

Ab initio methods in solid state physics

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Transition metals, lanthanides (rare earths), and actinides

Main-group Elements		Transition Metals												Main-group Elements	
H															
Li	Be														
Na	Mg													H	He
K	Ca	Sc	Tl	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Si	P	S
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pb	Ag	Cd	Ga	Ge	As	Se
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	In	Sn	Sb	Te
Fr	Ra	Ac	Rf	Ha	106	107	108	109				Tl	Pb	Bi	Po
														At	Rn

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/trans.php>



Electronic structure of Fe

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{3d^6} 4s^2$

BCC, α phase

$a_{\text{exp}} = 2.86 \text{ \AA}$

$m_{\text{exp}} = 2.22 \mu_B$

LDA

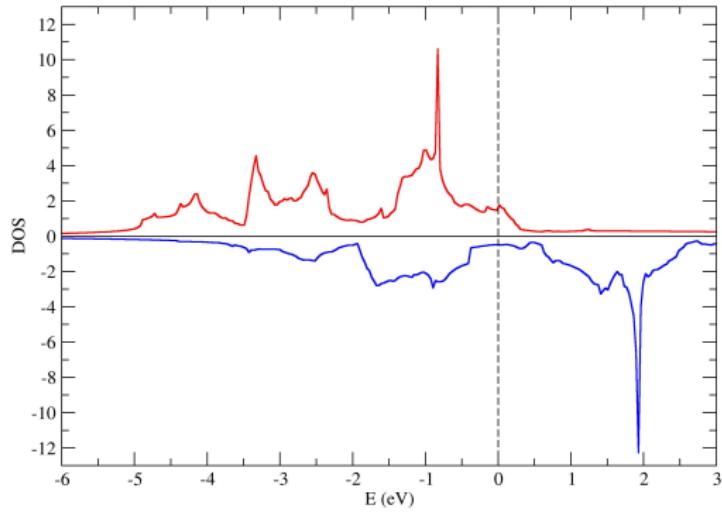
$a = 2.75 \text{ \AA}$

$m = 1.93 \mu_B$

GGA-PBE

$a = 2.83 \text{ \AA}$

$m = 2.19 \mu_B$



Charge and magnetic moment

Charge contained in a space Ω is calculated as the integral of electron density

$$\rho = \int_{\Omega} d\mathbf{r} [n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})]. \quad (1)$$

In a similar way, magnetization of a space Ω can be calculated as

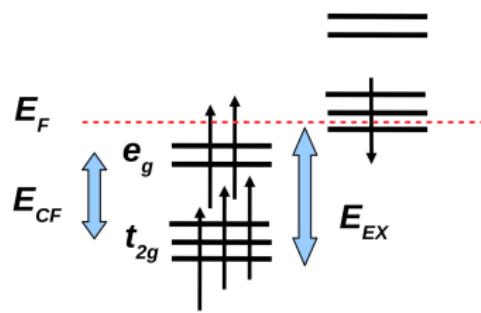
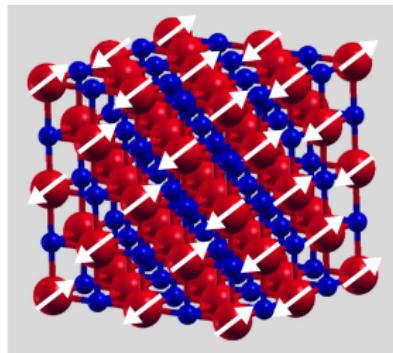
$$m = \int_{\Omega} d\mathbf{r} [n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})]. \quad (2)$$

Ion charges and magnetic moments can be calculated by the integration inside "atomic" spheres defined by the Wigner-Seitz radius. More accurate values can be obtained by the Bader partitioning scheme, which uses zero flux surfaces to divide atoms. A zero flux surface \mathcal{S} is a 2D surface exhibiting a local zero flux in the gradient vector field of the electron density

