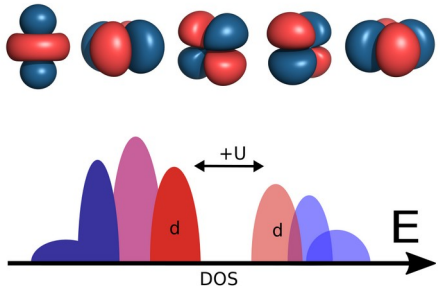
Intricacies of DFT+U, not only in a numeric atom centered orbital framework



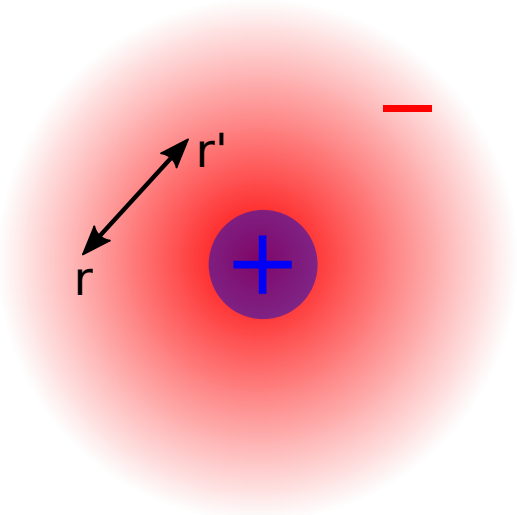
Overview

Part I: DFT+U in general

Part II: DFT+U in FHIaims

Motivation

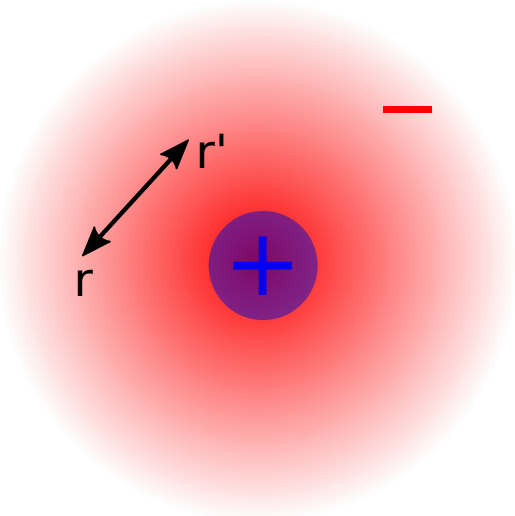
Self-interaction-error (SIE)



$$J\left[\rho\left(r\right)\right] = \frac{1}{2}\int\int\frac{\rho\left(r\right)\rho\left(r'\right)}{\left|r-r'\right|}drdr'$$

Motivation

Self-interaction-error (SIE)



Solution:

Hybrid-functionals

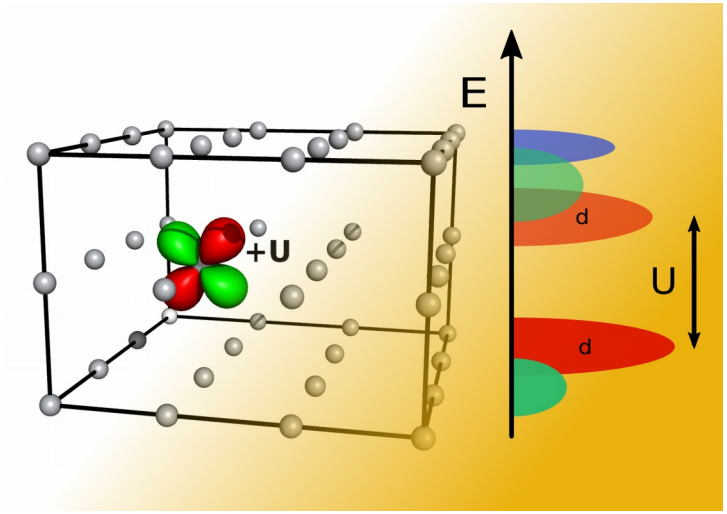
high-cost

DFT+U

low-cost
d-, f-electrons

Motivation - Theory

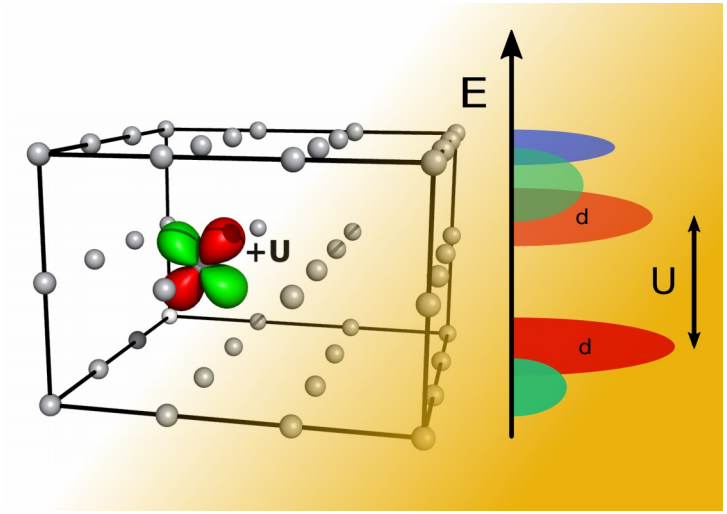
Hubbard-model



$$H_{\mathrm{U}} = U \sum_{i} c_{i\uparrow}^{\dagger} c_{i\uparrow} c_{i\downarrow}^{\dagger} c_{i\downarrow} - t \sum_{<ij>,\sigma} \left(c_{i\sigma}^{\dagger} c_{j\sigma} - c_{j\sigma}^{\dagger} c_{i\sigma} \right)$$

Motivation - Theory

General DFT+U Functional



$$E_{\mathrm{DFT+U}}\left[\rho\left(\mathbf{r}\right)\right] = E_{\mathrm{DFT}}\left[\rho\left(\mathbf{r}\right)\right] + E_{\mathrm{U}}^{0}\left[n_{Im}\right] - E_{\mathrm{dc}}\left[n_{Im}\right]$$

Motivation - Theory

Hubbard-Term

$$E_U^0\left[\{n_{mm'}\}\right] =$$

$$\frac{1}{2}\sum_{\sigma}\sum_{I}\sum_{\{m\}} < m,m''|\hat{V}_{ee}|m',m'' > n^{\sigma}_{Imm'}n^{-\sigma}_{Im''m'''}$$

$$+(< m,m'''|\hat{V}_{ee}|m',m''' >$$

$$- < m,m''|\hat{V}_{ee}|m''',m' >)n^{\sigma}_{Imm'}n^{\sigma}_{Im''m'''}$$

Motivation - Theory

Spherically averaged form of DFT+U

$$E_{\mathrm{U}}\left[\{n^{\sigma}_{Imm'}\}\right] = \frac{1}{2}\sum_{\sigma,I} U^{I}_{\mathrm{eff}}\left[Tr\left(\mathbf{n}^{\sigma}_{I}\right) - Tr\left(\mathbf{n}^{\sigma}_{I}\mathbf{n}^{\sigma}_{I}\right)\right]$$

