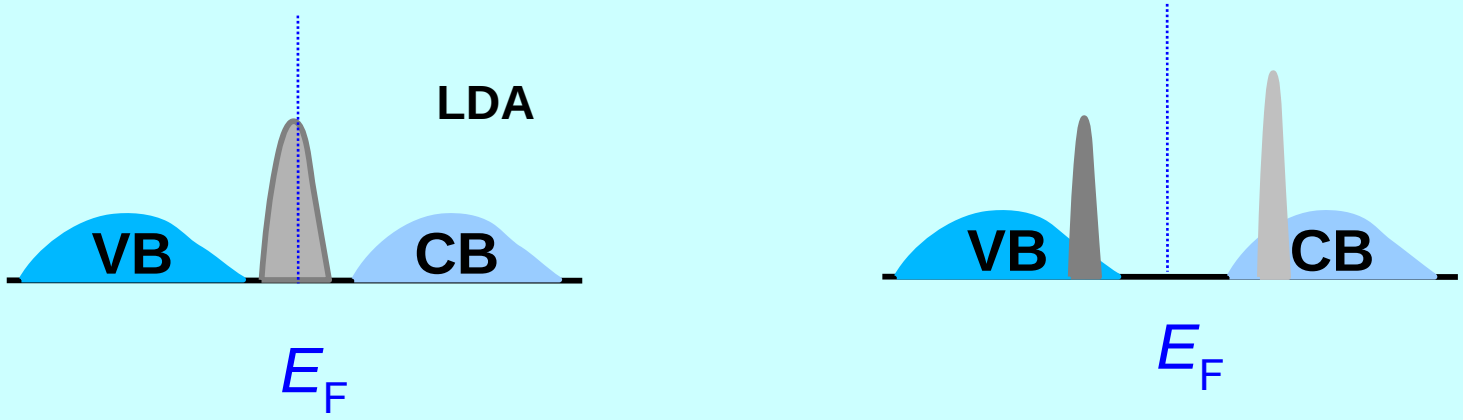
- Insulating in both anti-ferromagnetic ($T<T_c$) and paramagnetic ($T>T_c$)
- Band theory without symmetry breaking is doomed to fail
- Nature of the gap opening: Slater vs Mott model
- Small gap from LDA in AFM phase





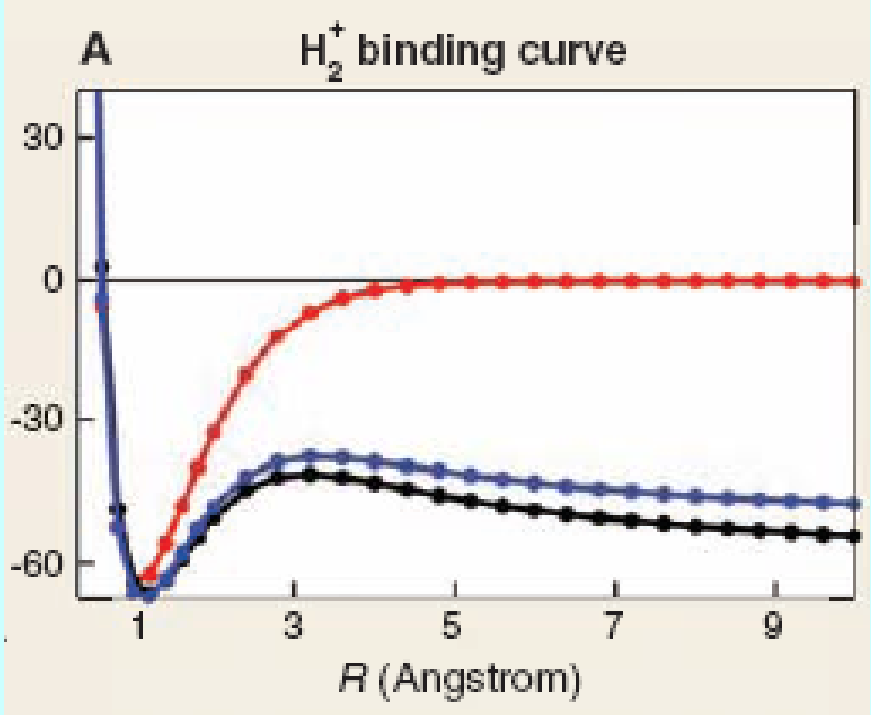


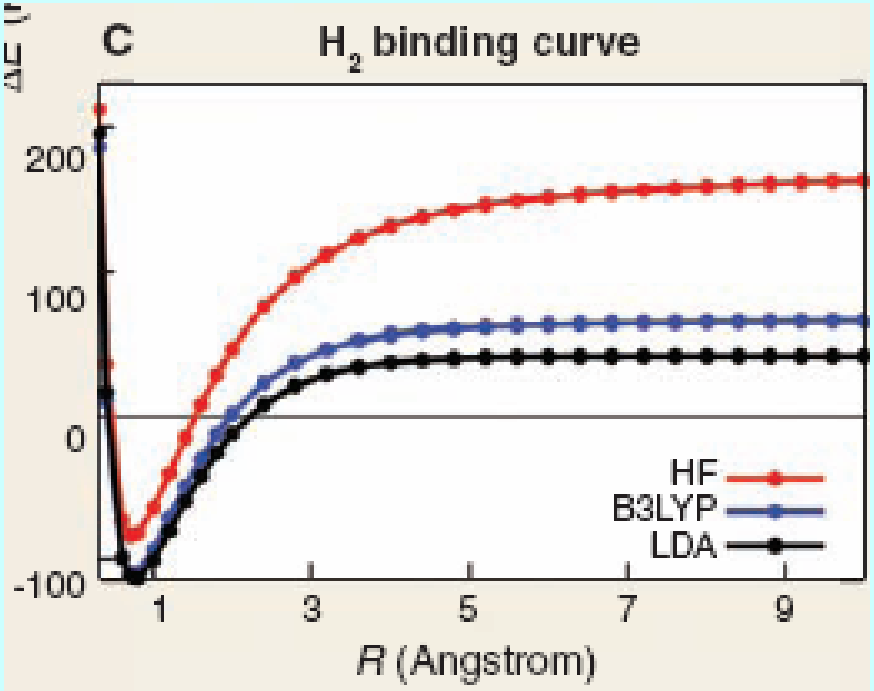
Failure of LDA/GGA and its extensions for correlated systems



Fundamental deficiencies of LDA/GGA

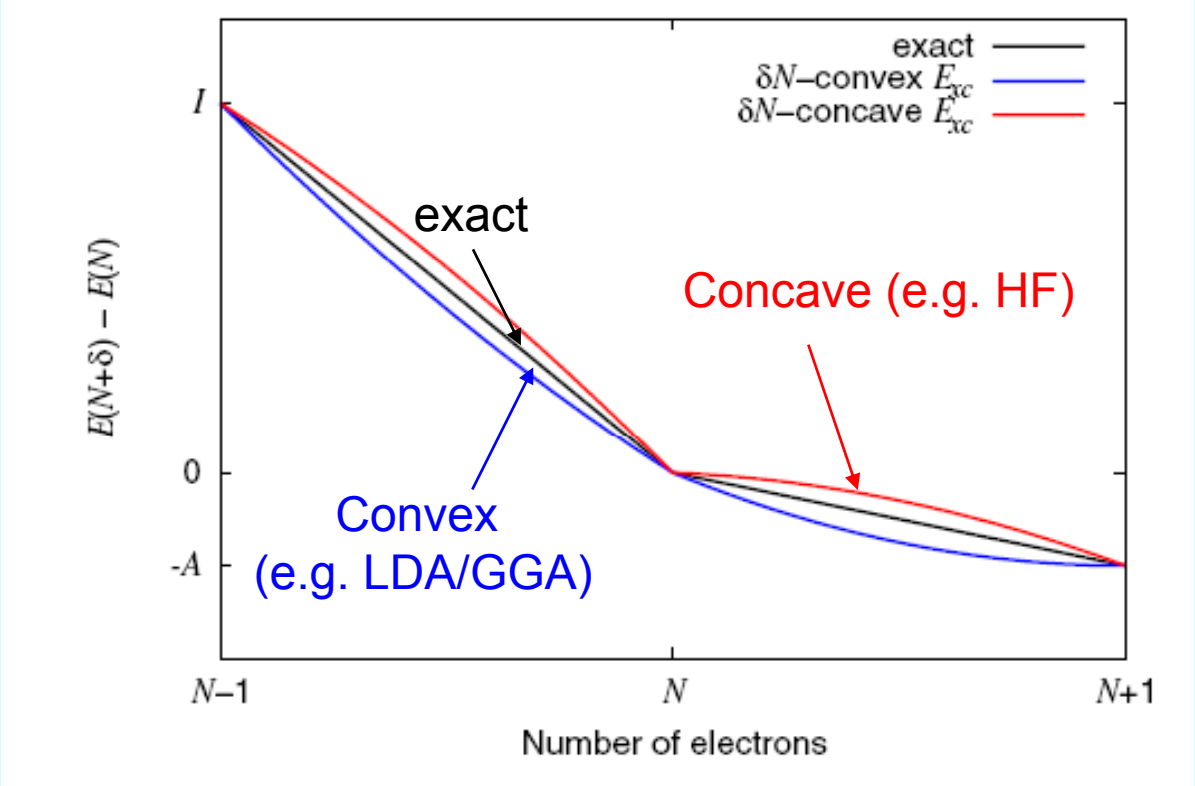
- underestimates E_{tot} for systems with factional charges
  - ➔ delocalization error (self-interaction)
- overestimates E_{tot} for systems with factional spins
  - ➔ static correlation error (strong correlation)





A. J. Cohen, P. Mori-Sanchez and W. Yang , *Science*, 321, 798 (2008)

DFT band gap problem



- More localized states have more severe delocalization error
- Open-shell *d/f*-electron systems: both fractional charge and fractional spin errors are present

Perdew et al. (1982); Mori Sanchez, Cohen and Yang, **PRL 77**, 115123(2008)

Beyond LDA/GGA

- SIC-LDA (Perdew amd Zunger (1981)

$$E_{\mathrm{tot}}^{\mathrm{SIC}}[n(\mathbf{r})] = E_{\mathrm{tot}}^{\mathrm{LDA}}[n(\mathbf{r})] - \sum_{i}^{\mathrm{occ}} \left(E_{\mathrm{H}}[n_i(\mathbf{r})] + E_{\mathrm{XC}}^{\mathrm{LDA}}[n_i(\mathbf{r})] \right)$$

