Electrons ($E^{(1)}$+$E^{(2)}$):

Theory and models

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Santander July 2017

Universidad de Cantabria

The energy in SP-DFT

We estimate the full DFT energy

$$E_{\mathrm{DFT}} = \sum_{j\vec{k}} o_{j\vec{k}} \left\langle \psi_{j\vec{k}} \right| \hat{t} + v_{\mathrm{ext}} \left| \psi_{j\vec{k}} \right\rangle + \frac{1}{2} \iint \frac{n(\vec{r})n'(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + E_{\mathrm{xc}}[n] + E_{\mathrm{nn}}$$

separating the density in reference and deformation contributions

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

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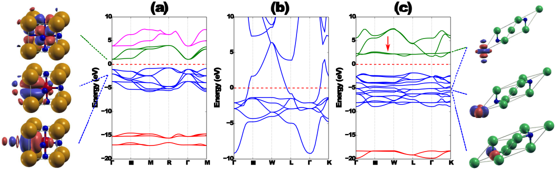
$$E_{\mathrm{DFT}} \approx \underbrace{E^{(0)}}_{\substack{\text{lattice} \\ n_0(\vec{r})}} + \underbrace{E^{(1)} + E^{(2)} + \ldots}_{\substack{\text{electron excitations} \\ \delta n(\vec{r})}}$$

Electron basis: Wannier functions

In order to express electron excitations we need basis:

Precise, small, material-adapted → Wannier-like functions



I. Souza et al.,*Phys. Rev. B*, 65, 035109 (2001)

$$|\chi_{\mathbf{a}}\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\vec{k} e^{-i\vec{k}\cdot\vec{R}_A}\sum_{m}^{M} B_{a,m\vec{k}}|\psi_{m\vec{k}}\rangle$$

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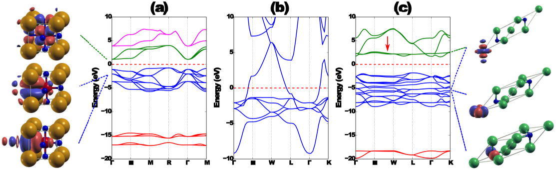

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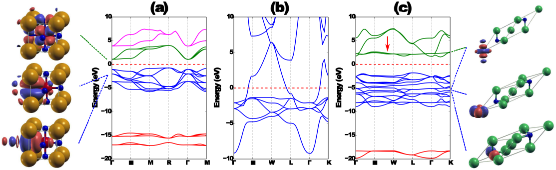

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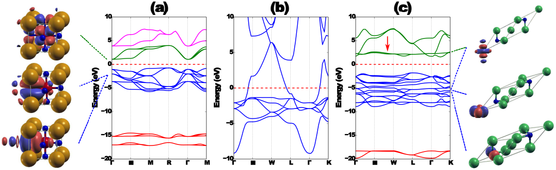

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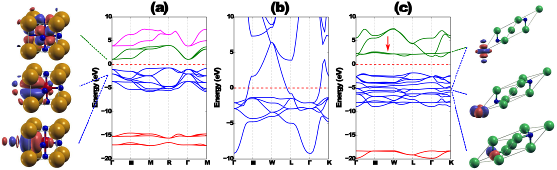

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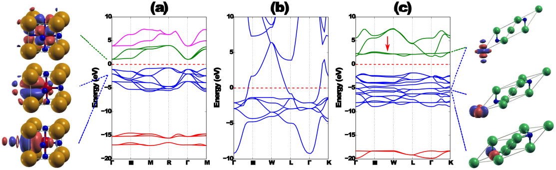

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2. allow disentanglement of electron degrees of freedom
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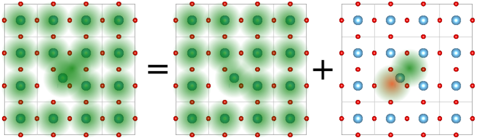
4. are orthogonal
5. are defined for all geometries

Electron basis: Density matrix in the WF basis

The different densities in the WF basis are:



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

Total	$n(\vec{r}) = \sum_{\mathbf{ab}} d_{\mathbf{ab}} \chi^*_{\mathbf{a}}(\vec{r})\chi_{\mathbf{b}}(\vec{r})$	$d_{\mathbf{ab}} = \sum_{j\vec{k}} o_{j\vec{k}} e^{i\vec{k}(\vec{R}_B - \vec{R}_A)} c^*_{ja\vec{k}} c_{jb\vec{k}}$
Reference	$n_0(\vec{r}) = \sum_{\mathbf{ab}} d^0_{\mathbf{ab}} \chi^*_{\mathbf{a}}(\vec{r})\chi_{\mathbf{b}}(\vec{r})$	$d^0_{ab} = \sum_{j\vec{k}} o^0_{j\vec{k}} e^{i\vec{k}(\vec{R}_B - \vec{R}_A)} \left(c^0_{ja\vec{k}}\right)^* c^0_{jb\vec{k}}$
Difference	$\delta n(\vec{r}) = \sum_{\mathbf{ab}} D_{\mathbf{ab}} \chi^*_{\mathbf{a}}(\vec{r})\chi_{\mathbf{b}}(\vec{r})$	$D_{\mathbf{ab}} = d_{\mathbf{ab}} - d^0_{\mathbf{ab}}$

