DE LA RECHERCHE À L'INDUSTRIE

Simulation of small polarons with ABINIT using functionalities related to correlated electrons

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CONTENT

1 – Reminder: what is a small polaron ?

2 – Computation of a self-trapped small polaron using DFT

3 – Small polaron hopping

I – Reminder: what is a small polaron ?

- **Context: semiconducting/insulating materials**
- **Introduction of additional charges (electron or holes) coming from point defects**
- **Different kinds of point defects:**

Donors
Liberate electrons

Example:
- **oxygen vacancy** in an insulating oxide

- **cation interstitial** in an insulating oxide

Acceptors
Liberate holes (i.e. catch electrons)

Example:
- **cationic vacancy** in an insulating oxide

- **aliovalent substitution of the cation** (by element of lower valence)

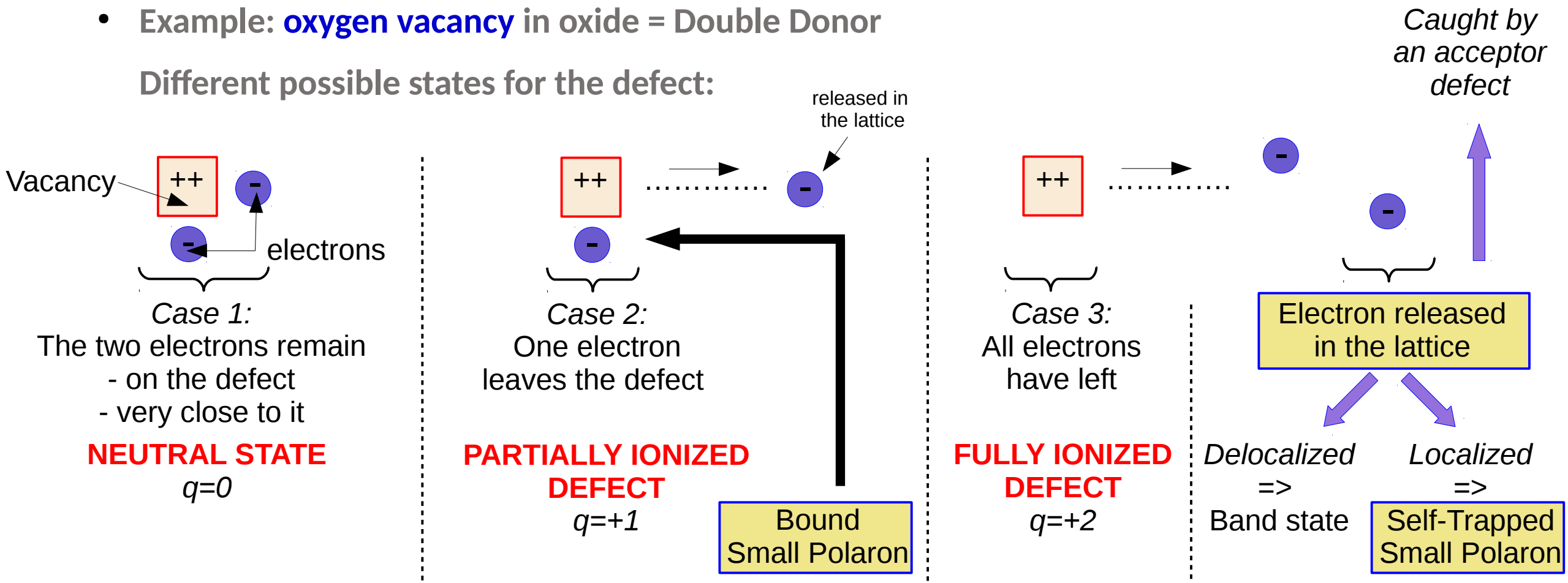
- **Single, double … donor**

Number of elementary charges released

I – Reminder: what is a small polaron ?

- **Example: oxygen vacancy in oxide = Double Donor**

  Different possible states for the defect:



- Small polaron = bound or self-trapped
- Depends on the electronic chemical potential μ_e (Fermi level)

- Example

Differen

Formation energy of the defect:

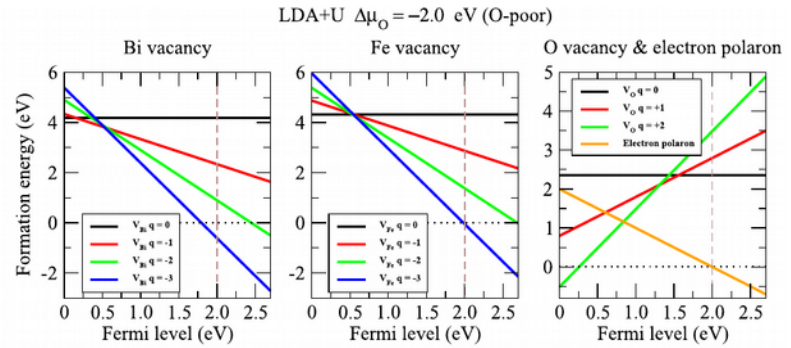
$$\Delta E_f = \text{intrinsic cost} + q\mu_e + \sum_i n_i \mu_i$$