- Hybrid functionals(Becke (1991); Perdew *et al*. (1996); Heyd et al. (2003))

$$E_{\mathrm{XC}}^{\mathrm{PBE0}}[n(\mathbf{r})] = a_{\mathrm{X}} E_{\mathrm{X}}^{\mathrm{HF}} + (1 - a_{\mathrm{X}}) E_{\mathrm{X}}^{\mathrm{PBE}} + E_{\mathrm{C}}^{\mathrm{PBE}}$$

$$E_{\mathrm{XC}}^{\mathrm{HSE}}[n(\mathbf{r})] = a_{\mathrm{X}} E_{\mathrm{X}}^{\mathrm{HF,SR}}(\omega) + (1 - a_{\mathrm{X}}) E_{\mathrm{X}}^{\omega\mathrm{PBE,SR}}(\omega) + E_{\mathrm{X}}^{\omega\mathrm{PBE,LR}}(\omega) + E_{\mathrm{C}}^{\mathrm{PBE}}$$

- LDA/GGA+*U* (Anisimov et al. (1991))

$$E^{\mathrm{LDA}+U}[\rho(\mathbf{r}), \hat{n}_l^a] = E^{\mathrm{LDA}}[\rho(\mathbf{r})] + E^{\mathrm{ee}}[\hat{n}_l^a] - E^{\mathrm{dc}}[\hat{n}_l^a]$$

- LDA+DMFT (Kotliar et. al. 2006)

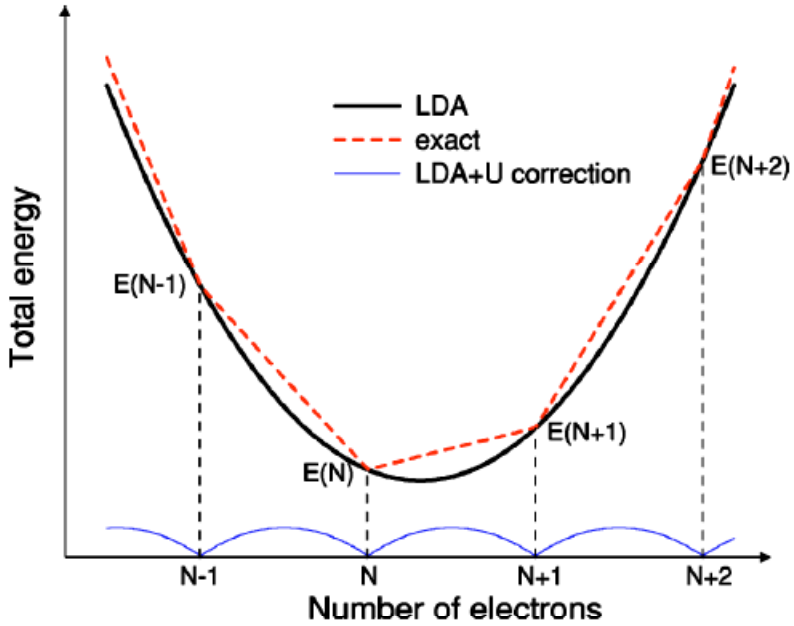
- LDA+Gutzwiller (Ho et al. 2008; Deng et al. 2008)

LDA+*U*: basic ideas

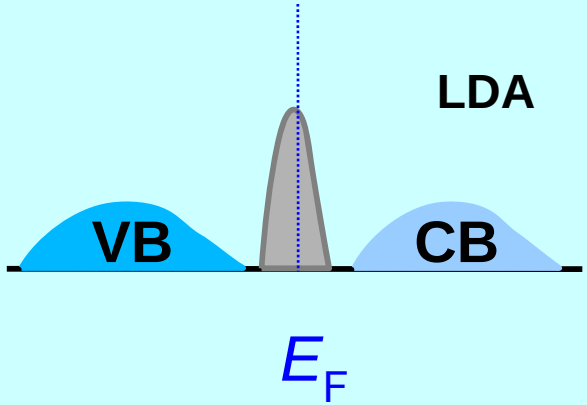
$$E = E_{LDA} - UN(N-1)/2 + \frac{1}{2}U\sum_{i\neq j} n_i n_j$$

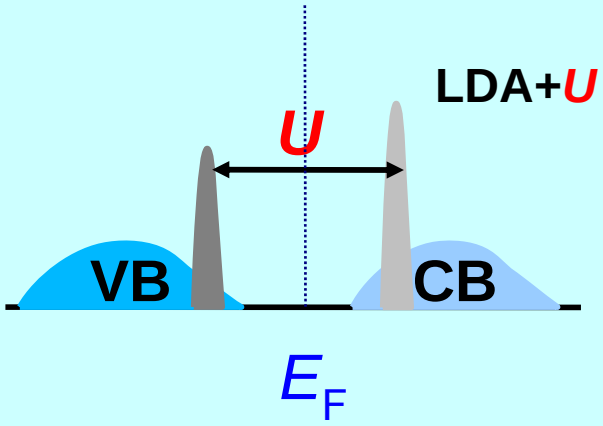
$$\epsilon_i = \partial E/\partial n_i = \epsilon_{LDA} + U\left(\frac{1}{2} - n_i\right).$$

$$V_i(r) = V_{LDA}(r) + U\left(\frac{1}{2} - n_i\right)$$



M. Cococcioni & S. de Gironicoli, PRB 71, 035105





LDA+*U* : a correction from the Hubbard Model

Hubbard model for local interaction:

$$\hat{H}_{ee} = \frac{U}{2} \sum_{m,m',\sigma} \hat{n}_m^{\sigma} \hat{n}_{m'}^{-\sigma} + \frac{U-J}{2} \sum_{m \neq m',\sigma} \hat{n}_m^{\sigma} \hat{n}_{m'}^{\sigma}$$

Hartree-Fock approximation:

$$E_{ee} = \frac{U}{2} \sum_{m,m',\sigma} n_m^{\sigma} n_{m'}^{-\sigma} + \frac{U-J}{2} \sum_{m \neq m',\sigma} n_m^{\sigma} n_{m'}^{\sigma}$$

For integer occupation

$$N_l^{\sigma} = \sum_m n_m^{\sigma}$$

$$\overline{E}_{ee} = \frac{U}{2} \sum_{\sigma} N_l^{\sigma} N_l^{-\sigma} + \frac{U-J}{2} \sum_{\sigma} N_l^{\sigma} (N_l^{\sigma} - 1)$$

$$\Delta E^{\mathrm{LDA+U}} \equiv E_{ee} - \overline{E}_{ee} = \frac{U-J}{2} \sum_{\sigma} \left\{ \mathrm{Tr}\left\{ \mathbf{n}^{\sigma} \right\} - \mathrm{Tr}\left\{ \mathbf{n}^{\sigma} \mathbf{n}^{\sigma} \right\} \right\}$$

Anisimov *et al.* (1993); Dudarev *et al.* (1998)

Assumptions within LDA+*U*

1. Identification of a local subsystem to which a correction is made

$$n^{\sigma}_{mm'} = \sum_i f^{\sigma}_i \langle \psi^{\sigma}_i | \hat{P}_{mm'} | \psi^{\sigma}_i \rangle$$

$$\hat{P}_{mm'} = |\phi_m\rangle \langle \phi_{m'}|$$

$$\phi_m(\mathbf{r}) \equiv u^I_{nl}(r) Y_{lm}(\hat{\mathbf{r}})$$

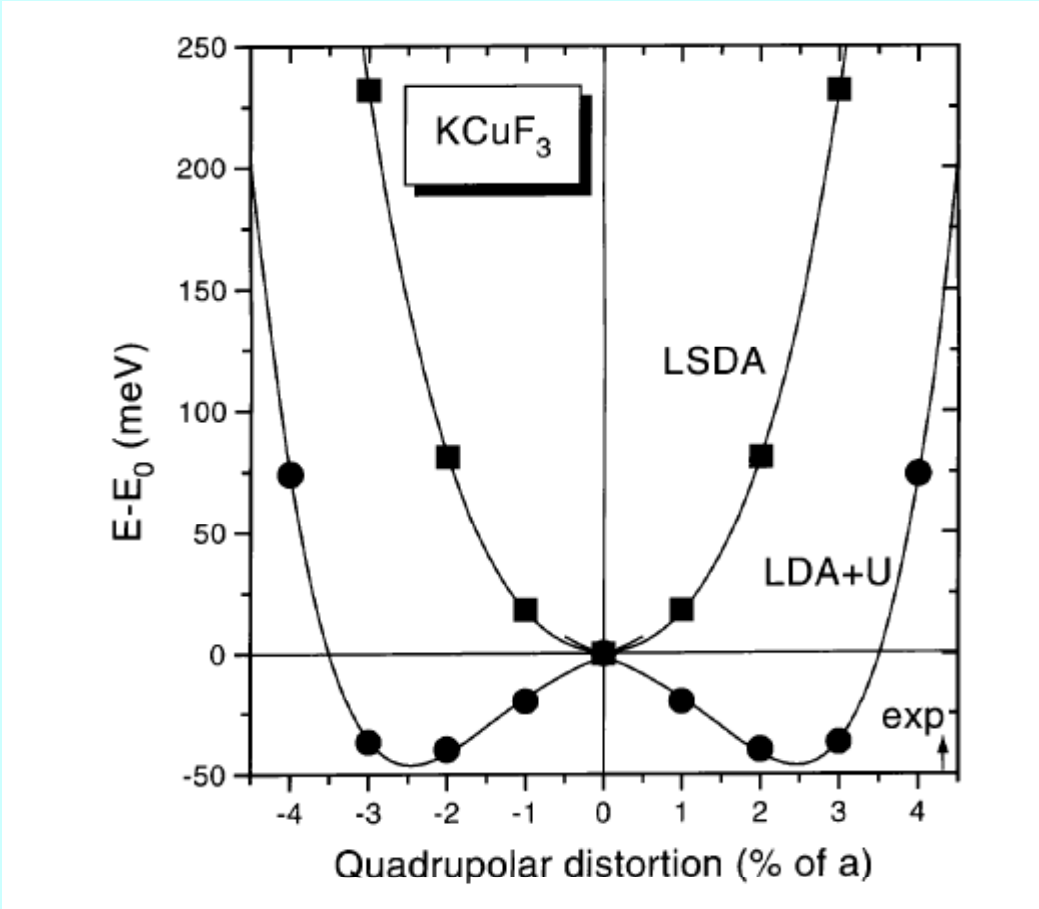
2. **A static mean-field approximation for the Hubbard model is adequate to describe many-body interaction in the local subsystem**
3. For the double-counting correction, the LDA interaction energy for the local subsystem can be described by the same parameters *U* and *J*