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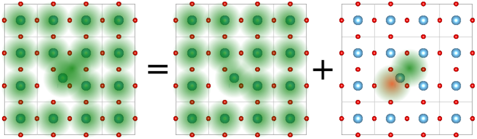

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Reference	$n_0(\vec{r}) = \sum_{\mathbf{ab}} d_{\mathbf{ab}}^0 \chi_{\mathbf{a}}^*(\vec{r}) \chi_{\mathbf{b}}(\vec{r})$	$d_{ab}^0 = \sum_{j\vec{k}} o_{j\vec{k}}^0 e^{i\vec{k}(\vec{R}_B - \vec{R}_A)} \left(c_{ja\vec{k}}^0\right)^* c_{jb\vec{k}}^0$
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    - Diagonal occupation of an orbital
    - Offdiagonal hybridization of two orbitals

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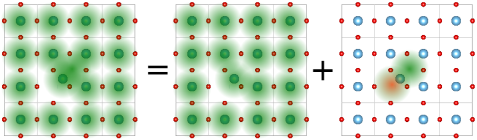

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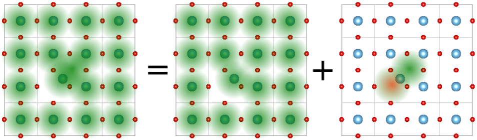

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2. The sign of $D_{\mathbf{ab}}$:
   - positive for excited electrons
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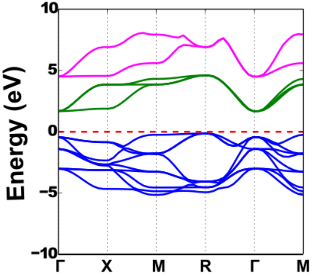
3. Density matrix for an insulator is diagonal In metals decays rationally
   $d_{\mathbf{ab}} = \delta_{\mathbf{ab}} o_{\mathbf{a}}$

Obtaining the WFs and their occupation

We transform sets of bands into WFs



Example: BaTiO$_3$

Wannier-Bloch transformation

$$|\chi_{\mathbf{a}}\rangle = \sum_{m}^{M} \frac{V}{2\pi^3} \int_{\mathrm{BZ}} d\vec{k} e^{-i\vec{k}\cdot\vec{R}_A} B_{a,m\vec{k}} |\psi_{m\vec{k}}\rangle$$

1. Select bands
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2. Minimize spread

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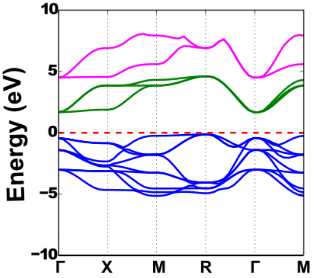

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Key property to understand how the reference is defined:

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

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

Reference state

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

$$E_{\text{DFT}} \approx \underbrace{E^{(0)}}_{\substack{\text{lattice} \\ n_0(\vec{r})}} + \underbrace{E^{(1)} + E^{(2)} + ...}_{\substack{\text{electron excitations} \\ \delta n(\vec{r})}}$$

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3. In the Wannier-function (WF) basis it is characterized by a fixed diagonal density matrix:

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

Density matrix in spin-polarized simulation

Spin-polarized simulations have up/down spin components

Density matrixes are expressed in two complementary ways

$$d^{U}_{\mathbf{ab}} = \frac{d^{\uparrow}_{\mathbf{ab}} + d^{\downarrow}_{\mathbf{ab}}}{2} \qquad d^{I}_{\mathbf{ab}} = \frac{d^{\uparrow}_{\mathbf{ab}} - d^{\downarrow}_{\mathbf{ab}}}{2}$$

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	Non-magnetic	Spin polarization
Total	$d_{\mathbf{ab}} = d^{U}_{\mathbf{ab}}$	$d^{\uparrow}_{\mathbf{ab}}, d^{\downarrow}_{\mathbf{ab}} \rightarrow d^{U}_{\mathbf{ab}}, d^{I}_{\mathbf{ab}}$
Reference	$d^{(0)}_{\mathbf{ab}}$	$d^{(0)}_{\mathbf{ab}}$
Difference	$D_{\mathbf{ab}} = D^{U}_{\mathbf{ab}}$	$D^{\uparrow}_{\mathbf{ab}}, D^{\downarrow}_{\mathbf{ab}} \rightarrow D^{U}_{\mathbf{ab}}, D^{I}_{\mathbf{ab}}$

Reference density and WF in the model xml file

They are associated to the ⟨atom ...⟩ ... ⟨ /atom ⟩ xml element

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$ vi srtio3_noelec.xml
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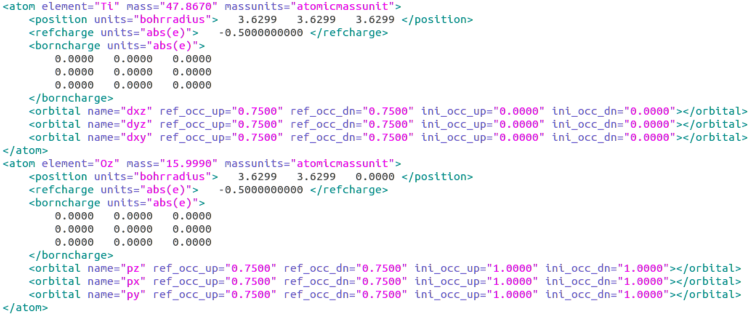