- Breaking/reforming bonds
- Interactions between released charges/defect
- Atomic distortions around the defect

Energy of the electron/hole released in the lattice

Energy of the atomic species (i) removed ($n_i>0$) or added ($n_i<0$)

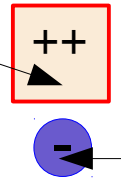
Ex: vacancies in $BiFeO_3$



$$\mu_e = E_{VBM} + \varepsilon_F$$ ← Fermi level

*G. Geneste, C. Paillard, B. Dkhil, Phys. Rev. B **99**, 024104 (2019)*

Vacancy



Case 1:
The two electrons remain
- on the defect
- very close to it

NEUTRAL STATE
q=0

Case 2:
One electron leaves the defect

PARTIALLY IONIZED DEFECT
q=+1

Bound Small Polaron

Case 3:
All electrons have left

FULLY IONIZED DEFECT
q=+2

Electron released in the lattice

Delocalized => Band state

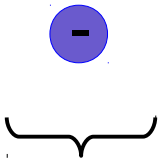
Localized => Self-Trapped Small Polaron

…
Other polaronic forms

- Small polaron = bound or self-trapped
- Depends on the electronic chemical potential μ_e (Fermi level)

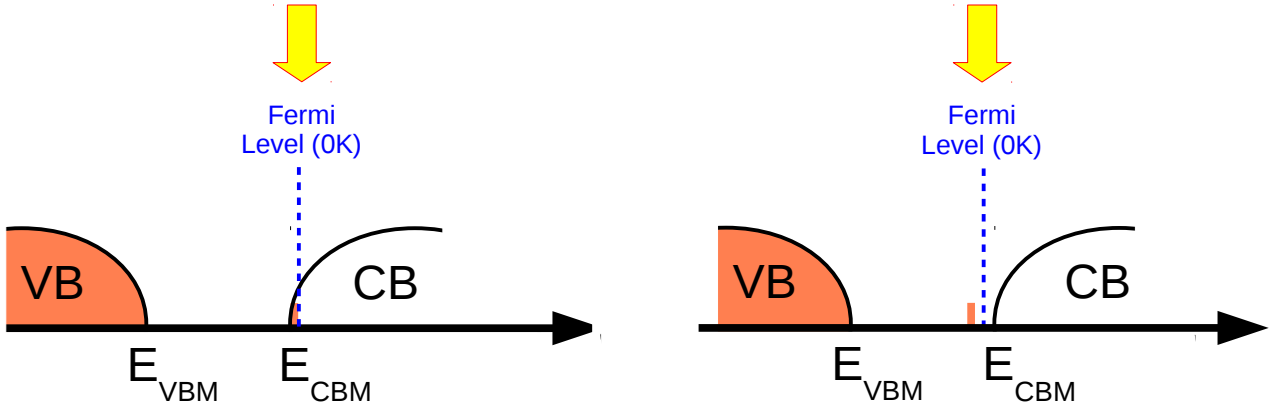
I – Reminder: what is a small polaron ?

Electron released in the lattice:



Delocalized => Band state

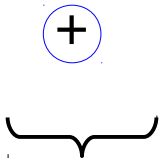
Localized => Self-Trapped Small Polaron (electron polaron)



Electron in band state
Delocalized throughout the crystal

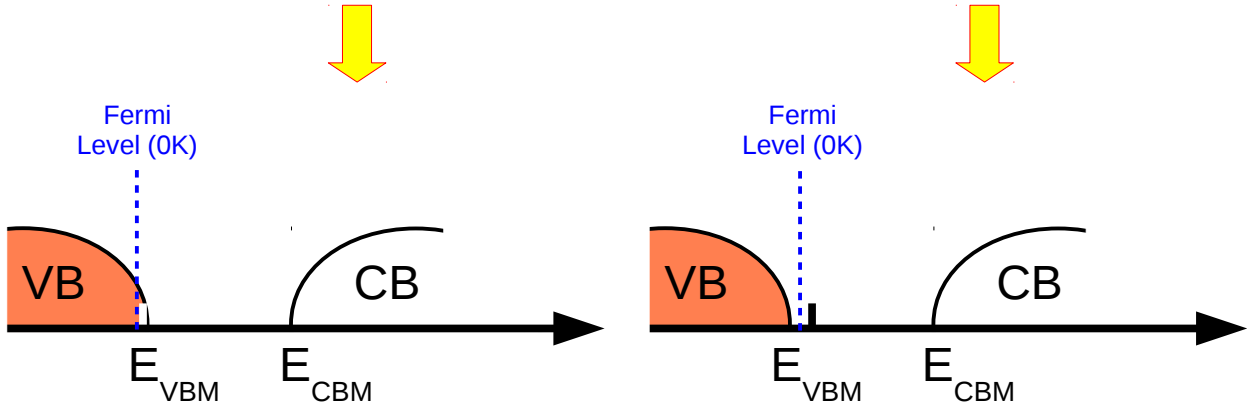
Electron state detached from CB
Localized in space
Distortions around the localized charge

Hole released in the lattice:



Delocalized => Band state

Localized => Self-Trapped Small Polaron (hole polaron)



Hole in band state
Delocalized throughout the crystal

Hole state detached from VB
Localized in space
Distortions around the localized charge

I – Reminder: what is a small polaron ?

