

Lecture on First-principles Computations (20): The DFT+ U method

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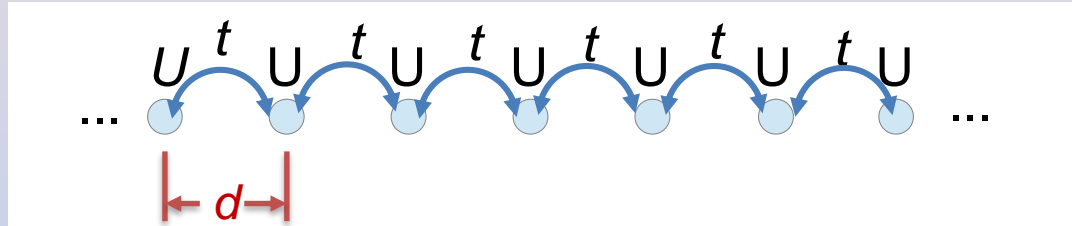
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Failure of band picture

The hydrogen chain model



- When d is small and t/U is large, the electrons can hop nearly freely between neighboring sites, and form a band. LDA and GGAs can describe this situation very well.
- As $d \rightarrow \infty$, the ratio t/U becomes vanishingly small, the system becomes insulating, this is the so-called atomic limit, where the band picture breaks down, and so do LDA and GGAs.

Mott insulators

- In 1937, de Boer and Verwey reported that a variety of transition metal oxides predicted to be conductors by band theory (because they have an odd number of electrons per unit cell) are insulators.
- In 1949, Mott proposed a model for NiO that could explain the formation of the energy gap:



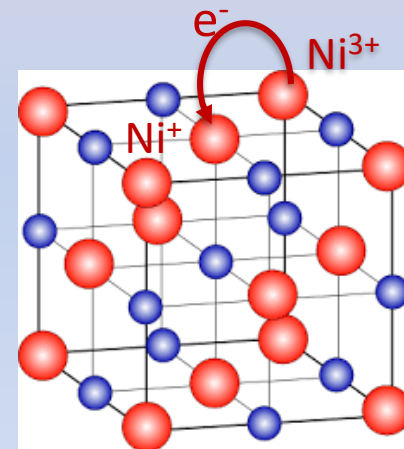
The energy cost for this virtual process:

Coordination number

$$\Delta E = U - 2zt$$

On-site Coulomb repulsion

Transfer integral



The energy gap of Mott insulators are caused by strong electron-electron Coulomb repulsion.

Real examples: late transition metal oxides

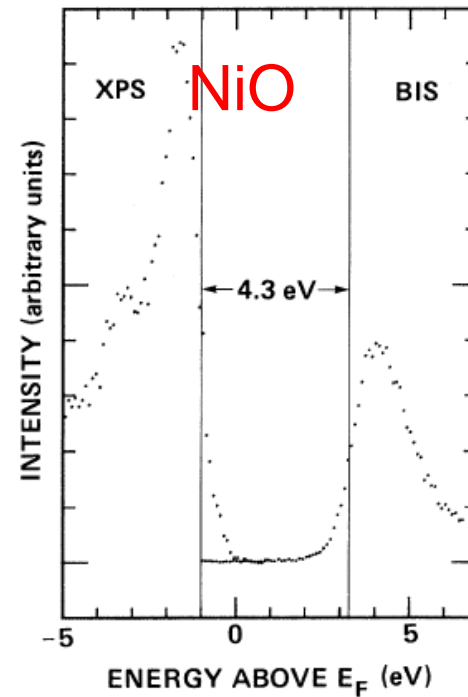
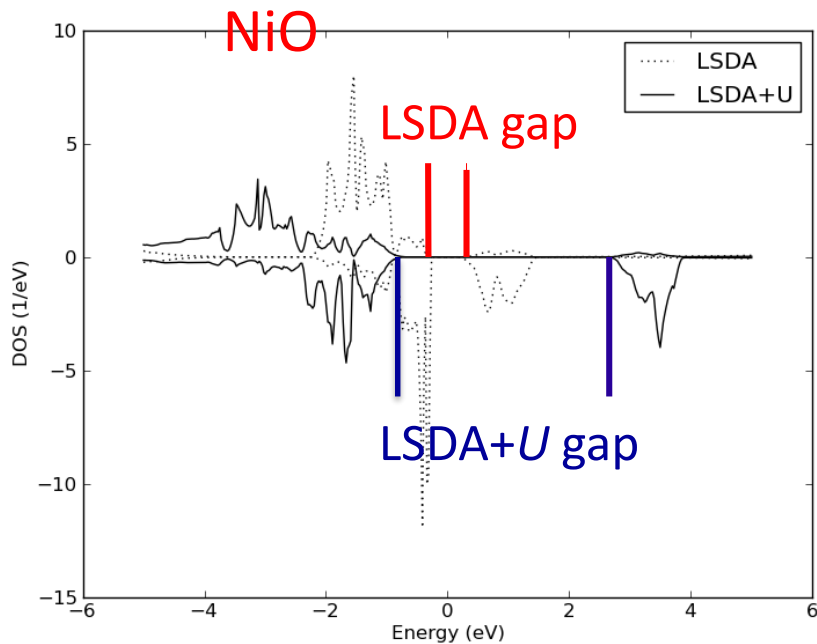
MnO, FeO, CoO, NiO

