A systematically improvable second-principles method including electron and lattice degrees of freedom

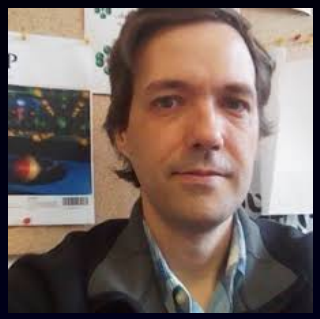
Javier Junquera

15th October 2015 - Bremen

Universidad de Cantabria

Collaborators

Cantabria University



Pablo
García-Fernández

Institut Ciència Materials Barcelona

Lattice Hamiltonian

Jorge Iñiguez

Now Luxembourg

Jacek Wojdeł

Cantabria University Campus

Funding

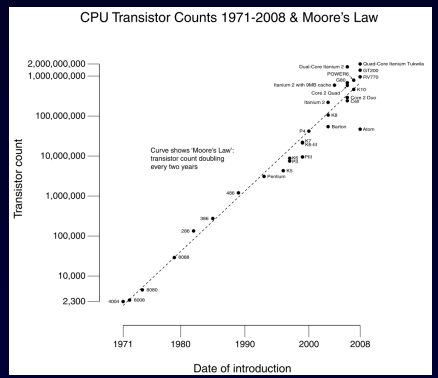
RyC programme

A happy and lasting marriage

Fast and recurrent increase of the computational power (hardware)

Bardeen, Shockley, and Brattain

(Nobel Prize in Physics, 1956)



Moore's law

Development of more efficient algorithm (software)
(Density Functional Theory; DFT)

W. Kohn

(Nobel Prize in Chemistry, 1998)

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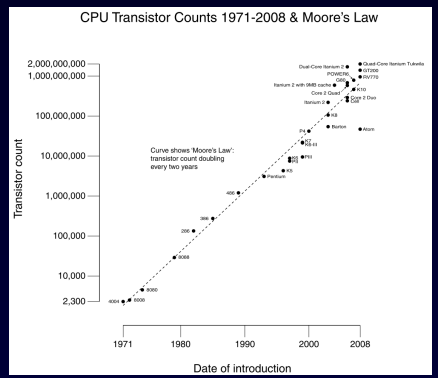

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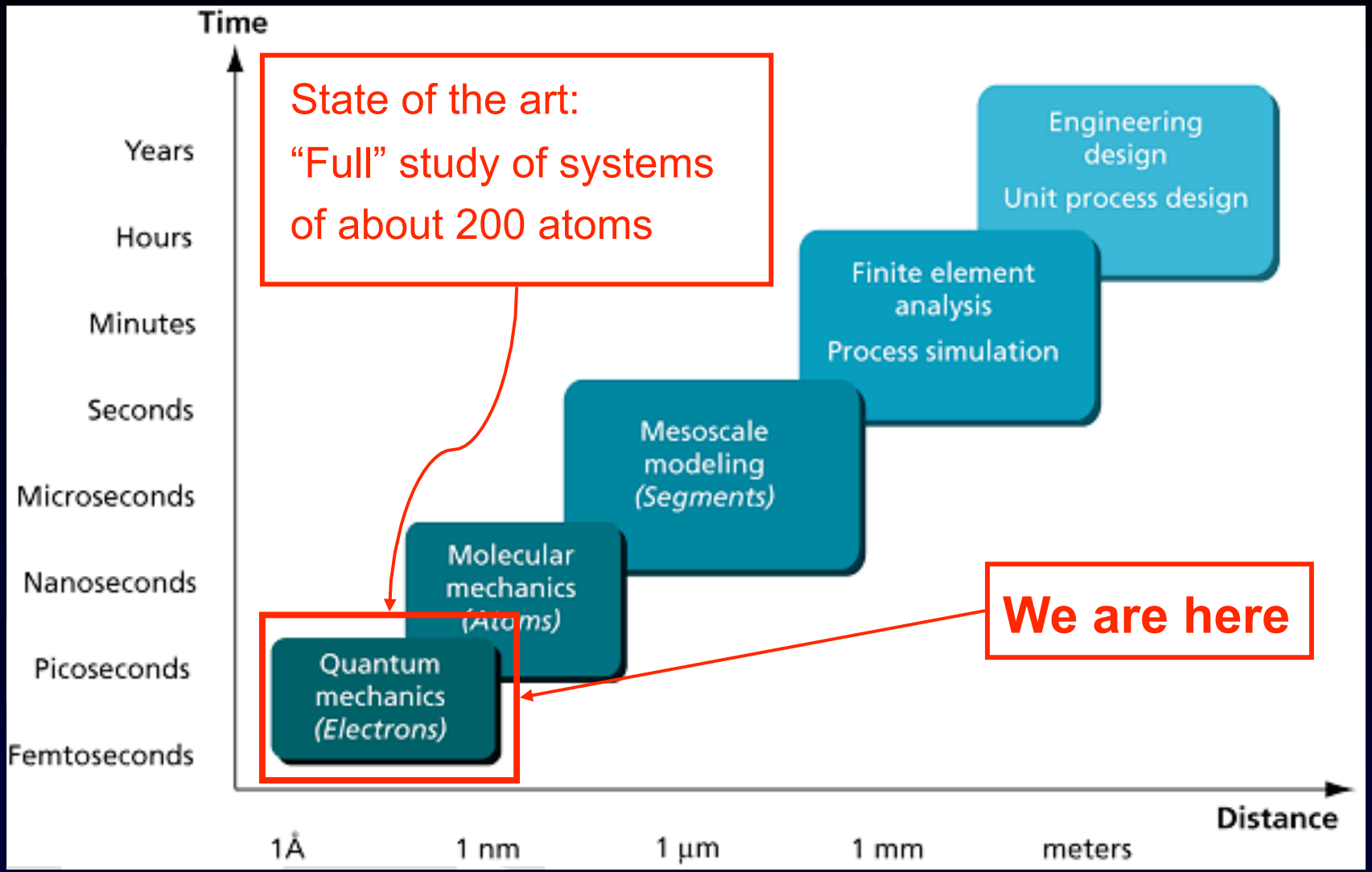
Simulation of materials with predictive-power from first-principles

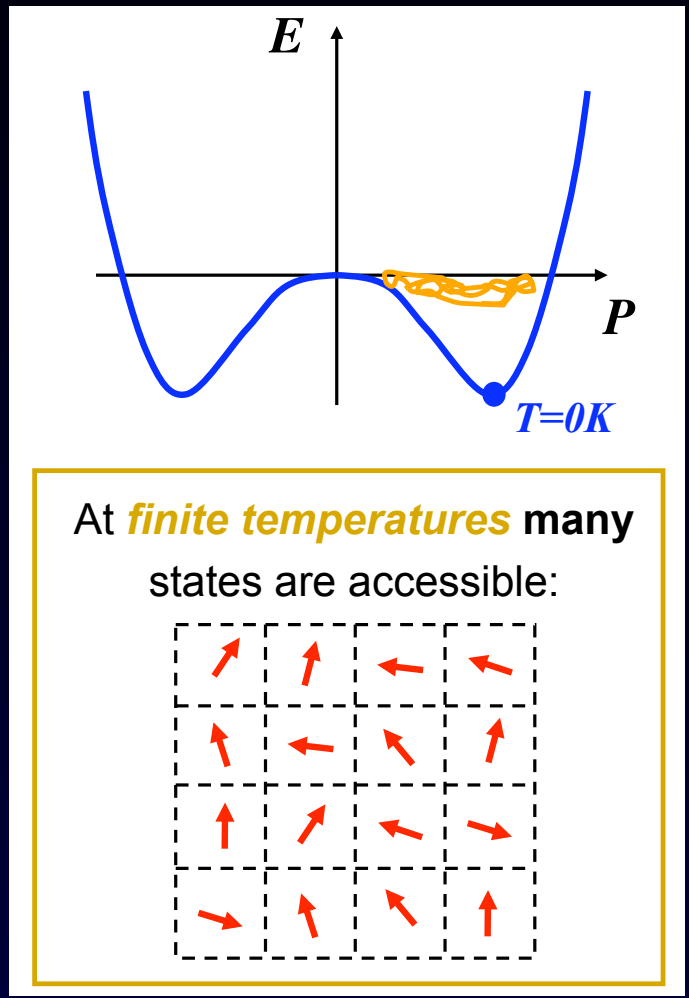
Challenge for first-principles simulations: the multiscale ladder



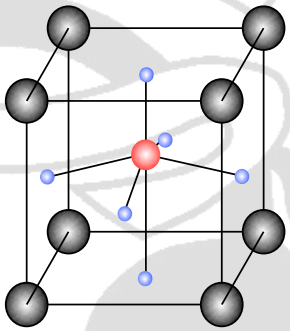
Courtesy of J. Íñiguez

Challenge for first-principles simulations: simulations at operating conditions

The equilibrium value of the polarization is a thermal average over all accessible states.



At *T=0K* only 1 state is accessible:

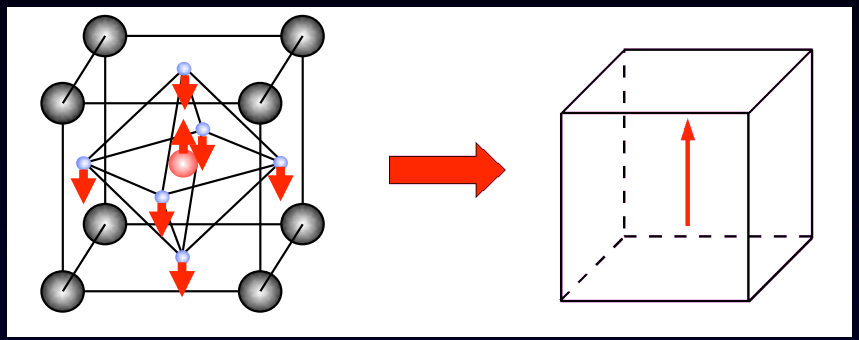


Courtesy of J. Íñiguez

Effective models for the lattice

$$\langle P \rangle = \frac{1}{Z} \sum_{\vec{x}} P\left[\vec{x}\right] e^{-E[\vec{x}]/k_{\mathrm{B}}T}$$

1. Identify the relevant degrees of freedom



local polar distortion associated to a FE instability

simplified version of the unit cell of our FE crystal

+ cell strains to capture ferroelastic and piezoelectric effects

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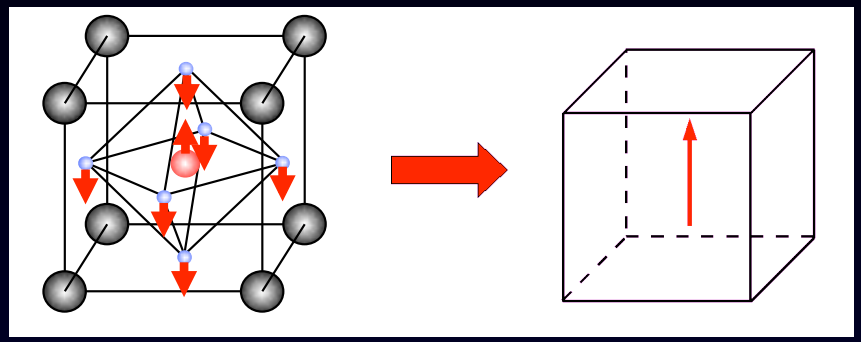

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$$\{\vec{x}\} \rightarrow \{\vec{u}\} \subset \{\vec{x}\}$$

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- Nice physical picture
- Reduce computational cost by factor 2-5

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2. Simple parametrization of the energy

$$E(\vec{u}) \rightarrow H_{\mathrm{eff}}\left[\vec{u}\right]$$

Taylor expansion of the energy as a function of the relevant degrees of freedom, around a reference configuration.