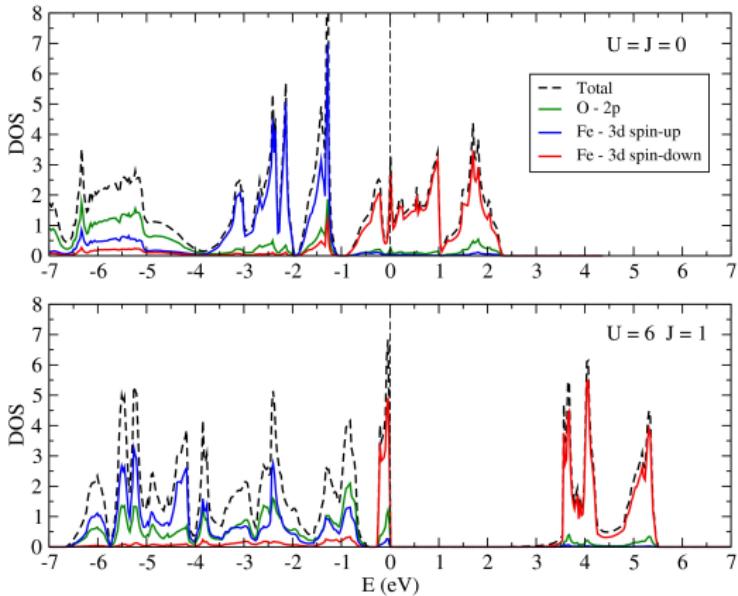
$$\nabla n(\mathbf{r}) \hat{\mathbf{N}}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in \mathcal{S}. \quad (3)$$

R. F. W. Bader, Theor. Chem. Acc. **105**, 276 (2001)

Electronic structure of FeO



Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
O: $1s^2 2s^2 2p^4$



Hubbard model

Hamiltonian of the electron system in second quantization has the form

$$\begin{aligned} H = H_1 + V &= \sum_{\sigma} \int d\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) h_1 \hat{\Psi}_{\sigma}(\mathbf{r}) \\ &+ \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma'}^{\dagger}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}_{\sigma'}(\mathbf{r}') \hat{\Psi}_{\sigma}(\mathbf{r}). \end{aligned} \quad (4)$$

The field operators can be expanded in Wannier orbital basis

$$\hat{\Psi}_{\sigma}(\mathbf{r}) = \sum_i c_{i\sigma} w_i(\mathbf{r}), \quad (5)$$

$$\hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) = \sum_i c_{i\sigma}^{\dagger} w_i^*(\mathbf{r}), \quad (6)$$

where $c_{i\sigma}$ and $c_{i\sigma}^{\dagger}$ are the annihilation and creation operators for site i and spin σ , which fulfill the anticommutation relations:

$$\{c_{i\sigma}, c_{j\sigma'}^{\dagger}\} = \delta_{ij} \delta_{\sigma\sigma'}, \quad \{c_{i\sigma}, c_{j\sigma'}\} = \{c_{i\sigma}^{\dagger}, c_{j\sigma'}^{\dagger}\} = 0. \quad (7)$$

Hubbard model

After substitution of field operators, Hamiltonian gets the tight binding form

$$H = H_1 + V = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{l\sigma'} c_{k\sigma}, \quad (8)$$

where hopping and interaction parameters are obtained from

$$t_{ij} = \int d\mathbf{r} w_i^*(\mathbf{r}) h_1 w_j(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k}} e^{-i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \varepsilon_{\mathbf{k}\sigma}, \quad (9)$$

$$V_{ijkl} = \int \int d\mathbf{r} d\mathbf{r}' w_i^*(\mathbf{r}) w_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} w_l(\mathbf{r}') w_k(\mathbf{r}). \quad (10)$$

After the Fourier transformation, H_1 transforms to

$$H_0 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}, \quad (11)$$

where $\varepsilon_{\mathbf{k}\sigma}$ describes the electronic band structure and $n_{\mathbf{k}\sigma} = c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$ is the operator of occupation numbers in the state \mathbf{k} and spin σ .

