Second Principles Density Functional Theory models: a procedure to obtain their tight-binding parameters automatically

nayara.carral@unican.es

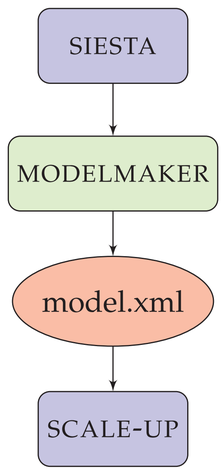
Nayara Carral-Sainz[1] , Javier Junquera[1] and Pablo García-Fernández[1]

[1]*Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria*

INTRODUCTION

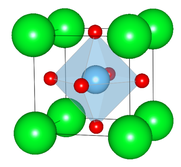
First-principles calculations allow to compute the energy and properties of a compound from essential information about its structure and composition. However, simulations at operating conditions as finite temperature or finite electric fields remain practically limited by computational resources to very small length scales (a few hundreds of atoms per cell) and time scales (a few picoseconds).

To overcome these limitations, a first-principles-based method called Second-Principles Density Functional Theory has been developed implemented in SCALE-UP [1]. This scheme relies on the usage of a force field to treat interatomic interactions. Later, it introduces the explicit treatment of the most relevant electronic degrees of freedom (**close to the bandgap**) in the form of a tight-binding model where the parameters are computed **AUTOMATICALLY** by MODELMAKER, reproducing as close as possible a set of first principles calculations (from SIESTA [2]). Since there is not input coming from the experiment, our method retains full **PREDICTIVE POWER**.



SYSTEM: $SrTiO_3$

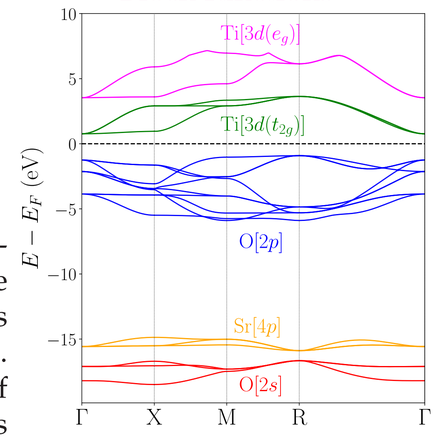
$SrTiO_3$ is an insulator system characterized by a perovskite structure.



WANNIERIZATION

In order to obtain localized functions in the real space storing the same information as the Bloch basis set, the Fourier transform is applied. The Fourier-transform partners of the Bloch functions are known as Wannier functions [3].

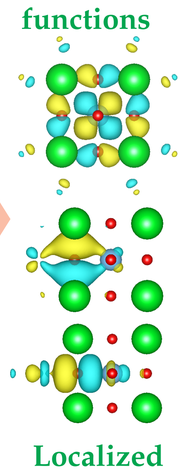
Bands computed in a basis of Bloch functions



Delocalized

FFT

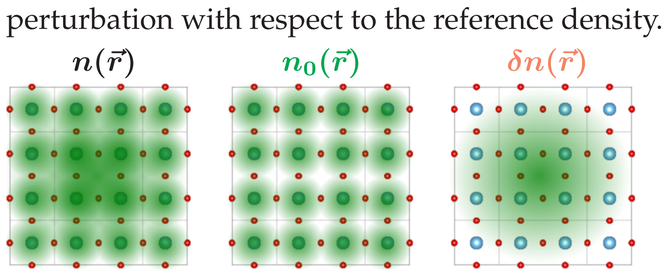
Wannier functions



Localized

SCALE-UP

Starting from the DFT energy expression [1], the total density is divided in two contributions: a **reference** contribution and a **deformation** contribution. The latter is considered a small perturbation with respect to the reference density.