LDA : All are metals

LSDA : FeO, CoO are metals;

MnO, NiO are small-gap (<0.5 eV) insulator

Exp : All are wide-gap (3-4 eV) insulator

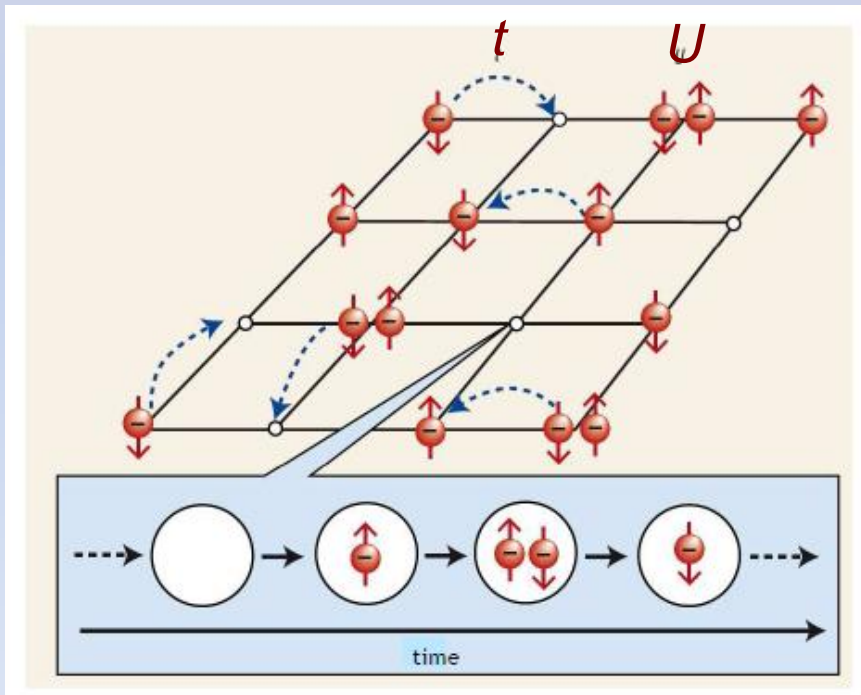


Sawatzky &
Allen, PRL
(1984)

The minimal model for strongly correlated systems

The Hubbard model

Hubbard (1963), Guzwiller (1963), Kanamori (1963)



$$\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

$$\hat{H}_0 = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} = \sum_{\mathbf{k}, \sigma} \epsilon_{\mathbf{k}\sigma} \hat{n}_{\mathbf{k}\sigma}$$

For 2-dimensional cubic lattice

$$\epsilon_{\mathbf{k}\sigma} = -2t(\cos k_x a + \cos k_y a)$$

$$\hat{H}_I = U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Mean-field (Hartree-Fock) solution of the Hubbard model

The Hubbard model represents a strongly correlated many-body problem, and is NOT exactly solvable (neither numerically nor analytically) in physically interesting 2D and 3D cases.

$$\hat{H}_I = U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad \text{Mean-field approximation} \rightarrow$$

$$\hat{H}_I^{\text{MF}} = U \sum_i [\langle \hat{n}_{i\downarrow} \rangle \hat{n}_{i\uparrow} + \langle \hat{n}_{i\uparrow} \rangle \hat{n}_{i\downarrow} - \langle \hat{n}_{i\uparrow} \rangle \langle \hat{n}_{i\downarrow} \rangle]$$