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    <borncharge units="abs(e)">
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        0.0000   0.0000   0.0000
        0.0000   0.0000   0.0000
    </borncharge>
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    <orbital name="dyz" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="0.0000" ini_occ_dn="0.0000"></orbital>
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    <borncharge units="abs(e)">
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        0.0000   0.0000   0.0000
        0.0000   0.0000   0.0000
    </borncharge>
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    <orbital name="px" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="1.0000" ini_occ_dn="1.0000"></orbital>
    <orbital name="py" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="1.0000" ini_occ_dn="1.0000"></orbital>
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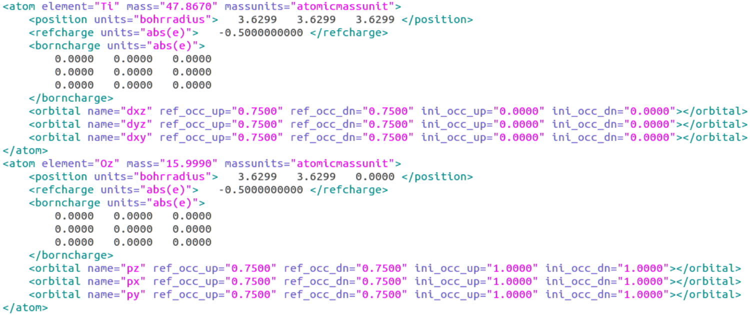

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    </borncharge>
    <orbital name="dxz" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="0.0000" ini_occ_dn="0.0000"></orbital>
    <orbital name="dyz" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="0.0000" ini_occ_dn="0.0000"></orbital>
    <orbital name="dxy" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="0.0000" ini_occ_dn="0.0000"></orbital>
</atom>
<atom element="Oz" mass="15.9990" massunits="atomicmassunit">
    <position units="bohrradius">   3.6299    3.6299    0.0000 </position>
    <refcharge units="abs(e)">   -0.5000000000 </refcharge>
    <borncharge units="abs(e)">
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        0.0000    0.0000    0.0000
        0.0000    0.0000    0.0000
    </borncharge>
    <orbital name="pz" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="1.0000" ini_occ_dn="1.0000"></orbital>
    <orbital name="px" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="1.0000" ini_occ_dn="1.0000"></orbital>
    <orbital name="py" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="1.0000" ini_occ_dn="1.0000"></orbital>
</atom>
```

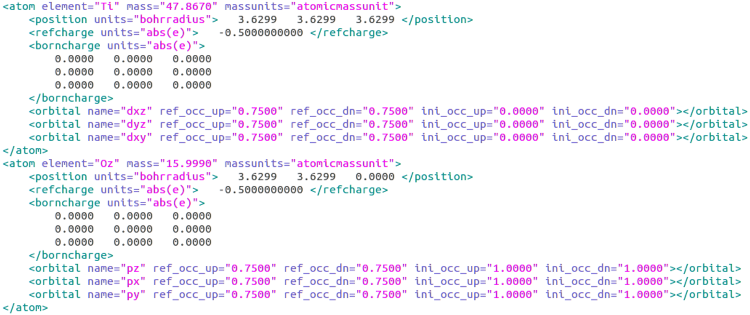
Each WF has its own ⟨orbital ...⟩ ... ⟨ /orbital ⟩ xml element

- It contains a name
- It contains the reference occupations ref_occ_up/ref_occ_dn
  Careful modifying these values!

Reference density and WF in the model xml file

They are associated to the ⟨atom ...⟩ ... ⟨ /atom ⟩ xml element

$ vi srtio3_noelec.xml



```
<atom element="Ti" mass="47.8670" massunits="atomicmassunit">
    <position units="bohrradius">   3.6299   3.6299   3.6299 </position>
    <refcharge units="abs(e)">   -0.5000000000 </refcharge>
    <borncharge units="abs(e)">
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        0.0000   0.0000   0.0000
        0.0000   0.0000   0.0000
    </borncharge>
    <orbital name="dxz" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="0.0000" ini_occ_dn="0.0000"></orbital>
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</atom>
<atom element="Oz" mass="15.9990" massunits="atomicmassunit">
    <position units="bohrradius">   3.6299   3.6299   0.0000 </position>
    <refcharge units="abs(e)">   -0.5000000000 </refcharge>
    <borncharge units="abs(e)">
        0.0000   0.0000   0.0000
        0.0000   0.0000   0.0000
        0.0000   0.0000   0.0000
    </borncharge>
    <orbital name="pz" ref_occ_up="0.7500" ref_occ_dn="0.7500" ini_occ_up="1.0000" ini_occ_dn="1.0000"></orbital>
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Reference density and WF in the model xml file

