

# *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,  $\alpha$  phase

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

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

LDA

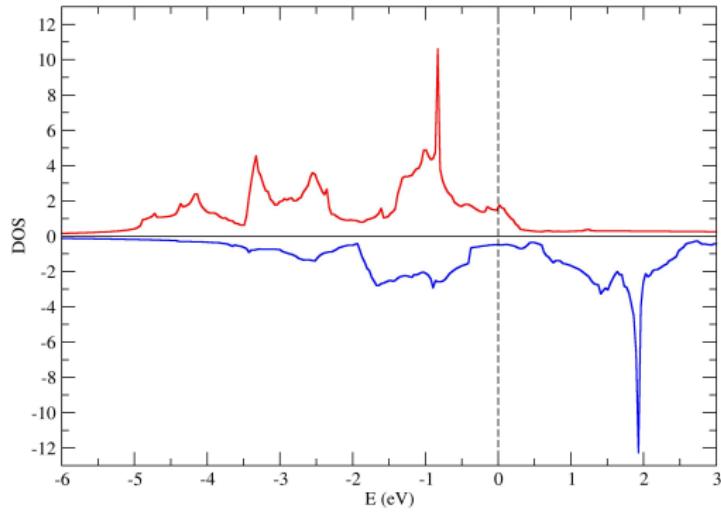
$a = 2.75 \text{ \AA}$

$m = 1.93 \mu_B$

GGA-PBE

$a = 2.83 \text{ \AA}$

$m = 2.19 \mu_B$



# Charge and magnetic moment

Charge contained in a space  $\Omega$  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  $\Omega$  can be calculated as

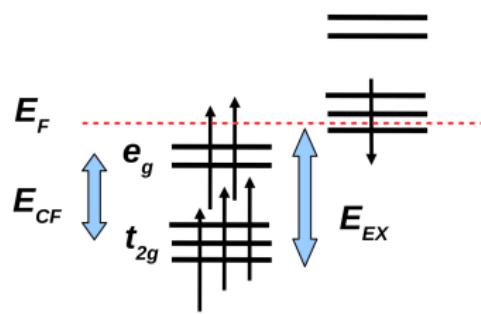
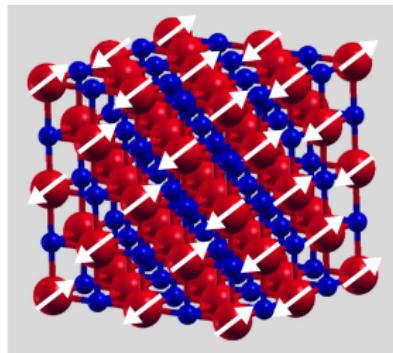
$$\mathbf{m} = \int_{\Omega} d\mathbf{r}[n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})]. \quad (2)$$

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

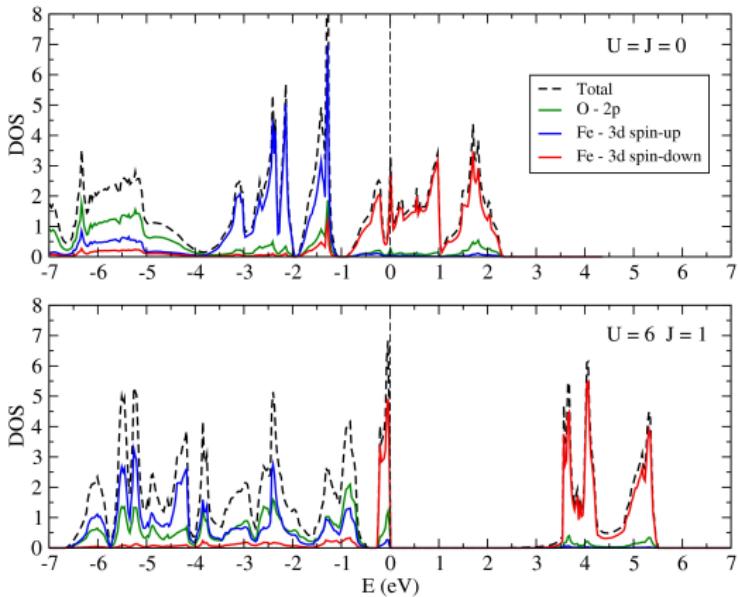
$$\nabla n(\mathbf{r}) \hat{\mathbf{N}}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in \mathcal{S}. \quad (3)$$

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  $\sigma$ , 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

$$H_1 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}, \quad (11)$$

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  $\sigma$ .