Main quantity: DFT+U occupation matrix $\mathbf{n}^{\sigma}_{I}$

Motivation - Theory

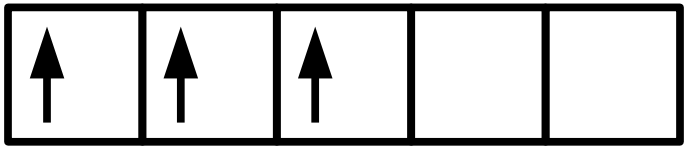
Spherically averaged form of DFT+U

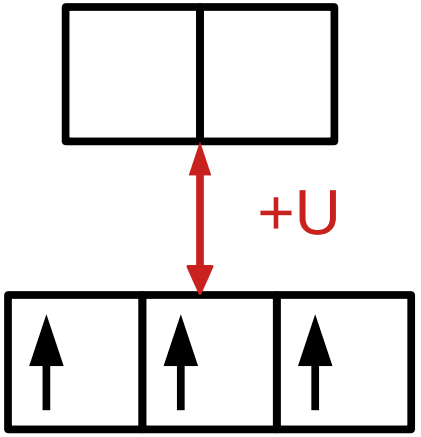
$$E_{\mathrm{U}}\left[\{n^{\sigma}_{Imm'}\}\right] = \frac{1}{2}\sum_{\sigma,I} U^{I}_{\mathrm{eff}}\left[Tr\left(\mathbf{n}^{\sigma}_{I}\right) - Tr\left(\mathbf{n}^{\sigma}_{I}\mathbf{n}^{\sigma}_{I}\right)\right]$$

Main quantity: DFT+U occupation matrix $\mathbf{n}^{\sigma}_{I}$

$\mathbf{n}^{\sigma}_{I}$: how many electrons at a certain lattice site

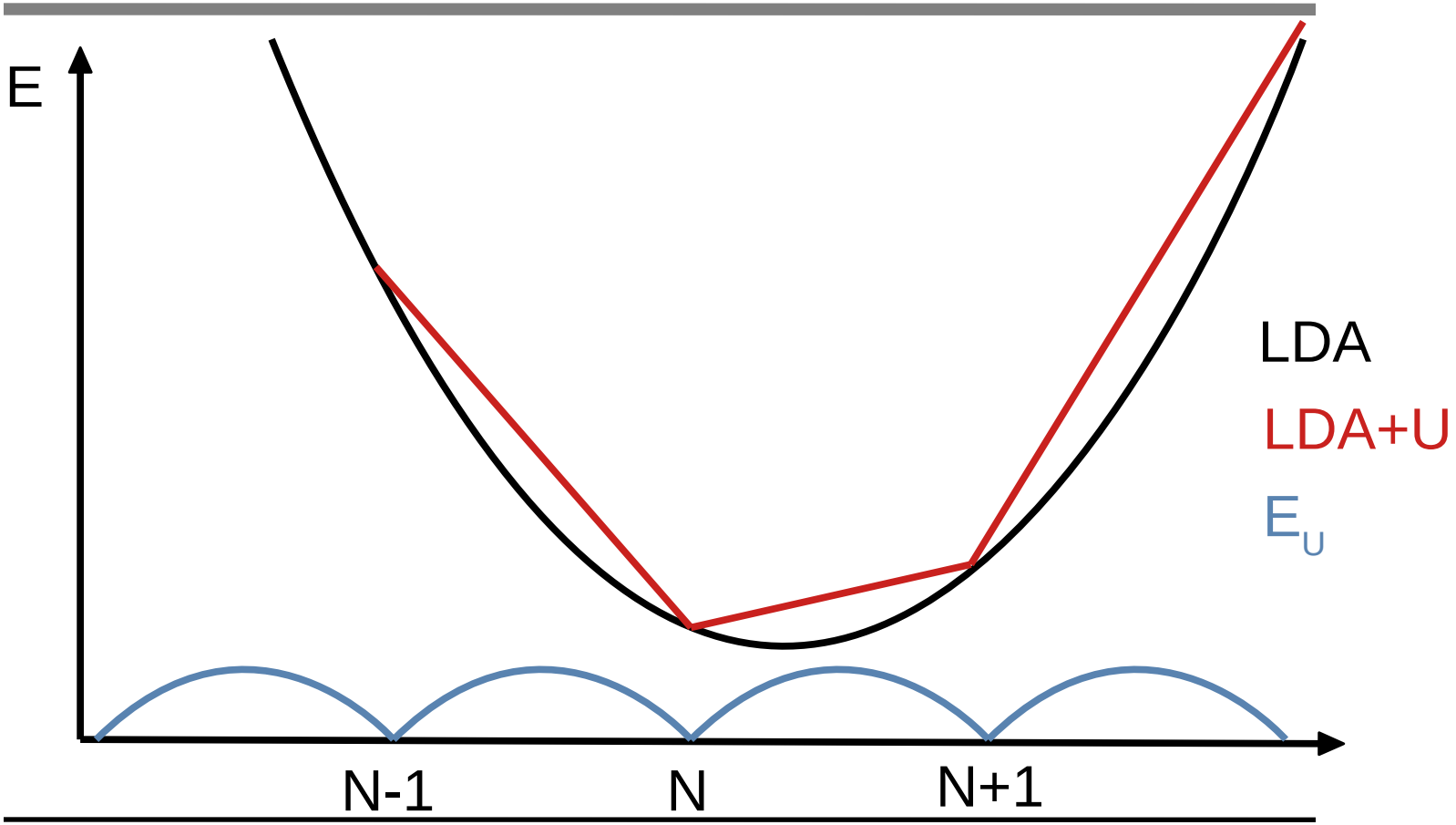
How does it work?





