Electron model construction in SCALE-UP

Pablo García-Fernández

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Universidad de Cantabria

Anatomy of a SP-DFT model

The full SP-DFT energy is:

$$E = E^{(0)}(\{\vec{u}_{\boldsymbol{\lambda}}\}, \overleftrightarrow{\eta}) + \sum_{\mathbf{ab}} D^U_{\mathbf{ab}}[\gamma^{\text{RAG,sr}}_{\mathbf{ab}} + \delta\gamma^{\text{el-lat,sr}}_{\mathbf{ab}}(\{\vec{u}_{\boldsymbol{\lambda}}\})]$$

$$+\frac{1}{2}\sum_{\mathbf{ab}}\sum_{\mathbf{a'b'}}\left(D^U_{\mathbf{ab}} D^U_{\mathbf{a'b'}} U^{\text{sr}}_{\mathbf{aba'b'}} - D^I_{\mathbf{ab}} D^I_{\mathbf{a'b'}} I_{\mathbf{aba'b'}}\right) + E^{\text{lg}}(\{D^U\})$$

1. $E^{(0)}(\{\vec{u}_{\boldsymbol{\lambda}}\}, \overleftrightarrow{\eta})$ is a force-field for the reference state
2. $\gamma^{\text{RAG,sr}}_{\mathbf{ab}}$ are the one-electron terms at the reference geometry
3. $\delta\gamma^{\text{el-lat,sr}}_{\mathbf{ab}}(\{\vec{u}_{\boldsymbol{\lambda}}\})$ are the electron-lattice coupling terms
4. $U^{\text{sr}}_{\mathbf{aba'b'}}$, $I_{\mathbf{aba'b'}}$ are the two-electron terms
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All parameters are defined at the reference state

$$\gamma_{\mathbf{ab}} = \langle \chi_{\mathbf{a}} | \, \hat{h}[n_0] \, | \chi_{\mathbf{b}} \rangle \qquad U_{\mathbf{aba'b'}} = \langle \chi_{\mathbf{a}} \chi_{\mathbf{a'}} | \, \hat{g} \, | \chi_{\mathbf{b}} \chi_{\mathbf{b'}} \rangle$$

$$g(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|} + \left.\frac{\delta^2 E_{\text{xc}}}{\delta n(\vec{r}) \delta n(\vec{r}')}\right|_{n_0}.$$

Reference state

The reference state is the base to make the SP-DFT expansion

$$E_{\mathrm{DFT}} \approx \underbrace{E_0}_{\substack{\text{lattice} \\ n_0(\vec{r})}} + \underbrace{E_1 + E_2 + \ldots}_{\substack{\text{electron excitations} \\ \delta n_0(\vec{r})}}$$

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1. n_0 is not spin-polarized (avoid bias between up/down states)
2. In the Wannier-function (WF) basis it is characterized by a diagonal density matrix:

$$n_0(\vec{r}) = \sum_{\mathbf{ab}} d^{(0)}_{\mathbf{ab}} \chi_{\mathbf{a}}(\vec{r}) \chi_{\mathbf{b}}(\vec{r}) = \sum_{\mathbf{a}} o^{(0)}_{\mathbf{a}} |\chi_{\mathbf{a}}(\vec{r})|^2 \Longleftrightarrow d^{(0)}_{\mathbf{ab}} = \delta_{\mathbf{ab}} o^{(0)}_{\mathbf{a}}$$

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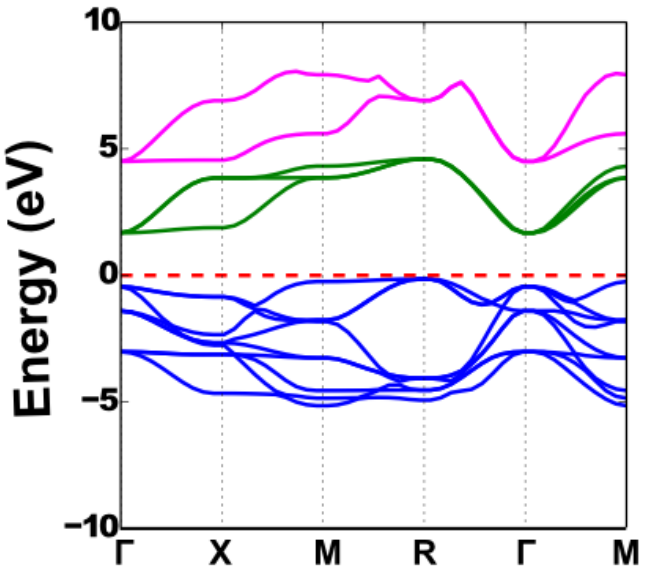
4. n_0 may be a real solution (DFT calculable) or be virtual

The key is the procedure to get WFs from first-principles

Obtaining the basis from first-principles

The tool we employ to obtain WFs is WANNIER90



Example: $BaTiO_3$

Wannier-Bloch transformation

$$\psi_{n\vec{k}} = \sum_{a\vec{R}} c_{an\vec{k}} e^{i\vec{k}\vec{R}} \chi_a(\vec{r} - \vec{R})$$

1. Select energy window
2. Select projections
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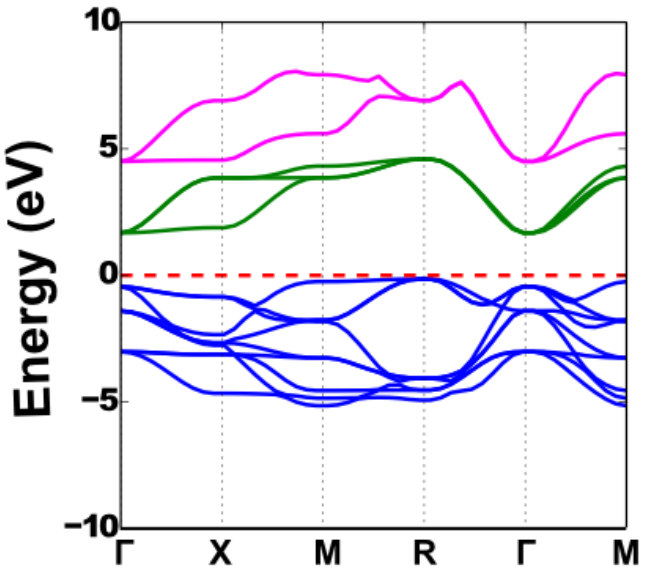