Hubbard model

The largest contribution to the interaction term is the Coulomb repulsion between electrons that occupy the same orbital

$$V_{iiii} = \int \int d\mathbf{r} d\mathbf{r}' |w_i(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |w_i(\mathbf{r}')|^2 = U. \quad (12)$$



Introducing the occupation number operator $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, we get the Hamiltonian

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (13)$$

It was first proposed by John Hubbard [Proc. Roy. Soc. Lond. **276**, 238 (1963)].

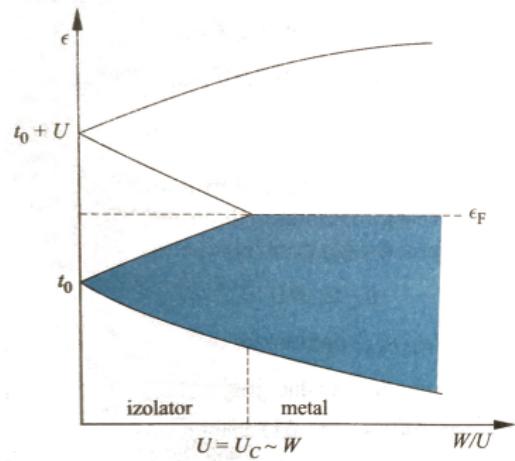
Hubbard model

The band width can be calculated from

$$W = \varepsilon_{\max} - \varepsilon_{\min} = 2 \left| \sum_{j(i)} t_{ij} \right|. \quad (14)$$

There are three regimes of electron behavior

- ① $U \ll W$ – metal,
- ② $U \approx W$ – metal-insulator transition,
- ③ $U \gg W$ – Mott insulator
 - electronic properties and the insulating gap are determined by strong Coulomb interactions. The energy gap calculated within the LDA or GGA (Δ_{KS}) is equal zero or is strongly underestimated.



J. Spałek, "Wstęp do fizyki materii skondensowanej", PWN 2015.

Mott insulators

The energy gap results from the discontinuity of the functional derivative (Δ_{xc}), which is related to the change of orbital occupation and it is proportional to the Hubbard interaction U :

$$E_g \sim U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n). \quad (15)$$

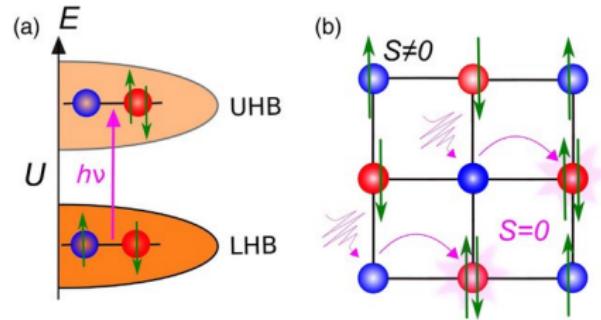


Figure : (a) The band structure of a Mott insulator with schematics of the electronic configuration corresponding to the lower (LHB) and upper Hubbard bands (UHB). (b) Magnetic structure of a Mott insulator subjected to the band gap excitation. Taken from D. Afanasiev *et al.*, Phys. Rev. X 9, 021020 (2019).

DFT+U method (LDA+U or GGA+U)

V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991)

V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993)

A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, 5467 (1995)

The total energy of a system can be written as follows

$$E_{\text{tot}} = E_{\text{DFT}} + E_U - E_{\text{dc}}, \quad (16)$$

where the interaction term is modeled as in the Hubbard Hamiltonian

$$\begin{aligned} E_U = & \frac{1}{2} \sum_{i,\{m\},\sigma} [\langle m, m'' | V_{ee} | m', m''' \rangle n_{i\sigma}^{mm'} n_{i-\sigma}^{m''m'''} \\ & + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{i\sigma}^{mm'} n_{i\sigma}^{m''m'''}], \end{aligned} \quad (17)$$

with the occupation numbers that are obtained by projection of occupied Kohn-Sham orbitals on the localized basis set

$$n_{i\sigma}^{mm'} = \sum_{\mathbf{k},j} f_{\mathbf{k}j}^{\sigma} \langle \psi_{\mathbf{k}j}^{\sigma} | \phi_{Im'} \rangle \langle \phi_{Im} | \psi_{\mathbf{k}j} \rangle. \quad (18)$$