Parameters computed once and for all from first-principles

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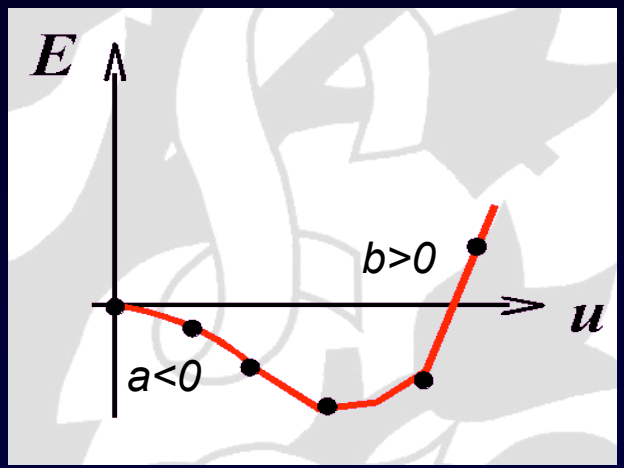

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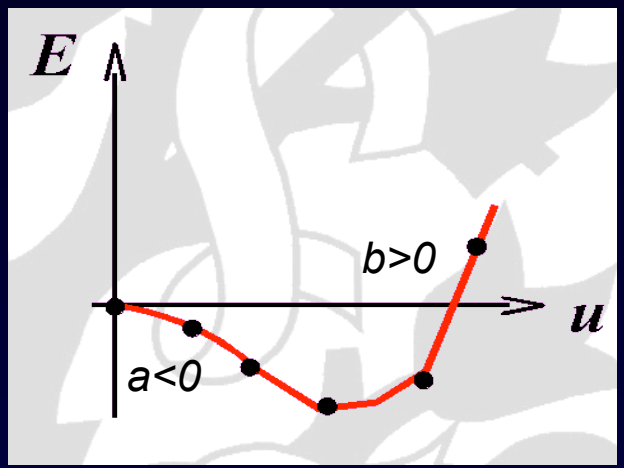

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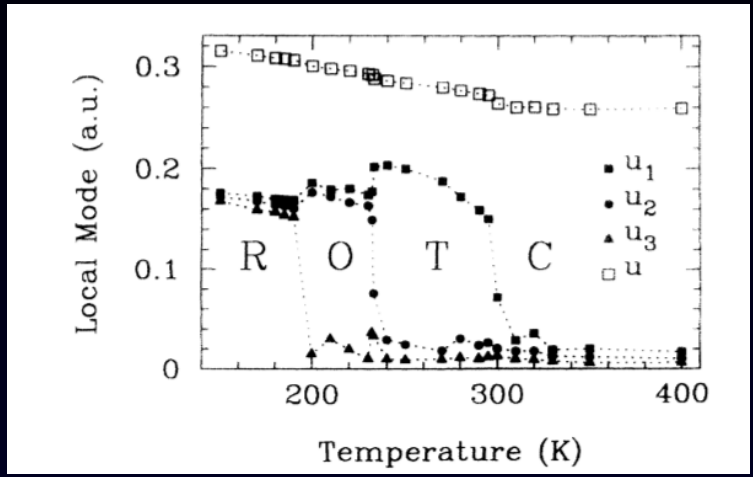
3. Calculate the thermal average with Molecular Dynamics or Monte Carlo simulations

$$\langle P \rangle = \frac{1}{Z} \sum_{\vec{u}} P\left[\vec{u}\right] e^{-H_{\mathrm{eff}}[\vec{u}]/k_{\mathrm{B}}T}$$

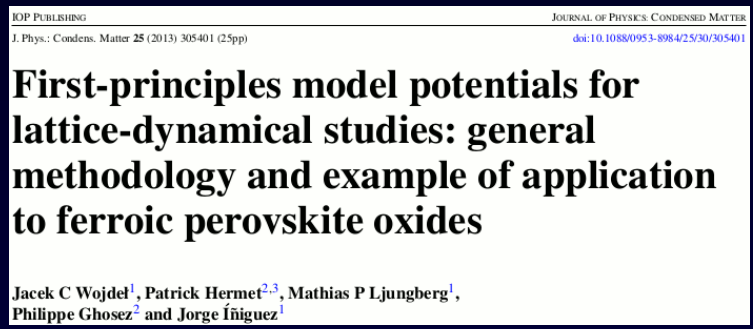
The pros and cons of the effective lattice models

- ✓ Larger time/space scales
- ✓ Statistics
- ✓ Capture the ferroelectric phase transitions



W. Zhong *et al.*,

Phys. Rev. Lett., 94, 1861 (1994)


IOP Publishing — Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **25** (2013) 305401 (25pp) — doi:10.1088/0953-8984/25/30/305401

First-principles model potentials for lattice-dynamical studies: general methodology and example of application to ferroic perovskite oxides

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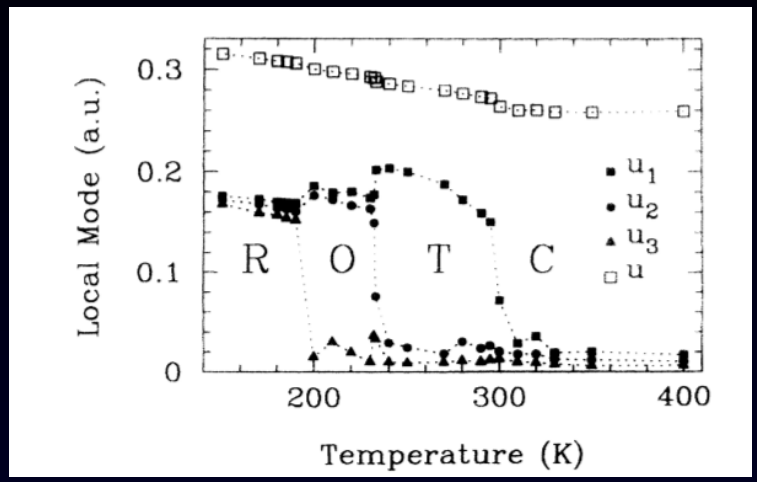

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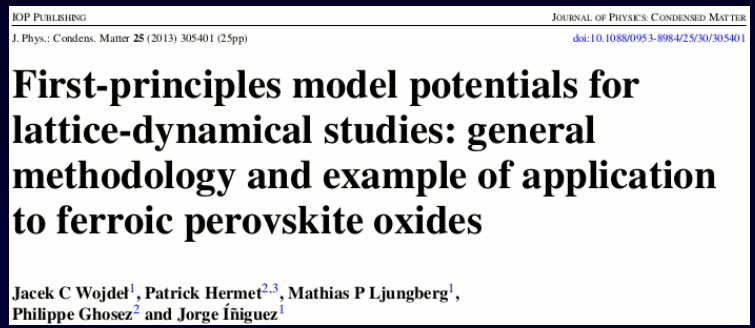
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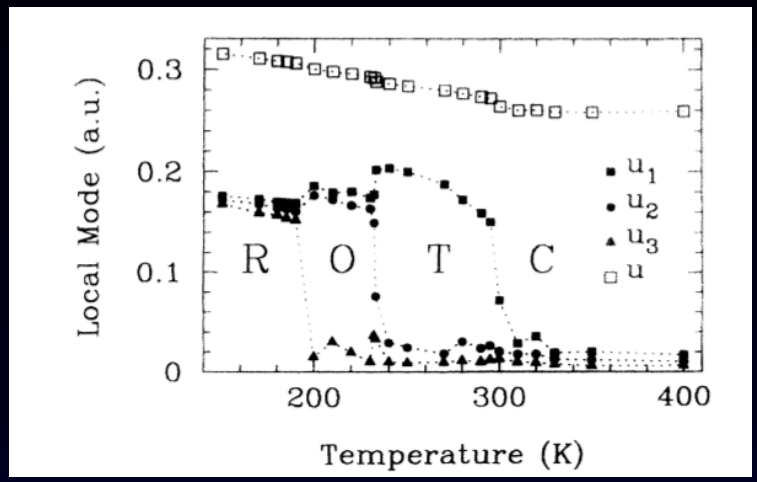

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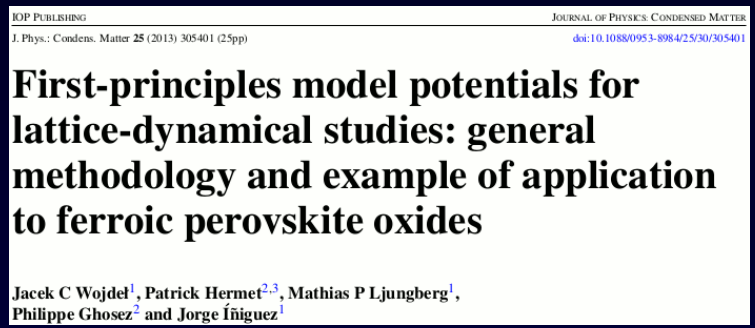
- ✓ Identification of the relevant degrees of freedom: consider all of them
- ✗ Lack of explicit consideration of electrons! Integrated out and considered implicitly during the fitting of parameters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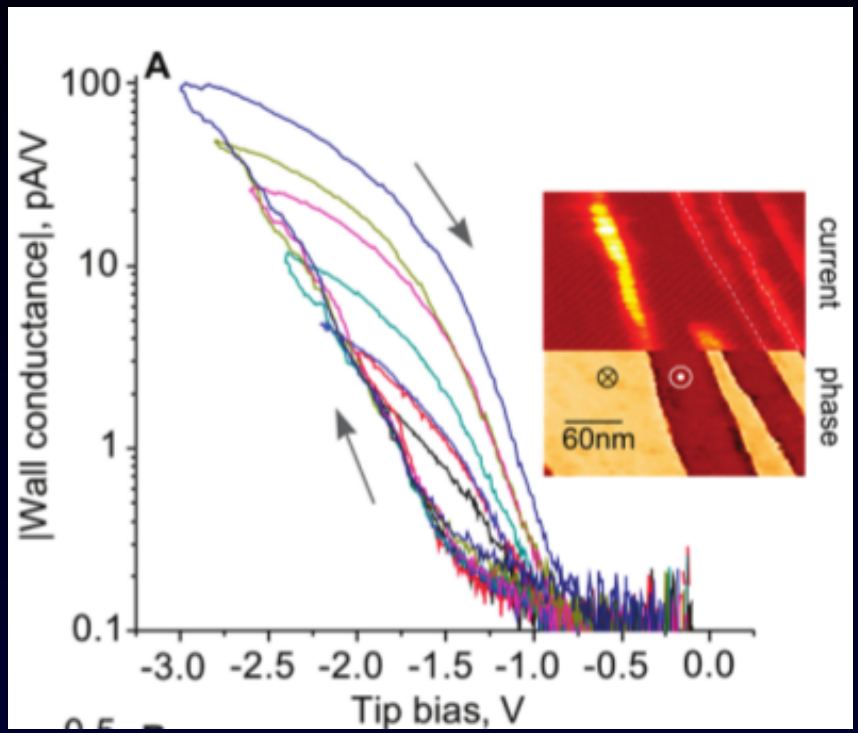
Many interesting problems require both lattice and electrons!



P. Maksymovuch *et al.*,
Nano Lett., 11, 1906 (2011)

- Conductivity domain walls
- Magnetic domains
- Switching of ferroelectrics
- Transport (polarons)
- Defects
- ...

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Development of a method to perform:

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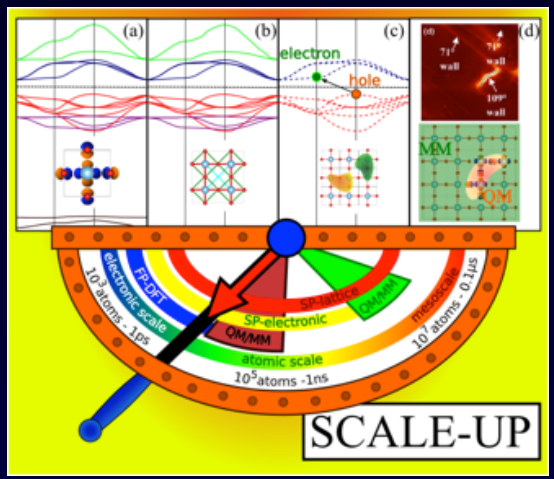
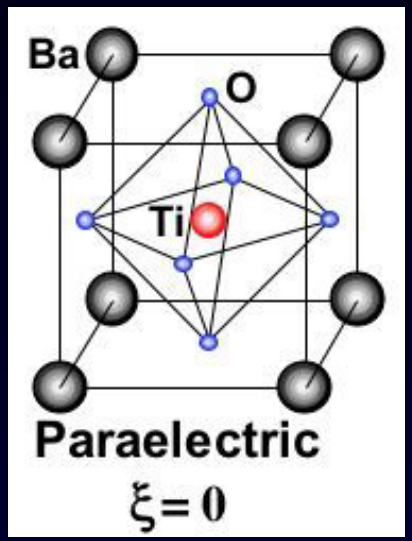


- Starting point: model atomic potentials for lattice-dynamics, including all degrees of freedom
- On top of this: relevant electronic degrees of freedom: tight-binding like Hamiltonian expressed in a basis of Wannier functions.