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Key property to understand how the reference is defined:

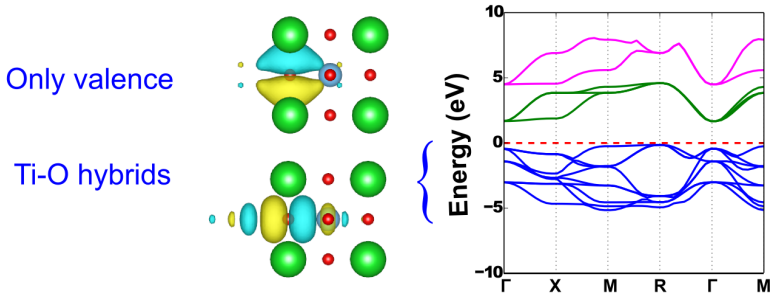
A diagonal density matrix is only obtained from the transformation of a set of Bloch states that are equally populated

$$o^{(0)}_{j\vec{k}} = o_{\mathcal{J}} \omega_{\vec{k}} \Longleftrightarrow d^{(0)}_{\mathbf{ab}} = o_{\mathcal{J}} \delta_{\mathbf{ab}}$$

Selecting energy window determines real/virtual reference state

Examples of reference states

Only valence bands



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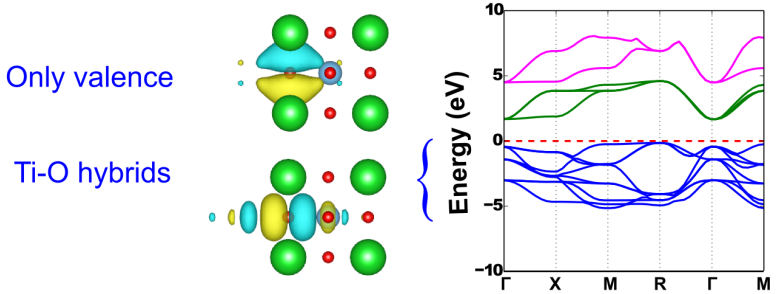

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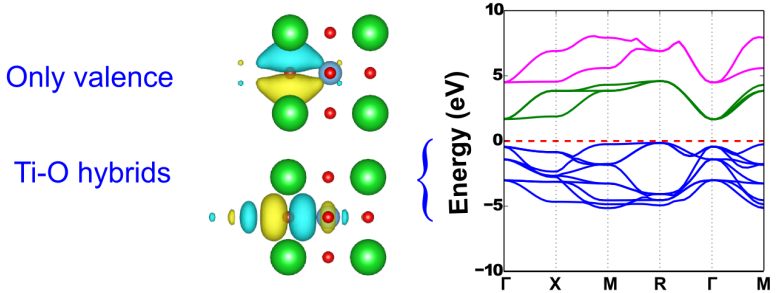

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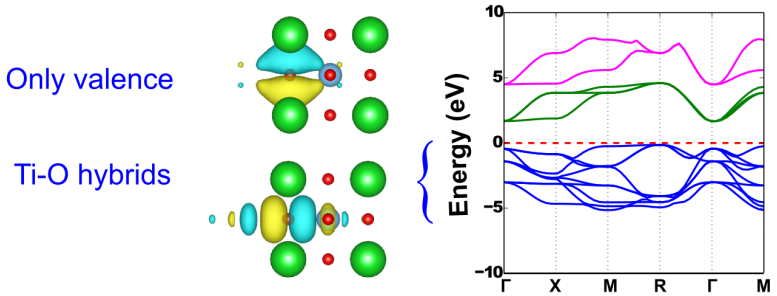

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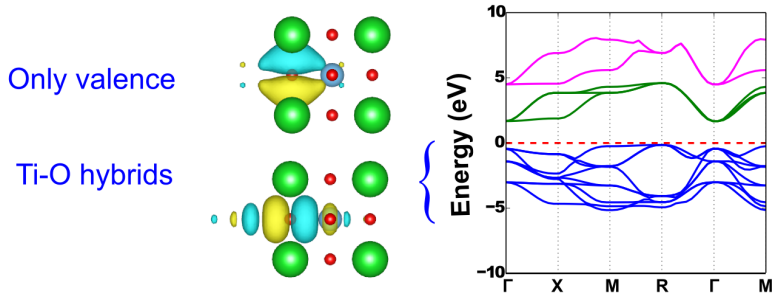

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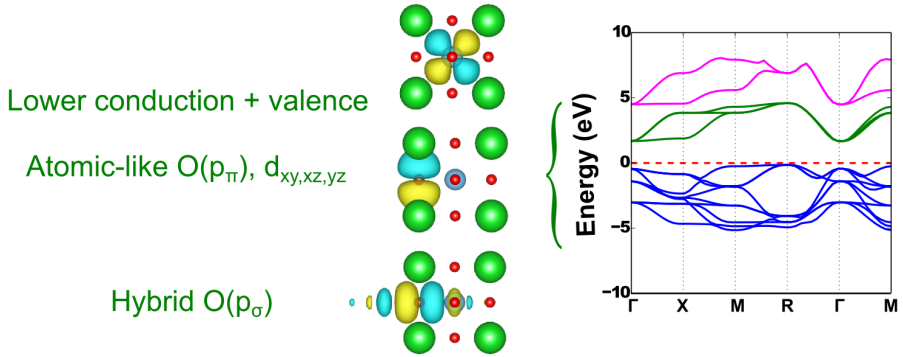

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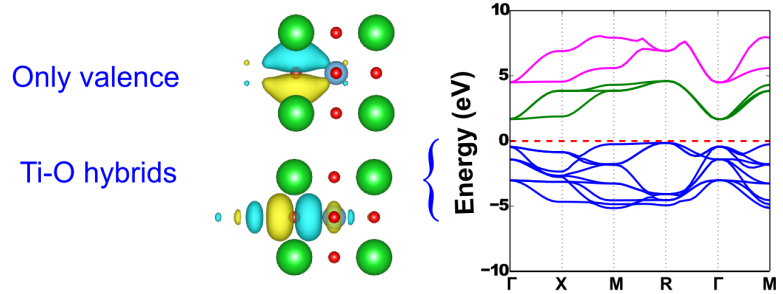