- **How can an excess electron/hole be localized on a single atom in the lattice (“self-trapped”)**

To pay:

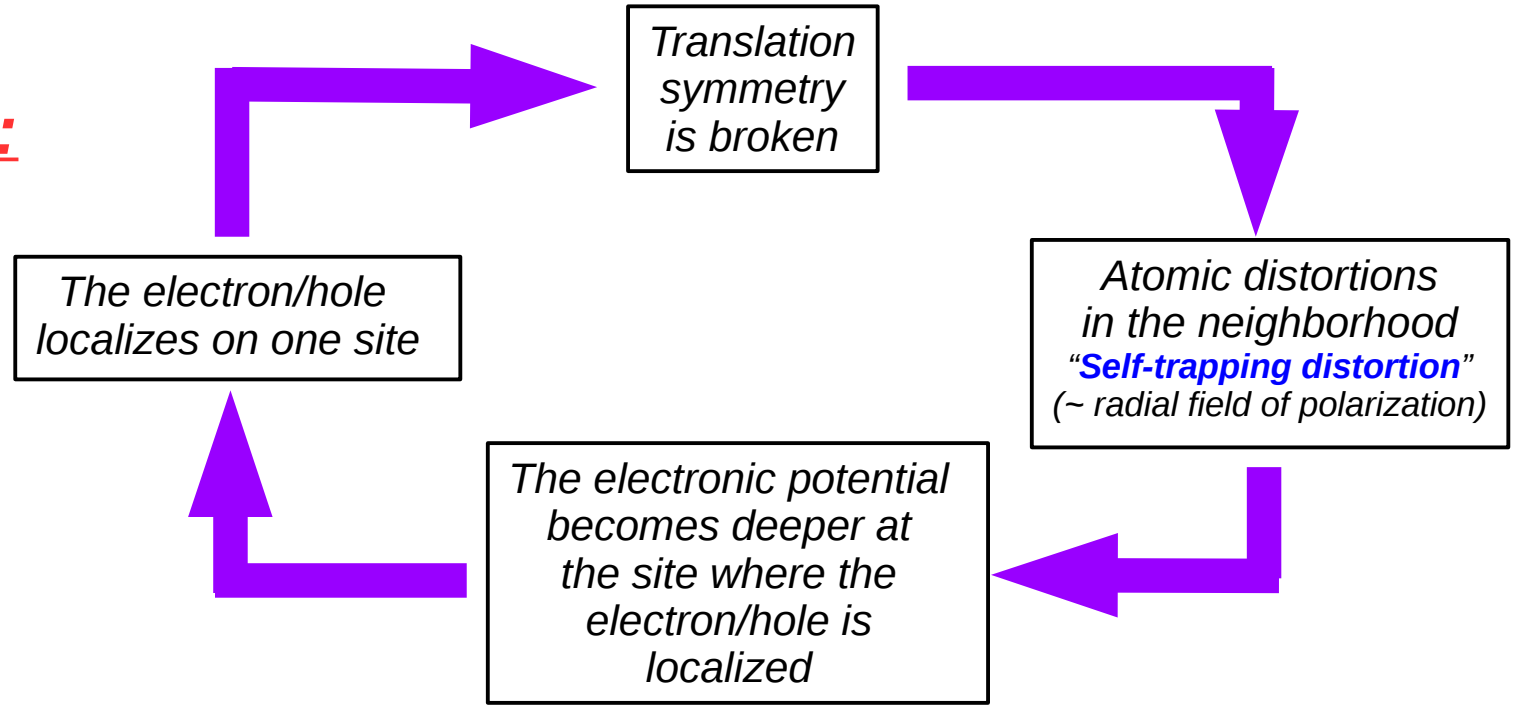
ZPE associated with quantum confinement

Atomic distortions around (optical phonons)
...

Can be compensated by:

Interaction between the charge and the ~ radial polarization field
...

Self-trapping mechanism:



Self-trapping energy (E_{st})=
Energy difference between total energies of **polaronic configuration** and **delocalized** one.

$E_{st} < 0$ => the **self-trapped polaron is stable**

II – Computation of a self-trapped small polaron using DFT

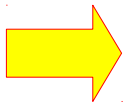
- **Add/remove electron => keyword *charge* (±1) (compensated by uniform background)**
- **XC functional:**

  LDA/GGA: trend to delocalization (self-interaction error);

  LDA/GGA can be OK for bound polarons, usually not for self-trapped ones;

  => DFT+*U* (*U* on atom type/angular momentum concerned by polaron) or Hybrid Functionals with HF (PBE0, HSE06…)

- **Rq: oxygen-type hole polarons in oxides => U on oxygen p**
- **Physical problems encountered:**
  - Small polaron alone in supercell
  - Small polaron close to defect, domain wall, etc
  - Small polaron hopping/reorientation



Choose atom by enforcing atomic distances to 1sr NN may be sufficient

…

But not always to enforce the orbital !