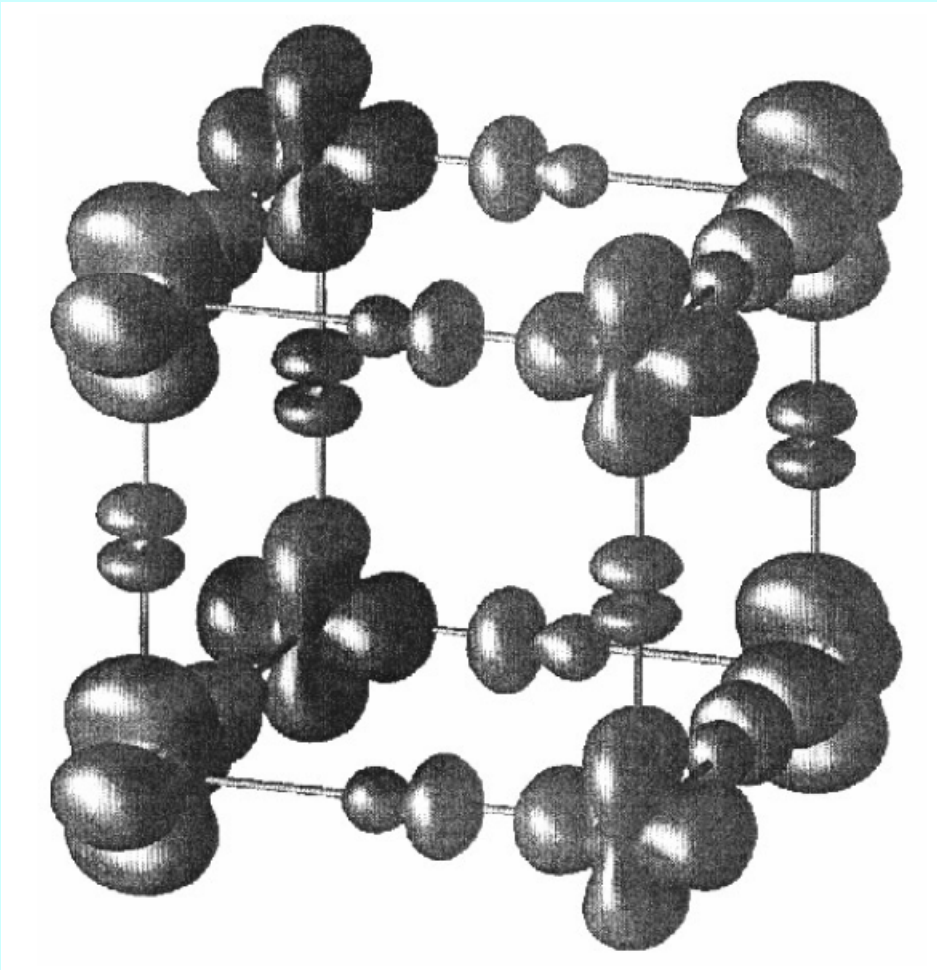
$$\overline{E}_{\mathrm{ee}}[n^{\sigma}] = \frac{1}{2} U N_l (N_l - 1) - \frac{1}{2} J \sum_{\sigma} N^{\sigma}_l (N^{\sigma}_l - 1)$$

➔ Assumptions similar to 1 and 3 are also made in LDA + DMFT or LDA + Gutzwiller

Anisimov, Aryasetiawan and Lichtenstein, JPCM (1997)

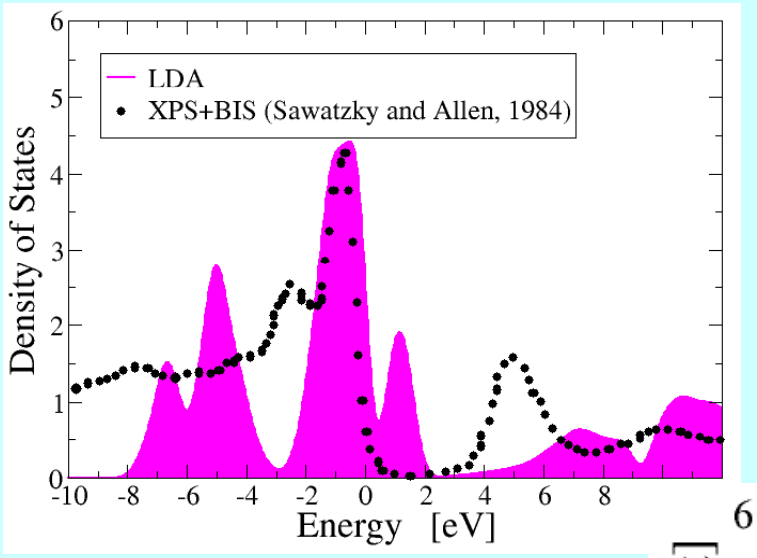
Example: Jahn-Teller distortion in in $KCuF_3$

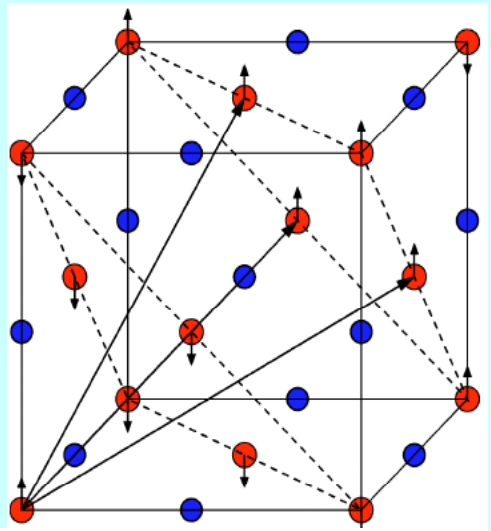


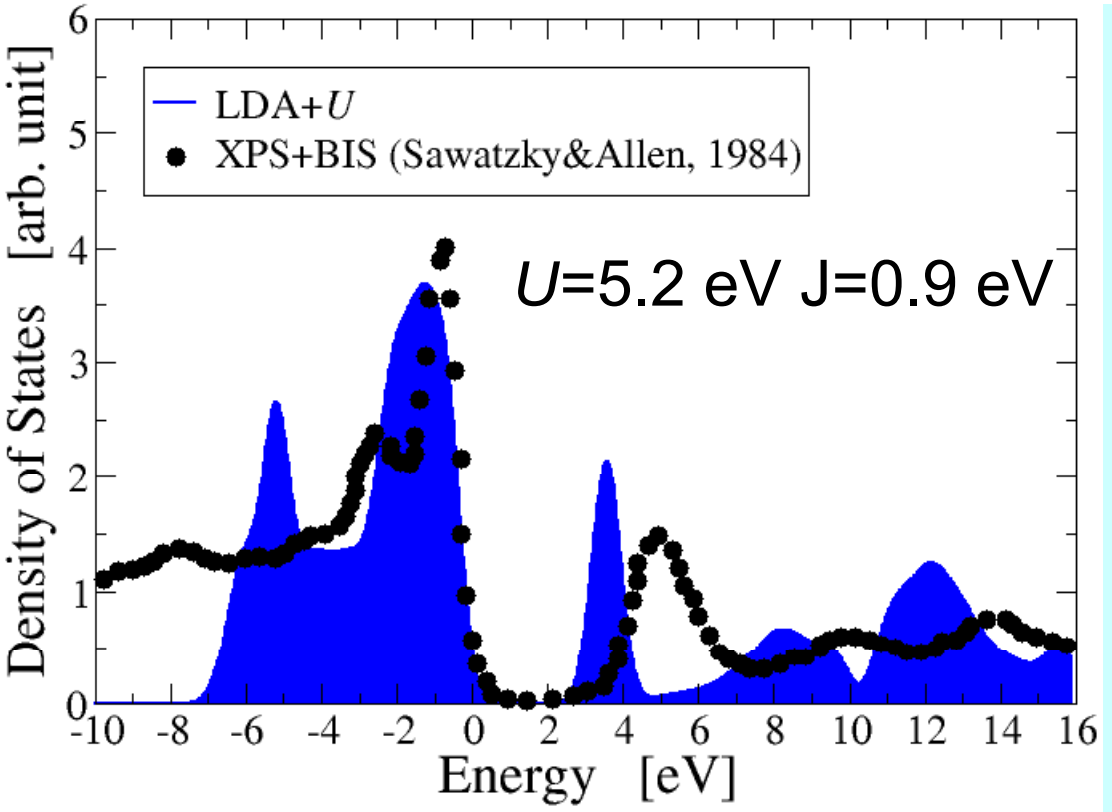


Lichtenstein, Anisimov, Zaanen (1995)