DFT+U method

The matrix elements of Coulomb interactions can be obtained from

$$\begin{aligned}\langle m, m'' | V_{ee} | m', m''' \rangle &= \int d\mathbf{r} d\mathbf{r}' \phi_{lm}^*(\mathbf{r}) \phi_{lm'}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{lm''}^*(\mathbf{r}') \phi_{lm'''}(\mathbf{r}') \\ &= \sum_p \frac{4\pi}{2p+1} \sum_{q=-p}^p \langle lm | Y_{pq} | lm' \rangle \langle lm'' | Y_{pq}^* | lm''' \rangle F^p.\end{aligned}\quad (19)$$

Slater integrals $F^p = \int d\mathbf{r} d\mathbf{r}' r^2 r'^2 R_{nl}^2(\mathbf{r}) \frac{r_1^p}{r_2^{p+1}} R_{nl}^2(\mathbf{r}')$,

$$(20)$$

$$U = \frac{1}{(2l+1)^2} \sum_{m,m'} \langle m, m' | V_{ee} | m, m' \rangle = F^0,$$
$$(21)$$

$$J = \frac{1}{2l(2l+1)} \sum_{m \neq m'} \langle m, m' | V_{ee} | m', m \rangle = \frac{F^2 + F^4}{14},$$
$$(22)$$

$$E_{dc} = \frac{1}{2} \left[\sum_i U n_i (n_i - 1) - J [n_{i\uparrow} (n_{i\uparrow} - 1) + n_{i\downarrow} (n_{i\downarrow} - 1)] \right].$$
$$(23)$$

Calculation of U – linear response

M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005)

We can calculate the total energy with the linear perturbation

$$E(\alpha_i) = \min\{E_{\text{DFT}} + \alpha_i n_i\}, \quad (24)$$

where α_i represents the strength of the perturbation and n_i is the value of the electron occupation at site i . Then we calculate the response function

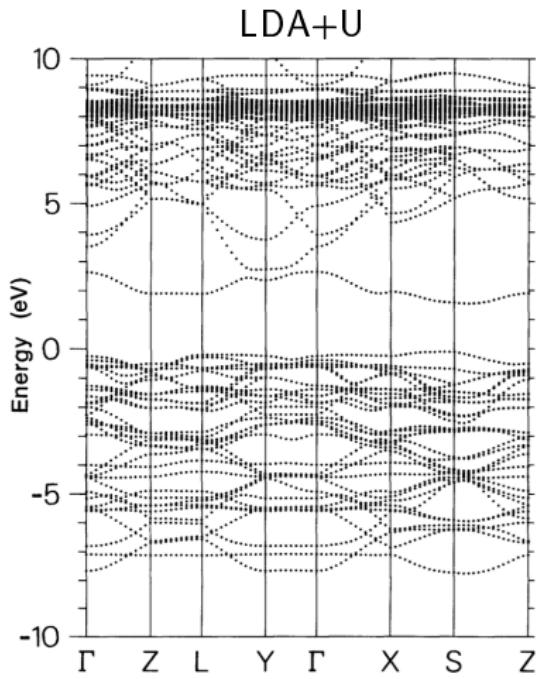
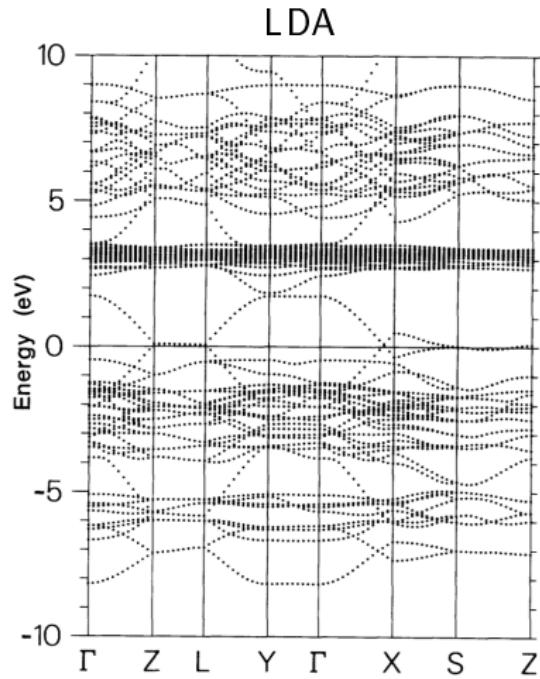
$$\chi = \frac{dn_i}{d\alpha_i}. \quad (25)$$