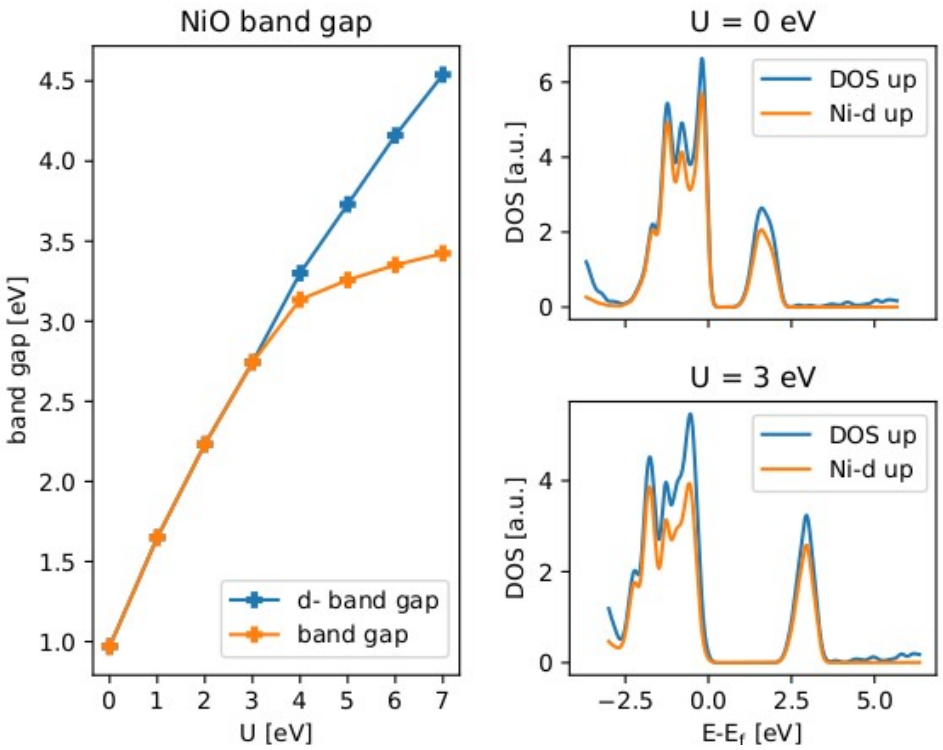
$$v_{mm'} = -U\left(n_{mm'} - \frac{1}{2}\right)$$

How does it work?



How does it work?