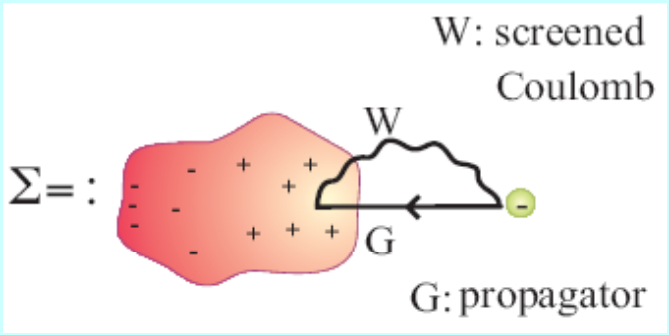
Example: Mott insulator NiO

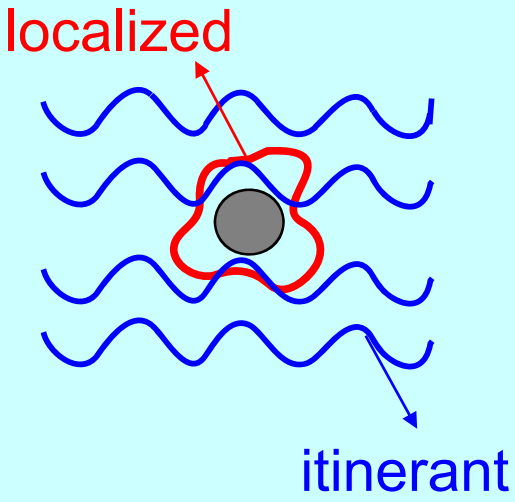






GW @LDA+*U* for *d*/*f*-electron System



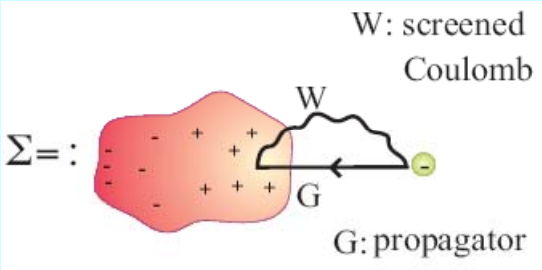


GW approximation for quasi-particle excitation

- **1st term** in a systematic MBPT expansion
- **Screening** in **quasi-particle picture**

=> accurate for itinerant electrons

- self-interaction treated at the exact exchange level



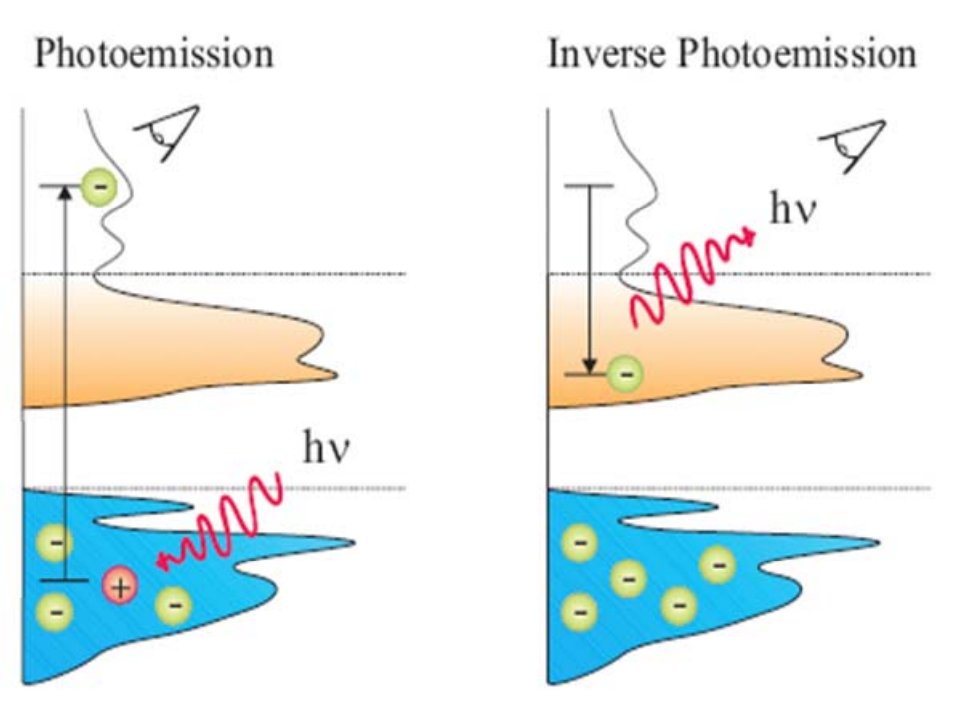
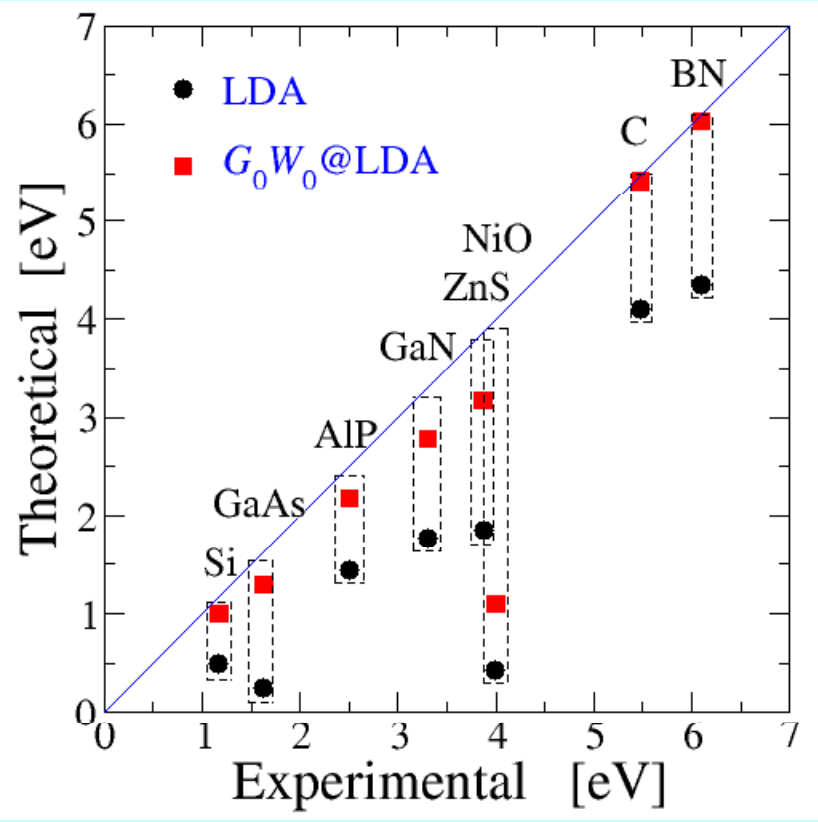
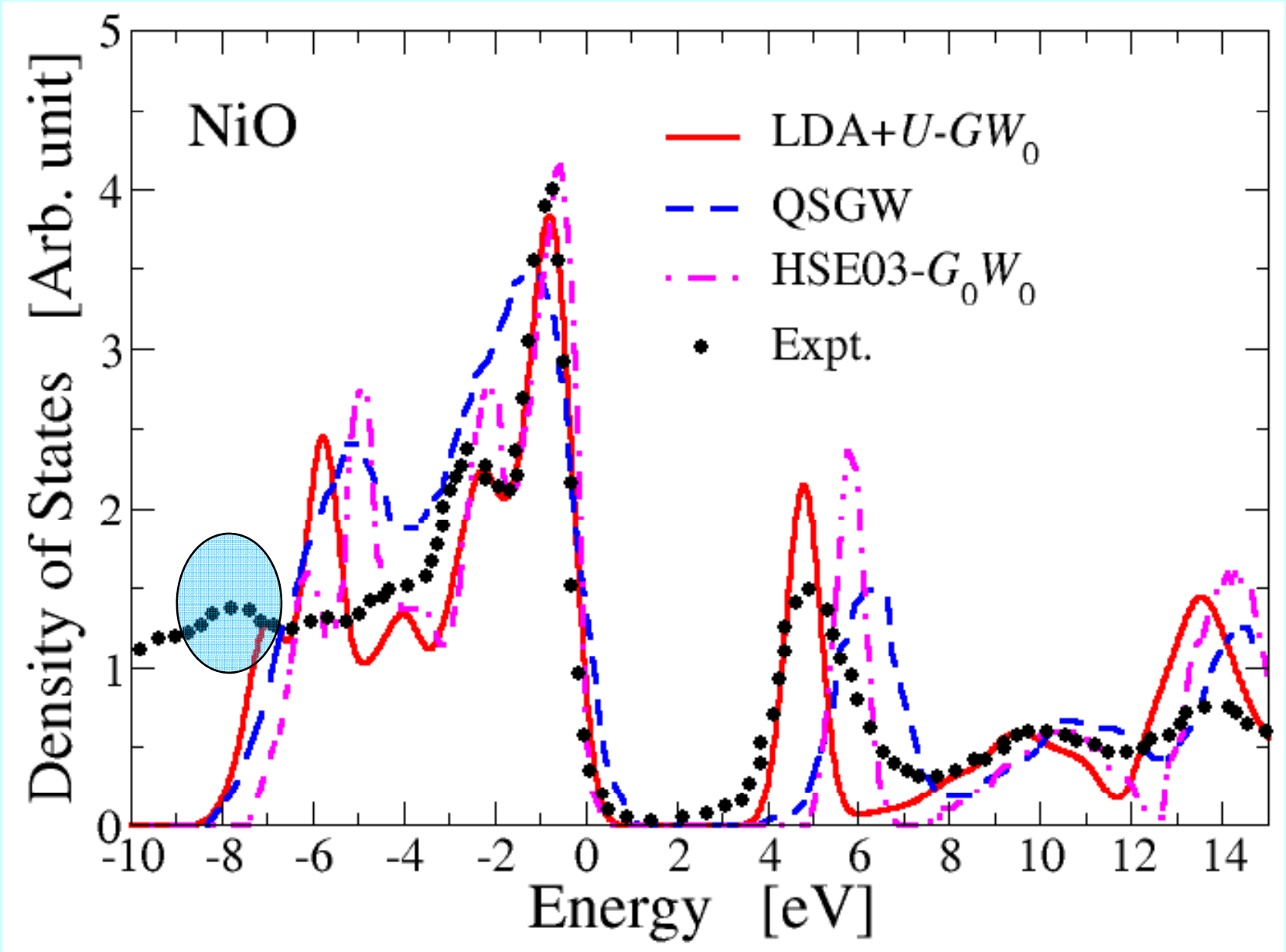


Figure from P. Rinke *et. al*. Ψ_k Newsletter No. 79, 163-189 (2007)



GW for *d*/*f*-electron systems



QSGW: T. Kotani, et al., PRB 76, 165106(2007).
HSE03-G_0W_0: C. Roedl et al. PRB 79, 235114(2009).