- **=> How to choose the atom / orbital on which le polaron is localized ?**

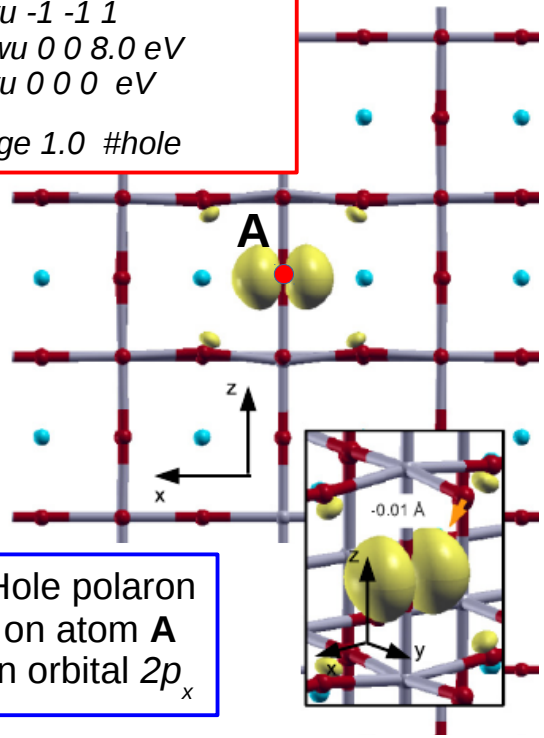
II – Computation of a self-trapped small polaron using DFT

- **ABINIT code DFT+U: occupation matrices of correlated orbitals**
  - Can be constrained over a given number of electronic steps
  - During 1st or all ionic steps

- **Two-step procedure to enforce small polaron on given atom in given orbital**

usepawu 1
znucl 56 50 8 #BaSnO3
lpawu -1 -1 1
upawu 0 0 8.0 eV
jpawu 0 0 0 eV

charge 1.0 #hole



Hole polaron on atom **A** in orbital $2p_x$

(1) Create the ST distortion

- **enforce localization** with occupation matrices, constrained over all electronic steps

usedmatpu -30 #neg value: constr over all ionic steps
nstep 30
dmatpawu
...
#atom A
0.8 0.0 0.0
0.0 0.8 0.0
0.0 0.0 0.0 #hole (y,z,x)
...

- **structurally optimize**

ionmov 2 ntime 100
tolmxf 5.0d-4
#need not to be fully optimized

(2) Final structural optimization

start with geometry obtained at the end of (1)

- relax previous constraint by imposing occ matrices only at beginning of 1st ionic step

usedmatpu 30
nstep 100
dmatpawu
...
#atom A
0.8 0.0 0.0
0.0 0.8 0.0
0.0 0.0 0.0 #hole (y,z,x)
...

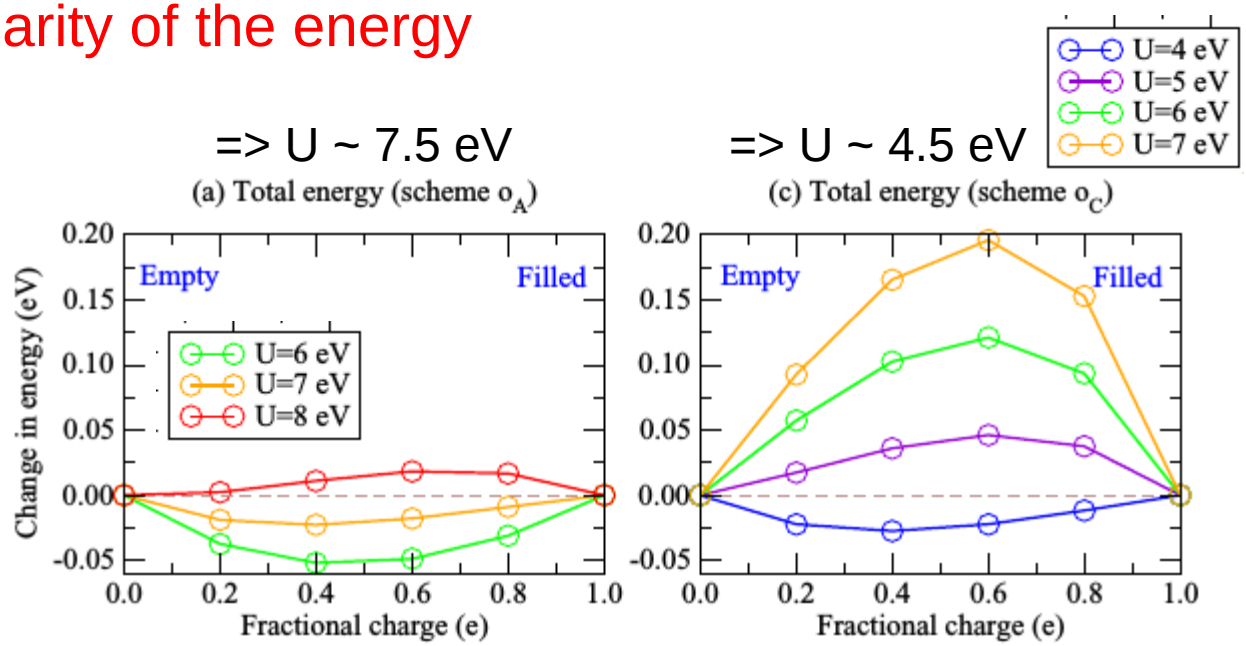
- terminate **structural optimization**

ionmov 2 ntime 100
tolmxf 1.0d-4 #fully optimized

*G. Geneste, B. Amadon, M. Torrent, G. Dezanneau, Phys. Rev. B **96**, 134123 (2017)*