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```
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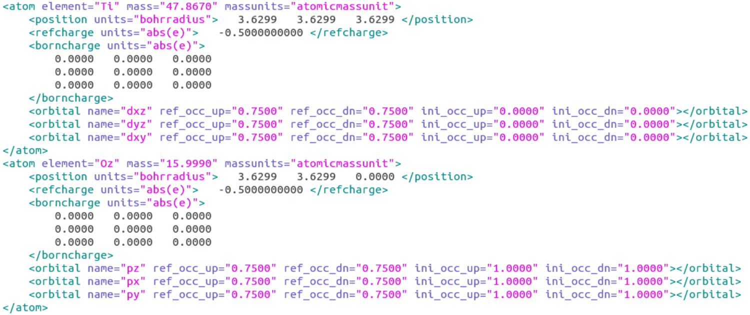
```



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        0.0000   0.0000   0.0000
        0.0000   0.0000   0.0000
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        0.0000   0.0000   0.0000
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  Can be modified to converge to particular states
  Also check read_orbocc in input

The SP-DFT total energy

The full SP-DFT energy is:

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

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

Electron energy terms:

1. $\gamma^{\text{RAG,sr}}_{\mathbf{ab}}$ are the one-electron terms at the reference geometry
2. $\delta\gamma^{\text{el-lat,sr}}_{\mathbf{ab}}(\{\vec{u}_{\boldsymbol{\lambda}}\})$ are the electron-lattice coupling terms
3. $U^{\text{sr}}_{\mathbf{aba'b'}}$, $I_{\mathbf{aba'b'}}$ are the two-electron terms
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All parameters are well-defined and evaluated at reference state

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

$$U_{\mathbf{aba'b'}} = \langle\chi_{\mathbf{a}}\chi_{\mathbf{a'}}|\,\hat{g}\,|\chi_{\mathbf{b}}\chi_{\mathbf{b'}}\rangle$$

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

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What is the associated one-electron hamiltonian?

The SP-DFT real-space Hamiltonian

The SP-DFT is *formally* equivalent to Hartree-Fock

The real-space one-electron Hamiltonian is a central part of the code

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

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This expression contains the main parameters for the electron part:

1. $\gamma^{\text{RAG,sr}}_{\mathbf{ab}}$ short-range tight-binding

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The electron bands trivially obtained by going to reciprocal space:

$$h^{s}_{ab,\vec{k}} = \sum_{\vec{R}_B - \vec{R}_A} e^{i\vec{k}\cdot\left(\vec{R}_B - \vec{R}_A\right)} h^{s}_{\mathbf{ab}} \longrightarrow \sum_{b} h^{s}_{ab,\vec{k}}\, c^{s}_{jb\vec{k}} = \varepsilon^{s}_{j\vec{k}}\, c^{s}_{ja\vec{k}},$$

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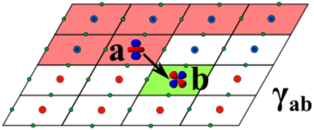
Let's check them in detail...

The reference one-electron terms in the model xml file

The SCALE-UP input: one-, two- and electron-lattice interactions.



One-electron interaction, $\gamma_{\mathbf{ab}}$

orbital 1 $\Longleftrightarrow$ orbital 2

cell hop $\Longrightarrow$ 3 integers

Value $\Longrightarrow$ $\gamma_{\mathbf{ab}}$ (eV)

Position $\Longrightarrow$ $\int \chi_{\mathbf{a}} \vec{r} \chi_{\mathbf{b}} d^3 r$

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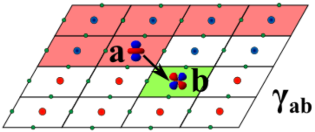

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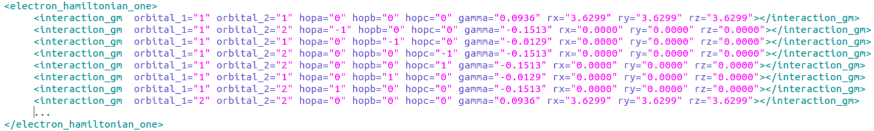
Example:

```
$ vi srtio3_noelec.xml
```



```
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     <interaction_gm  orbital_1="1" orbital_2="2" hopa="-1" hopb="0" hopc="0" gamma="-0.1513" rx="0.0000" ry="0.0000" rz="0.0000"></interaction_gm>
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     <interaction_gm  orbital_1="1" orbital_2="2" hopa="0" hopb="0" hopc="-1" gamma="-0.1513" rx="0.0000" ry="0.0000" rz="0.0000"></interaction_gm>
     <interaction_gm  orbital_1="1" orbital_2="2" hopa="0" hopb="0" hopc="1" gamma="-0.1513" rx="0.0000" ry="0.0000" rz="0.0000"></interaction_gm>
     <interaction_gm  orbital_1="1" orbital_2="1" hopa="0" hopb="1" hopc="0" gamma="-0.0129" rx="0.0000" ry="0.0000" rz="0.0000"></interaction_gm>
     <interaction_gm  orbital_1="1" orbital_2="2" hopa="1" hopb="0" hopc="0" gamma="-0.1513" rx="0.0000" ry="0.0000" rz="0.0000"></interaction_gm>
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     ...
</electron_hamiltonian_one>
```

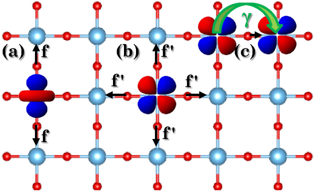
Composed of:

⟨electron_hamiltonian_one ...⟩ ... ⟨ /electron_hamiltonian_one ⟩ xml section

⟨interaction_gm ...⟩ ... ⟨ /interaction_gm ⟩ xml elements

Geometry dependence - Introduction

WFs depend on geometry $\Rightarrow \gamma$ is expanded on atomic positions:



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U,I should also depend on $\delta\vec{r} \rightarrow$ neglected

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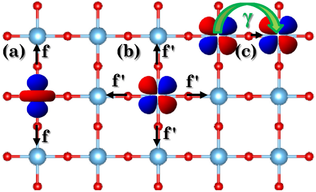

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These terms have two main effects:

1. lattice→electron $h_{\mathbf{ab}}$ depends on geometry
2. electron→lattice Forces depend on density

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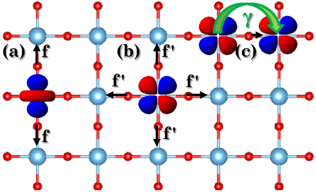

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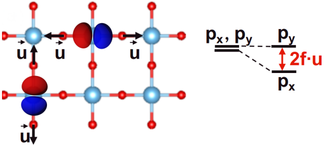
Closely related to Jahn-Teller Hamiltonian

Geometry dependence - Lattice→Electron

$\vec{f}$ and $\overleftrightarrow{g}$ influence electronic structure in 3 main ways:

1. Diagonal terms $h_{\mathbf{aa}}$ level-shift



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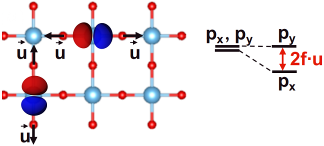
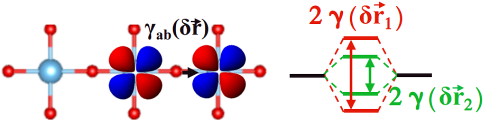


2. Off-diagonal terms same-type orbitals $h_{\mathbf{ab}}$ band width



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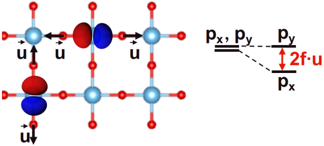

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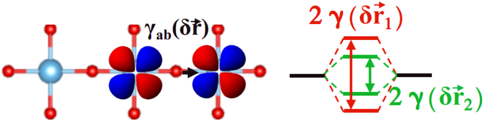
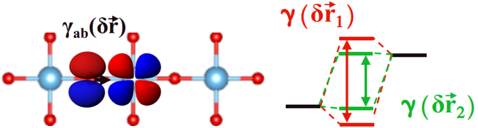
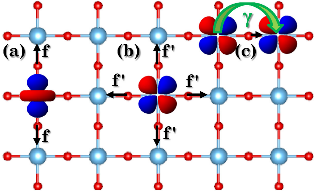


③ Off-diagonal terms different-type orbitals $h_{\mathbf{ab}}$ hybridization



Geometry dependence - Electron→Lattice

Depending where electrons are placed they produce forces:



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

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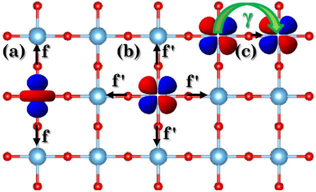

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The forces are :

$$\vec{F}_{\lambda} = -\vec{\nabla}_{\lambda} E = -\vec{\nabla}_{\lambda} E^{(0)} - \sum_{\mathbf{ab}} D_{ab} \vec{\nabla}_{\lambda} \gamma_{\mathbf{ab}}$$

$$= \vec{F}^{(0)}_{\lambda} + \sum_{\mathbf{ab}} D_{ab} \sum_{\boldsymbol{\upsilon}} \left(\vec{f}_{\mathbf{ab},\boldsymbol{\lambda\upsilon}} - \overset{\leftrightarrow}{g}_{\mathbf{ab},\boldsymbol{\lambda\upsilon}} \cdot \delta\vec{r}_{\boldsymbol{\lambda\upsilon}} + \ldots \right)$$

Depending where electron excitations are, force field is corrected

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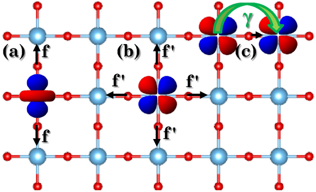

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Depending where electron excitations are, force field is corrected

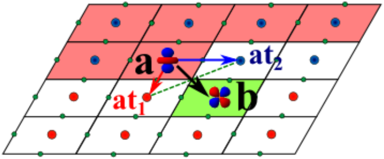
$\vec{f}_{\mathbf{ab}}$ represents the force when that interaction is occupied

$\overset{\leftrightarrow}{g}_{\mathbf{ab},\boldsymbol{\lambda\upsilon}}$ corrects the force with distortion

The electron-lattice terms in the model xml file

Electron-lattice interactions change $h_{\mathbf{ab}}$ based on atomic positions:

$$\gamma_{\mathbf{ab}}^{\mathrm{sh}} = \gamma_{\mathbf{ab}}^{0,\mathrm{sh}} + \sum_{\boldsymbol{\lambda\upsilon}} \left[-\vec{f}_{\mathbf{ab},\boldsymbol{\lambda\upsilon}} \cdot \delta\vec{r}_{\boldsymbol{\lambda\upsilon}} + \sum_{\boldsymbol{\lambda'\upsilon'}} \delta\vec{r}_{\boldsymbol{\lambda\upsilon}} \left(g\right)_{\mathbf{ab},\boldsymbol{\lambda\upsilon\lambda'\upsilon'}} \delta\vec{r}_{\boldsymbol{\lambda'\upsilon'}} + ... \right],$$



Electron-lattice interaction

Interaction $\Longleftrightarrow \gamma_{\mathbf{ab}}$

Atoms $\Longrightarrow$ from **a**

Linear $\Longrightarrow \vec{f}_{\mathbf{ab},\boldsymbol{\lambda\upsilon}}$ (eV/Å)

Quadratic $\Longrightarrow (g)_{\mathbf{ab},\boldsymbol{\lambda\upsilon\lambda'\upsilon'}}$ (eV/Å^2)

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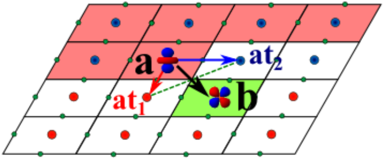

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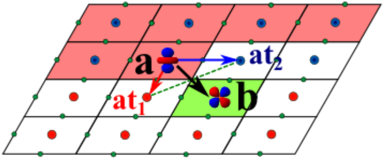

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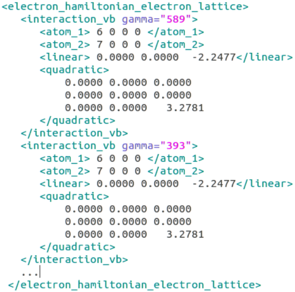

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      <atom_2> 7 0 0 0 </atom_2>
      <linear> 0.0000 0.0000  -2.2477</linear>
      <quadratic>
          0.0000 0.0000 0.0000
          0.0000 0.0000 0.0000
          0.0000 0.0000   3.2781
      </quadratic>
   </interaction_vb>
   <interaction_vb gamma="393">
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      <atom_2> 7 0 0 0 </atom_2>
      <linear> 0.0000 0.0000  -2.2477</linear>
      <quadratic>
          0.0000 0.0000 0.0000
          0.0000 0.0000 0.0000
          0.0000 0.0000   3.2781
      </quadratic>
   </interaction_vb>
   ...|
 </electron_hamiltonian_electron_lattice>
```

```
$ vi li2o2_latticeelectrons_mod.xml
```