NiO



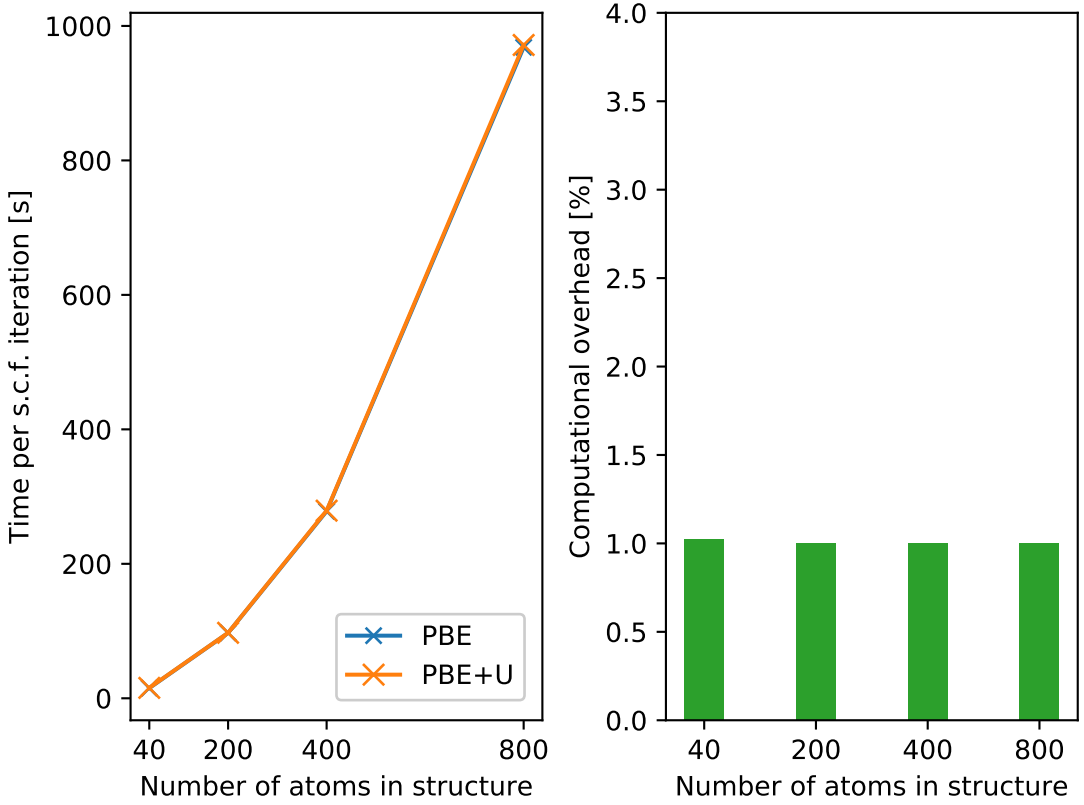
DFT+U Occupation Matrix

Problem: How to identify localized states from the KS-spectrum

$$\mathrm{n}^{\sigma}_{Imm'} = \sum_{\gamma} f_{\gamma} < \Psi^{\sigma}_{\gamma} | \hat{P}^{\sigma}_{Imm'} | \Psi^{\sigma}_{\gamma} >$$

Computational cost is negligible, evaluation of $\mathbf{n}^{\sigma}_{I}$ is reduced to finding the correct entries of the density matrix

DFT+U Occupation Matrix



DFT+U Occupation Matrix

Problem: How to identify localized states from the KS-spectrum

$$\mathrm{n}^{\sigma}_{Imm'} = \sum_{\gamma} f_{\gamma} < \Psi^{\sigma}_{\gamma} | \hat{P}^{\sigma}_{Imm'} | \Psi^{\sigma}_{\gamma} >$$

on-site

$$\hat{P}^{\sigma}_{Imm'} = |\tilde{\phi}^{\sigma}_{Im'} >< \tilde{\phi}^{\sigma}_{Im}|$$

$$|\tilde{\phi}^{\sigma}_{Im} >= \sum_{q} c^{\sigma}_{Imq} |\tilde{\psi}^{\sigma}_{Imq} >$$