LDA+*U* as an "approximation" to *GW*

Assumptions

- **static approximation**: frequency dependence in W can be neglected
- **LDA for itinerant states**: QP correction are important only for localized d/f-states
- **fully localization limit** : localized *d/f*-states are "orthogonal" from itinerant states

$$\Sigma^{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int d\omega' G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega')$$

$$\Sigma^{\mathrm{CHSX}}(\mathbf{r},\mathbf{r}') = \sum_{n\mathbf{k}}\left(\frac{1}{2}-f_{n\mathbf{k}}\right)\psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}')^* W(\mathbf{r},\mathbf{r}';0) - \frac{1}{2}\sum_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}')^* v(\mathbf{r}-\mathbf{r}')$$

$$\delta\Sigma \simeq \sum_{m,m'}|m\rangle\,\delta\Sigma_{mm'}\,\langle m'|$$

$$\delta\Sigma_{mm'} = \sum_{m_1m_2}\left(\frac{1}{2}-n_{m_1m_2}\right)\langle mm_2|\,W(0)\,|m_1m'\rangle - \sum_{m_1m_2}\langle mm_2|\,v\,|m_1m'\rangle - \langle m|\,V_{\mathrm{xc}}\,|m'\rangle$$

$$\delta\Sigma_{mm'} - \delta_{mm'}\left(\frac{1}{2}-n_m\right)U$$

Anisimov *et al.* JPCM(1997)

GW @LDA+*U* method

LDA+*U* as the starting point of G_0W_0

- Simplest extension of *GW*@LDA
- LDA+*U* overcome the major failure of LDA for localized states
- LDA+*U* single-particle Hamiltonian as the reference, all states are treated on the same footing ➔ no double counting issue
- Dependence on *U* implicitly

$$\mathcal{E}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \Re\left[\langle\psi_{n\mathbf{k}}|\,\Sigma^{\mathrm{xc}}(\mathcal{E}_{n\mathbf{k}}) - V_{\mathrm{xc}} - \delta\hat{V}^{U}\,|\psi_{n\mathbf{k}}\rangle\right]$$

GW @LDA+*U* method

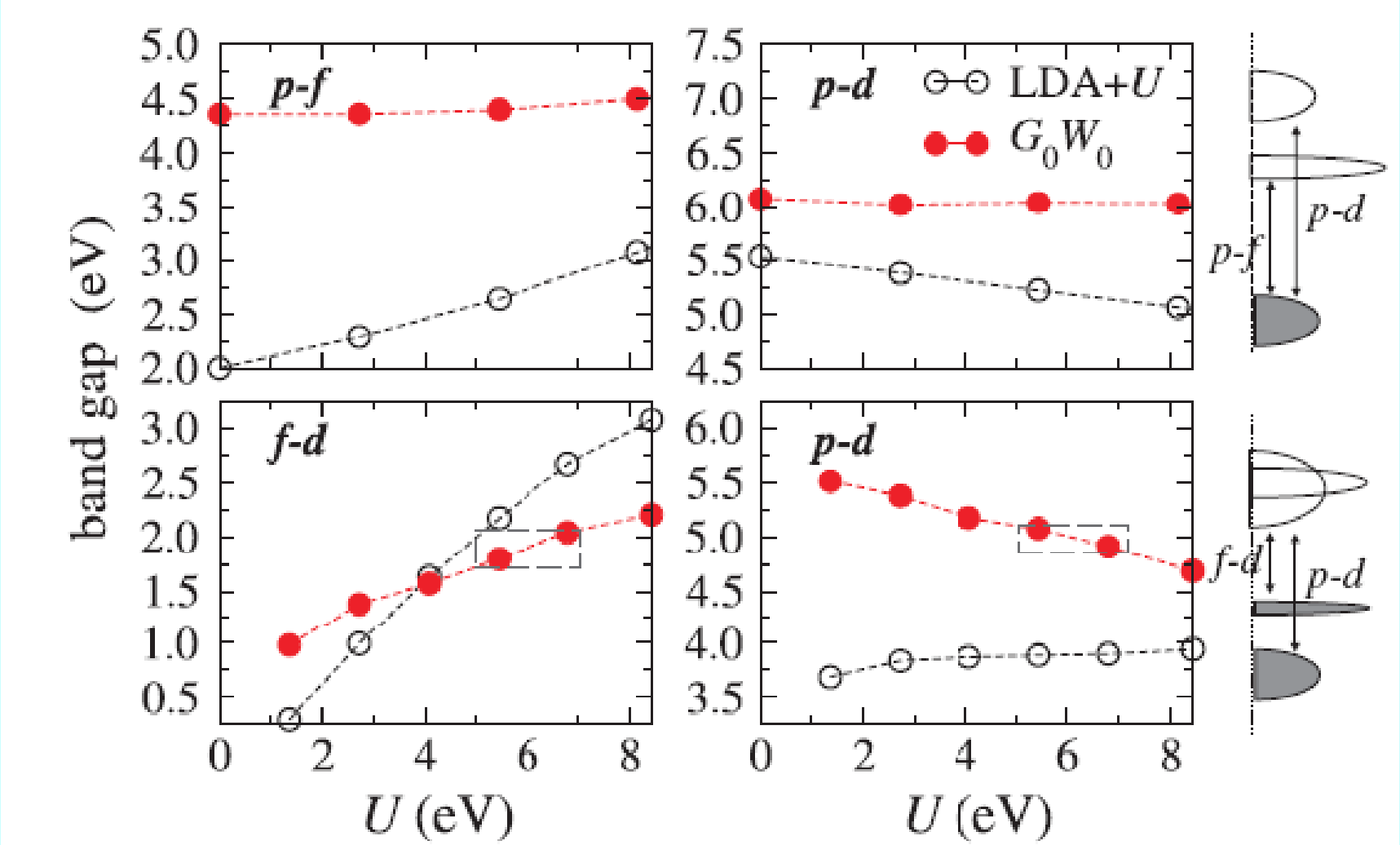
$$\mathcal{E}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \Re\left[\langle\psi_{n\mathbf{k}}|\,\Sigma^{\mathrm{xc}}(\mathcal{E}_{n\mathbf{k}}) - V_{\mathrm{xc}} - \delta\hat{V}^{U}\,|\psi_{n\mathbf{k}}\rangle\right]$$

$$\begin{aligned}\epsilon^{\mathrm{LDA}+U}_{n\mathbf{k}} &= \langle\psi_{n\mathbf{k}}|-\frac{1}{2}\nabla^2 + V^{\mathrm{LDA}} + \delta\hat{V}^{U}\,|\psi_{n\mathbf{k}}\rangle \\ &= \bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + \delta\hat{V}^{U}_{n\mathbf{k}}\end{aligned}$$

$$\begin{aligned}\mathcal{E}_{n\mathbf{k}} &= \epsilon^{\mathrm{LDA}+U}_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\mathcal{E}_{n\mathbf{k}}) \\ &\simeq \bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + \delta\hat{V}^{U}_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}) \\ &\quad + \delta\Sigma'_{n\mathbf{k}}(\bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}})(\mathcal{E}_{n\mathbf{k}} - \bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}).\end{aligned}$$

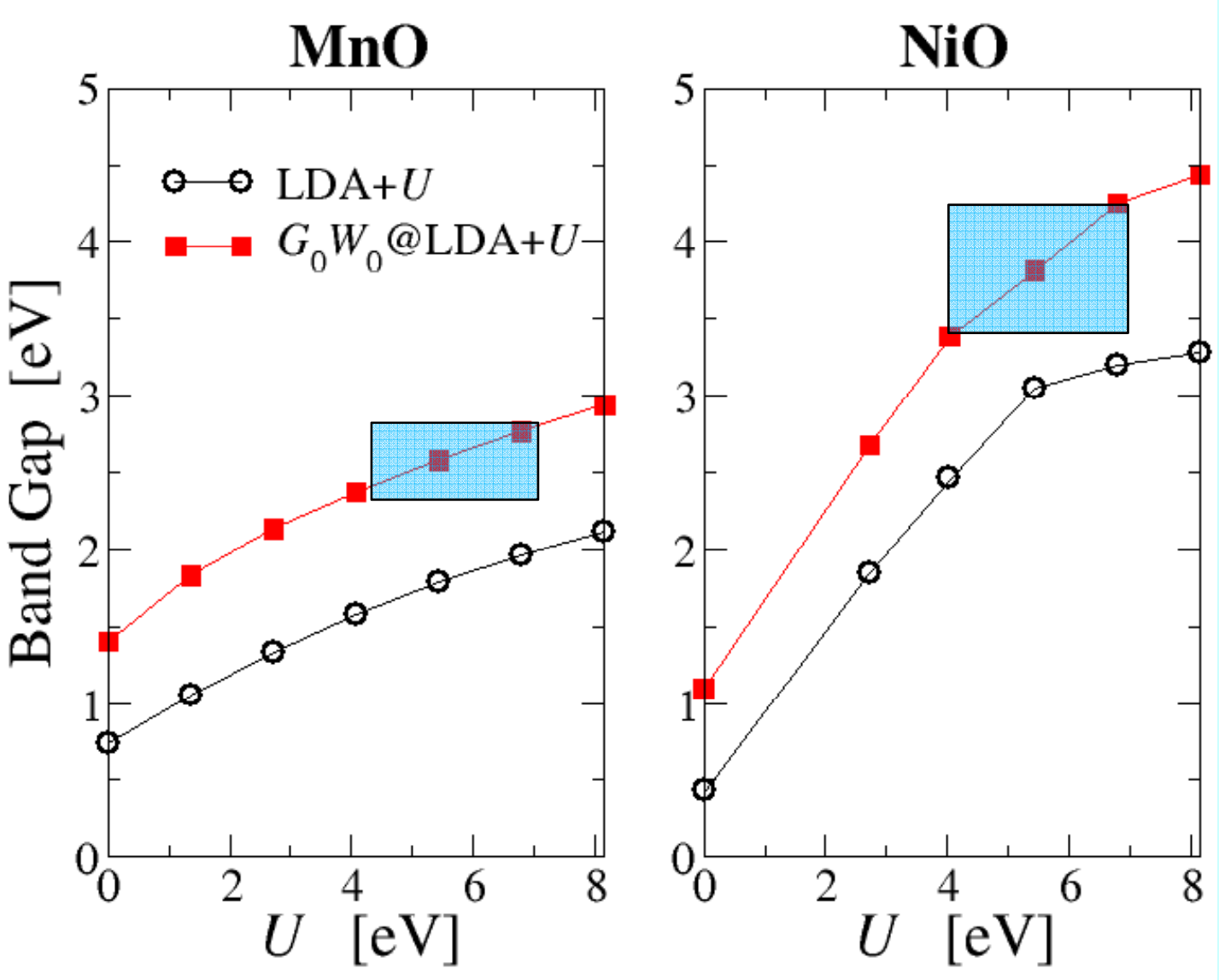
$$\mathcal{E}_{n\mathbf{k}} = \bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}\right)\left[\Sigma^{\mathrm{xc}}_{n\mathbf{k}}\left(\bar{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}\right) - V^{\mathrm{xc}}_{n\mathbf{k}}\right]$$