Introduce: $\langle \hat{n}_{i\uparrow} \rangle + \langle \hat{n}_{i\downarrow} \rangle = \langle \hat{n}_i \rangle$, $\langle \hat{n}_{i\uparrow} \rangle - \langle \hat{n}_{i\downarrow} \rangle = \langle \hat{m}_i \rangle \rightarrow$

$$\langle \hat{n}_{i\uparrow} \rangle = \frac{\langle \hat{n}_i \rangle + \langle \hat{m}_i \rangle}{2} \quad \langle \hat{n}_{i\downarrow} \rangle = \frac{\langle \hat{n}_i \rangle - \langle \hat{m}_i \rangle}{2}$$

$$\hat{H}_I^{\text{MF}} = \frac{U}{2} \sum_i \left[\langle \hat{n}_i \rangle (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}) - \langle \hat{m}_i \rangle (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}) - \frac{1}{2} (\langle \hat{n}_i \rangle^2 - \langle \hat{m}_i \rangle^2) \right]$$

Feature of the mean-field solution

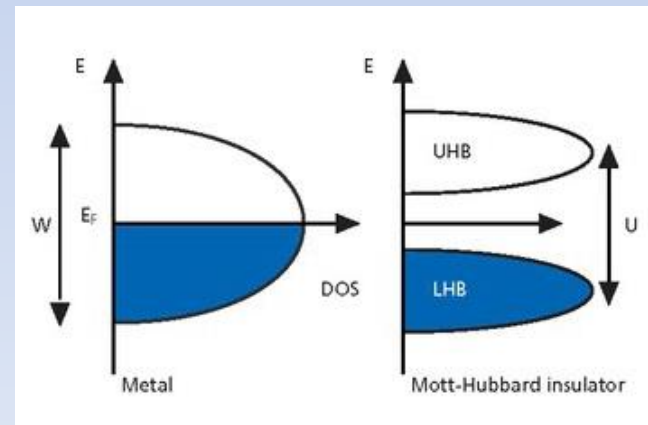
$$\hat{H}_I^{\text{MF}} = \frac{U}{2} \sum_i \left[\langle \hat{n}_i \rangle (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}) - \langle \hat{m}_i \rangle (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}) - \frac{1}{2} (\langle \hat{n}_i \rangle^2 - \langle \hat{m}_i \rangle^2) \right]$$

$$\langle \hat{H}_I^{\text{MF}} \rangle = \frac{U}{4} \sum_i [\langle \hat{n}_i \rangle^2 - \langle \hat{m}_i \rangle^2]$$

At half-filling $\langle \hat{n}_i \rangle = 1$, the paramagnetic state $\langle \hat{m}_i \rangle = 0$ is at too high in energy ($\Delta E = U/4$), compared to the complete spin polarization solution $\langle \hat{m}_i \rangle = 1$, where $E = 0$.

The single-particle potential:

$$V_{i\sigma} = \frac{\partial \langle \hat{H}_I^{\text{MF}} \rangle}{\partial \langle \hat{n}_{i\sigma} \rangle} = \frac{U}{2} [\langle \hat{n}_i \rangle - \sigma \langle \hat{m}_i \rangle]$$

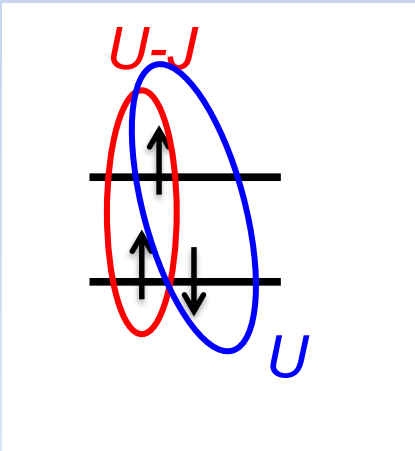


The multi-band Hubbard model

Suitable for 3d transition metals and their oxides

$$\hat{H} = \sum_{\langle i,j \rangle, m, m', \sigma} t_{mm'} c_{im\sigma}^\dagger c_{jm'\sigma} + \frac{U}{2} \sum_{i, m, m', \sigma} \hat{n}_{im\sigma} \hat{n}_{im'-\sigma} + \frac{(U-J)}{2} \sum_{i, m \neq m', \sigma} \hat{n}_{im\sigma} \hat{n}_{im'\sigma}$$

i, j : site index
 m, m' : orbital index



The Hund's rule coupling

Mean-field solution can be easily found in analogy to the single-band case.