II – Computation of a self-trapped small polaron using DFT

- **Choice of U to simulate small polarons**
  - U generally chosen to reproduce bulk properties (bandgap), or directly calculated
  - Small polarons: U can be chosen to cancel self-interaction error
- **Idea: polaron = additional charge q=±1, how does the energy vary when going continuously from 0 to q ?**
- The energy varies linearly as a function of the number of electrons between two consecutive integer values = piecewise linearity of the energy
- In practise:
  - freeze a polaronic configuration
  - Compute total energy by varying *charge* from 0 to q=±1 by fractional value
  - Plot energy change w/r to linearity as a function of fractional charge
  - Choose U to be as close as possible to linearity (chang



*M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005)*
*P. Erhart, A. Klein, D. Åberg, and B. Sadigh, Phys. Rev. B **90**, 035204 (2014)*

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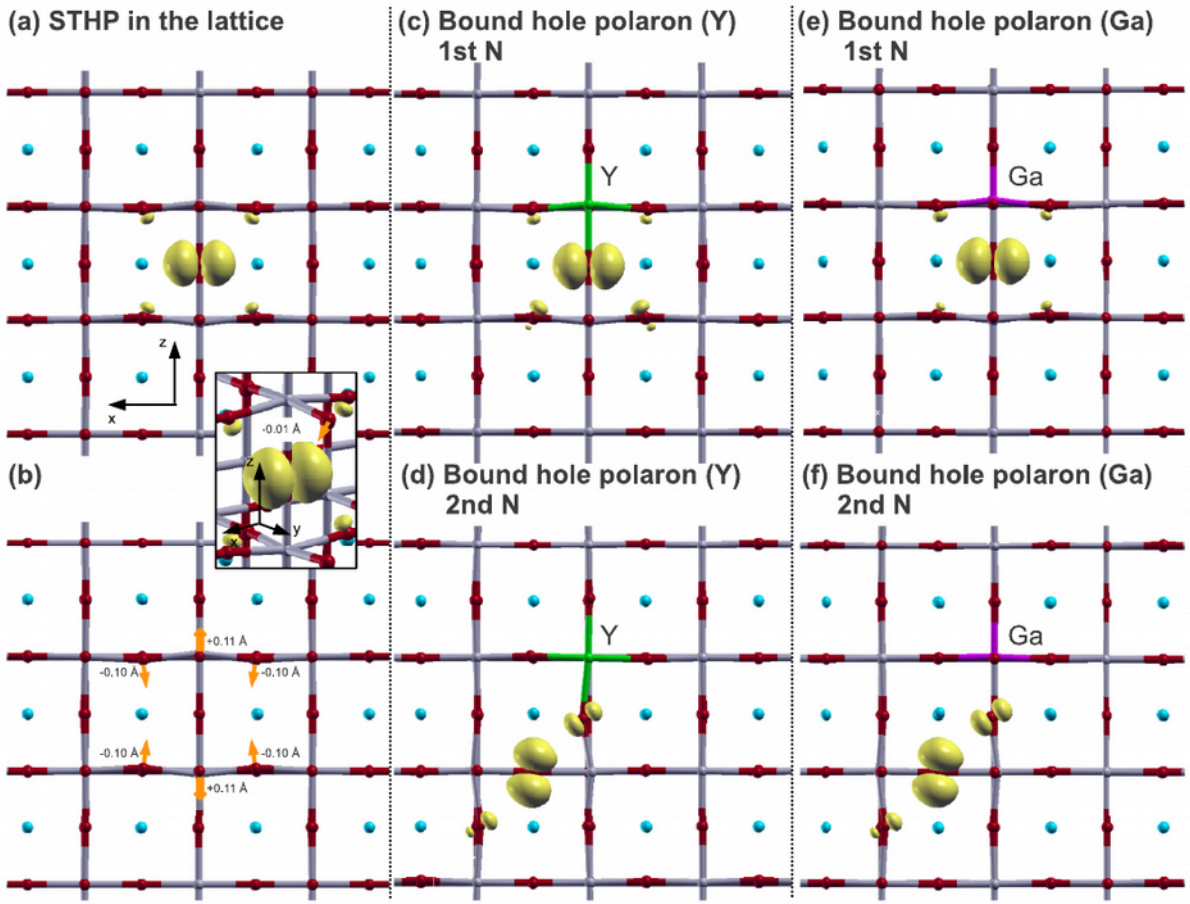
Example 1: Hole polaron in $BaSnO_3$