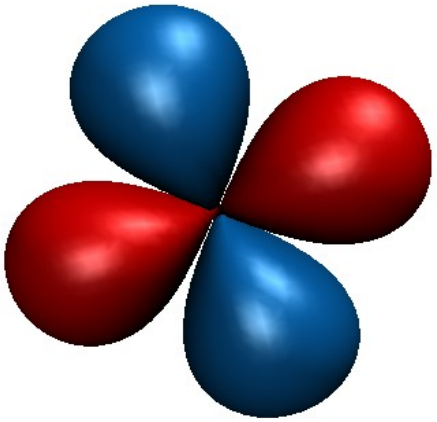
Part II: DFT+U in FHIaims

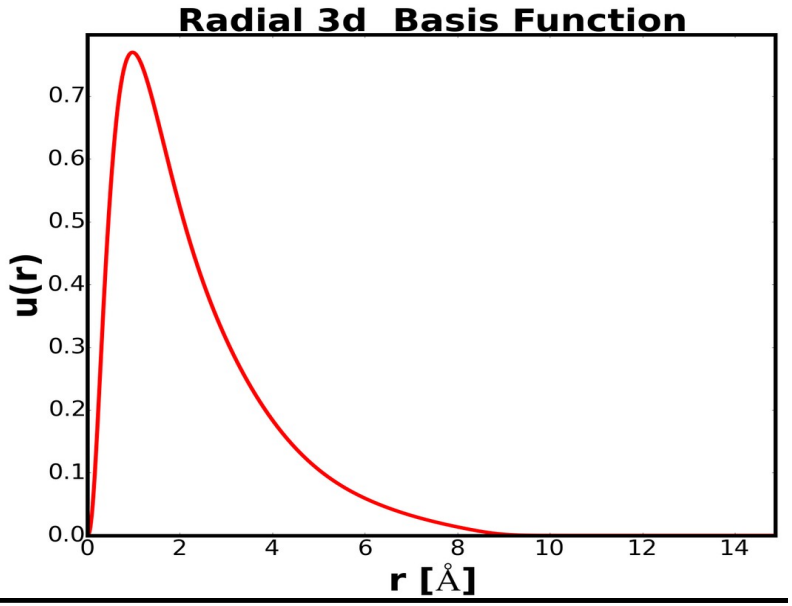
(or DFT+U in electronic structure codes with localized basis functions)

Hubbard Projectors

$$\psi_i(r) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

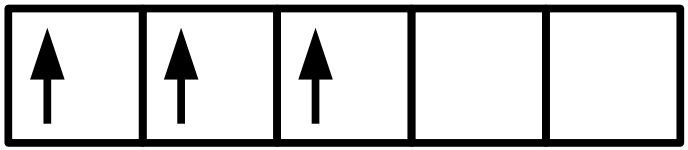
“minimal basis set is default”

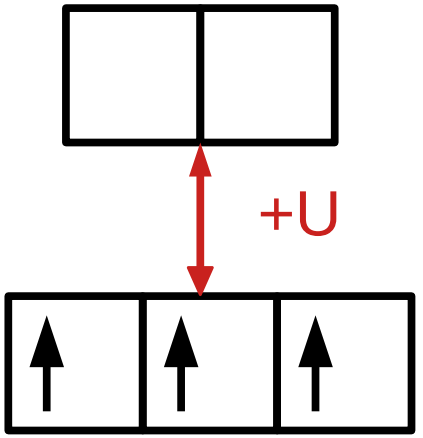




Hubbard Projectors

Not “fully true” anymore





penalize basis functions

better to speak of a correlated subspace

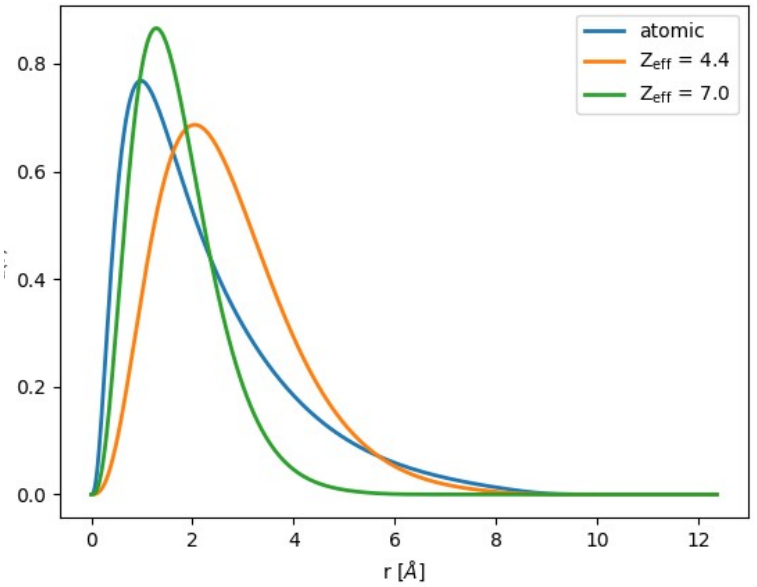
$$v_{mm'} = -U\left(n_{mm'} - \frac{1}{2}\right)$$