First basic ingredient: The reference atomic geometry (RAG)



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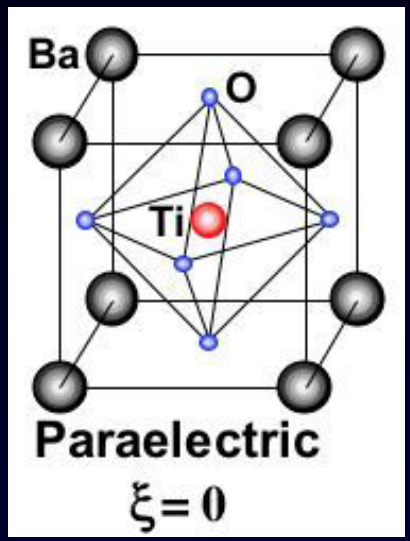

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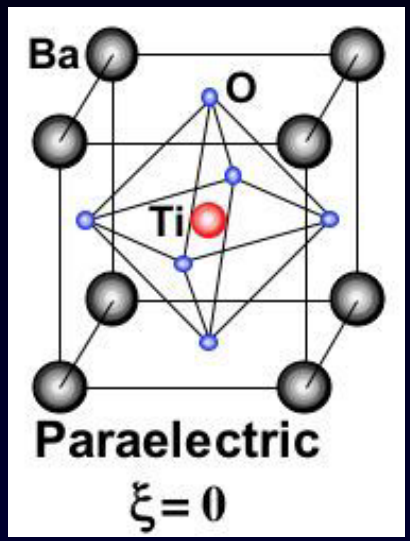
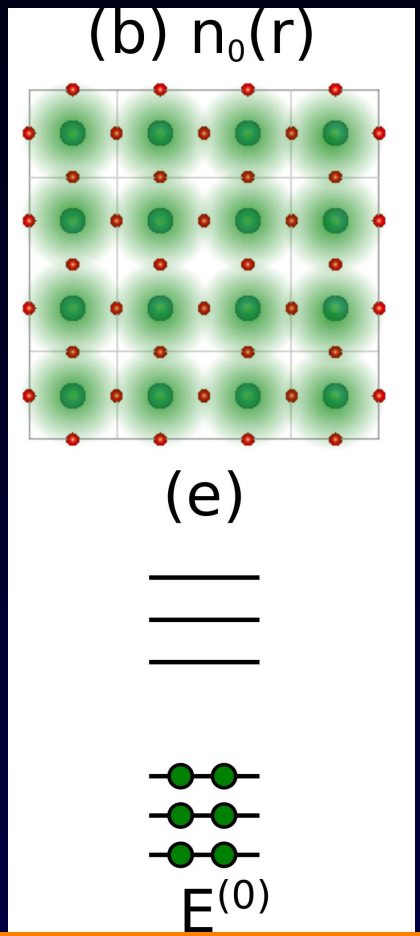


1. reference atomic geometry: One particular configuration of the nuclei that we will use as reference to describe any other configuration
2. No restrictions are impossed
3. Convenient to employ the ground state or a suitably chosen high-symmetry configurations
   - Corresponding forces and stresses are zero
   - The fewer the coupling terms required to describe the system

Second basic ingredient:
The reference electron density (RED)

In most cases, the self-consistent electron density can be split

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



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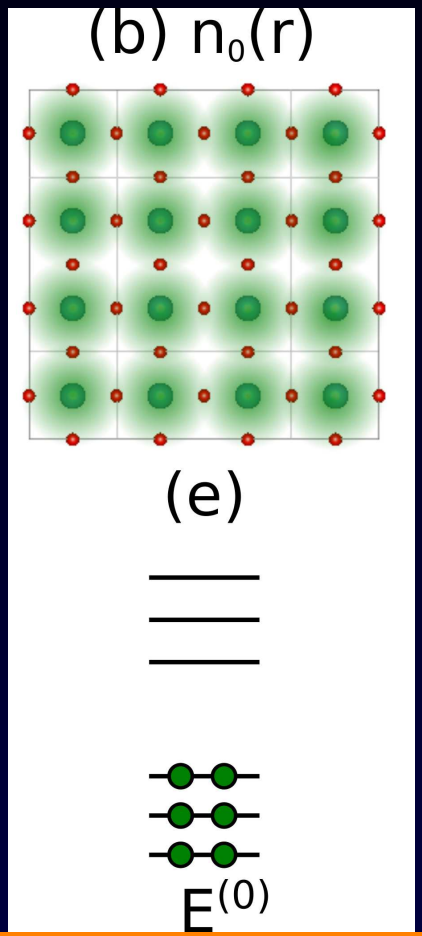

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   - Valence bands full
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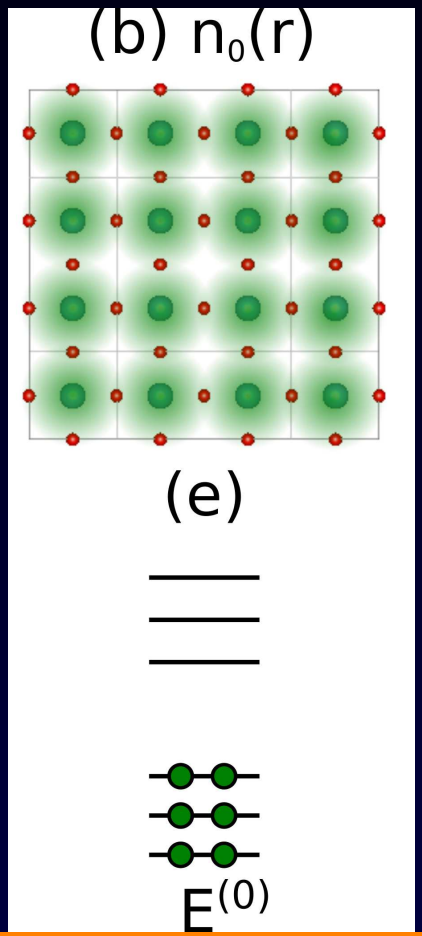

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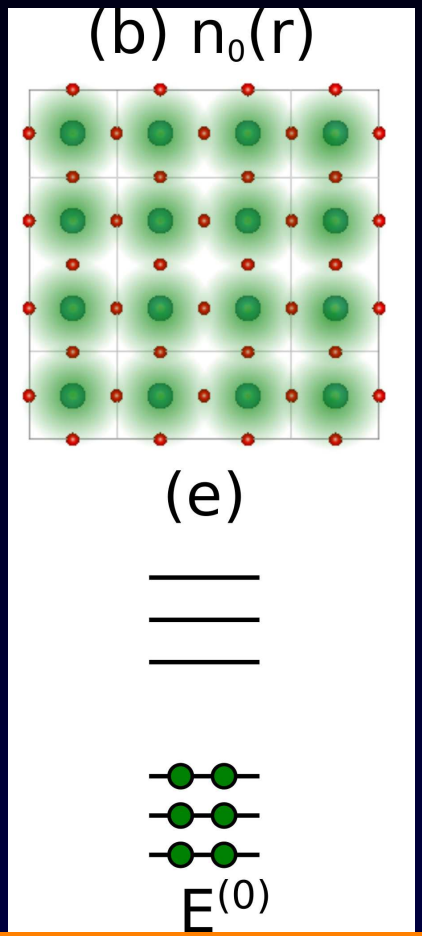

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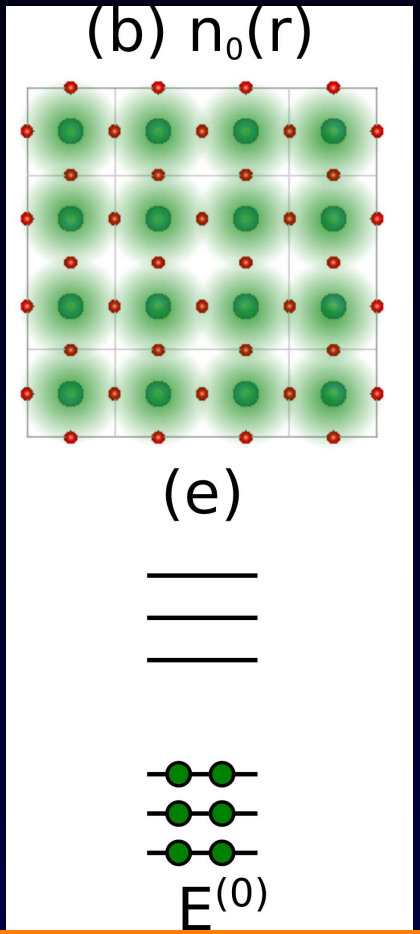

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2. Typically, it will be the actual solution of the electronic problem
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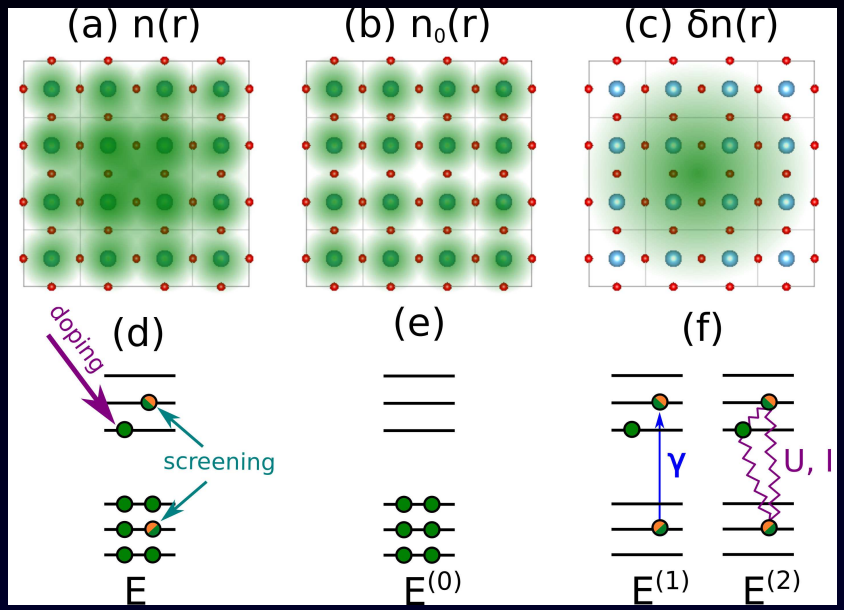
4. The method does not require the explicit calculation of $n_0(\vec{r})$

Technologically relevant applications: Doping of semiconductors and insulators with e^- or h^+



- The doping electron will occupy states at the bottom of the conduction band

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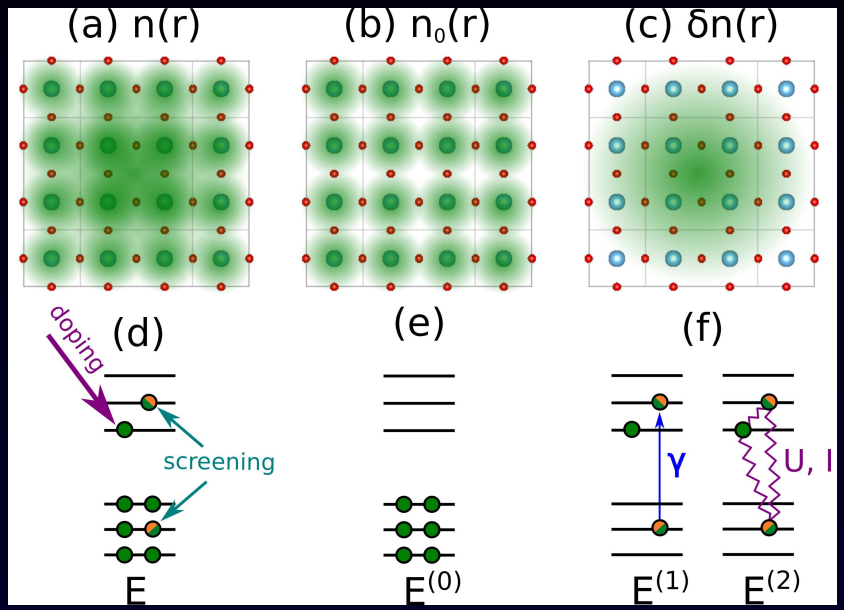