Composed of:

⟨electron_hamiltonian_electron_lattice ⟩ xml section

⟨interaction_vb ...⟩ ... ⟨ /interaction_gm ⟩ xml elements

The two-electron constants

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

The Hubbard two-electron constant:

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

1. Contains all classical electrostatic terms (Hartree)

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2. They are corrected (screened) by exchange and correlation

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1. Contains all classical electrostatic terms (Hartree)
2. They are corrected (screened) by exchange and correlation

The Stoner one-electron constant:

$$g_I(\vec{r},\vec{r}') = \frac{1}{2}\left[\left.\frac{\delta^2 E_{\text{xc}}}{\delta n(\vec{r},\uparrow)\delta n(\vec{r}',\downarrow)}\right|_{n_0} - \left.\frac{\delta^2 E_{\text{xc}}}{\delta n(\vec{r},\uparrow)\delta n(\vec{r}',\uparrow)}\right|_{n_0} \right]$$

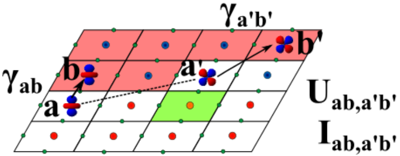
1. Magnetic interactions
2. Pure quantum origin (exchange and correlation)

The two-electron terms in the model xml file

The two-electron interactions modify the one-electron values:

$$h_{\mathbf{ab}} = \gamma_{\mathbf{ab}} + \sum_{\mathbf{a'b'}} D_{\mathbf{a'b'}} U_{\mathbf{ab},\mathbf{a'b'}}$$

Describes how bands change when occupations change



Two-electron interaction

interactions $\Longleftrightarrow \gamma_{\mathbf{ab}},\ \gamma_{\mathbf{a'b'}}$

cell hop $\Longrightarrow$ 3 integers

Hubbard $\Longrightarrow U_{\mathbf{ab},\mathbf{a'b'}}$ (eV)

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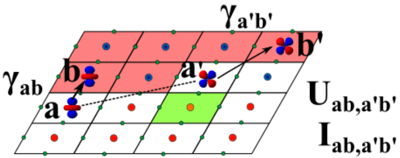

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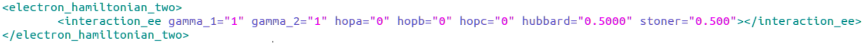
Example:



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</electron_hamiltonian_two>
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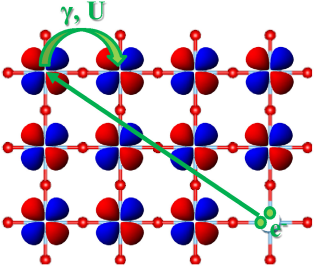
Composed of:

⟨electron_hamiltonian_two ...⟩ ... ⟨ /electron_hamiltonian_two ⟩ xml section

⟨interaction_ee ...⟩ ... ⟨ /interaction_ee ⟩ xml elements

Electrostatics

All interactions in the model are between localized objects:



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Hartree/electron-nucleus

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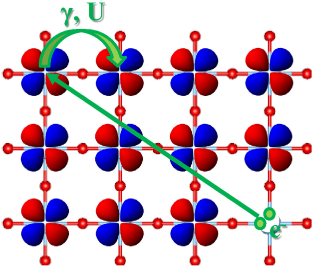

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Multipolar expansion!