Hubbard Projectors

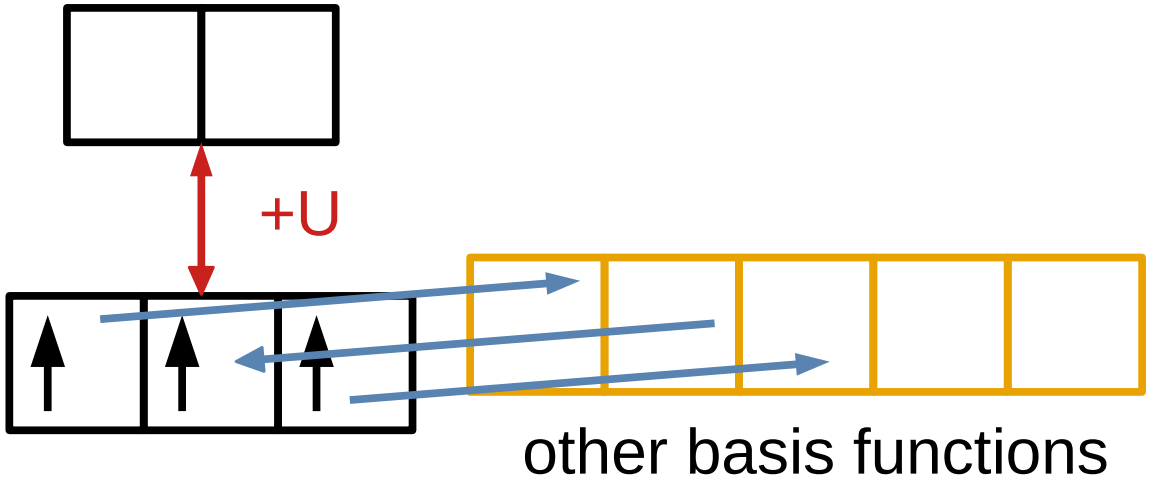
Titanium basis set

```
#"First tier"
    hydro 4 f 8
    hydro 3 d 2.7
    ionic 4 p auto
    hydro 5 g 11.6
    ionic 4 s auto
#"Second tier"
    hydro 3 d 4.4

    ...
```



My electrons disappear



Energy penalty depending on the occupation numbers

My electrons disappear

What can I do?

adjust U value

initial structure is bad

use DFT+U occupation matrix control

Include other basis functions also in DFT+U description

Matrix Control

Fix $\mathbf{n}_I^\sigma$ for entire run will fix DFT+U potential and increases stability

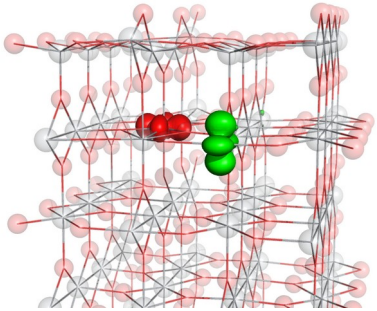
$$v_{mm'} = -U_{\text{eff}} \left(n_{mm'} - \frac{1}{2} \right)$$

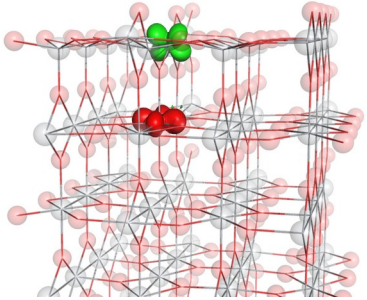
Occupation numbers from a PBE run, HSE06 run or completely user defined