# 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

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

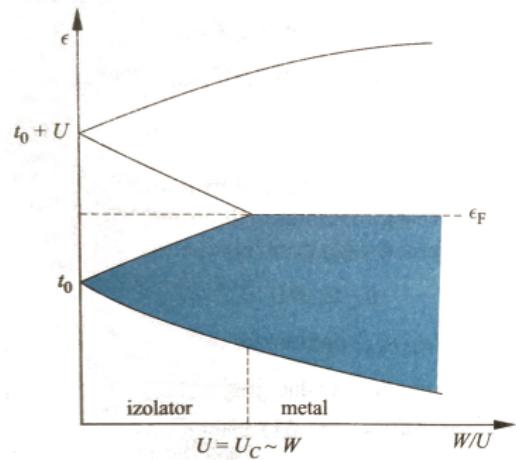
# Metal-insulator transition

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 ( $\Delta_{KS}$ ) is equal zero or is strongly underestimated.



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

## 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

$$E_{\text{tot}} = E_{\text{DFT}} + E_U - E_{\text{dc}}, \quad (15)$$

where the interaction term is modeled as in the Hubbard Hamiltonian

$$\begin{aligned} E_U = & \frac{1}{2} \sum_{i,\{m\},\sigma} [\langle m, m'' | V_{ee} | m', m''' \rangle n_{i\sigma}^{mm'} n_{i-\sigma}^{m''m'''} \\ & + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{i\sigma}^{mm'} n_{i\sigma}^{m''m'''}], \end{aligned} \quad (16)$$

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

$$n_{i\sigma}^{mm'} = \sum_{\mathbf{k},j} f_{\mathbf{k}j}^{\sigma} \langle \psi_{\mathbf{k}j}^{\sigma} | \phi_{Im'} \rangle \langle \phi_{Im} | \psi_{\mathbf{k}j} \rangle. \quad (17)$$

# DFT+U method

The matrix elements of Coulomb interactions can be obtained from

$$\begin{aligned}\langle m, m'' | V_{ee} | m', m''' \rangle &= \int d\mathbf{r} d\mathbf{r}' \phi_{lm}^*(\mathbf{r}) \phi_{lm'}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{lm''}^*(\mathbf{r}') \phi_{lm'''}(\mathbf{r}') \\ &= \sum_p \frac{4\pi}{2p+1} \sum_{q=-p}^p \langle lm | Y_{pq} | lm' \rangle \langle lm'' | Y_{pq}^* | lm''' \rangle F^p.\end{aligned}\quad (18)$$

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

$$\quad (19)$$

$$U = \frac{1}{(2l+1)^2} \sum_{m,m'} \langle m, m' | V_{ee} | m, m' \rangle = F^0,\quad (20)$$

$$J = \frac{1}{2l(2l+1)} \sum_{m \neq m'} \langle m, m' | V_{ee} | m', m \rangle = \frac{F^2 + F^4}{14},\quad (21)$$

$$E_{dc} = \frac{1}{2} \left[ \sum_i U n_i (n_i - 1) - J [n_{i\uparrow} (n_{i\uparrow} - 1) + n_{i\downarrow} (n_{i\downarrow} - 1)] \right].\quad (22)$$

# 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

$$E(\alpha_i) = \min\{E_{\text{DFT}} + \alpha_i n_i\}, \quad (23)$$

where  $\alpha_i$  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

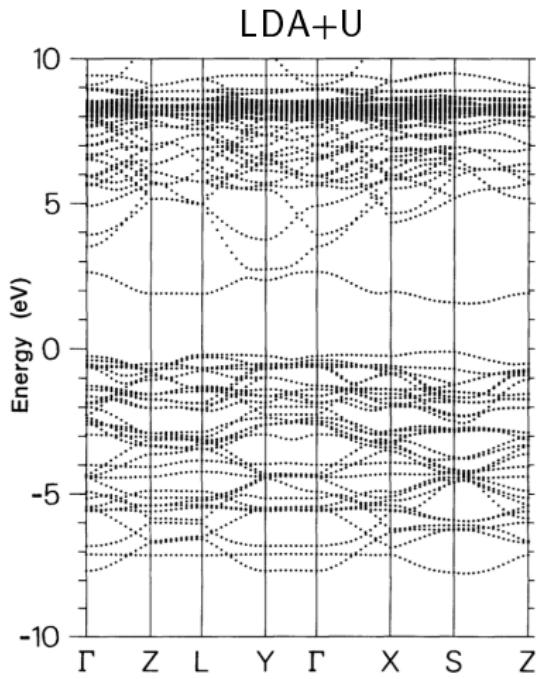
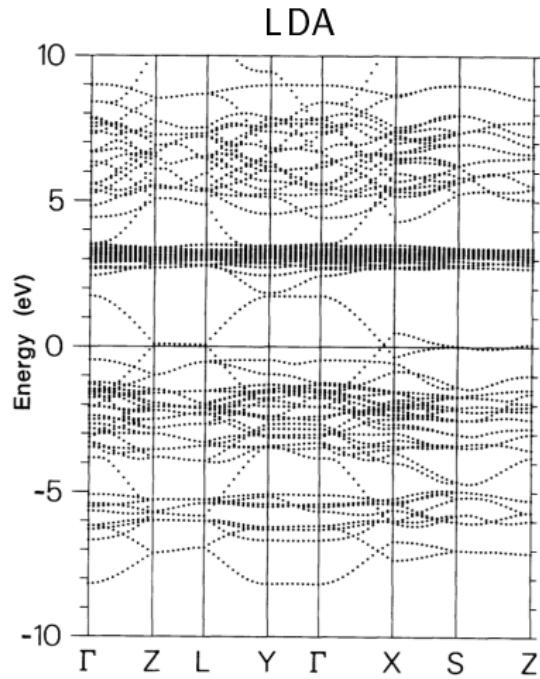
$$\chi = \frac{dn_i}{d\alpha_i}. \quad (24)$$