The LDA+ U method

Phys. Rev. B **44**, 943 (1991)

Band theory and Mott insulators: Hubbard U instead of Stoner I

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We propose a form for the exchange-correlation potential in local-density band theory, appropriate for Mott insulators. The idea is to use the “constrained-local-density-approximation” Hubbard parameter U as the quantity relating the single-particle potentials to the magnetic- (and orbital-) order parameters. Our energy functional is that of the local-density approximation plus the mean-field approximation to the remaining part of the U term. We argue that such a method should make sense, if one accepts the Hubbard model and the success of constrained-local-density-approximation parameter calculations. Using this *ab initio* scheme, we find that all late-3d-transition-metal monoxides, as well as the parent compounds of the high- T_c compounds, are large-gap magnetic insulators of the charge-transfer type. Further, the method predicts that LiNiO_2 is a low-spin ferromagnet and NiS a local-moment p -type metal. The present version of the scheme fails for the early-3d-transition-metal monoxides and for the late 3d transition metals.

The LDA+U method

V. I. Anisimov et al., *Phys. Rev. B* **44**, 943 (1991)

$$E^{\text{LDA}+U} = E^{\text{LDA}} + \frac{U}{2} \sum_{i,m,m',\sigma} (\langle \hat{n}_{im\sigma} \rangle - n_0) (\langle \hat{n}_{im'\bar{\sigma}} \rangle - n_0) \\ + \frac{(U-J)}{2} \sum_{i,m \neq m',\sigma} (\langle \hat{n}_{im\sigma} \rangle - n_0) (\langle \hat{n}_{im'\sigma} \rangle - n_0)$$

$$n_0 = \sum_{m\sigma} \frac{\langle n_{m\sigma} \rangle}{N} \quad (N = 10 \text{ for } d \text{ orbitals, } 14 \text{ for } f \text{ orbitals})$$

In contrast to

$$E^{\text{LSDA}} = E^{\text{LDA}} + E_{xc}[n_{\uparrow}, n_{\downarrow}] - E_{xc}[n]$$

The LDA+ U method

The exchange-correlation potential:

$$V_{m\sigma}^{\text{LDA}+U} = V_{xc}^{\text{LDA}} + U \sum_{m'} (\langle n_{m',-\sigma} \rangle - n^0) + (U - J) \sum_{m'(\neq m)} (\langle n_{m',\sigma} \rangle - n^0)$$

$$V_{\uparrow}^{\text{LDA}+U} - V_{\downarrow}^{\text{LDA}+U} \sim U$$

Occupied orbitals and unoccupied orbitals are separated by an energy U !