The Hubbard U is obtained from the inverse of the response function

$$U = -\chi^{-1} + \chi_0^{-1}, \quad (26)$$

where χ_0 measures the response of the system due to the modification of the electronic states upon perturbation. It is obtained from the variation of on-site occupation at the non-selfconsistent iteration.

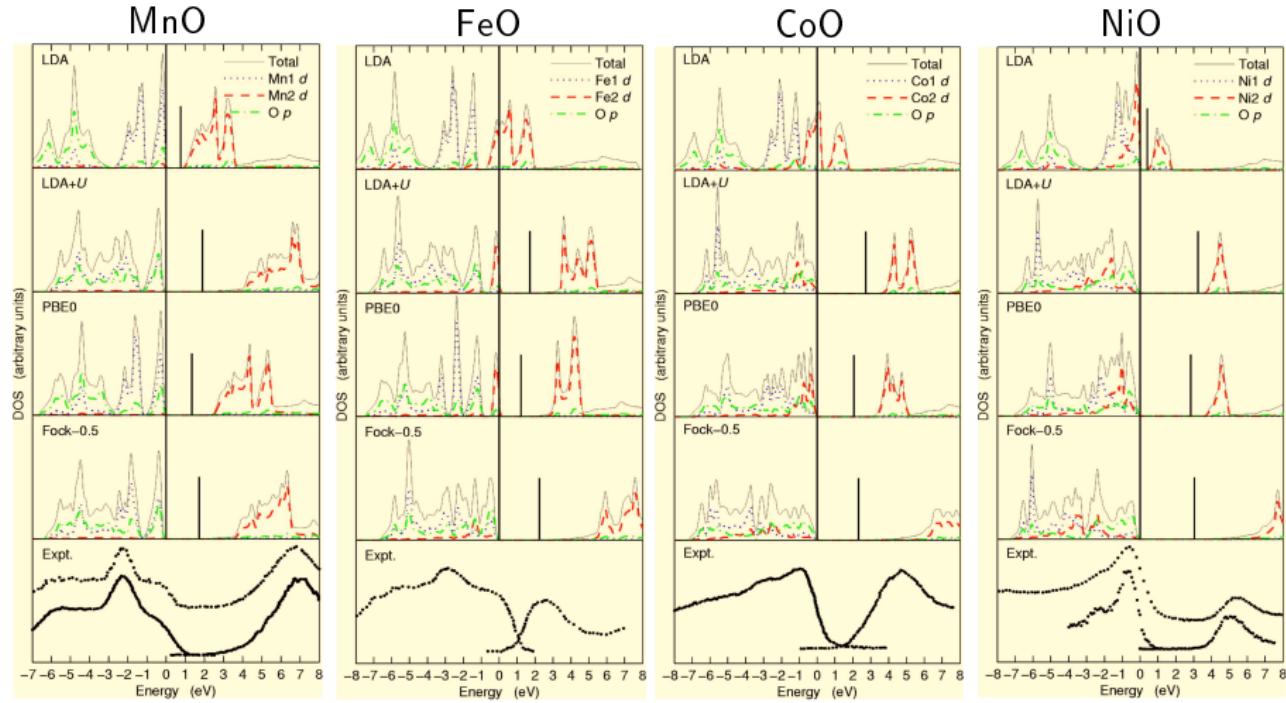
Example: La_2CuO_4



M. T. Czyzyk and G. A. Sawatzky, Phys. Rev. B **49**, 14 211 (1994)

Transition-metal monoxides