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

$$U = -\chi^{-1} + \chi_0^{-1}, \quad (25)$$

where  $\chi_0$  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: $\text{La}_2\text{CuO}_4$

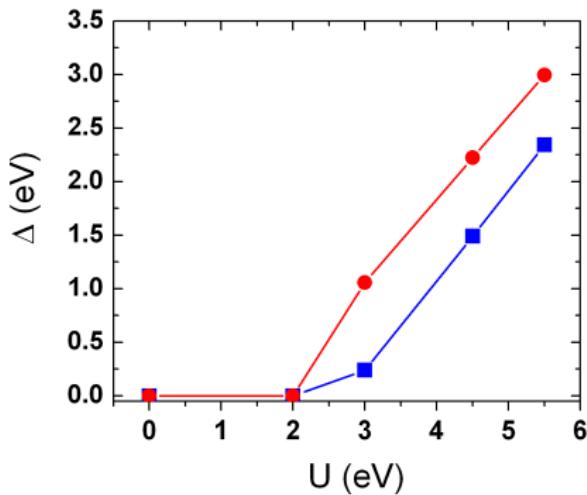
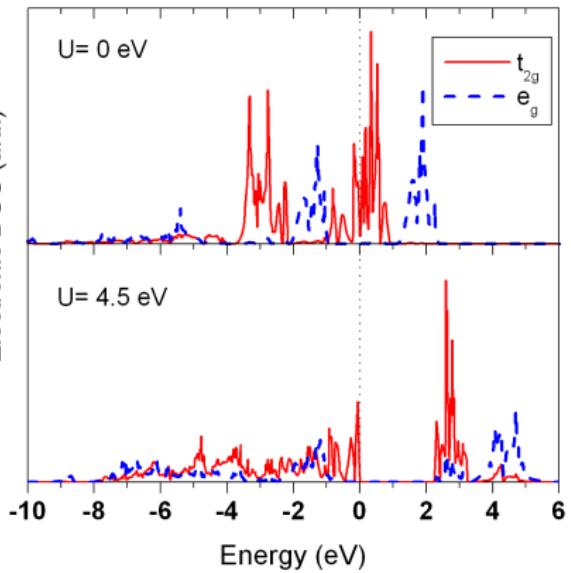


M. T. Czyzyk and G. A. Sawatzky, Phys. Rev. B **49**, 14 211 (1994)

# Example: $\text{Fe}_2\text{SiO}_4$

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.)

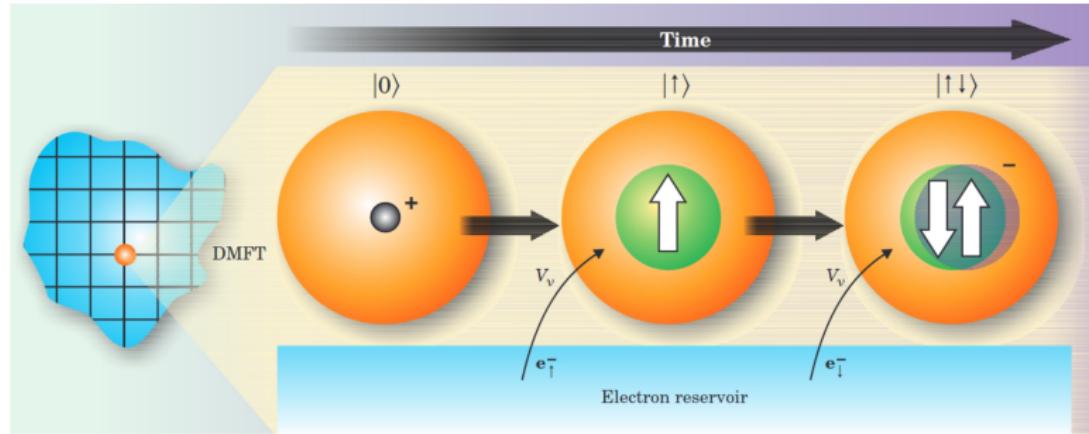


$U < W \approx 2 \text{ eV}$  – metal

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

# Dynamical mean-field theory (DMFT)

*Strongly Correlated Materials: Insights From Dynamical Mean-Field Theory*  
G. Kotliar and D. Vollhardt, Physics Today 57, 53 (2004)



DMFT replaces the full lattice of atoms and electrons with a single impurity atom existing in a bath of electrons. The approximation captures the dynamics of electrons on a central atom as it fluctuates among different electron configurations.