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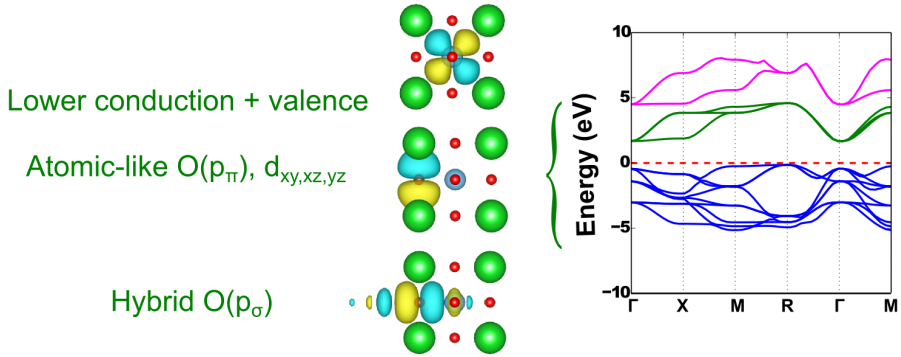

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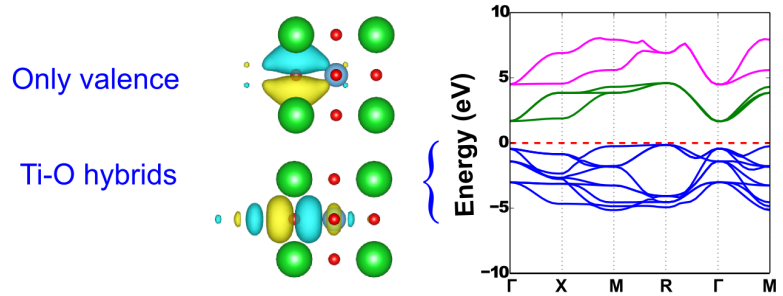

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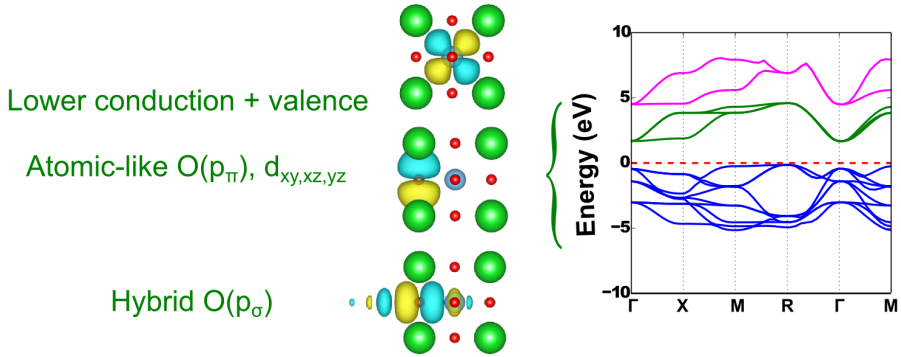

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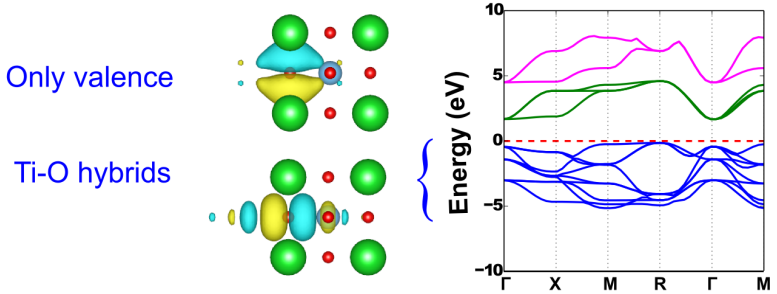

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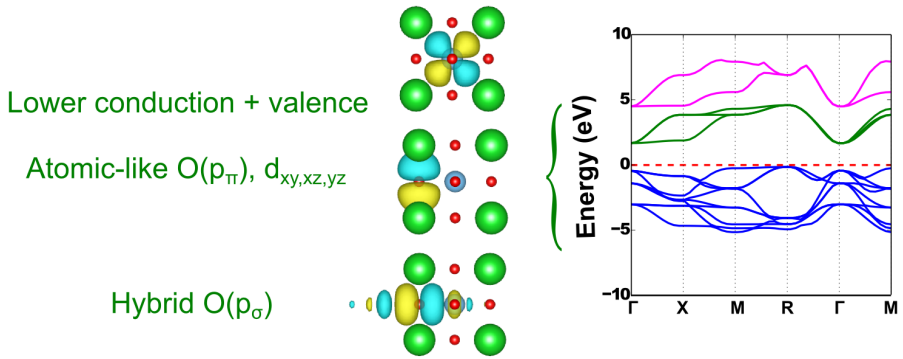

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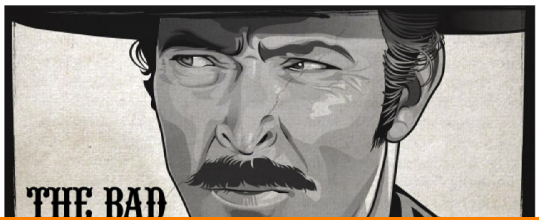
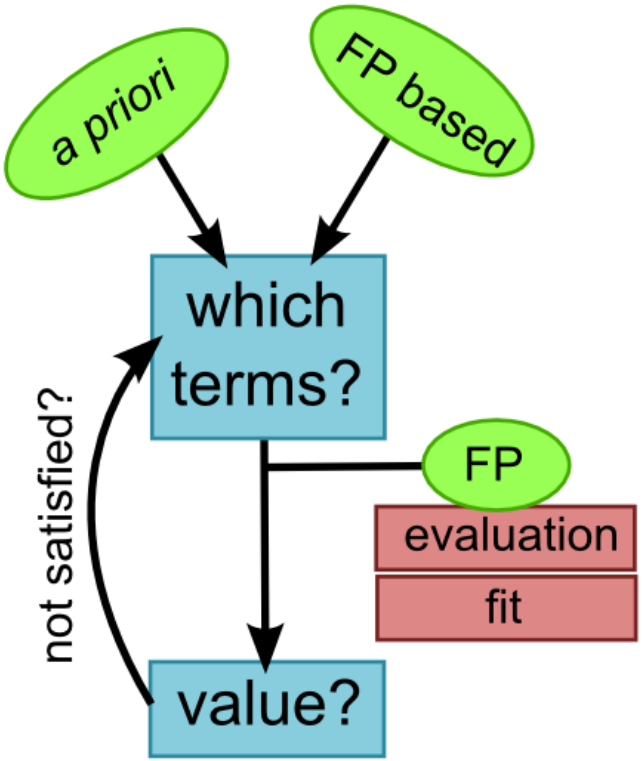
Model construction is hugely restricted due to WANNIER90 constraints