$$n(\vec{r}) = n_0(\vec{r}) + \delta n(\vec{r})$$

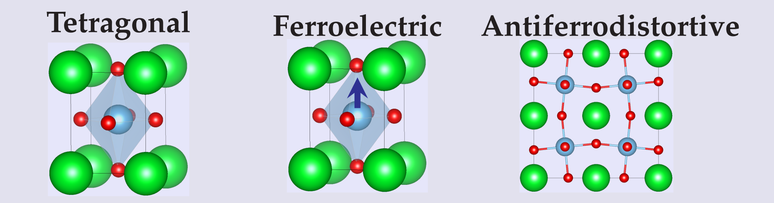
The energy is computed according to the expansion

$$E \approx E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

The **first-order** correction due to electron excitations expressed in the localized Wannier basis is:

$$E^{(1)} = \sum_{ab} D^{U}_{ab} \left[\gamma^{\mathrm{RAG,sr}}_{ab} + \delta\gamma^{\mathrm{el-lat,sr}}_{ab}(\{\vec{u}_{\lambda}\}) \right]$$

ABO_3 systems are prone to be stable in different phases depending on pressure and temperature conditions:



Changes in geometries → Alteration of the bonds → **Electron-lattice** coupling corrections, $\delta\gamma^{\mathrm{el-lat}}_{ab}$

The electron-lattice coupling is expanded in terms of the atomic coordinates:

$$\delta\gamma^{\mathrm{el-lat,sr}}_{ab}(\{\vec{u}_{\lambda}\}) = \sum_{\lambda\upsilon} \Big[-\vec{f}_{ab,\lambda\upsilon}{}^{T} \delta\vec{r}_{\lambda\upsilon} + \sum_{\lambda'\upsilon'} \delta\vec{r}^{\,T}_{\lambda\upsilon} \overleftrightarrow{g}_{ab,\lambda\upsilon\lambda'\upsilon'} \delta\vec{r}_{\lambda'\upsilon'} \Big]$$

These terms have two main effects [4]:

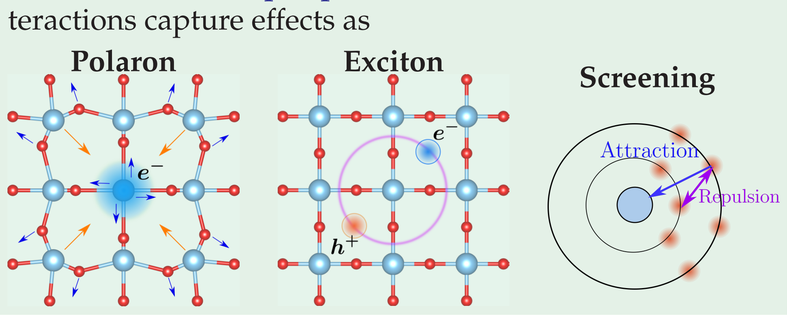
- lattice → electron Energy depends on geometry
- electron→lattice Forces depend on density

The **second-order** correction is:

$$E^{(2)} = \frac{1}{2} \sum_{ab} \sum_{a'b'} \left\{ D^{U}_{ab} D^{U}_{a'b'} U_{aba'b'} - D^{I}_{ab} D^{I}_{a'b'} I_{aba'b'} \right\}$$

Different occupations → Band structure changes → **Electron-electron** coupling corrections, $\delta\gamma^{\mathrm{el-el}}_{ab}$

It takes into account the energy required to **add/remove electrons** and the **spin-polarization**. The two-electron interactions capture effects as



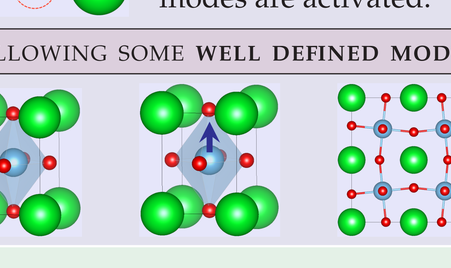
MODELMAKER

The model hamiltonian

$$h^{s}_{ab} = \gamma^{\mathrm{RAG,sr}}_{ab} + \gamma^{\mathrm{lr}}_{ab} + \sum_{\lambda\upsilon} \left[-\vec{f}^{T}_{ab,\lambda\upsilon} \delta\vec{r}_{\lambda\upsilon} + \sum_{\lambda'\upsilon'} \delta\vec{r}^{\,T}_{\lambda\upsilon} \overleftrightarrow{g}_{ab,\lambda\upsilon\lambda'\upsilon'} \delta\vec{r}_{\lambda'\upsilon'} \right] + \sum_{a'b'} \left(D^{U}_{a'b'} U_{aba'b'} - D^{I}_{a'b'} I_{aba'b'} \right)$$