Use the obtained restart information to make it self-consistently

Matrix Control: Examples

localize excess electrons in TiO_2





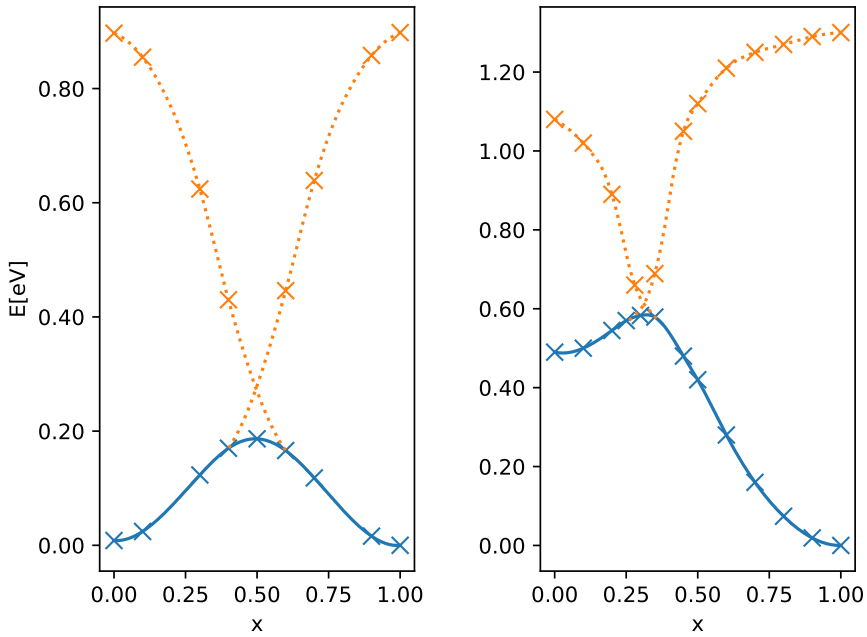
a) Ti 3d

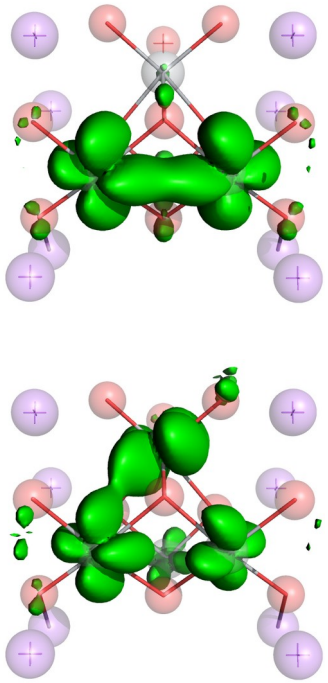
0.12	0.00	0.04	0.00	0.00
0.00	0.13	0.00	0.04	0.00
0.04	0.00	0.09	0.00	0.00
0.00	0.04	0.00	0.13	0.00
0.00	0.00	0.00	0.00	0.09

b) Ti 3d modified

0.12	0.00	0.04	0.00	0.00
0.00	0.13	0.00	0.04	0.00
0.04	0.00	1.00	0.00	0.00
0.00	0.04	0.00	0.13	0.00
0.00	0.00	0.00	0.00	0.09

Matrix Control: Examples





calculation of polaron hopping barriers and transition states

Conclusion

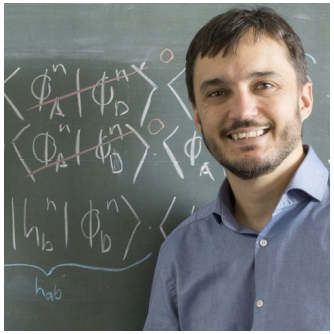
DFT+U corrects SIE (similar to hybrid functionals)

Ambiguities come mainly from the projector functions

Negligible computational cost compared to LDA/GGA

Occupation matrix control extremly powerful
Enables the treatment of systems which otherwise are pathologically

Thank you for your attention!



DFG Deutsche Forschungsgemeinschaft

Implementation