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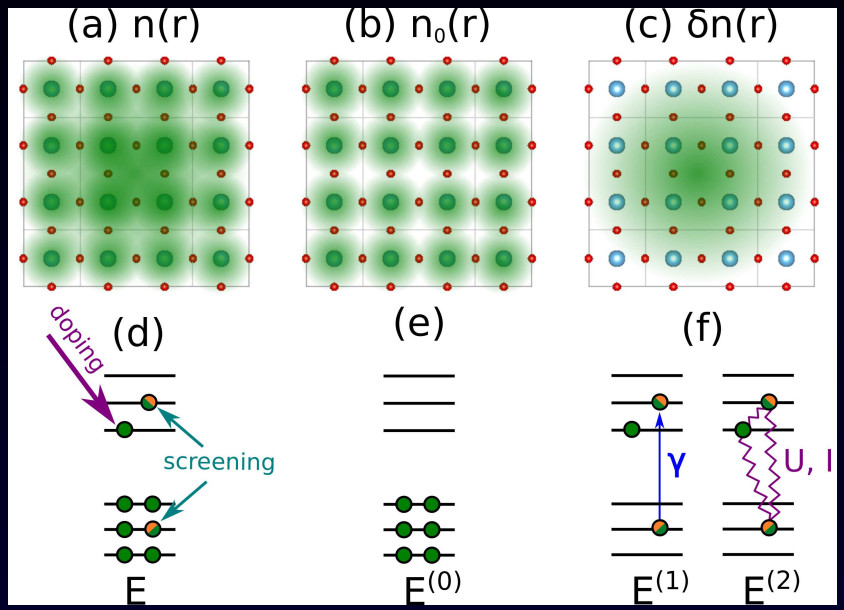

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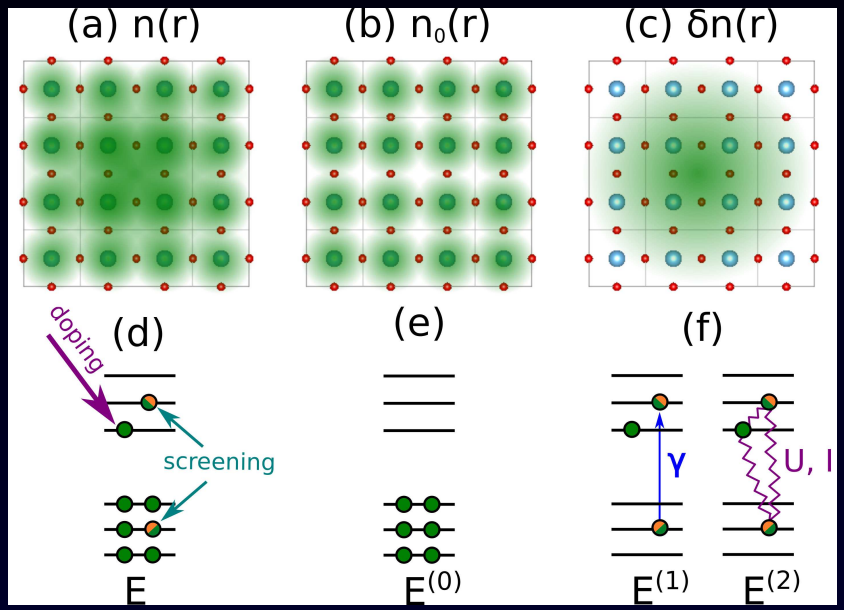

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- $\delta n(\vec{r}) \equiv$ doping + redistribution

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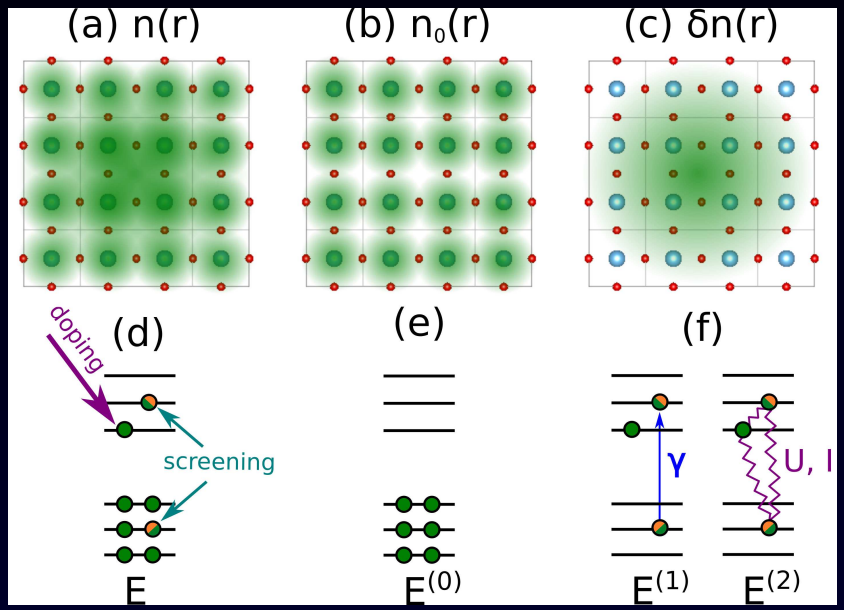

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- It will produce a response of the electronic cloud...
- ...that can be described from an admixture of the occupied and unoccupied states of the reference configuration
- $\delta n(\vec{r}) \equiv$ doping + redistribution

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and after a Taylor expansion of the exchange-correlation

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M. Elstner *et al.*, Phys. Rev. B 58 7260 (1998)

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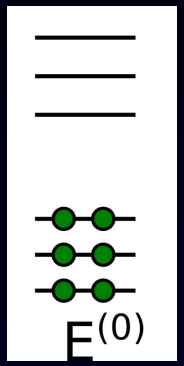
$$E_{\text{DFT}} \approx E^{(0)} + E^{(1)} + E^{(2)} + \cdots$$

The method is systematically improvable

$E^{(0)}$ - Energy of the reference state

Correspond, without approximation, to the full DFT energy for the reference density $n_0(\vec{r})$



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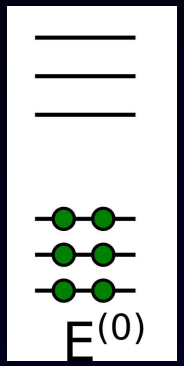

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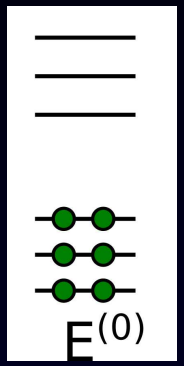

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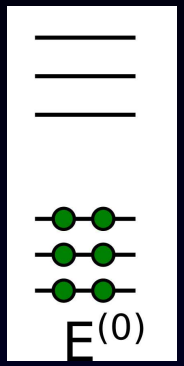

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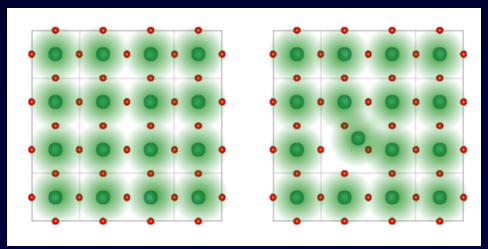


RED defined for all geometries

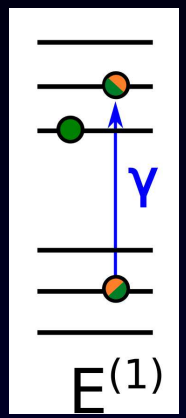
Huge gains with respect to other treatments: no need to

- Accurate treatment of the electronic interactions yielding the RED
- Solve numerically for $E^{(0)}$ and n_0

$E^{(1)}$ - One-electron excitations

$E^{(1)}$ contains the differences in one-electron energies

It involves the one-electron excitations as captured by the deformation density



$$E^{(1)} = \sum_{j\vec{k}} \left[o_{j\vec{k}} \left\langle \psi_{j\vec{k}} \right| \hat{h}_0 \left| \psi_{j\vec{k}} \right\rangle - o^{(0)}_{j\vec{k}} \left\langle \psi^{(0)}_{j\vec{k}} \right| \hat{h}_0 \left| \psi^{(0)}_{j\vec{k}} \right\rangle \right]$$

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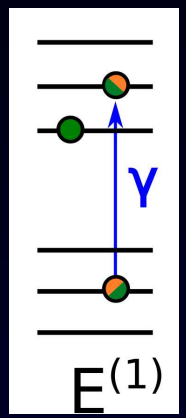

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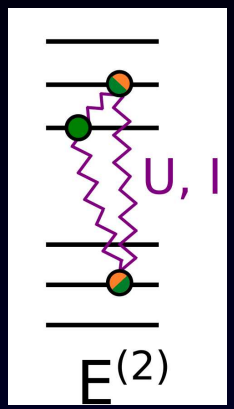
- Typical DFTB schemes include a sum of one-electron energies
- Here we deal with the difference between the value of this quantity for the actual system and the reference one
- Such a difference is a much smaller quantity, more amenable to accurate calculations

$E^{(2)}$ - Two-electron excitations

$E^{(2)}$ only contains interactions between 2 electrons



$$E^{(2)} = \frac{1}{2} \int d^3r \int d^3r' g(\vec{r},\vec{r}') \delta n(\vec{r}) \delta n(\vec{r}')$$

where the screened electron-electron interaction operator, $g(\vec{r},\vec{r}')$, is

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

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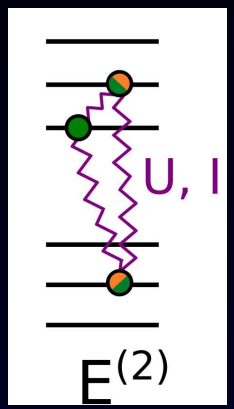

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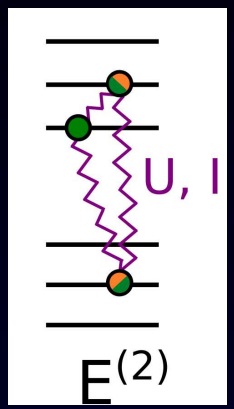

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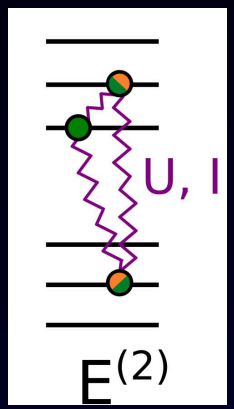

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We can deal with strongly-correlated and magnetic systems

Basis set of Wannier functions

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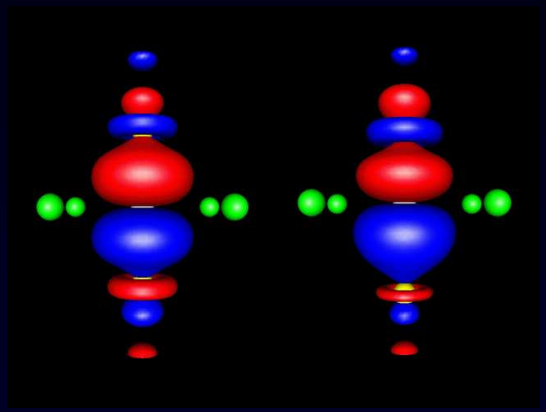

Maximally Localized Wannier function in $BaTiO_3$.
One of the 9 originated from the composite group of the O $2p$ bands.