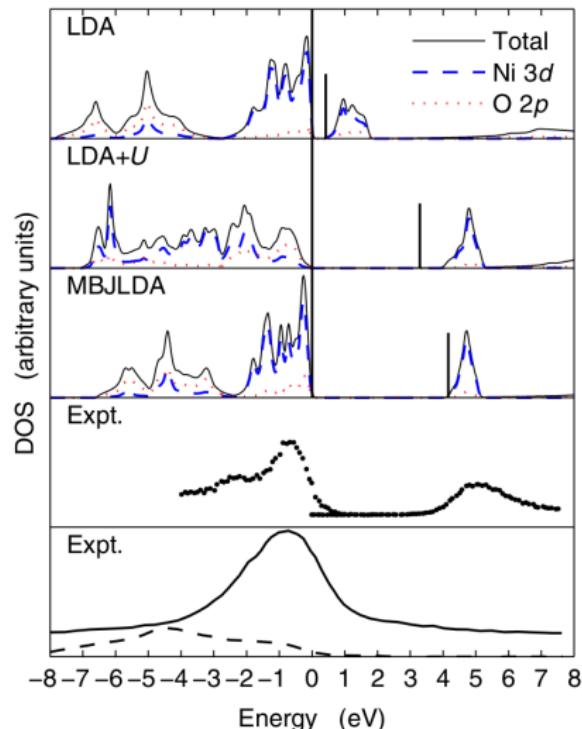
F. Tran, P. Blaha, and K. Schwarz, Phys. Rev. B **74**, 155108 (2006)



Example: meta-GGA mBJ potential vs LDA+U for NiO

F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)

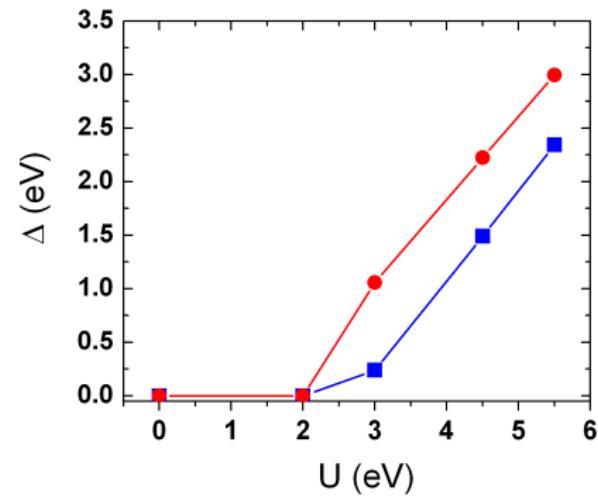
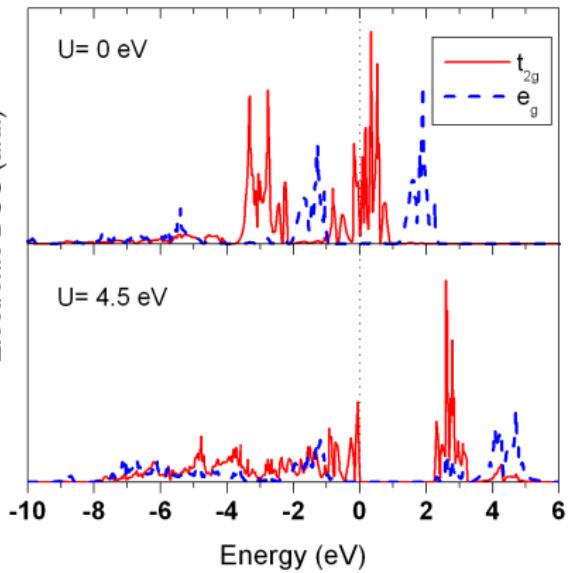
LDA+U, $U = 8$ eV, $J = 0.95$ eV



Example: Fe_2SiO_4

M. Derzsi, P. Piekarz, P. T. Jochym, J. Łążewski, M. Sternik, A. M. Oleś,
and K. Parlinski, Phys. Rev. B **79** 205105 (2009)

Electronic DOS (au.)