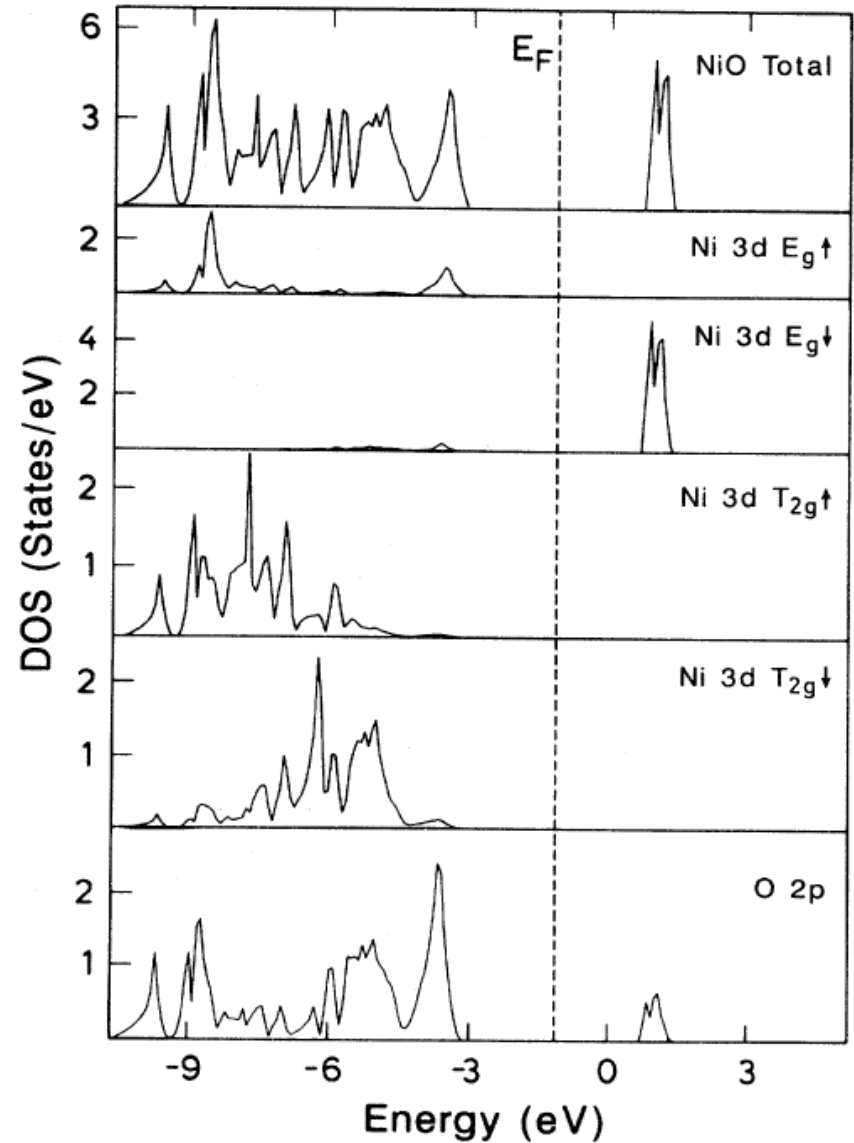
In contrast to

$$V_{xc,\sigma}^{\text{LSDA}} = \frac{\delta E_{xc}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}}$$

$$V_{\uparrow}^{\text{LSDA}} - V_{\downarrow}^{\text{LSDA}} \sim J \quad (J \text{ is similar to the Stoner parameter } I)$$

Example:

Density of states
of NiO obtained by
LDA+ U



LDA+ U band gaps and magnetic moments

Table 1. Experimental (exp) and calculated (LDA + U and LSDA) spin moment (m in μ_B) and energy gap (E in eV) values of the late-3d-transition-metal oxides.

	E_{LSDA}	E_{LDA+U}	E_{exp}	m_{LSDA}	m_{LDA+U}	m_{exp}
CaCuO ₂	0.0	2.10	1.5	0.0	0.66	0.51
CuO	0.0	1.9	1.4	0.0	0.74	0.65
NiO	0.2	3.1	4.3, 4.0	1.0	1.59	1.77, 1.64, 1.90
CoO	0.0	3.2	2.4	2.3	2.63	3.35, 3.8
FeO	0.0	3.2	2.4	3.4	3.62	3.32
MnO	0.8	3.5	3.6–3.8	4.61	1.67	4.79, 4.58

V.I. Anisimov, F. Aryasetiawan, S. Lichtenstein,
J. Phys. Condens. Matter **9**, 767 (1997)

Simple understanding of LDA+U

$$E_{\text{LDA}+U} = E_{\text{LDA}} - UN(N+1)/2 + \frac{U}{2} \sum_{i \neq j} \langle \hat{n}_i \rangle \langle \hat{n}_j \rangle$$

$$n_i = \langle \hat{n}_i \rangle, N = \sum_i n_i$$

$$\epsilon_i^{\text{LDA}+U} = \frac{\partial E_{\text{LDA}+U}}{\partial n_i} = \epsilon_i^{\text{LDA}} + U \left(\frac{1}{2} - n_i \right)$$

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

For occupied states: $n_i = 1$, $\epsilon_i^{\text{LDA}+U} = \epsilon_i^{\text{LDA}} - U/2$

For unoccupied states: $n_i = 0$, $\epsilon_i^{\text{LDA}+U} = \epsilon_i^{\text{LDA}} + U/2$

What about U ?

$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$$

- Constrained LDA method:

O. Gunnarsson, Phys. Rev. B **41**, 514 (1990)

$$U = \delta^2 E_{tot} / \delta n_d^2$$

Fix the occupation of d orbitals, and let all other electrons relax. Set $t_{d,r} = 0$.