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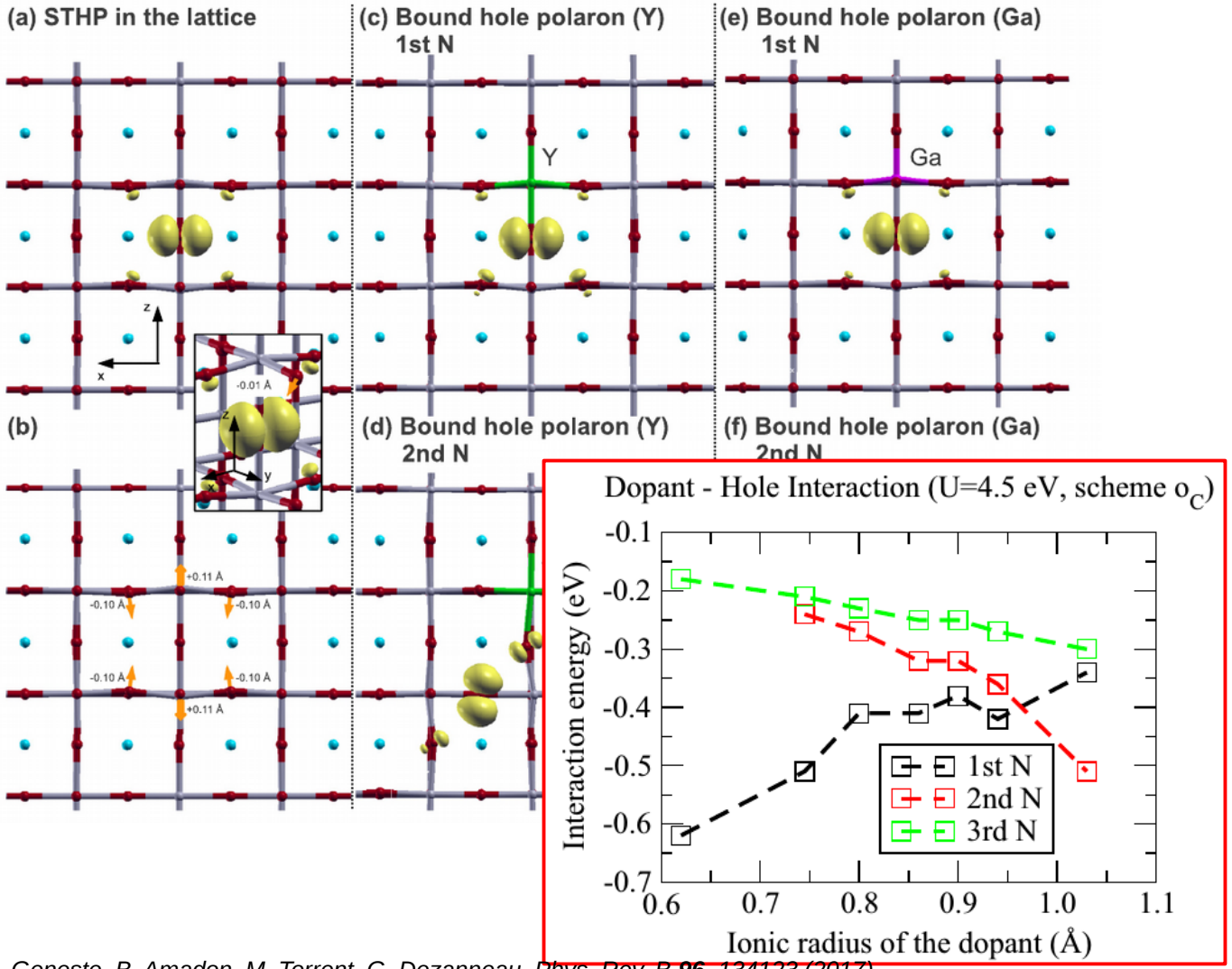

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II – Computation of a self-trapped small polaron using DFT