Constructing a model

Main questions building a SP model:

1. Which terms enter the model?
   Symmetry-Adapted-Terms (SAT)
2. What value do they take?



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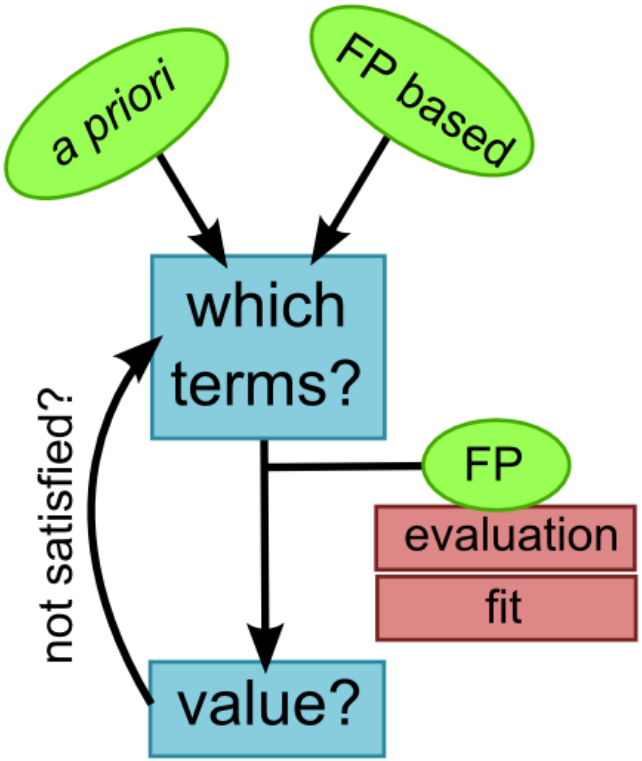

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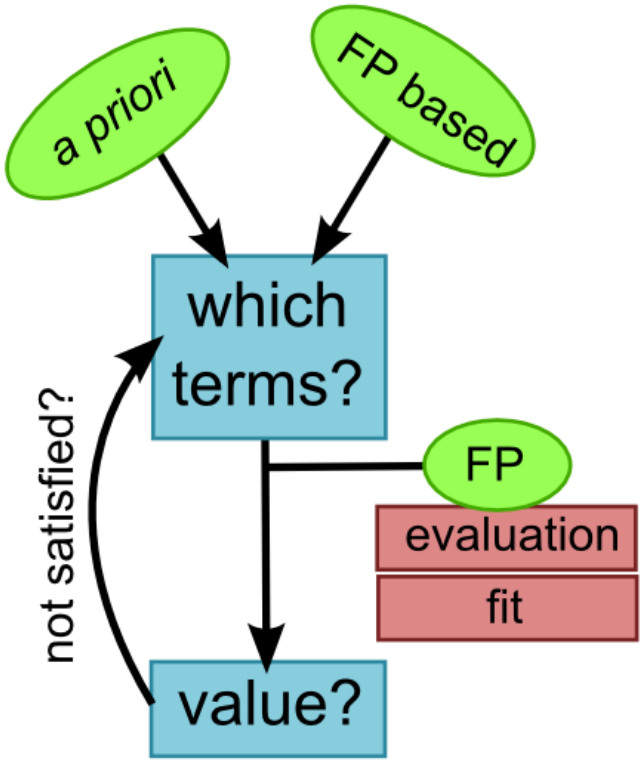

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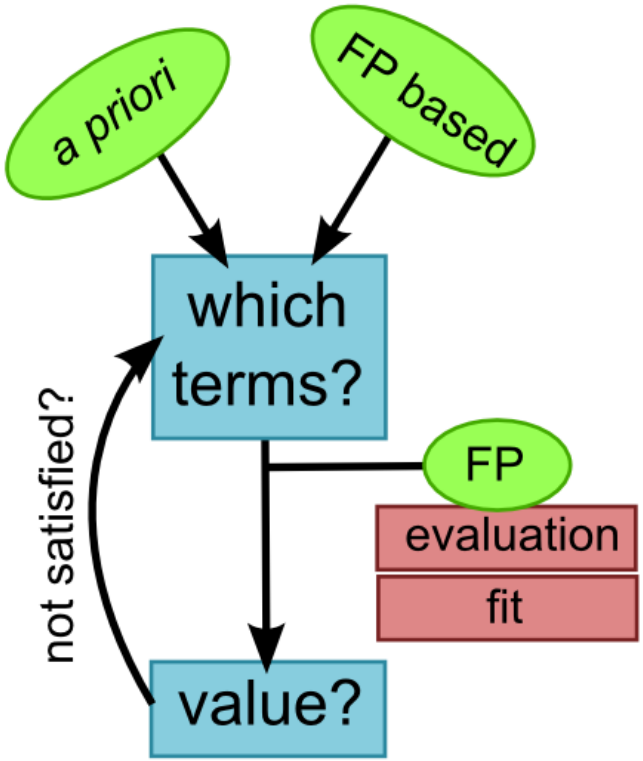