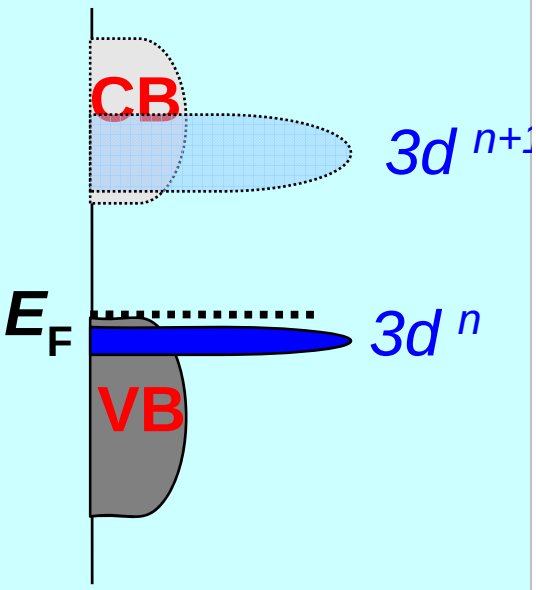
U-dependence: CeO_2 and Ce_2O_3

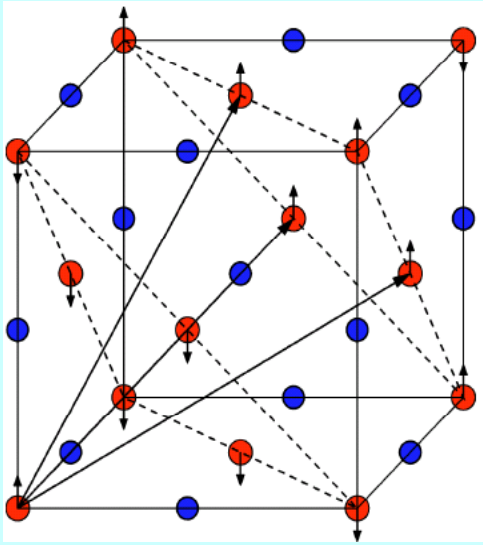


- **LDA+*U*:** *f-d* gap strongly depends on *U*
- **G_0W_0 @LDA+*U*:** both *f-d* and *p-d* gaps depend on *U* weakly
- Around “physical value” of *U* (~5-7 eV), the uncertainty ~ 0.2 eV

U-dependence: MnO and NiO

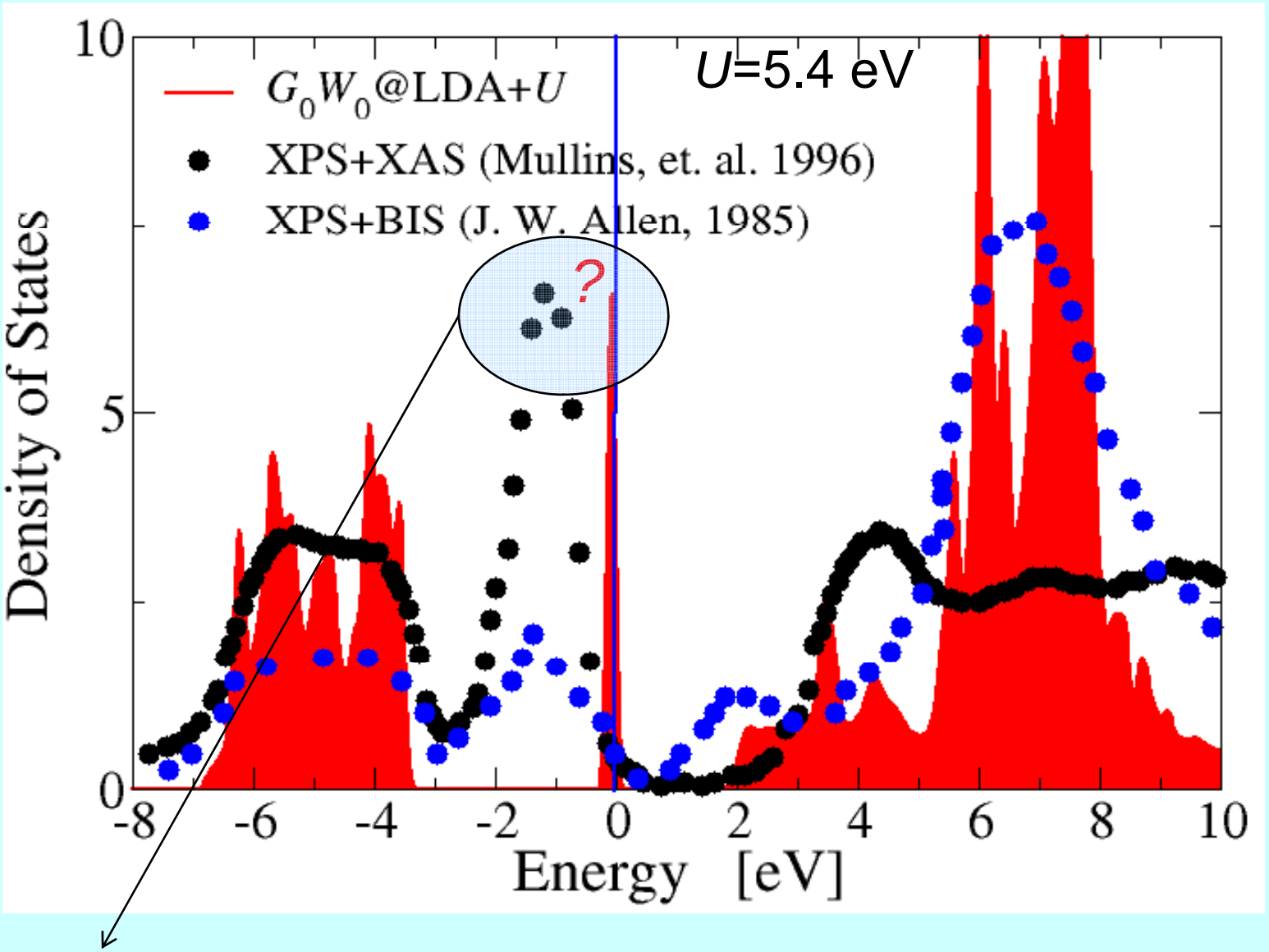






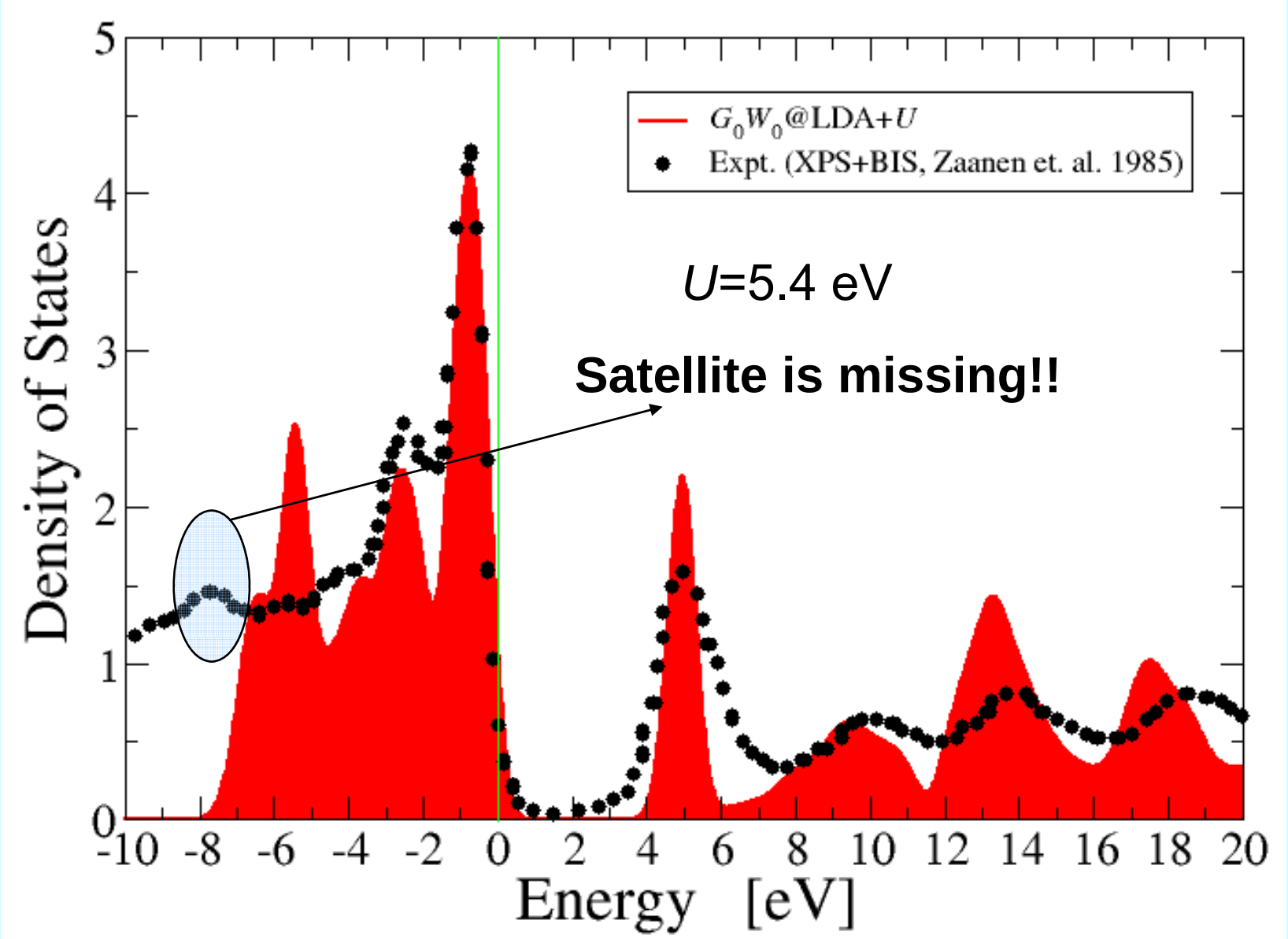
AFM-II

Ce_2O_3 : Compare G_0W_0 and Expt.



f^{occ} state binding energy is underestimated!!