We approximate the full charge density by a field of point charges and dipoles localized at the reference geometry

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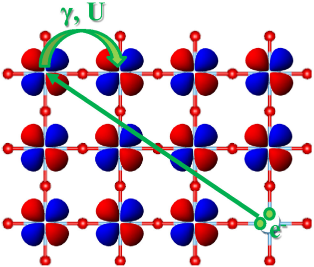

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Model parameters are separated in long and short contributions.

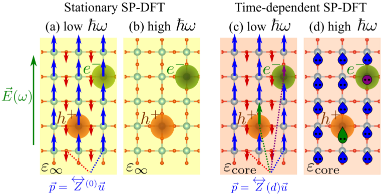
$$\gamma_{\mathbf{ab}} = \gamma^{\mathrm{sr}}_{\mathbf{ab}} + \gamma^{\mathrm{lr}}_{\mathbf{ab}}$$

$$U_{\mathbf{aba'b'}} = U^{\mathrm{sr}}_{\mathbf{aba'b'}} + U^{\mathrm{lr}}_{\mathbf{aba'b'}}$$

The short-range part → quickly converging to zero

Electrostatics:

The present electrostatics in code extend beyond original paper:



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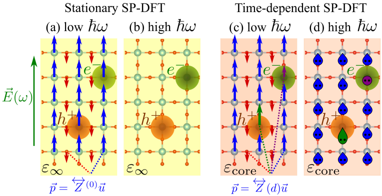

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Same basics - the far-field potential

$$v_\text{elec}[n](\vec{r}) = \sum_{\boldsymbol{\lambda}} \frac{Z_{\boldsymbol{\lambda}}}{|\vec{r} - \vec{r}_{\boldsymbol{\lambda}}|} + \int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3r \approx \sum_{\boldsymbol{\lambda}} \frac{q_{\boldsymbol{\lambda}}}{|\vec{r} - \vec{r}_{\boldsymbol{\lambda}}|} + \sum_{\boldsymbol{\lambda}} \vec{p}_{\boldsymbol{\lambda}} \frac{\vec{r} - \vec{r}_{\boldsymbol{\lambda}}}{|\vec{r} - \vec{r}_{\boldsymbol{\lambda}}|^3}$$

Dipole definition changes

$$q_{\boldsymbol{\lambda}} = Z_{\boldsymbol{\lambda}} - \sum_{\mathbf{a}' \in \boldsymbol{\lambda}} d_{\mathbf{a}'\mathbf{a}'} \qquad \vec{p}_{\boldsymbol{\lambda}} = Z_{\boldsymbol{\lambda}} \vec{u}_{\boldsymbol{\lambda}} - \sum_{\mathbf{a}' \in \boldsymbol{\lambda}} \left[\sum_{\mathbf{b}'} \left(d_{\mathbf{a}'\mathbf{b}'} \vec{r}_{\mathbf{a}'\mathbf{b}'} \right) - d_{\mathbf{a}'\mathbf{a}'} \vec{r}_{\boldsymbol{\lambda}} \right]$$

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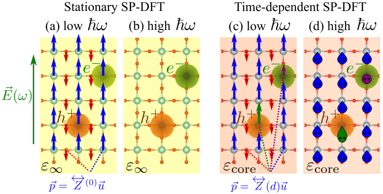

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Definition of dipoles is consistent with modern theory of polarization

Electrostatics: Matrix elements

Previously electrostatic matrix elements were just diagonal in $\hat{h}$

To calculate matrix element expand mid-way between WFs

$$v_{\mathrm{FF}}(\vec{r},t) \approx v_{\mathrm{FF}}\left(\frac{\vec{r}_{\mathbf{a}}+\vec{r}_{\mathbf{b}}}{2},t\right) - \vec{E}_{\mathsf{int}}\left(\frac{\vec{r}_{\mathbf{a}}+\vec{r}_{\mathbf{b}}}{2},t\right)\hat{\vec{r}} + \ldots$$

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We now see the existence of diagonal and off-diagonal elements

$$h^{\mathrm{lr}}_{\mathbf{ab}} \approx \underbrace{-e v_{\mathrm{FF}}\left(\frac{\vec{r}_{\mathbf{a}}+\vec{r}_{\mathbf{b}}}{2},t\right)\langle\chi_{\mathbf{a}}|\,\chi_{\mathbf{b}}\rangle}_{\text{diagonal}} + \underbrace{e\left[\vec{E}_{\mathrm{ext}}(t) + \vec{E}_{\mathrm{int}}\left(\frac{\vec{r}_{\mathbf{a}}+\vec{r}_{\mathbf{b}}}{2},t\right)\right]\vec{r}_{\mathbf{ab}}}_{\text{off-diagonal}}$$