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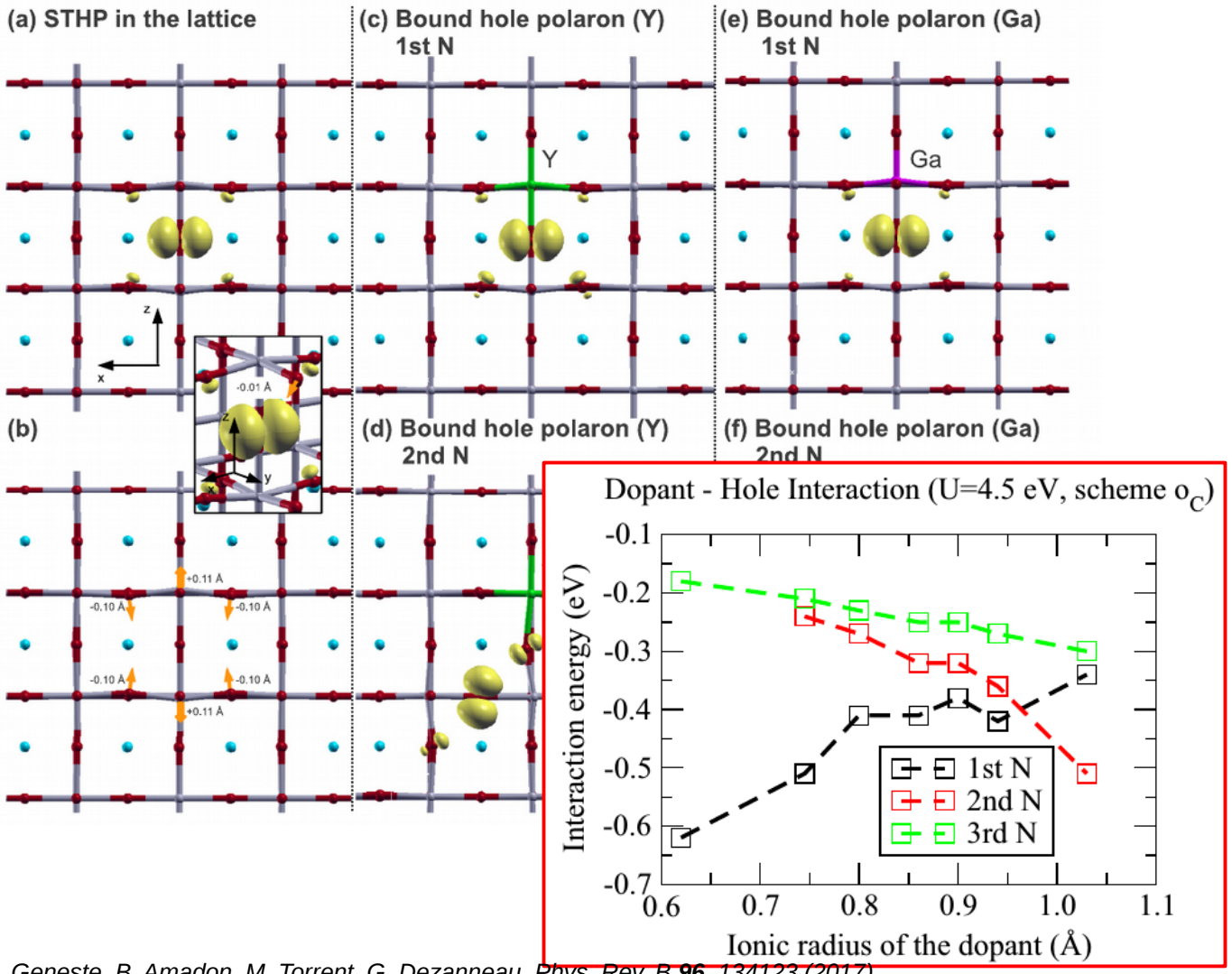

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Example 2: electron polaron in $BiFeO_3$

Localizes on Fe, 3d orbital $Fe^{3+} + e^- \rightarrow Fe^{2+}$

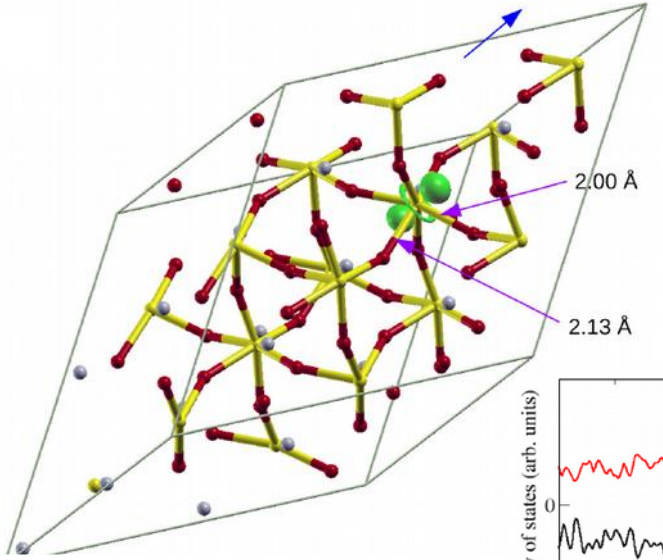
Fe^{3+}: $3d^5$ high-spin => 5 possibilities, which one ?

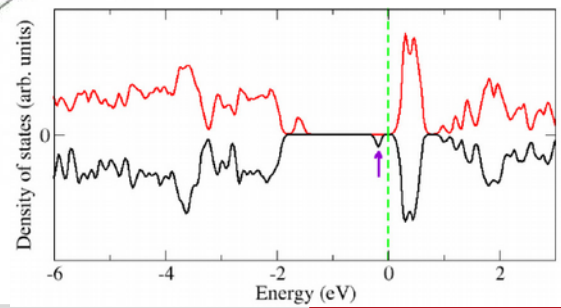
Risk of being blocked in metastable state (DFT +U)

=> Exploration by two-step-procedure of the 5 possibilities

The most stable is retained

E_{st}=-0.50 eV





*G. Geneste, C. Paillard, B. Dkhil, Phys. Rev. B **99**, 024104 (2019)*

III – Small polaron hopping

- **Small polaron hopping = thermally activated process**

  Thermal agitation of atoms, since the electron/hole remains in its GS !
- **Transfer: tunneling process in specific configurations = COINCIDENCE**
- **Two limits**
  - If tunneling time << coincidence timescale: **ADIABATIC** transfer