N. Marzari and D. Vanderbilt,
First-principles calculations for ferroelectrics, 436, 146 (1998)

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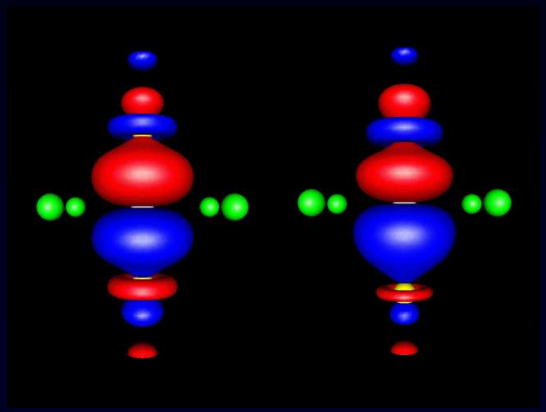

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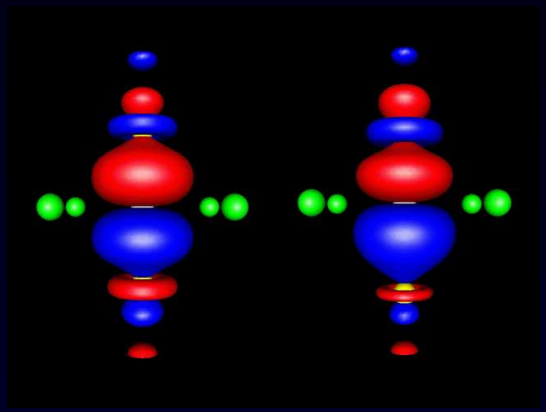

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3. Orthogonal $\Rightarrow$ no need to compute overlaps
4. Flexible description of the electronic band structure $\Rightarrow$ selection of appropriate bands (small number of basis set to be included)

We can deal accurately and cheaply with very large systems

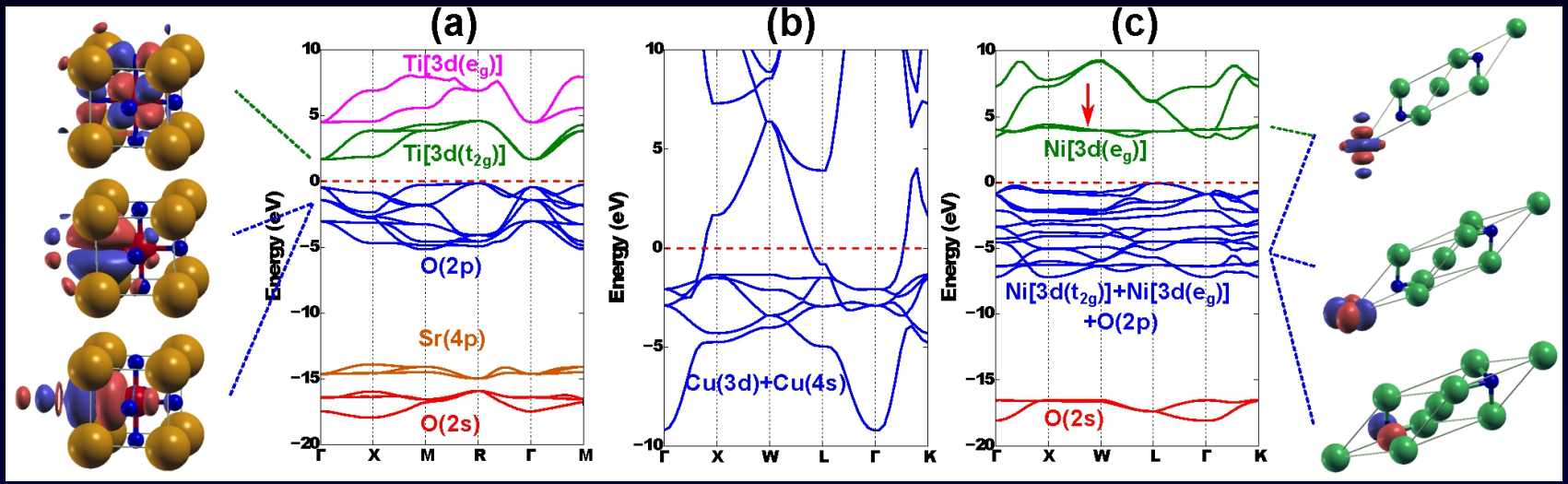
Maximally localized Wannier functions

The idea is to get localized packages in real space using a very broad superposition of states at $\vec{k}$ space.

N. Marzari *et al.*,

Rev. Mod. Phys., 84, 1419 (2012)

$$|\chi_{\boldsymbol{a}}\rangle \equiv |\vec{R}_A a\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\vec{k}\; e^{-i\vec{k}\cdot\vec{R}_A}\sum_{m=1}^{J} T_{ma}^{(\vec{k})}|\psi_{m\vec{k}}^{(0)}\rangle$$



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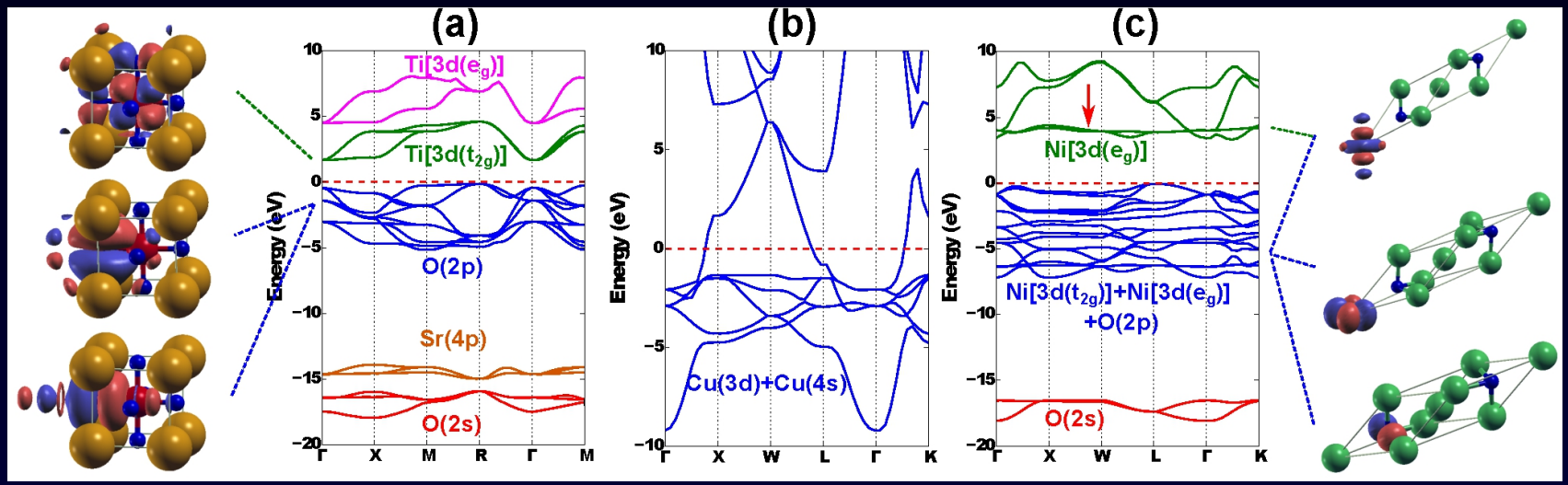

The electronic states can be effectively splitted into:

- an active set playing an important role in the properties under study
- a background set that will be integrated out from explicit treatment

Expressions of charge densities in terms of a Wannier functions

Expression of the eigenstates of the perturbed state in terms of a Wannier basis

$$|\psi_{j\vec{k}}\rangle = \sum_{\boldsymbol{a}} c_{ja\vec{k}} e^{i\vec{k}\cdot\vec{R}_A} |\chi_{\boldsymbol{a}}\rangle$$

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Charge density of the perturbed state in terms of Wannier functions

$$\begin{aligned} n(\vec{r}) &= \sum_{j\vec{k}} o_{j\vec{k}} |\psi_{j\vec{k}}(\vec{r})|^2 = \sum_{j\vec{k}} o_{j\vec{k}} \psi^*_{j\vec{k}}(\vec{r}) \psi_{j\vec{k}}(\vec{r}) \\ &= \sum_{j\vec{k}} \sum_{\boldsymbol{ab}} o_{j\vec{k}} c^*_{ja\vec{k}} c_{jb\vec{k}} e^{i\vec{k}(\vec{R}_B - \vec{R}_A)} \chi_{\boldsymbol{a}}(\vec{r}) \chi_{\boldsymbol{b}}(\vec{r}). \\ &= \sum_{\boldsymbol{ab}} d_{\boldsymbol{ab}} \chi_{\boldsymbol{a}}(\vec{r}) \chi_{\boldsymbol{b}}(\vec{r}) \end{aligned}$$

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where we have introduced the reduced density matrix

$$d_{\boldsymbol{ab}} = \sum_{j\vec{k}} o_{j\vec{k}} c^*_{j\boldsymbol{a}\vec{k}} c_{j\boldsymbol{b}\vec{k}} e^{i\vec{k}(\vec{R}_B - \vec{R}_A)}$$

The deformation occupation matrix

Repeating the for the RED density

$$n(\vec{r}) = \sum_{\boldsymbol{ab}} d_{\boldsymbol{ab}} \chi_{\boldsymbol{a}}(\vec{r}) \chi_{\boldsymbol{b}}(\vec{r})$$

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$$D_{\boldsymbol{ab}} = d_{\boldsymbol{ab}} - d^{(0)}_{\boldsymbol{ab}}$$

Energy expressions in term of the deformation occupation matrix: $E^{(1)}$

$$
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&= \sum_{j\vec{k}} \left[o_{j\vec{k}} \sum_{\boldsymbol{ab}} c^{*}_{aj\vec{k}} c_{bj\vec{k}} e^{i\vec{k}(\vec{R}_B - \vec{R}_A)} \langle \chi_{\boldsymbol{a}} | \hat{h}_0 | \chi_{\boldsymbol{b}} \rangle \right. \\
&\quad \left. - o^{(0)}_{j\vec{k}} \sum_{\boldsymbol{ab}} \left(c^{(0)}_{aj\vec{k}} \right)^{*} c^{(0)}_{bj\vec{k}} e^{i\vec{k}(\vec{R}_B - \vec{R}_A)} \langle \chi_{\boldsymbol{a}} | \hat{h}_0 | \chi_{\boldsymbol{b}} \rangle \right] \\
&= \left[\sum_{\boldsymbol{ab}} d_{\boldsymbol{ab}} \langle \chi_{\boldsymbol{a}} | \hat{h}_0 | \chi_{\boldsymbol{b}} \rangle - \sum_{\boldsymbol{ab}} d^{(0)}_{\boldsymbol{ab}} \langle \chi_{\boldsymbol{a}} | \hat{h}_0 | \chi_{\boldsymbol{b}} \rangle \right] \\
&= \sum_{\boldsymbol{ab}} D_{\boldsymbol{ab}} \gamma_{\boldsymbol{ab}}
\end{aligned}
$$

where $\gamma_{\boldsymbol{ab}}$ is one of the primary parameters defined in our model

$$
\gamma_{\boldsymbol{ab}} = \langle \chi_{\boldsymbol{a}} | \, \hat{h}_0 \, | \chi_{\boldsymbol{b}} \rangle = \int d^3 r \; \chi_{\boldsymbol{a}}(\vec{r}) \; \hat{h}_0 \; \chi_{\boldsymbol{b}}(\vec{r})
$$

Energy expressions in term of the deformation occupation matrix: $E^{(2)}$

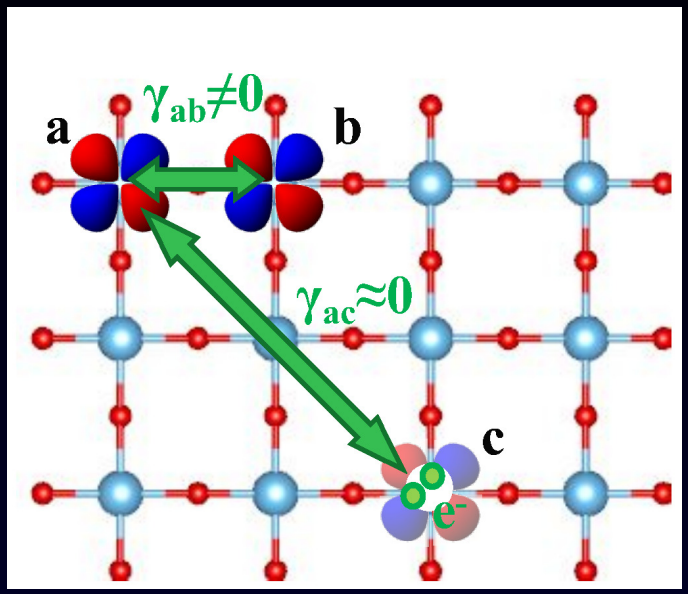
$$E^{(2)} = \frac{1}{2}\int d^3r \int d^3r' g(\vec{r},\vec{r}')\delta n(\vec{r})\delta n(\vec{r}')$$
$$= \frac{1}{2}\sum_{ab}\sum_{a'b'} D_{ab}D_{a'b'}\langle \chi_a\chi_{a'}|\hat{g}|\chi_b\chi_{b'}\rangle$$
$$= \frac{1}{2}\sum_{ab}\sum_{a'b'} D_{ab}D_{a'b'}U_{aba'b'},$$

where $U_{aba'b'}$ is the second primary parameter defined in our model

$$U_{aba'b'} = \langle \chi_a\chi_{a'}|\hat{g}|\chi_b\chi_{b'}\rangle$$
$$= \int d^3r \chi_a(\vec{r})\chi_b(\vec{r}) \int d^3r' \chi_{a'}(\vec{r}')\chi_{b'}(\vec{r}')\hat{g}(\vec{r},\vec{r}')$$