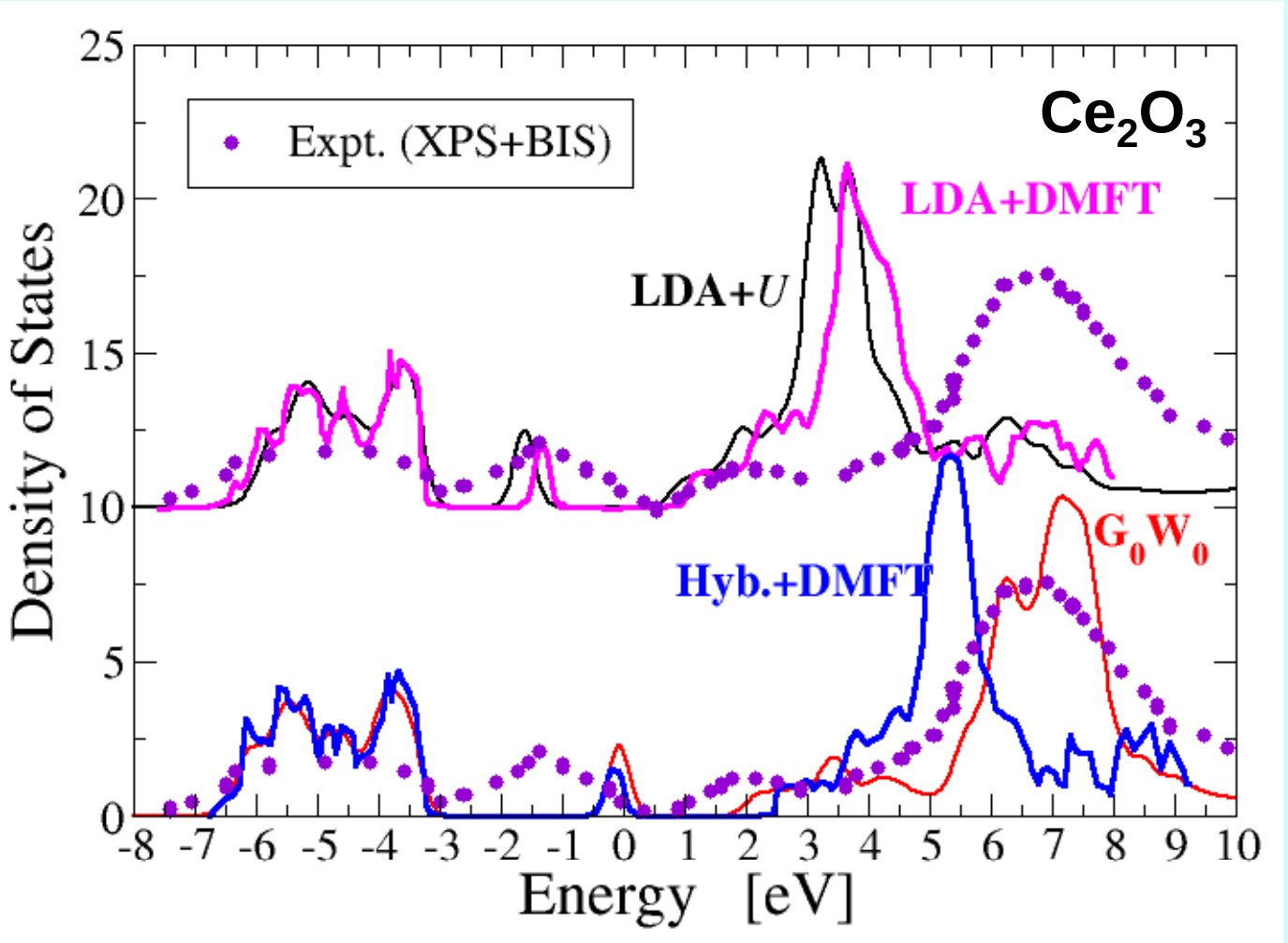
NiO: G_0W_0@LDA+U vs expt.



Jiang, Gomez-Abal, Rinke and Scheffler, in preparation.

GW@LDA+*U* vs LDA+DMFT

- Both consider dynamic correction to LDA+*U*
- DMFT: strong correlation among localized states only
- *GW* considers all states on the same footing

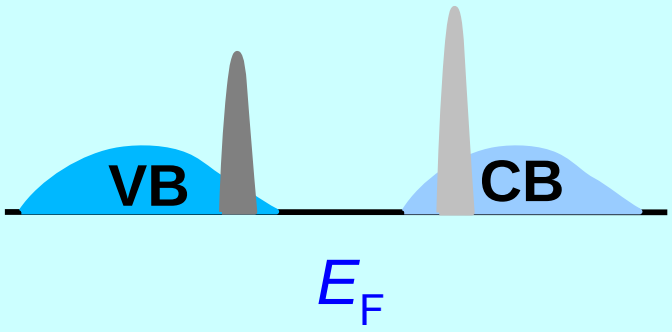


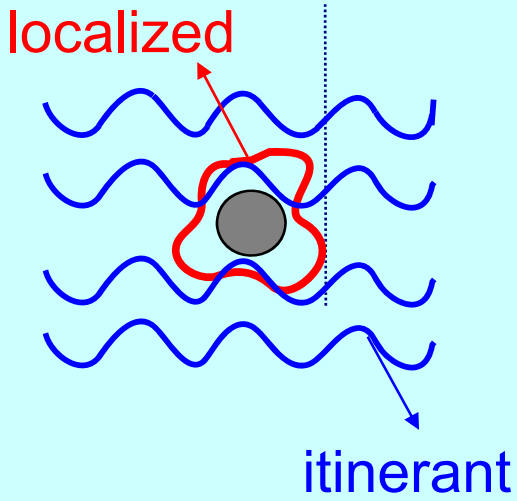
DMFT: D. Jacob et al. EPL **84**, 57009(2008); Expt.: J. W. Allen, J. Magn. Magn. Mater. 47/48, 168 (1985)

Limitations of *GW*@LDA+*U*

- ***U*-dependence**
  - Allow operational investigation of interaction effects
  - Often quite weak for Ln_2O_3, but stronger for late TMO
  - For quantitative prediction, one needs “first-principles” approaches to determine *U*
- **Change of wave functions**
  - LDA+*U* wave functions may not be good enough ➔off-diagonal contributions of self-energy are important
- **More Fundamental problems (fail for strong correlation?)**
  - Binding energy of occupied localized states significantly underestimated
  - Satellite structure missing

Mott insulator in *GW*?





What is a Mott insulator?

- A material which exhibits a radical breakdown of conventional band theory
- A material whose insulating gap is due primarily to the one-site Coulomb repulsion U
- A material with properties similar to NiO

- An ordinary magnetic insulator

B. H. Brandow, Advance in Physics, 26, 651 (1977)

Slater vs Mott: Are they really incompatible?

- **Slater model**: gap opening due to the anti-ferromagnetic ordering (breaking the spin symmetry)

➔ Can not explain the gap in the paramagnetic ordering

➔ What is the cause of the anti-ferromagnetic ordering?

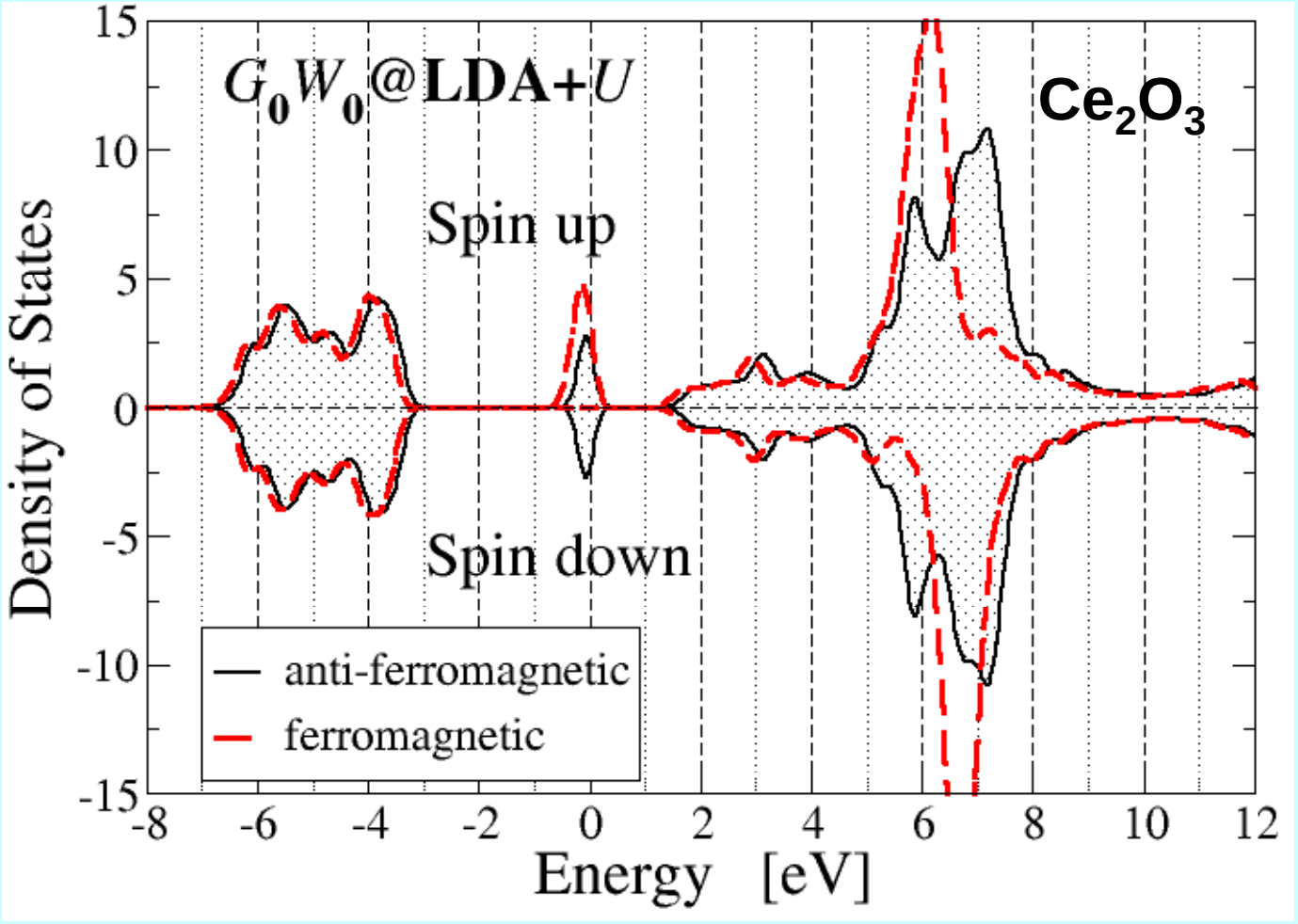
- **Mott model:** gap opening due to the strong on-site interaction