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We perform all electrostatic calculations on atomic centers

$$\vec{E}_{\mathrm{int}}\left(\frac{\vec{r}_{\mathbf{a}}+\vec{r}_{\mathbf{b}}}{2},t\right) \approx \frac{1}{2}\left[\vec{E}_{\mathrm{int}}\left(\vec{r}_{\mathbf{a}},t\right) + \vec{E}_{\mathrm{int}}\left(\vec{r}_{\mathbf{b}},t\right)\right]$$

During parameterization, the total matrix element is:

$$h^{DFT}_{\mathbf{ab}} \approx h^{SP-DFT}_{\mathbf{ab}} = h^{\mathrm{lr}}_{\mathbf{ab}} + h^{\mathrm{sr}}_{\mathbf{ab}}$$

Electrostatics: local dipoles

The local dipole on an atom is:

$$\vec{p}_{\boldsymbol{\lambda}} = Z_{\boldsymbol{\lambda}} \vec{u}_{\boldsymbol{\lambda}} - \sum_{\mathbf{a}' \in \boldsymbol{\lambda}} \left[\sum_{\mathbf{b}'} \left(d_{\mathbf{a}'\mathbf{b}'} \vec{r}_{\mathbf{a}'\mathbf{b}'} \right) - d_{\mathbf{a}'\mathbf{a}'} \vec{r}_{\boldsymbol{\lambda}} \right]$$

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Noting that:

1. Reference and difference densities

$$d_{\mathbf{ab}} = o_{\mathbf{a}}\delta_{\mathbf{ab}} + D_{\mathbf{ab}}$$

Electrostatics: local dipoles

The local dipole on an atom is:

$$\vec{p}_{\boldsymbol{\lambda}} = Z_{\boldsymbol{\lambda}} \vec{u}_{\boldsymbol{\lambda}} - \sum_{\mathbf{a'} \in \boldsymbol{\lambda}} \left[\sum_{\mathbf{b'}} \left(d_{\mathbf{a'b'}} \vec{r}_{\mathbf{a'b'}} \right) - d_{\mathbf{a'a'}} \vec{r}_{\boldsymbol{\lambda}} \right]$$

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$$d_{\mathbf{ab}} = o_{\mathbf{a}} \delta_{\mathbf{ab}} + D_{\mathbf{ab}}$$

2. WF real position (displaced from atom)

$$\vec{r}_{\mathbf{ab}} = \delta_{\mathbf{ab}} \left(\vec{r}_{\boldsymbol{\lambda}(\mathbf{a})} + \vec{u}_{\boldsymbol{\lambda}(\mathbf{a})} \right) + \delta \vec{r}_{\mathbf{ab}}$$

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- $Z_{\boldsymbol{\lambda}}\vec{u}_{\boldsymbol{\lambda}}$ Born dipole for reference state

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- $Z_{\boldsymbol{\lambda}} \vec{u}_{\boldsymbol{\lambda}}$ Born dipole for reference state
- $\vec{p}^{(0)}_{\boldsymbol{\lambda}}$ is intrinsic dipole by WF position

Electrostatics: local dipoles

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- ion is dipole by displacing charge

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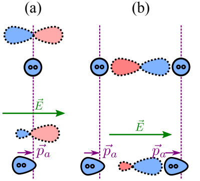
- $Z_{\boldsymbol{\lambda}}\vec{u}_{\boldsymbol{\lambda}}$ Born dipole for reference state
- $\vec{p}^{(0)}_{\boldsymbol{\lambda}}$ is intrinsic dipole by WF position
- ion is dipole by displacing charge
- hybridization is dipole by mixing of orbitals



Scaling

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

Building the matrix...

1. full elements $\longrightarrow$ N^4 (N = basis-size)

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Building the matrix...

1. full elements $\longrightarrow$ N^4 (N = basis-size)
2. range limited $\longrightarrow$ $\mathrm{N}\cdot\mathrm{n}^3$ (n = interactions per element)

In SCALE-UP only non-null interactions are taking into account

Scaling in matrix-building is linear!

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

Building the matrix...

1. full elements ⟶ N^4 (N = basis-size)
2. range limited ⟶ $N \cdot n^3$ (n = interactions per element)

In SCALE-UP only non-null interactions are taking into account

Scaling in matrix-building is linear!

Diagonalization:

1. Full scaling is N^3 (very slow)
2. Lanczos has better scaling (not implemented yet)
3. Other methods are being explored (using TD)

Summary of electron hamiltonians

The electron part of SP-DFT is based on a real-space approach:

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

It contains the following terms:

1. $\gamma^{\text{RAG,sr}}_{\mathbf{ab}}$ short-range tight-binding
2. $\gamma^{\text{lr}}_{\mathbf{ab}}$ long-range electrostatic interactions
3. $U_{\mathbf{aba'b'}}$ Hubbard two-electron parameter (RAG)
4. $I_{\mathbf{aba'b'}}$ Stoner two-electron parameter (RAG)
5. $\delta\gamma^{\text{el-lat,sr}}_{\mathbf{ab}}(\{\vec{u}_{\boldsymbol{\lambda}}\})$ electron-lattice terms (out of RAG)

SP-DFT is *formally* equivalent to Hartree-Fock

Range-limited terms would allow to obtain linear scaling