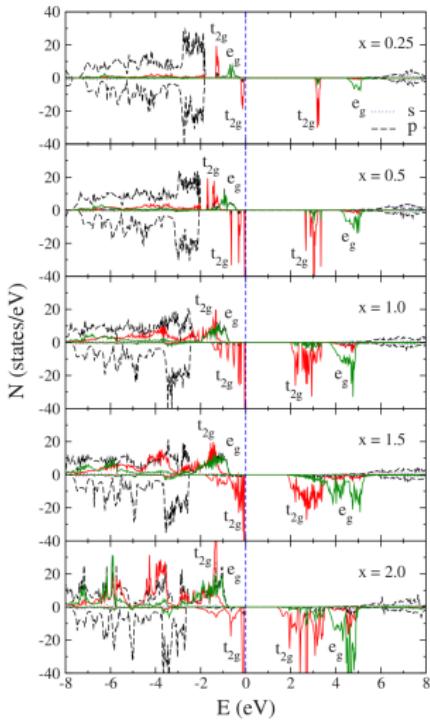
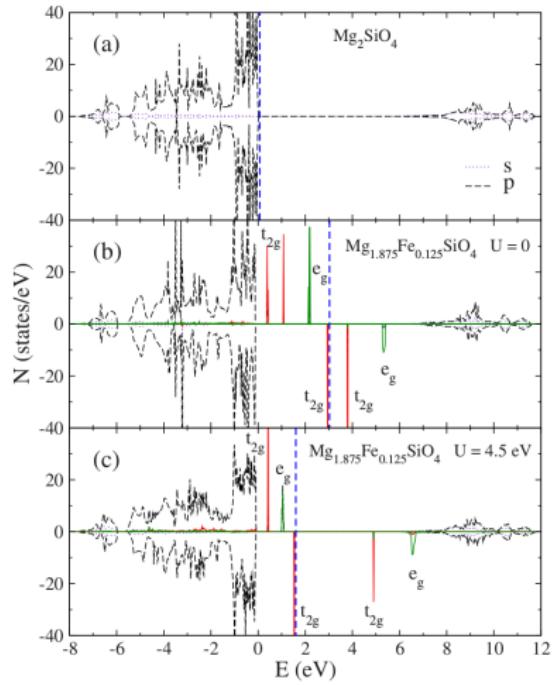


$U < W \approx 2 \text{ eV}$ – metal

$U > W \approx 2 \text{ eV}$ – insulator

Example: $Mg_{2-x}Fe_xSiO_4$

K. Tokár *et al.*, Phys. Rev. B **82**, 195116 (2010)



Relativistic effects

Relativistic effects of electrons in atoms or solids are described by Dirac equation.
In DFT calculations, three relativistic corrections can be included in the total Hamiltonian

$$H = T + V + H_{\text{Darwin}} + H_{\text{SO}}. \quad (27)$$

① Kinetic energy correction

$$T = \sqrt{p^2 c^2 + m_e^2 c^4} - m_e c^2 \approx \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3 c^2} + \dots \quad (28)$$