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

Electrostatics



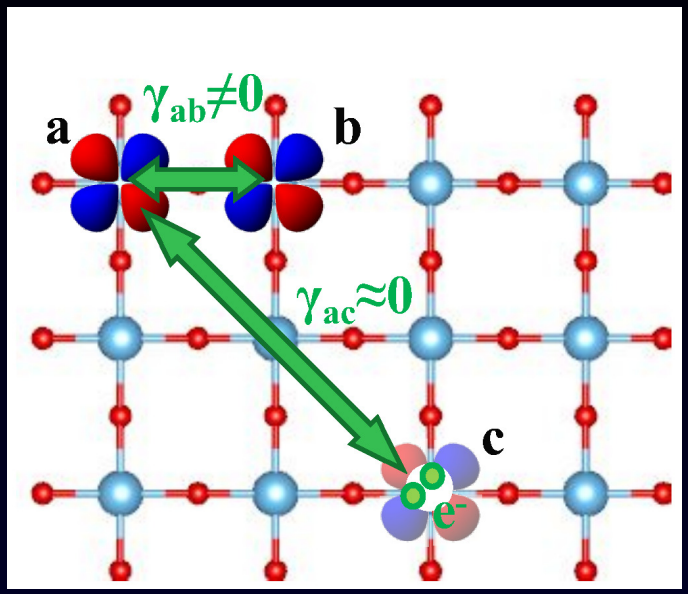
The one-electron integrals gathers Coulomb interactions associated with the long-range electrostatic potentials

$$\gamma_{\boldsymbol{ab}}^{\text{elec,e}} \equiv \langle \chi_{\boldsymbol{a}} | \, v_{\text{H}}(n_0;\vec{r}) \, | \chi_{\boldsymbol{b}} \rangle$$

$$= \int \chi_{\boldsymbol{a}}(\vec{r}) \left(\int \frac{n_0(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' \right) \chi_{\boldsymbol{b}}(\vec{r}) d^3r$$

$$= \int \chi_{\boldsymbol{a}}(\vec{r}) \left(\int \frac{\sum_{\boldsymbol{c}} o_{\boldsymbol{c}}^{(0)} |\chi_{\mathbf{c}}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d^3r' \right) \chi_{\boldsymbol{b}}(\vec{r}) d^3r$$

Electrostatics



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The Coulomb electron-electron interaction can be split into
[A. Demkov *et al.*, Phys. Rev. B **52**, 1618 (1995)]

- Near field
- Far field: the electrostatic potential can be expressed as a multipole expansion

$$v_{\text{H}}(n_0;\vec{r}) = \sum_{\mathbf{c}} o_{\mathbf{c}}^{(0)} \int \frac{|\chi_{\mathbf{c}}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d^3r' \approx \sum_{\mathbf{c}} \frac{q_{\mathbf{c}}}{r} + \sum_{\mathbf{c}} \frac{\vec{p}_{\mathbf{c}} \cdot \vec{r}}{r^3} + \ldots .$$

Electrostatics

Doing the same for the potential associated with the nuclei,

$$v_{\rm ext}(\vec{r}) - v_{\rm app}(\vec{r}) \approx -\sum_{\boldsymbol{\lambda}} \frac{Z_{\boldsymbol{\lambda}}}{r} - \sum_{\boldsymbol{\lambda}} \frac{(Z_{\boldsymbol{\lambda}}\vec{u}_{\boldsymbol{\lambda}})\cdot\vec{r}}{r^3} + \ldots$$

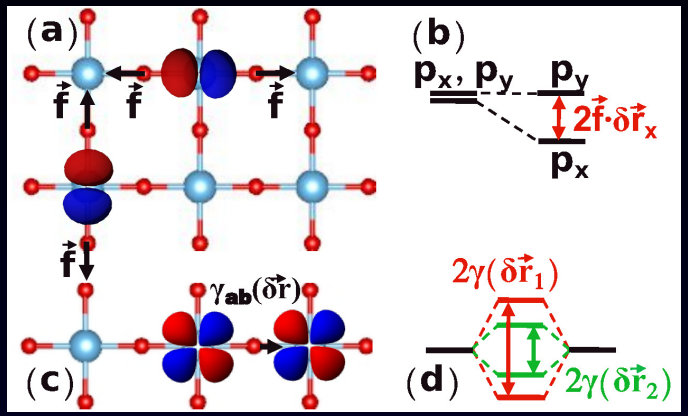
and adding all the far-field contributions, taking into account that the interactions take place in a material at its reference electronic density

$$v_{\rm FF}(\vec{r}_{\boldsymbol{a}}) \approx -\sum_{\boldsymbol{\lambda}} \left[\vec{e}^{\,T}_{\boldsymbol{\lambda a}}(\overleftrightarrow{\epsilon_\infty})^{-1}\vec{e}_{\boldsymbol{\lambda a}}\right] \frac{q_{\boldsymbol{\lambda}}}{|\vec{r}_{\boldsymbol{\lambda}} - \vec{r}_{\boldsymbol{a}}|} - \sum_{\boldsymbol{\lambda}} \frac{[\vec{p}_{\boldsymbol{\lambda}}(\overleftrightarrow{\epsilon_\infty})^{-1}\vec{e}_{\boldsymbol{\lambda a}}]}{|\vec{r}_{\boldsymbol{\lambda}} - \vec{r}_{\boldsymbol{a}}|^2}$$

Finally, considering that the Wannier functions are extremely localized, we define the long-range contribution as being only diagonal

$$\gamma^{\rm lr}_{\boldsymbol{ab}} = v_{\rm FF}(\vec{r}_{\boldsymbol{a}})\delta_{\boldsymbol{ab}} \qquad\qquad \gamma^{\rm sr}_{\boldsymbol{ab}} = \gamma_{\boldsymbol{ab}} - \gamma^{\rm lr}_{\boldsymbol{ab}}$$

Electron-lattice coupling



The dependence of the model parameters on the atomic configuration is captured by the electron-lattice couplings

$$\gamma_{ab}^{\mathrm{sr}} = \gamma_{ab}^{0,\mathrm{sr}} + \sum_{\lambda\upsilon}\Big[-\vec{f}_{ab,\lambda\upsilon}\cdot\delta\vec{r}_{\lambda\upsilon} + \sum_{\lambda'\upsilon'}\delta\vec{r}_{\lambda\upsilon}\overleftrightarrow{g}_{ab,\lambda\upsilon\lambda'\upsilon'}\delta\vec{r}_{\lambda'\upsilon'} + \ldots\Big],$$

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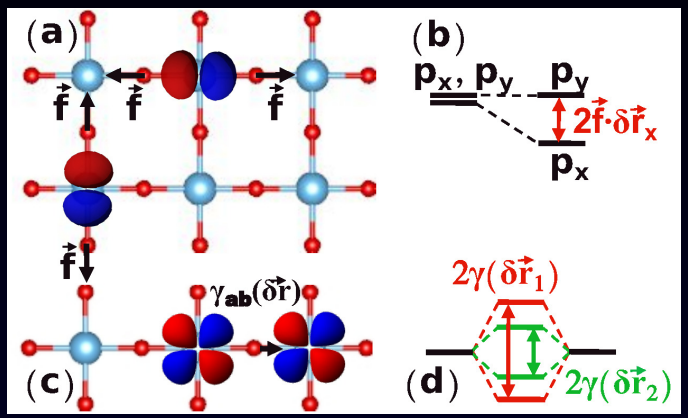

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Including quadratic constants: enough to describe typical changes in γ

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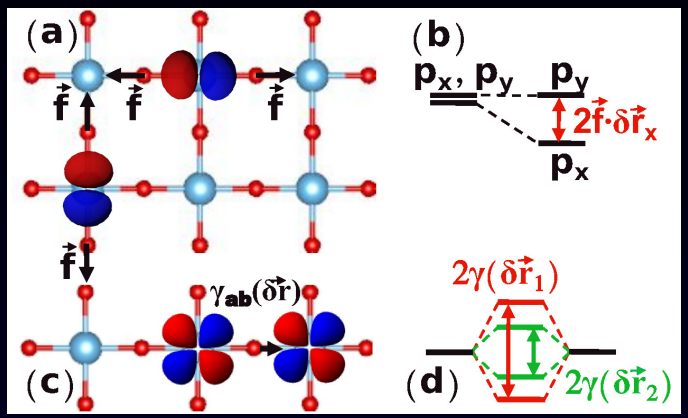

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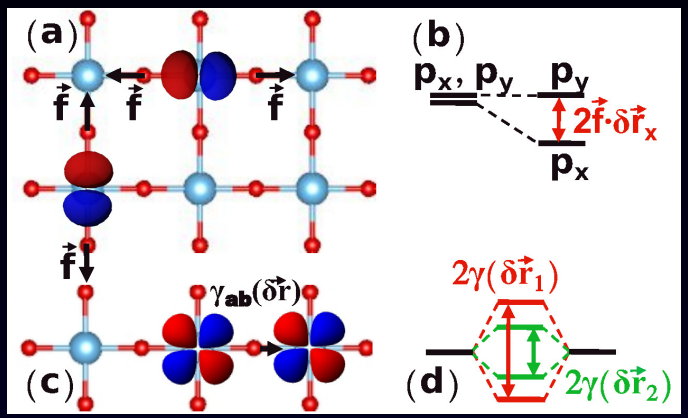

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- Off-diagonal terms in $\vec{f}$ describe the mixing of two WFs upon an atomic distortion, and thus quantify changes in covalency (pseudo Jahn-Teller vibronic constants and are, involved in ferroelectricity).

Self-consistent equations

The total energy depends on the deformation occupation matrix, that depends on the coefficients of the wave functions in the basis of Wannier functions, the only variational parameter of the method

$$\sum_b h^s_{ab,\vec{k}}\, c^s_{jb\vec{k}} = \varepsilon^s_{j\vec{k}}\, c^s_{ja\vec{k}}$$

where the corresponding Hamiltonian matrix is

$$h^s_{ab,\vec{k}} = \sum_{\vec{R}_B - \vec{R}_A} e^{i\vec{k}\cdot\left(\vec{R}_B - \vec{R}_A\right)} h^s_{\boldsymbol{ab}}$$

and the real-space Hamiltonian is

$$h^s_{\boldsymbol{ab}} = \gamma_{\boldsymbol{ab}} + \sum_{\boldsymbol{a'b'}} \Big[\left(D^s_{\boldsymbol{a'b'}} + D^{-s}_{\boldsymbol{a'b'}}\right) U_{\boldsymbol{aba'b'}} + \left(D^{-s}_{\boldsymbol{a'b'}} - D^s_{\boldsymbol{a'b'}}\right) I_{\boldsymbol{aba'b'}} \Big] .$$

Total energy, forces, and stress

Adding together the expressions for the one-electron and two-electron integrals, we get the total energy

$$\begin{aligned} E =& E^{(0)} + \sum_{\boldsymbol{ab}} D^{U}_{\boldsymbol{ab}} \gamma^{\mathsf{sr}}_{\boldsymbol{ab}} \\ &+ \frac{1}{2} \sum_{\boldsymbol{ab}} \sum_{\boldsymbol{a'b'}} D^{U}_{\boldsymbol{ab}} D^{U}_{\boldsymbol{a'b'}} U^{\mathsf{sr}}_{\boldsymbol{aba'b'}} \\ &+ \sum_{\boldsymbol{a}} D^{U}_{\boldsymbol{aa}} \left(v_{\mathrm{FF}}(\vec{r}_{\boldsymbol{a}}) + \frac{1}{2} \sum_{\boldsymbol{a'}} D^{U}_{\boldsymbol{a'a'}} U^{\mathsf{lg}}_{\boldsymbol{aaa'a'}} \right) . \end{aligned}$$