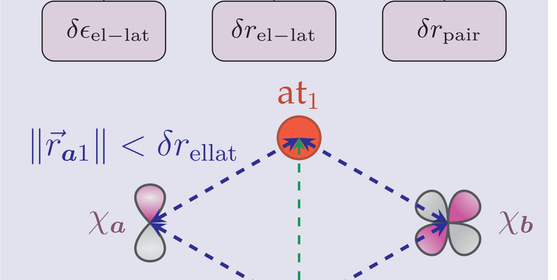
1. REFERENCE WANNIER HAMILTONIAN

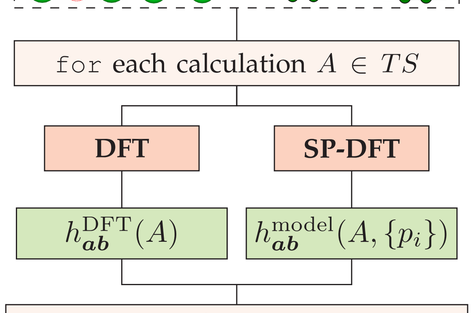
The model generation starts running the SIESTA calculation for the system at the selected Reference Atomic Geometry (RAG) and Reference Atomic Density (RED).



2. SYMMETRY GROUPS

MODELMAKER groups interactions h^{s}_{ab} equivalent by symmetry .

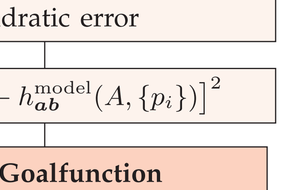




The previous interactions transform each other by a mirror plane.

3. SELECTING INTERACTIONS

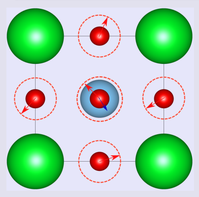
The h_{ab} elements should decay fast with the distances between the Wanniers, ie, they can be neglected at a given distance cutoff δr_{h}). For the filtered h_{ab}, the values of $\gamma^{\mathrm{RAG}}_{ab}$ are selected from the RAG.



4. CREATING A TRAINING SET (TS)

The TS to obtain the electron-lattice parameters is composed by SIESTA calculations where the **lattice has been distorted**. Distortions can be performed in two ways:

MOVING ATOMS RANDOMLY



The random structure can be written as a linear combination of all the normal modes. So all the modes are activated.

FOLLOWING SOME WELL DEFINED MODES

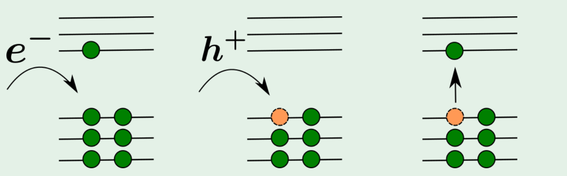
TS for electron-electron parameters

First principles simulations(SIESTA)

Beyond the Born-Oppenheimer surface

Modifying the occupations of the WF

ELECTRON DOPING | HOLE DOPING | EXCITATIONS



5. SELECT CUTOFFS AND FIND TERMS

CUTOFFS ELECTRON-LATTICE (EL-LAT)

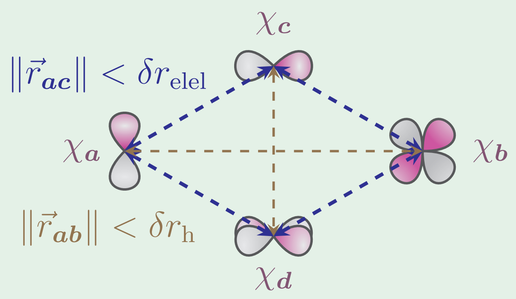
Select the strongest and most relevant **WFs-atoms** interactions