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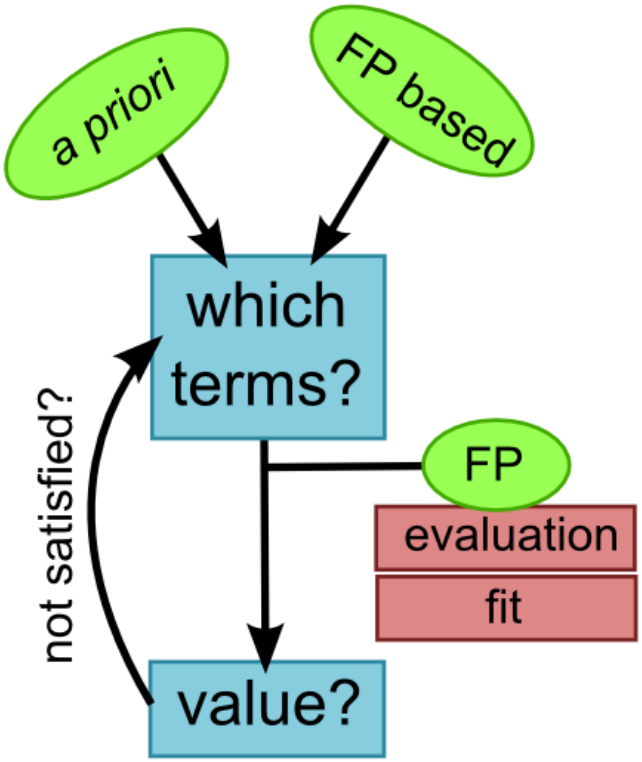

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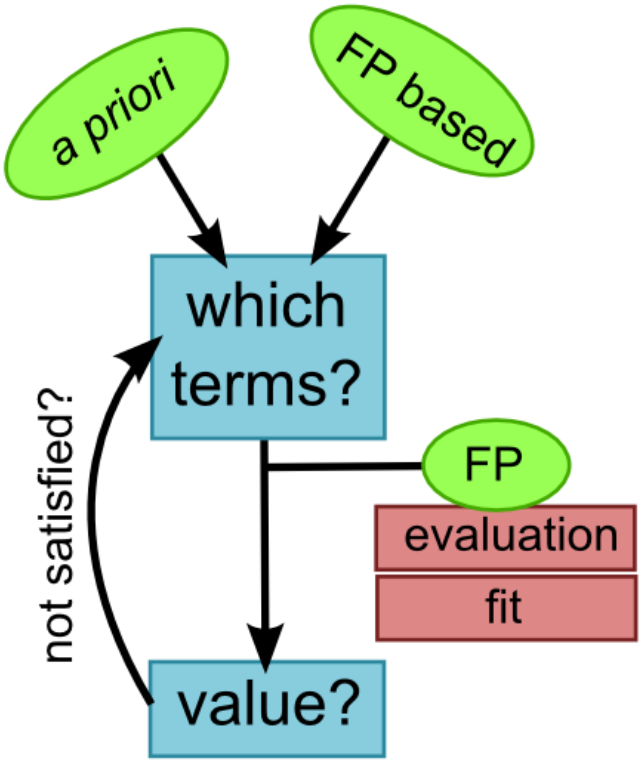

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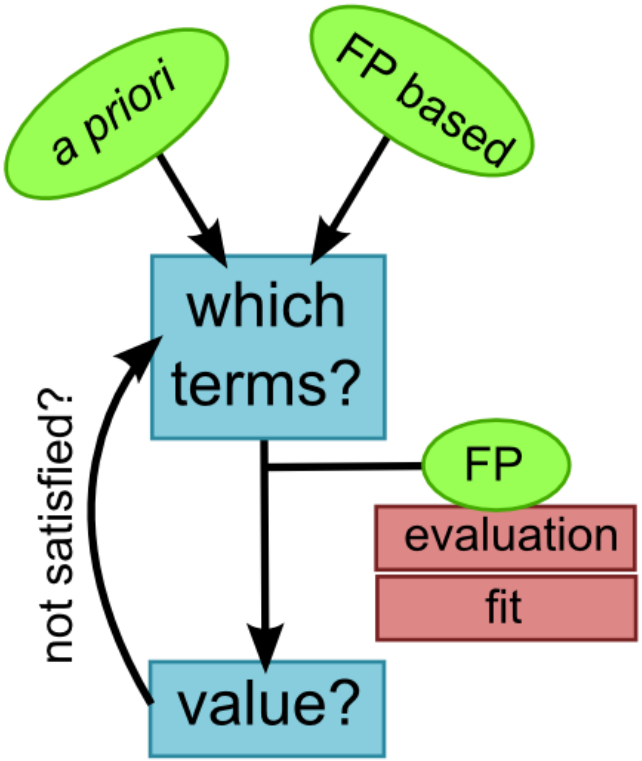

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Problems:

1. WF from WANNIER90 do not have symmetry
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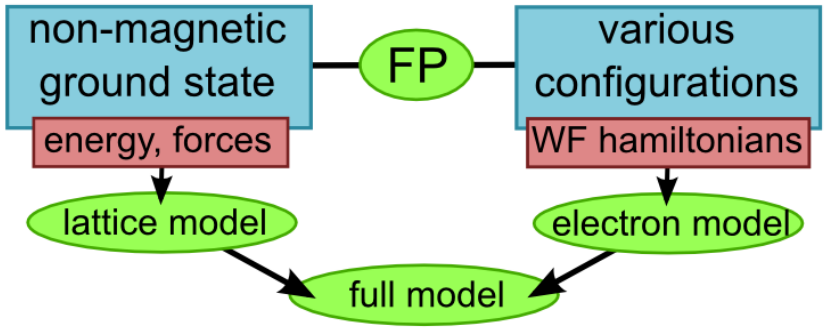
2. Training-set approaches may be intrinsically biased or difficult

Separation of electron and lattice degrees of freedom



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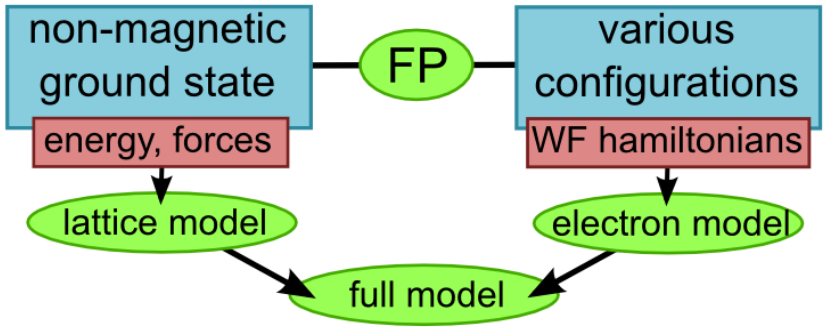