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Forces and stresses can be computed by direct derivation of the total energy with respect to atomic positions and cell strains

$$\vec{F}_{\boldsymbol{\lambda}} = -\vec{\nabla}_{\boldsymbol{\lambda}} E = -\vec{\nabla}_{\boldsymbol{\lambda}} E^{(0)} - \sum_{\boldsymbol{ab}} D^U_{\boldsymbol{ab}} \vec{\nabla}_{\boldsymbol{\lambda}} \gamma_{\boldsymbol{ab}}$$

$$S_{\alpha\beta} = -\frac{1}{V} \left[\frac{\partial E^{(0)}}{\partial \eta_{\alpha\beta}} + \sum_{\boldsymbol{ab}} D^U_{\boldsymbol{ab}} \frac{\partial \gamma^{sr}_{\boldsymbol{ab}}}{\partial \eta_{\alpha\beta}} + \frac{\partial E^{\mathrm{elec}}}{\partial \eta_{\alpha\beta}} \right]$$

Parametrization

This method allows for large scale material simulations assuming that some parameters describing one-electron and two-electrons are known before hand

$$\gamma_{\boldsymbol{ab}} = \langle \chi_{\boldsymbol{a}} | \, \hat{h}_0 \, | \chi_{\boldsymbol{b}} \rangle = \int d^3r \, \chi_{\boldsymbol{a}}(\vec{r}) \, \hat{h}_0 \, \chi_{\boldsymbol{b}}(\vec{r})$$

$$U_{\boldsymbol{aba'b'}} = \langle \chi_{\boldsymbol{a}} \chi_{\boldsymbol{a'}} | \hat{g} | \chi_{\boldsymbol{b}} \chi_{\boldsymbol{b'}} \rangle = \int d^3r \chi_{\boldsymbol{a}}(\vec{r}) \chi_{\boldsymbol{b}}(\vec{r}) \int d^3r' \chi_{\boldsymbol{a'}}(\vec{r'}) \chi_{\boldsymbol{b'}}(\vec{r'}) \hat{g}(\vec{r}, \vec{r'})$$

Since the chosen basis functions are localized in space, the required calculations could be performed on small supercells

A direct calculation to obtain the parameters is, in principle, feasible (but would require significant effort)

Parametrization: practical approach

1. Identify a training set: relevant atomic and electronic configurations from which the model parameters will identified and computed.
   - Magnetic systems: different spin arrangements
   - Bands sensitive to atomic structure: different geometries
   - Doping effects: DFT simulations on charged systems

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$$h^s_{\boldsymbol{ab}} = \frac{(2\pi)^3}{V} \int_{\mathrm{BZ}} d^3k \left[\sum_j \left[T^{s(\vec{k})}_{ja} \right]^\star \varepsilon^s_{j\vec{k}} T^{s(\vec{k})}_{jb} \right] e^{i\left(\vec{R}_A - \vec{R}_B\right)\vec{k}}$$

Routinely provided by WANNIER90 code
A. Mostofi *et al.* Comput. Phys. Commun. **178**, 685 (2008)

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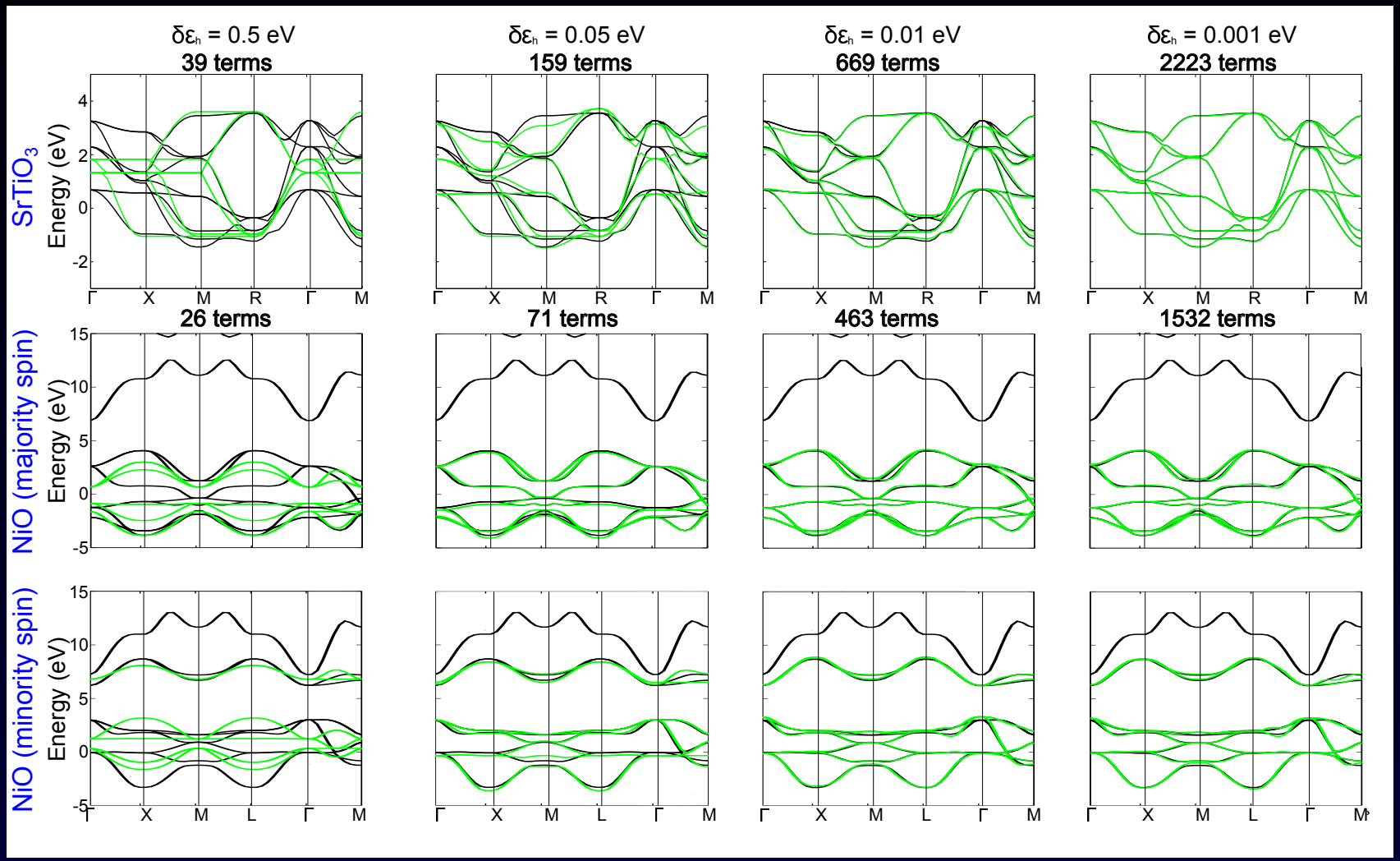
4. Fit the γ, U and I to reproduce the $\{h^s_{\boldsymbol{ab}}\}$ matrix elements above

$$h^s_{\boldsymbol{ab}}(i) = \gamma_{\boldsymbol{ab}} + \sum_{\boldsymbol{a'b'}} \Big[\left(D^s_{\boldsymbol{a'b'}}(i) + D^{-s}_{\boldsymbol{a'b'}}(i) \right) U_{\boldsymbol{aba'b'}} + \left(D^{-s}_{\boldsymbol{a'b'}}(i) - D^s_{\boldsymbol{a'b'}}(i) \right) I_{\boldsymbol{aba'b'}} \Big]$$

Parametrization: practical approach



SCALE-UP

This method is currently implemented in our new code:

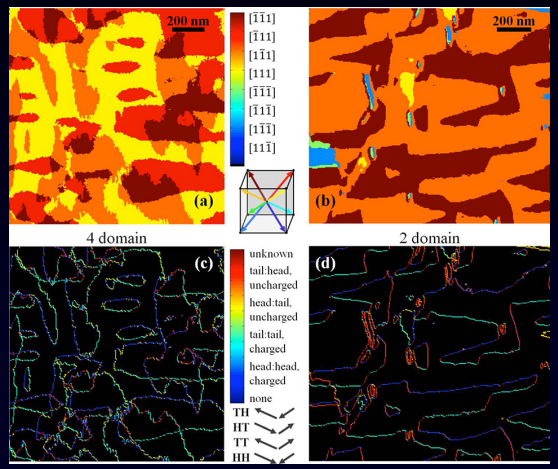
Second-principles Computational Approach for Lattice and Electrons

- Single and composite materials
- MPI paralellization
- Full and Lanczos diagonalization
- Geometry optimization
- Dynamics
- Trivial QM/MM (simply put basis functions in some of the atoms)

Available soon!

Head-to-head tail-to-tail domains in $PbTiO_3$

The field of ferroelectric domain walls is currently very exciting due to possible applications in electronics.



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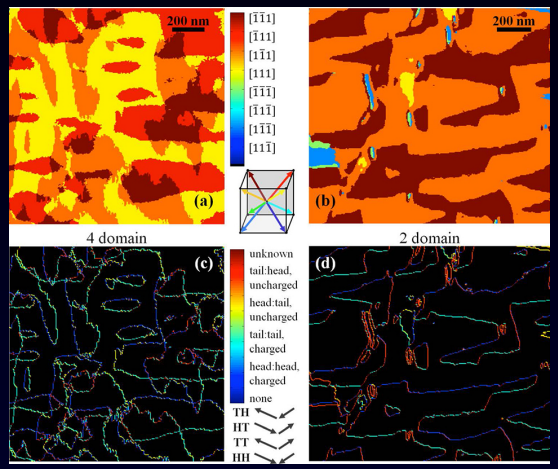

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Their morphology and properties can be dynamically altered with e.g. electric fields

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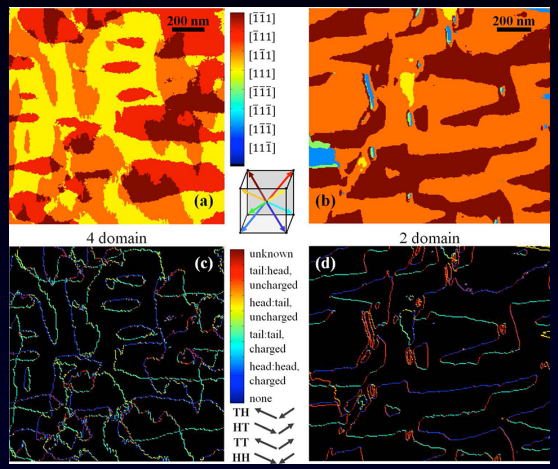

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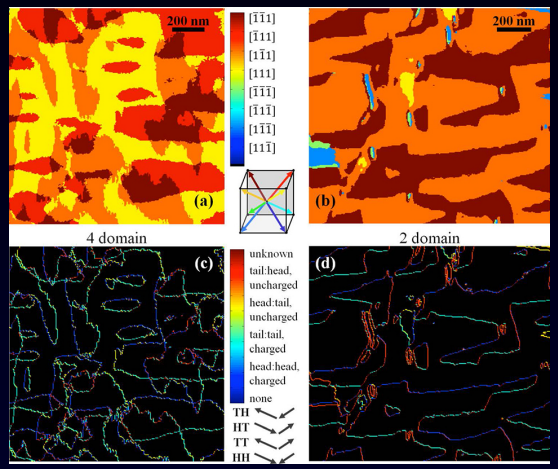

Some domain wall are conducting

Their morphology and properties can be dynamically altered with e.g. electric fields

Problem: Strong controversy about the origin of the conductivity.