② Darwin term

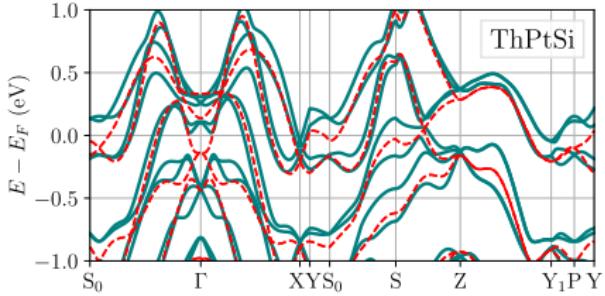
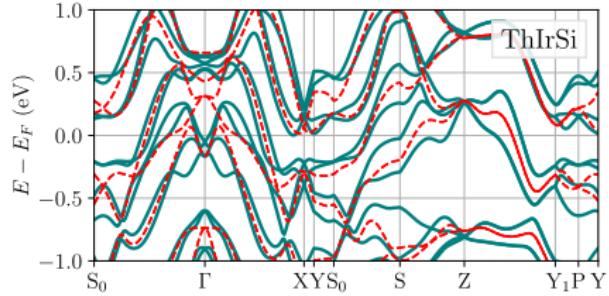
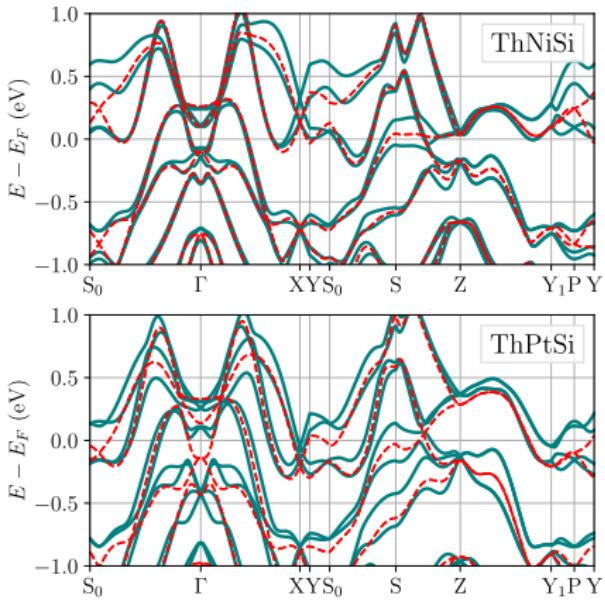
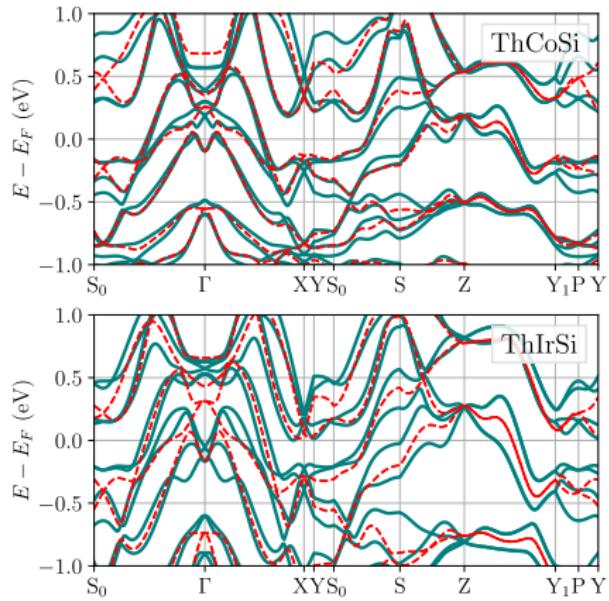
$$H_{\text{Darwin}} = \frac{Z \hbar^2 e^2}{8m_e^2 c^2 \varepsilon_0} \delta^3(\mathbf{r}). \quad (29)$$

③ Spin-orbit coupling

$$H_{\text{SO}} = \frac{\hbar^2}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \boldsymbol{\sigma}. \quad (30)$$

Example: spin-orbit coupling in ThXSi

A. Ptok, K. Domieracki, K. J. Kapcia, J. Łązewski, P. T. Jochym, M. Sternik, P. Piekarz, and D. Kaczorowski Phys. Rev. B **100**, 165130 (2019)



Example: spin-orbit coupling in ThXSi

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