TABLE I. Coulomb (U) and exchange parameters (J) and the splitting between the d^{n-1} and d^{n+1} high-spin states (U^{eff}), calculated using the constrained-density-functional method, compared to empirical estimates (Ref. 42) ($U_{\text{emp}}, U_{\text{emp}}^{\text{eff}}$). Further, the (diagonal) splittings between the highest occupied and lowest unoccupied d state, as well as the splitting between the O $2p$ level and the lowest unoccupied d state in the converged mean-field solution, are shown (U_{SCF} and Δ_{SCF} , respectively). For comparison, we also show the empirical p - d splitting (Ref. 42) (Δ_{emp}). All energies are in eV.

	U	J	U^{eff}	U_{emp}	$U_{\text{emp}}^{\text{eff}}$	Δ_{emp}	U_{SCF}	Δ_{SCF}
CaCuO ₂	7.5	0.98	6.5				4.3	2.5
NiO	8.0	0.95	7.1	6.7	6.1	6.0	5.7	4.0
CoO	7.8	0.92	6.9	5.3	4.9	5.4	5.8	5.1
FeO	6.8	0.89	5.9	5.1	3.5	6.1	5.2	4.9
MnO	6.9	0.86	10.3	7.8	8.8	8.9	9.2	5.5
VO	6.7	0.81	5.9	4.0	4.8	9.9		
TiO	6.6	0.78	5.8	3.5	2.9	8.3		

Constrained RPA method

Irreducible polarizability (non-interacting response function)

$$P(\mathbf{r}, \mathbf{r}', \omega) = \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) \times \left[\frac{1}{\omega - \epsilon_j + \epsilon_i + 0^+} - \frac{1}{\omega + \epsilon_j - \epsilon_i - i0^+} \right]$$