One strong difficulty is that the scale is too large for ab initio

We have carried preliminary calculations to check whether the method can simulate these systems

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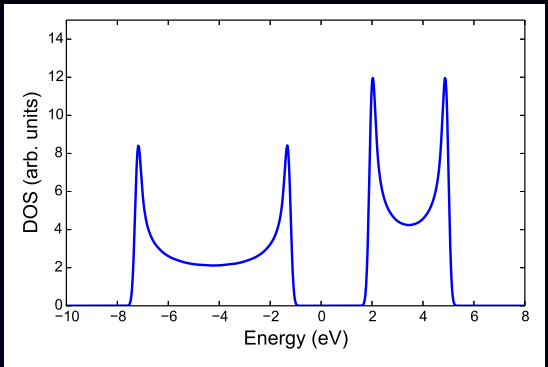
We describe neutral $PbTiO_3$:



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- Occupied Wannier on O_z
- Empty Wannier on Ti
- Correct band gap of 3.2eV

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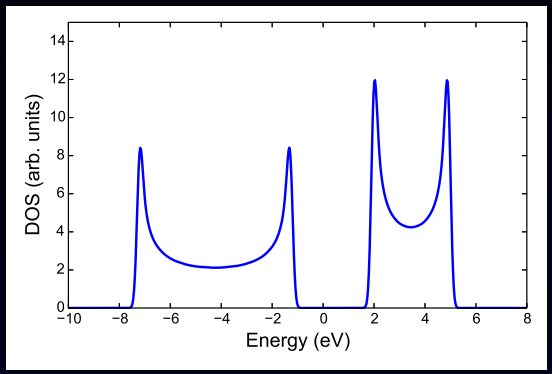

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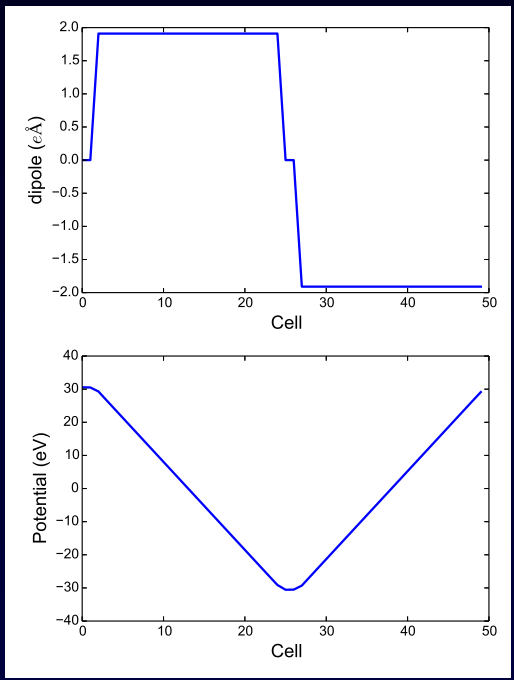
We take a $1 \times 1 \times 50$ supercell... 250 atoms



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   Without electrons electrostatic potential sends system to paraelectric phase

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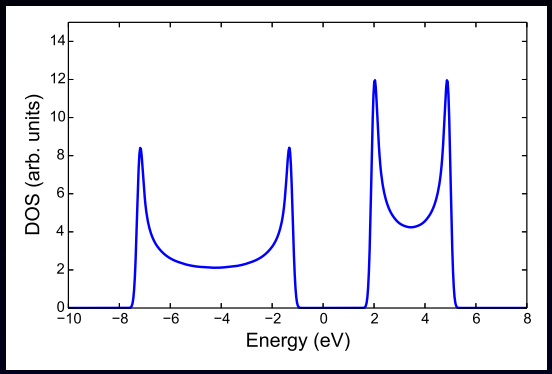

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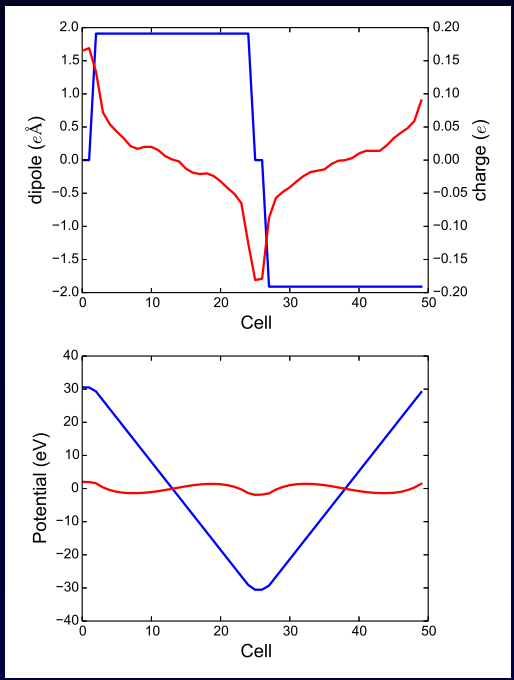

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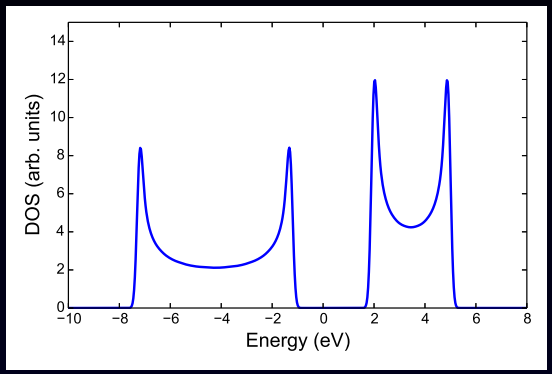

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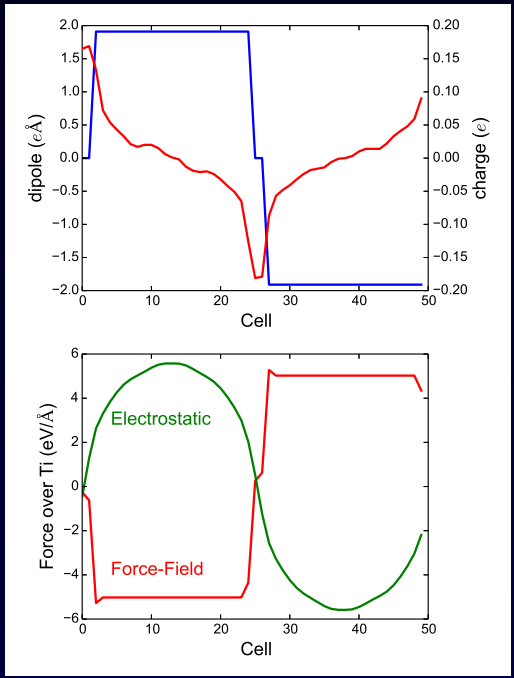

1. We optimize the monodomain phase
2. From that structure we build a 25/25 head-to-head domains
   Without electrons electrostatic potential sends system to paraelectric phase
   Band crossing and electron transfer!
   Then forces are largely compensated

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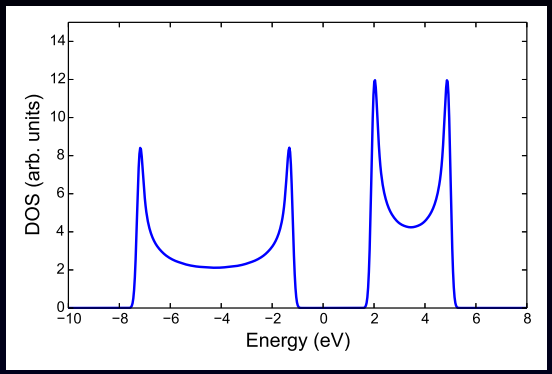

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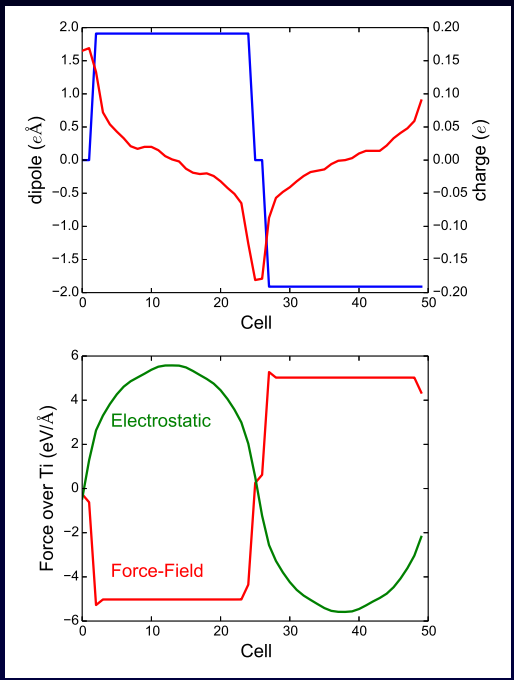
- Correct band gap of 3.2eV

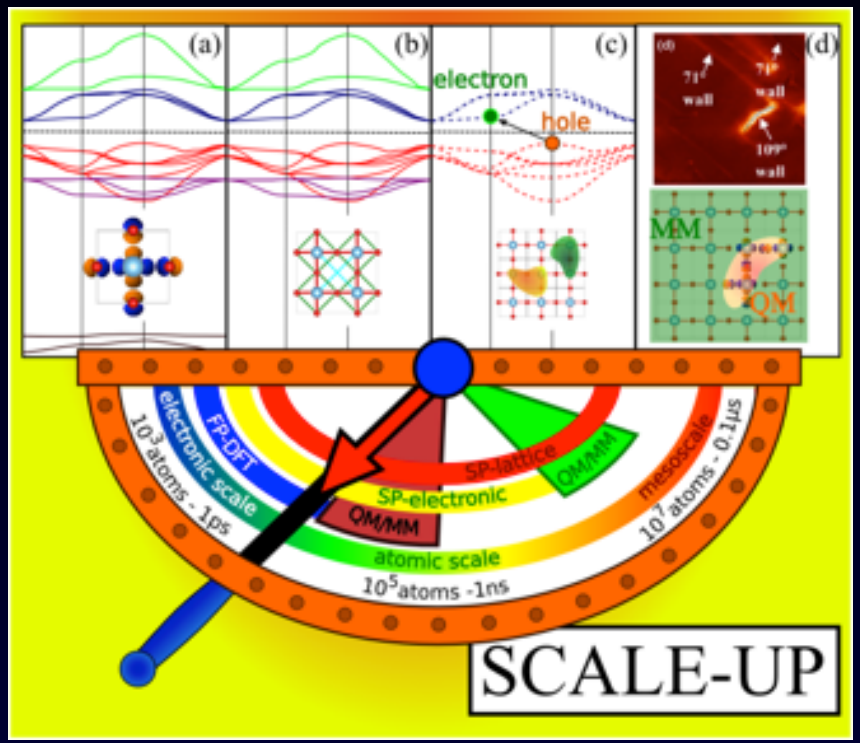
We take a $1 \times 1 \times 50$ supercell... 250 atoms



1. We optimize the monodomain phase
2. From that structure we build a 25/25 head-to-head domains
   Without electrons electrostatic potential sends system to paraelectric phase
   Band crossing and electron transfer!
   Then forces are largely compensated
3. Runtime: 1.8 minutes

Conclusions

New "second-principles" method for large scale simulations combining electron and lattice degrees of freedom



This offers the opportunity to move continuously from a fully first-principles description (considering explicitly all electrons and ions) to a coarse grained model in which the electronic degrees of freedom are integrated out.

- Magnetic systems
- Strongly correlated electrons
- Electron lattice coupling
- More to come (spin-orbit, TDDFT, ...)

Most important reference

Second-principles method including electron and lattice degrees of freedom

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We introduce a new non-empirical multi-scale method for material simulation with predictive power under operating conditions (finite temperature, applied external fields, etc.) including both lattice and electron degrees of freedom on the same footing. The method is firmly based on higher-level first-principles theory, treating all lattice degrees of freedom, and the relevant electronic ones, with a similar accuracy, that can be systematically improved to match that of Density Functional Theory (DFT), at a very modest computational cost. It is free of adjustable parameters coming from experiment (and therefore, retains the predictive power of first-principles), but requires some input from previous *ab-initio* simulations. That is why we coined the term *"second-principles"* to refer to them. The rudiments of the approach involve (i) identify an underlying lattice or bonding topology that is not broken during the course of the simulation, (ii) split the total electron density in reference and deformation contributions, and (iii) use the latter to write the total DFT energy. We show that an adequate choice of the reference density allows to rigorously describe the ensemble of the nuclei plus the vast majority of the electrons using an accurate force-field that is then corrected through the self-consistent calculation of the small deformation density. The latter is achieved using a basis of Wannier-like functions that provides a very efficient representation of the electron/hole excitations produced with respect to the reference electron system. Moreover, we have developed an strategy to build models in an automatic fashion for each material using a reduced number of small-scale first-principles calculations. This procedure allows for a methodical enhancement of the parameters towards full DFT quality. Details of the practical implementations of the method in computers programs to fit the parameters or to carry out the second-principles simulations are given. We illustrate the accuracy of the resulting scheme with the calculation of the stability of various magnetic phases in NiO and the simulation of distribution of metallic electrons at the $LaAlO_3/SrTiO_3$ interface.

PACS numbers: 71.15.-m,71.23.An,71.15.Pd,71.38-k

Ph.D. position might be available to work on "second-principles".
Deadline next week