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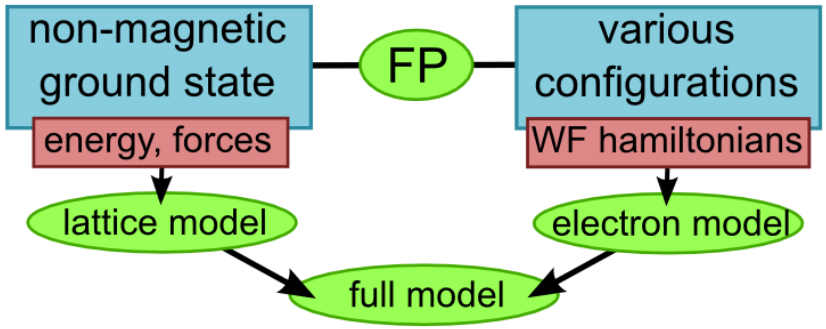

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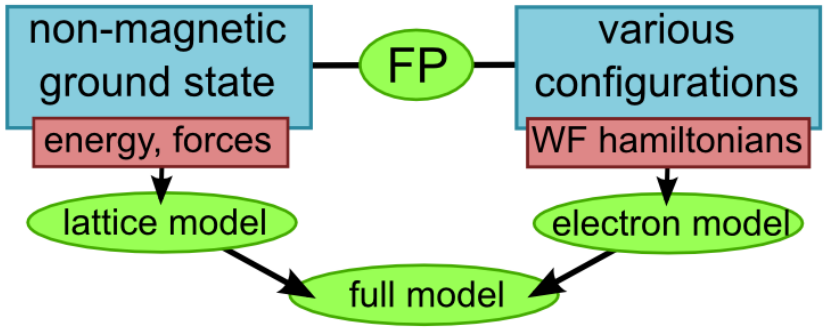

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Reference configuration in electron model may not match that for lattice model!

What if ground state and reference do not match?

The DFT ground state energy matches that of the lattice model:

$$E_{\mathrm{DFT}}^{(\mathrm{ground})} = E_{\mathrm{lattice}}$$

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At the same time this also corresponds with the SPDFT energy:

$$E_{\mathrm{DFT}}^{(\mathrm{ground})} \approx E^{(0)} + \underbrace{E^{(1)} + E^{(2)} + \ldots}_{\text{electrons in GS}}$$

Thus, the correct $E^{(0)}$ takes the value:

$$E^{(0)} \approx E_{\mathrm{lattice}} - \underbrace{(E^{(1)} + E^{(2)} + \ldots)}_{\text{electrons in GS}}$$

where the electron correction is only dependent on the geometry.

This is equivalent to correcting the force-field

Currently we correct the harmonic part of the lattice model

Working on the anharmonic part (or something better)!

Real space WF Hamiltonians

The basis of SP electron calculations is the real-space Hamiltonian

$$h^s_{\mathbf{ab}} = \gamma^{\text{RAG,sr}}_{\mathbf{ab}} + \delta\gamma^{\text{el-lat,sr}}_{\mathbf{ab}}(\{\vec{u}_{\boldsymbol{\lambda}}\}) + \sum_{\mathbf{a'b'}} \left(D^{U,s}_{\mathbf{a'b'}} U_{\mathbf{aba'b'}} + D^{I,s}_{\mathbf{a'b'}} I_{\mathbf{aba'b'}} \right) + \gamma^{\text{lr}}_{\mathbf{ab}}$$

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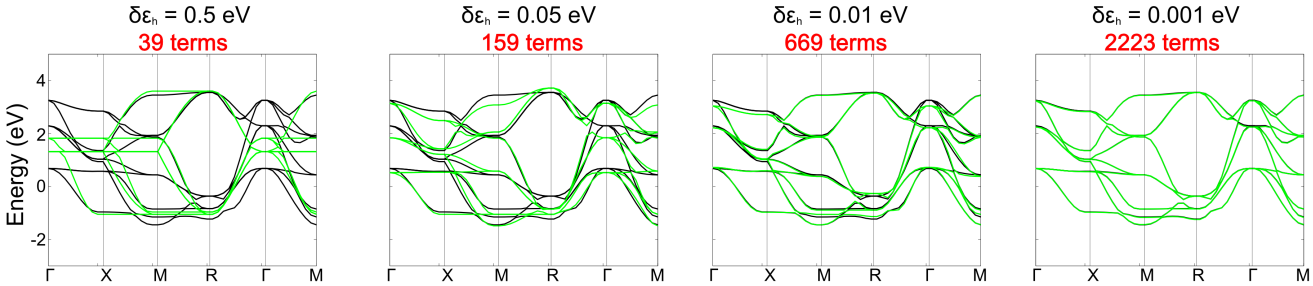

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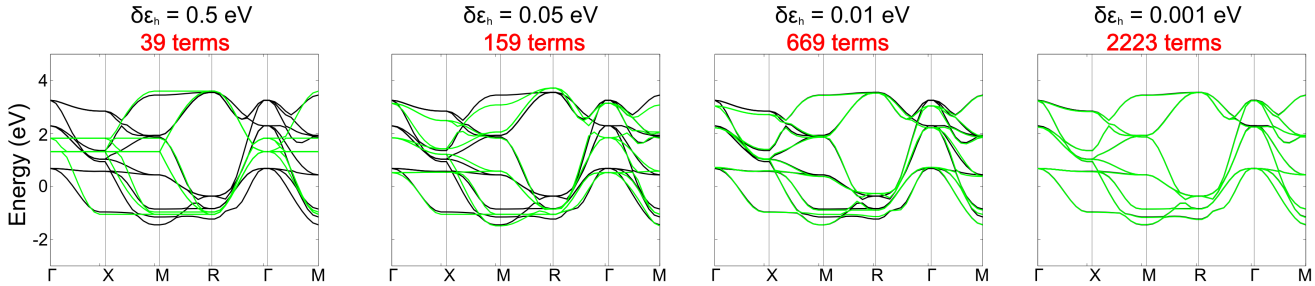

3. Find how $h^s_{\mathbf{ab}}$ changes. Superimposed:
   - Two-electron: Different electron state
     Doping, magnetic state,...
   - Electron-lattice: Change geometry in reference

Not always easy to separate!