# Anderson impurity model

$$H = H_{\text{imp}} + \sum_{i,\sigma} \varepsilon_{i,\sigma}^{\text{bath}} n_{i,\sigma}^{\text{bath}} + \sum_{i,\sigma} V_i c_{0,\sigma}^\dagger a_{i,\sigma}^{\text{bath}} + h.c., \quad (26)$$

The hybridization function  $\Delta(\omega)$  plays the role of a mean field

$$\Delta(\omega) = \sum_i \frac{|V_i|^2}{\omega - \varepsilon_{i,\sigma}^{\text{bath}}}, \quad (27)$$

which is determined from the self-consistency condition

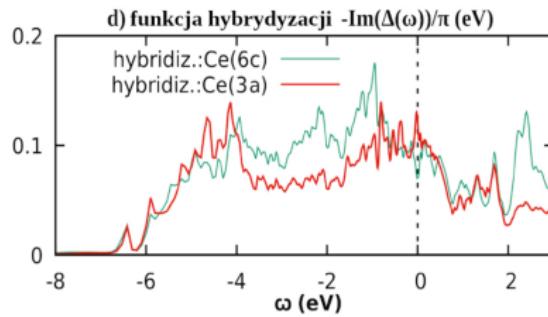
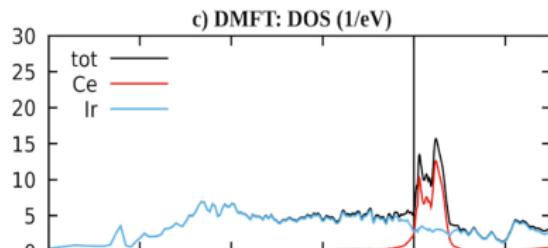
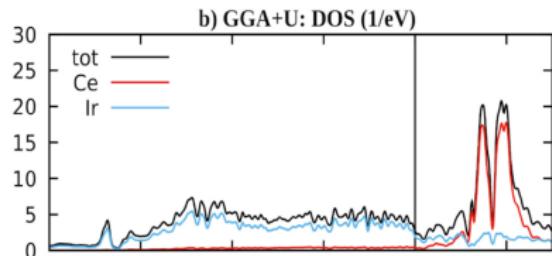
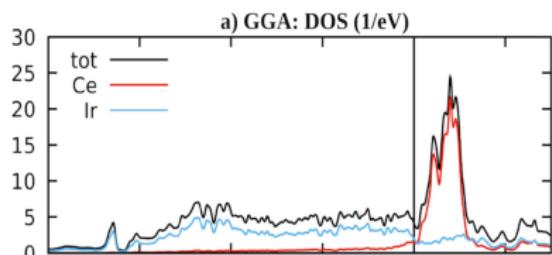
$$G[\Delta(\omega)] = \sum_k \frac{1}{\omega - \Sigma[\Delta(\omega)] - t_k}, \quad (28)$$

where  $t_k$  is the Fourier transform of the hopping parameter  $t_{ij}$  of the solid and the self-energy is given by the equation

$$\Sigma[\Delta(\omega)] = \Delta(\omega) - \frac{1}{G[\Delta(\omega)]} + \omega. \quad (29)$$

# DFT+DMFT. Example: $\text{CeIr}_3$

$$E[n] \rightarrow E[n, G] = T[n, G] + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n, G]$$



S. Gutowska, B. Wiendlocha, J. Magn. Magn. Mat. 547, 168917 (2022)

# Relativistic effects

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

$$H = T + V + H_{\text{Darwin}} + H_{\text{SO}}. \quad (30)$$

## ① Kinetic energy correction

$$T = \sqrt{p^2 c^2 + m_e^2 c^4} - m_e c^2 \approx \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3 c^2} + \dots \quad (31)$$

## ② Darwin term

$$H_{\text{Darwin}} = \frac{Z \hbar^2 e^2}{8m_e^2 c^2 \varepsilon_0} \delta^3(\mathbf{r}). \quad (32)$$

## ③ Spin-orbit coupling

$$H_{\text{SO}} = \frac{\hbar^2}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \boldsymbol{\sigma}. \quad (33)$$

# 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)