$\delta\epsilon_{\mathrm{el-lat}}$ | $\delta r_{\mathrm{el-lat}}$ | δr_{pair}

CUTOFFS ELECTRON-ELECTRON (EL-EL)

Select the strongest and most relevant **WFs-WFs** interactions

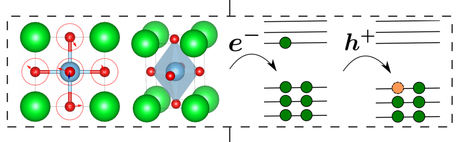
$\delta\epsilon_{\mathrm{el-el}}$ | $\delta r_{\mathrm{el-el}}$



6. DETERMINING PARAMETERS

Set of parameters : $\{p_1, \dots, p_N\}$

Training set calculations



for each calculation $A \in TS$

DFT → $h^{\mathrm{DFT}}_{ab}(A)$ | SP-DFT → $h^{\mathrm{model}}_{ab}(A, \{p_i\})$

Quadratic error

$$\left[h^{\mathrm{DFT}}_{ab}(A) - h^{\mathrm{model}}_{ab}(A, \{p_i\}) \right]^2$$

Total Goalfunction

$$\sum_A \sum_{ab} \left[h^{\mathrm{DFT}}_{ab}(A) - h^{\mathrm{model}}_{ab}(A, \{p_i\}) \right]^2$$

Looking for the parameters which minimize GF most effectively

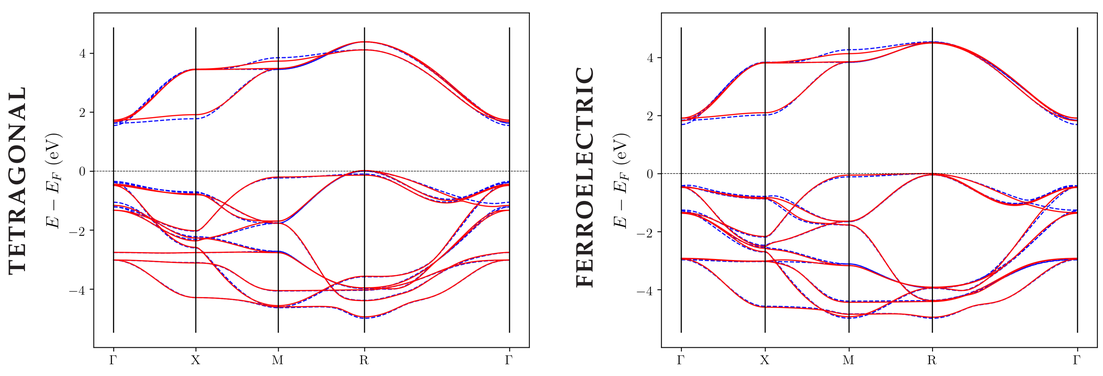
STEP WISE PROCEDURE WITH FORWARD SELECTION

- Best model 1 parameter $\{p_1\}$
- Best model 2 parameters $\{p_1, p_2\}$
- ...

RESULTS

The validation of the models is based on the comparison of the band diagram representations obtained from first principles calculations (**SIESTA**) versus second principles calculations (which employ the output model) for configurations out of the training set (**SCALE-UP**).

We can see the SCALE-UP bands fit properly with the bands from SIESTA.



REFERENCES

[1] P. García-Fernández, J. C. Wojdeł, J. Íñiguez, and J. Junquera. *Phys. Rev. B*, 93:195137, 2016.

[2] A. García, N. Papior, A. Akhtar, E. Artacho, et al. *The Journal of chemical physics*, 152(20):204108, 2020.

[3] D. Vanderbilt. *Berry Phases in Electronic Structure Theory*. Cambridge University Press, 2018.

[4] I. Bersuker. *The Jahn-Teller effect*. Cambridge University Press, 2006.