The method's steps

In each step we apply some user-input cutoff:

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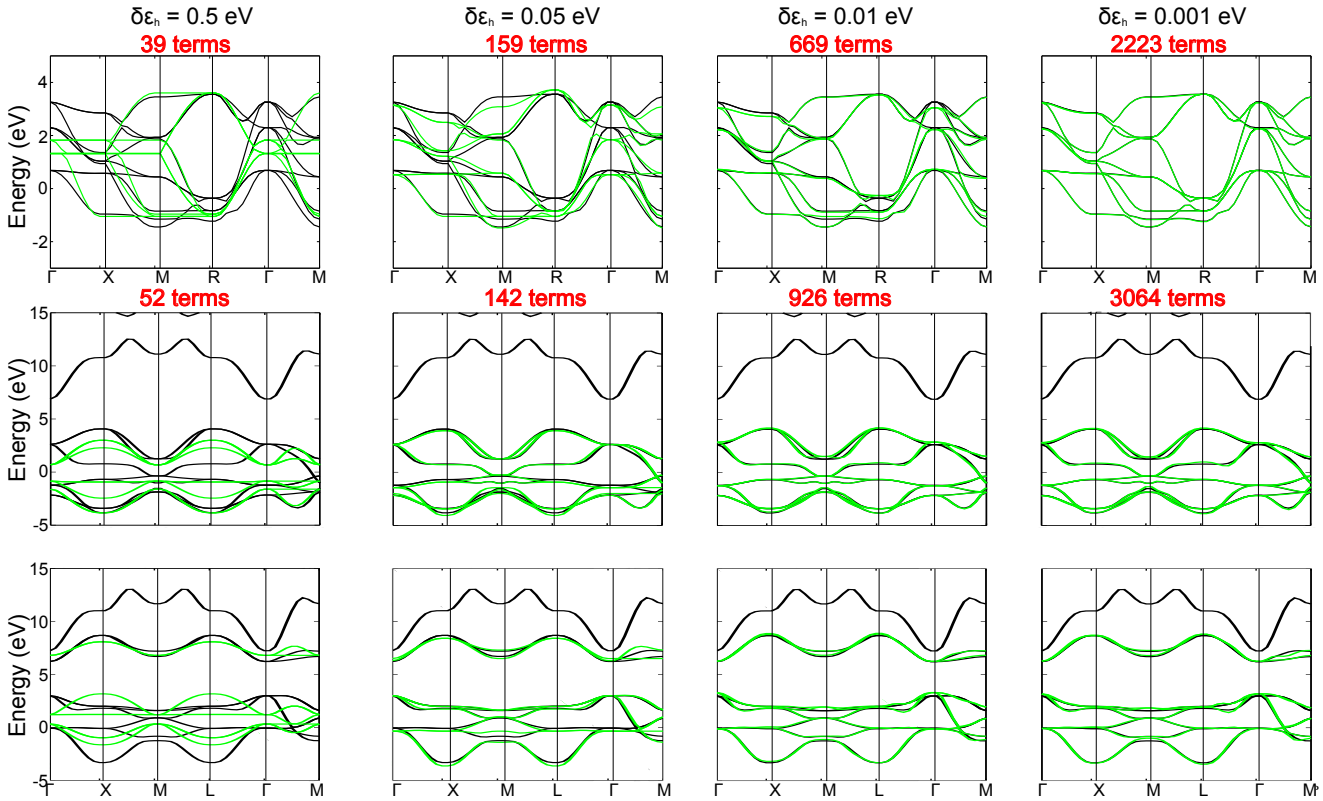

$\delta\varepsilon_h$ controls the balance of quality vs computational efficiency

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$$|D^{\uparrow}_{a'b'} + D^{\downarrow}_{a'b'}| > \delta D$$

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Two-electron terms

Involve screened electron-electron interactions:

$$X_{\mathbf{aba'b'}} = \int d^3r \chi_{\mathbf{a}}(\vec{r})\chi_{\mathbf{b}}(\vec{r}) \int d^3r' \chi_{\mathbf{a'}}(\vec{r'})\chi_{\mathbf{b'}}(\vec{r'}) g_X(\vec{r},\vec{r'}) \quad X = U, I$$

with the operators,

$$g_{U,I}(\vec{r},\vec{r'}) = \frac{1}{2}\left[\pm \left.\frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\vec{r},\uparrow)\delta n(\vec{r'},\uparrow)}\right|_{n_0} + \left.\frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\vec{r},\uparrow)\delta n(\vec{r'},\downarrow)}\right|_{n_0} \right]$$

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They follow a strict hierarchy:

TERM	ORIGIN	SYMMETRY	POSITION $h_{\mathbf{ab}}$
$X_{\mathbf{aaaa}} = \langle\chi_{\mathbf{a}}\chi_{\mathbf{a}}\vert\,\hat{g}_X\,\vert\chi_{\mathbf{a}}\chi_{\mathbf{a}}\rangle$	self-interaction	always	diagonal
$X_{\mathbf{aaa'a'}} = \langle\chi_{\mathbf{a}}\chi_{\mathbf{a'}}\vert\,\hat{g}_X\,\vert\chi_{\mathbf{a}}\chi_{\mathbf{a'}}\rangle$	charge-charge	always	diagonal
$X_{\mathbf{aaa'b'}} = \langle\chi_{\mathbf{a}}\chi_{\mathbf{a'}}\vert\,\hat{g}_X\,\vert\chi_{\mathbf{a}}\chi_{\mathbf{b'}}\rangle$	charge-dipole	$\gamma_{\mathbf{ab}}$	on/off-diagonal
$X_{\mathbf{aba'b'}} = \langle\chi_{\mathbf{a}}\chi_{\mathbf{a'}}\vert\,\hat{g}_X\,\vert\chi_{\mathbf{b}}\chi_{\mathbf{b'}}\rangle$	dipole-dipole	depends	off-diagonal