Screened Coulomb interaction

$$W = \frac{v}{1 - vP}$$

$$P = P_d + P_r$$

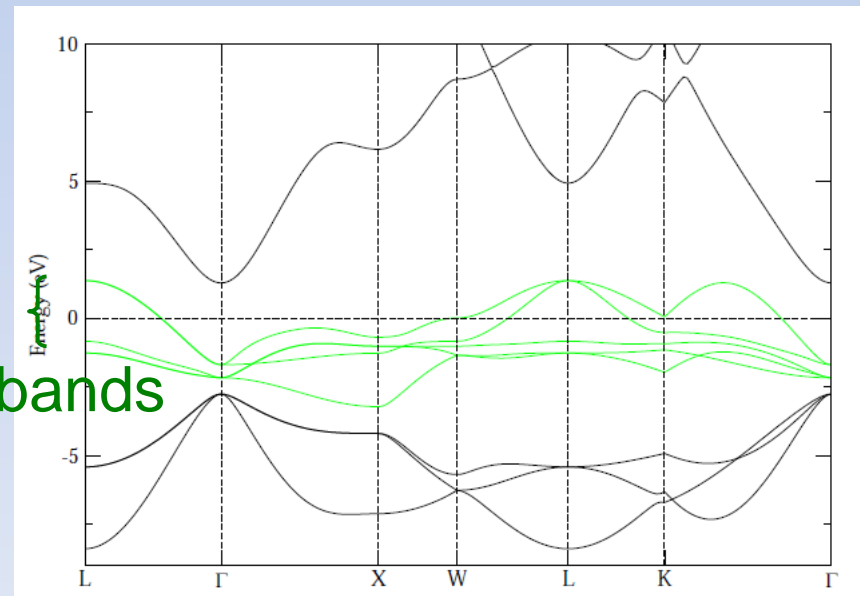
$$W = [1 - W_r P_d]^{-1} W_r$$

$$W_r = [1 - vP_r]^{-1} v$$

$$U(\omega) = \langle \phi\phi | W_r(\omega) | \phi\phi \rangle$$

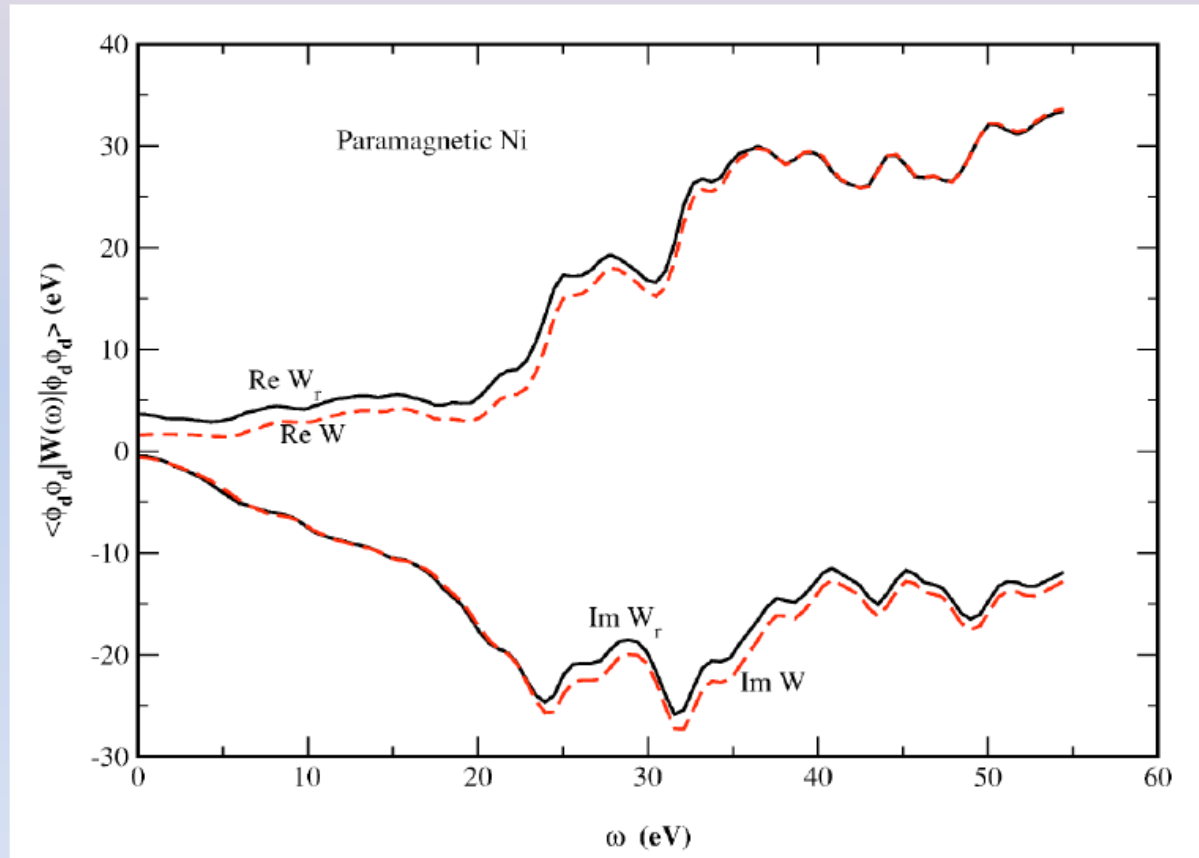
P P_d d bands

LDA band structure of NiO



W_r versus W

Paramagnetic metal d orbitals



Static $U = U(\omega = 0)$ parameter

	MnO	FeO	CoO	NiO
U	9.2	9.5	9.8	10.3
$U_{t_{2g}}$	8.9	9.2	9.5	10.0
U_{e_g}	9.7	10.0	10.3	10.8
U'	7.7	7.9	8.1	8.6
J	0.7	0.8	0.8	0.9
U_p	6.8	6.8	6.8	6.6
U'_p	5.4	5.5	5.4	5.2
J_p	0.7	0.7	0.6	0.6
U_{dp}	1.1	1.2	1.2	1.2

	Mn	Fe	Co	Ni
U	4.8	4.9	4.3	3.9
U'	3.5	3.5	2.9	2.5
J	0.6	0.7	0.7	0.7
U	4.8	4.7	4.3	3.5
U'	3.6	3.4	2.9	2.1
J	0.6	0.7	0.7	0.7

Sakuma and Aryasetiawan,
Phys. Rev. B **87**, 165118 (2013)

Discussion:

LDA+ U versus the hybrid functional method

- Both methods mitigate the self-interaction error, suitable for d - and f -electron systems. Hybrid functionals can also be used for other types of systems.
- LDA+ U needs to define a local-orbital subspace, while hybrid functionals don't.
- U, J parameters need to be computed within LDA+ U .
- Computationally LDA+ U is more efficient, comparable to LDA, whereas the cost of hybrid functional is comparable to Hartree-Fock.

Homework IV

Please discuss the deficiencies of local-density and generalized gradient approximations. Describe your understandings of the following methodologies:

hybrid functionals

DFT+ U

DFT-D/vdW-DF

RPA

Especially discuss in what aspects the problems of LDA and GGAs can be fixed by the above beyond-LDA/GGA methods.