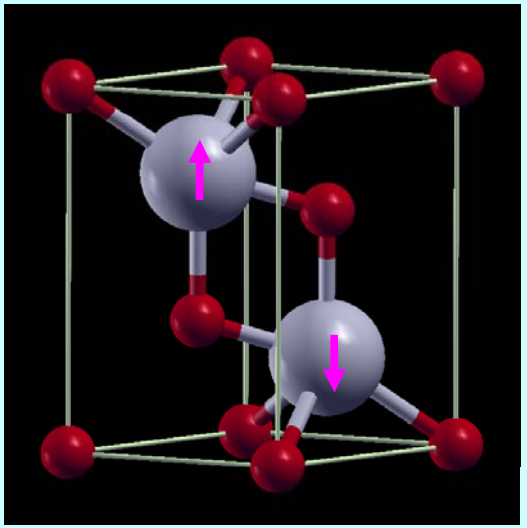
➔ The gap opening is not related to magnetic ordering, but there is always a local magnetic moment even in the paramagnetic phase

➔ symmetry is broken

➔ How to incorporate this basic physics in a band theoretical framework?

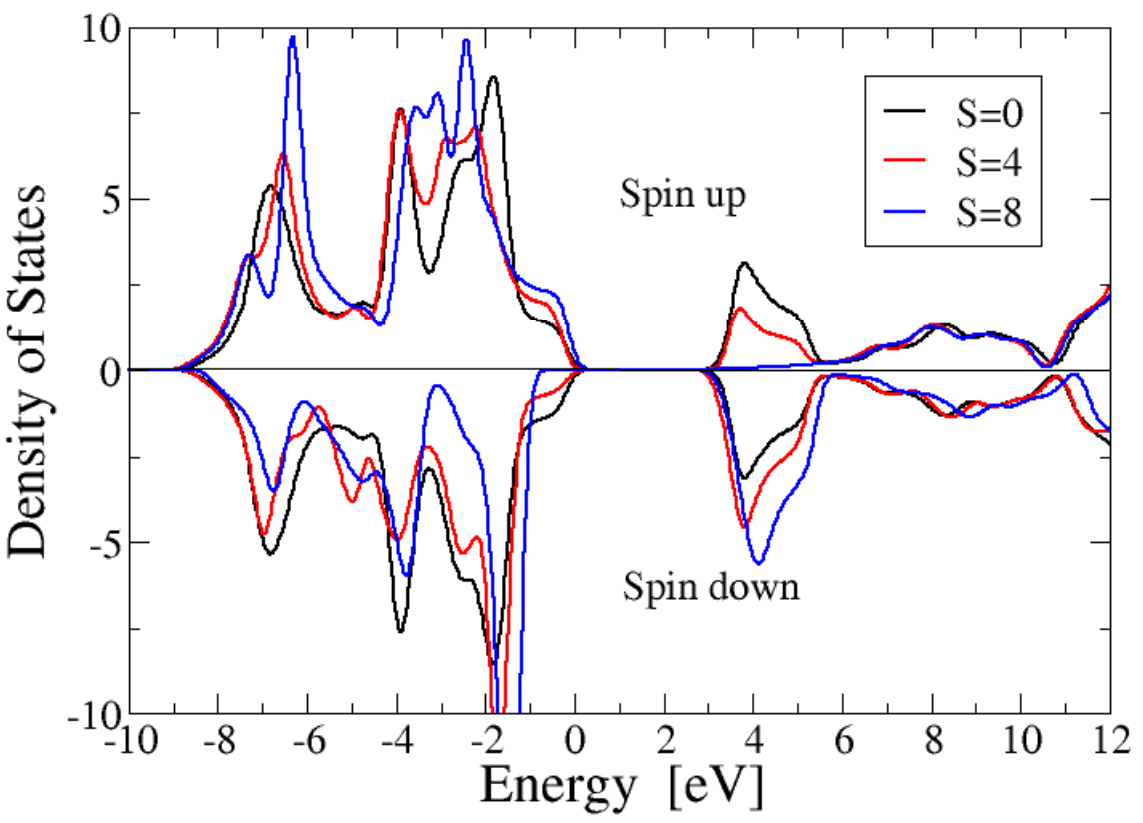
Ce_2O_3 in FM and AFM

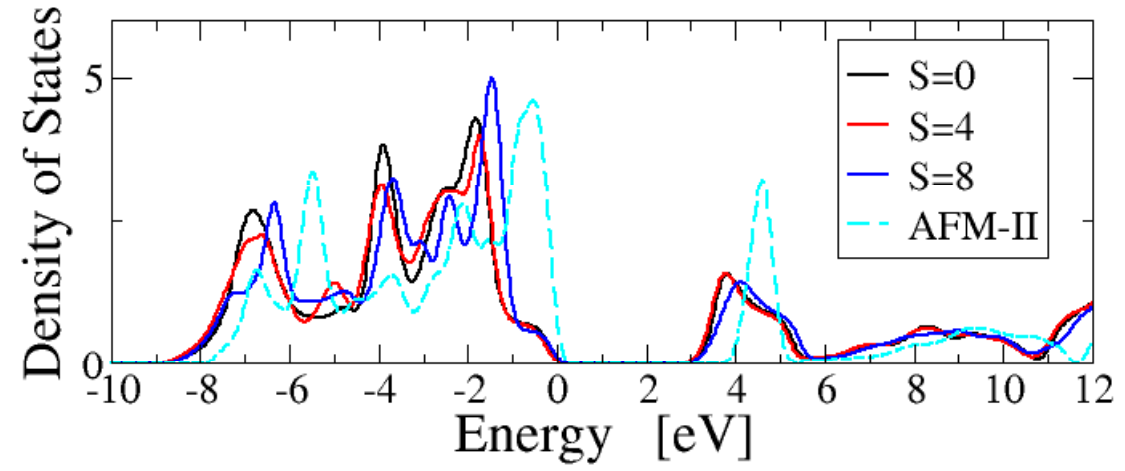


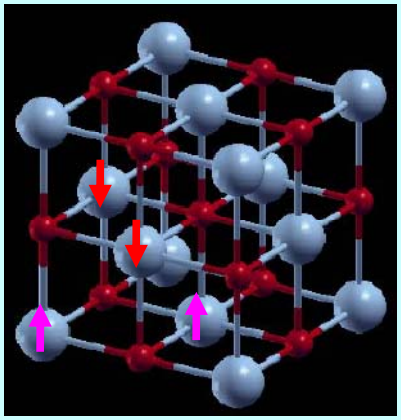


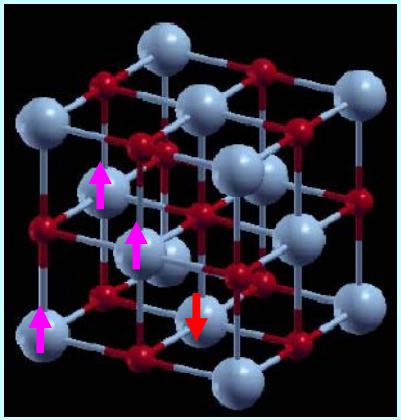
➔ Electronic density of states is essentially impendent of spin-ordering !

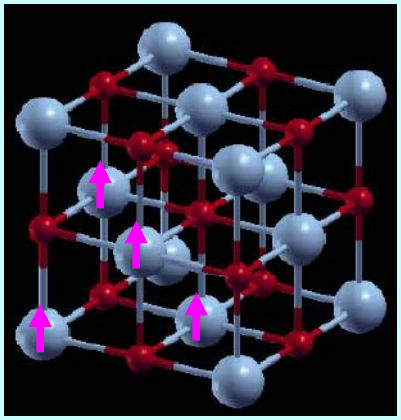
NiO in different spin configuration











Role of symmetry breaking: a unified view?

- static correlation can be (partly?) described by breaking symmetry (spin, orbital, structure)

  e.g. spin unrestricted LSDA or HF for H_2 dissociation

- The essence of the (generalized) Slater model is symmetry breaking, not anti-ferromagnetism

- Symmetry breaking is real: Peiers transition, Jahn-Teller distortion...

- "Strong correlation" can be regarded as one possible mechanism to drive such symmetry breaking

➔ "Strong correlation" is compatible with the band theory

A proposal: strong interaction vs strong correlation

Weak correlation

- LDA/GGA for total energy
- LDA-G_0W_0 for quasiparticle energy works well

Strong interaction

- Delocalization (self-interaction) error is severe, but can be essentially overcome by orbital-dependent corrections
- *GW* with proper starting point or approximate self-consistency for QP energies
- Broken symmetry if necessary

Strong correlation

- Truly many-body treatment beyond single-particle picture needed

Concluding remarks

- Accurate first-principles modelling of d/f-electron systems requires a unified treatment of localized and itinerant states
- The state-of-the-art *GW,* either using improved reference as the input for G_0W_0, or with approximate self-consistency, can generally describe electronic band structure of *d/f*-electron systems quite well, but the satellite structure is still absent, and occupied localized states binding energy tend to be overestimated ➔ high order correlation effects are important
- Symmetry breaking makes the band-theory description of *d/f*-electron systems compatible with strong local Coulomb interaction ➔ a unified treatment of localized and itinerant states is possible