In general it is easy to propose two-electron terms to build a model

We can use ligand-field (+U) to reduce amount of degrees of freedom

Electron-lattice

Electron-lattice terms are extremely sensitive to symmetry:

$$\gamma^{\mathrm{sr}}_{\mathbf{ab}} = \gamma^{0}_{\mathbf{ab}} + \sum_{\boldsymbol{\lambda v}} - \left[\vec{f}_{\mathbf{ab},\boldsymbol{\lambda v}} \cdot \delta\vec{r}_{\boldsymbol{\lambda v}} + \delta\vec{r}_{\boldsymbol{\lambda v}} \cdot \overset{\leftrightarrow}{g}_{\mathbf{ab},\boldsymbol{\lambda v}} \cdot \delta\vec{r}_{\boldsymbol{\lambda v}} + \ldots \right]$$

Calculation$\rightarrow$ observe change in WANNNIER90 $h_{\mathbf{ab}}$ with geometry

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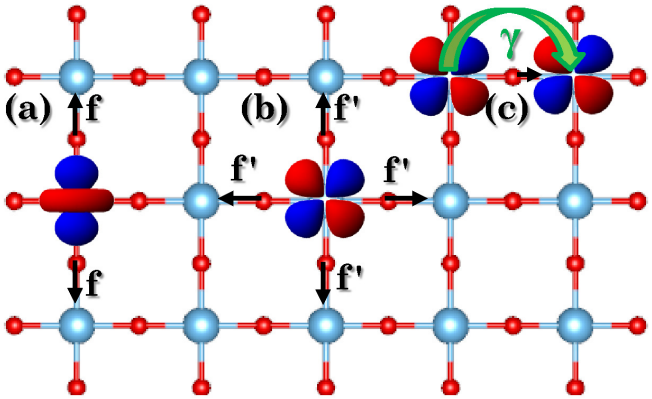

$$\vec{f}_{\mathbf{ab},\boldsymbol{\lambda\upsilon}} = - \langle \chi_{\mathbf{a}} | \vec{\nabla}_{\vec{u}_{\boldsymbol{\lambda}} - \vec{u}_{\boldsymbol{\upsilon}}} h | \chi_{\mathbf{b}} \rangle$$

Orbital shape strongly influences forces

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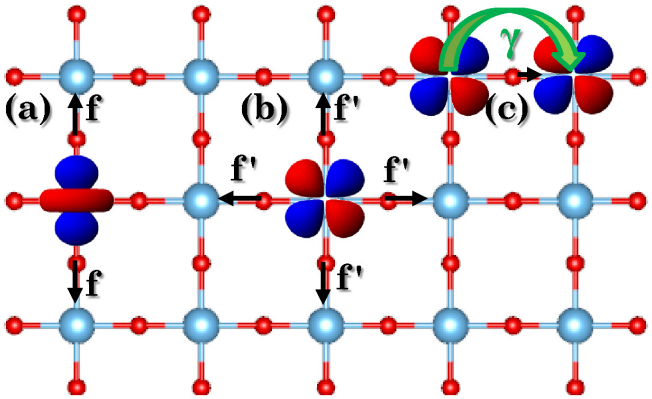

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Orbital shape strongly influences forces

Lack symmetry in WANNIER90 hinders making electron-lattice SATs

Orlando Aquije atixvector.deviantart.com

We are limited to *a priori* Jahn-Teller models/Slater-Koster variations

Example: NiO

The first complex example for electronic structure:

Simple training set:

2 magnetic states of 2 atom cell
(FM/AFM2)

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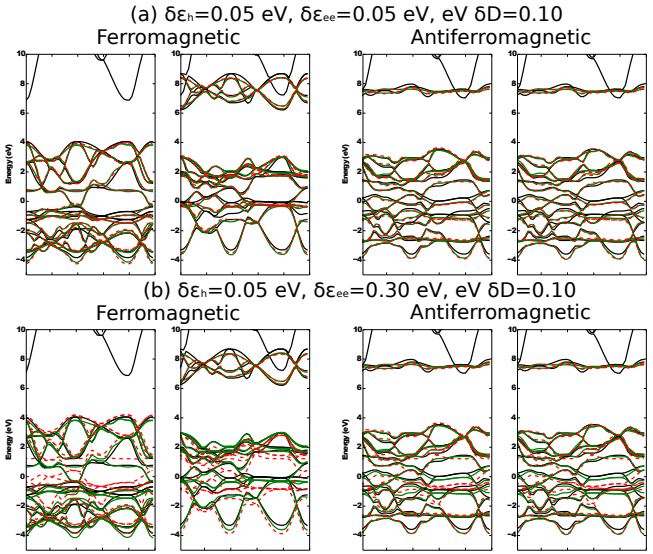

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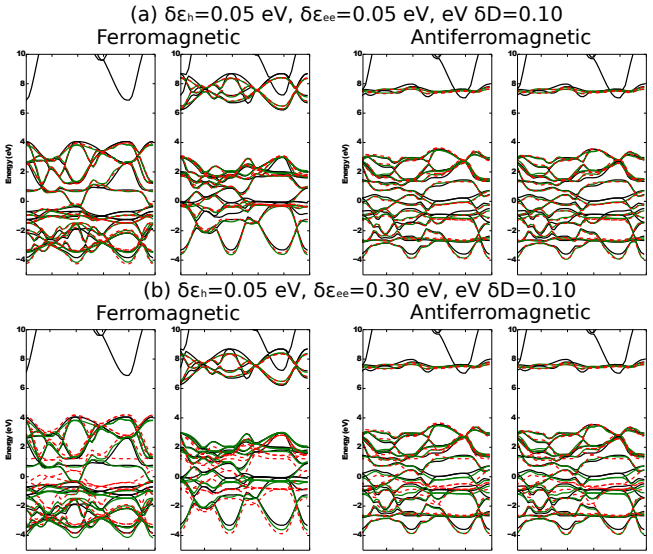

Method	J_1 (meV)	J_2 (meV)
neutron	1.4	-19.0
LDA+U	2.6	-17.5
SP-$Ni(e_g)$	-0.2	-19.1
SP-$Ni(3d)$	-0.0	-19.1
SP-$Ni(3d) + O(2p)$	3.3	-17.6

Model building tool: MODELMAKER

Philosophy to run it: Running modes

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8. Write the model to the SCALE-UP format in the file given by mmfilename name_of_file

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Automatized tools linked to ab initio codes could significantly improve the procedure

This is an area where active development is taking place