    The adiabatic approximation remains valid at coincidence.
  - If tunneling time >> coincidence timescale: **NON-ADIABATIC** transfer
- **Hopping can be computed by NEB or String Method**

  with assumption that the adiabatic approximation is valid all along the process
- **ABINIT DFT+U: occupation matrices can be constrained**

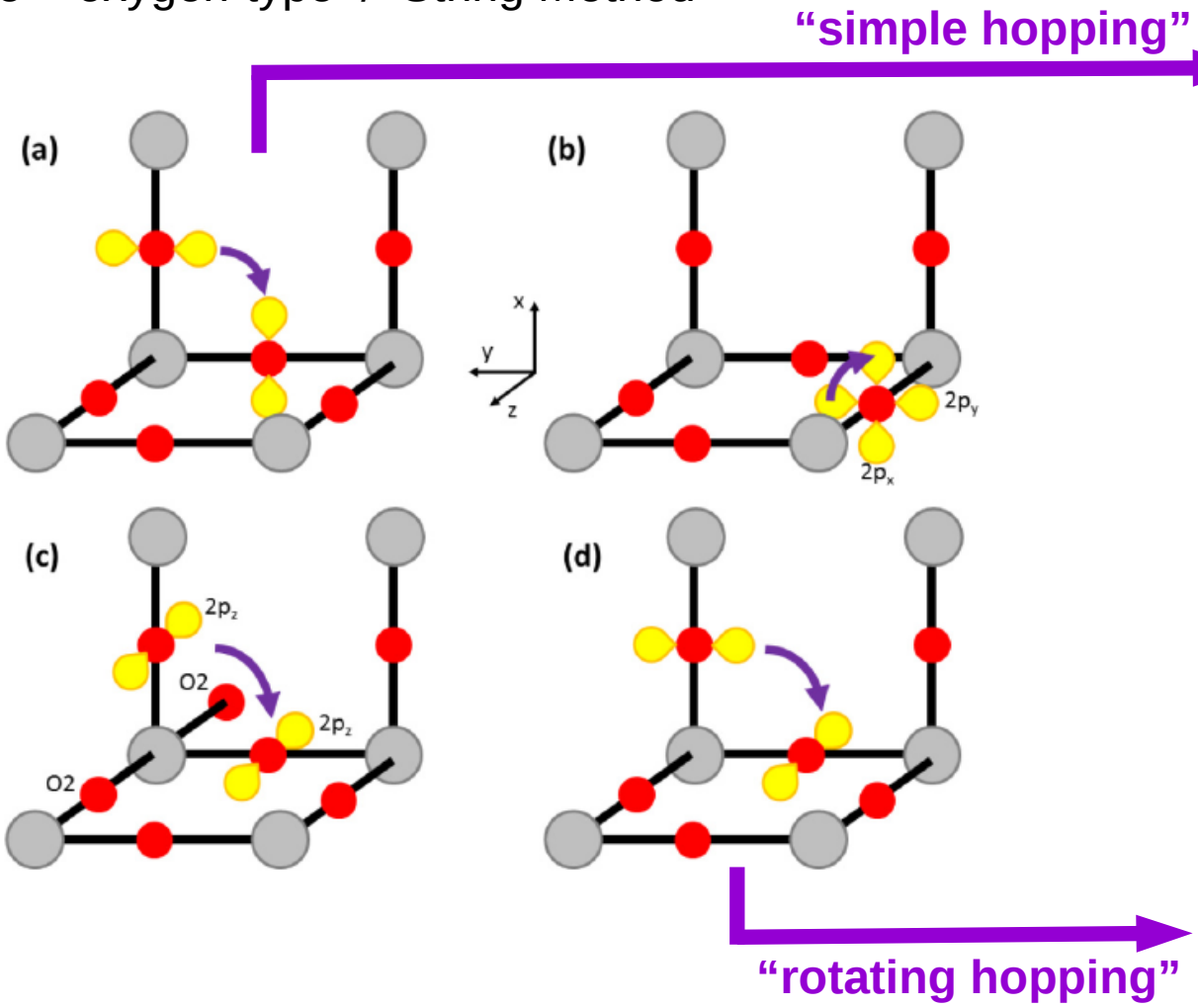
  dmatpawu_1img ..... dmatpawu_lastimg

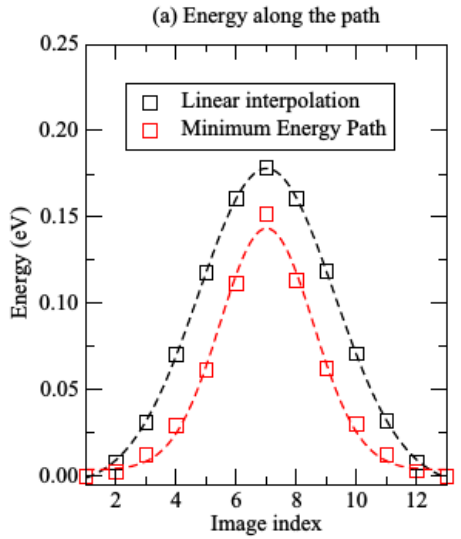
  ... ...

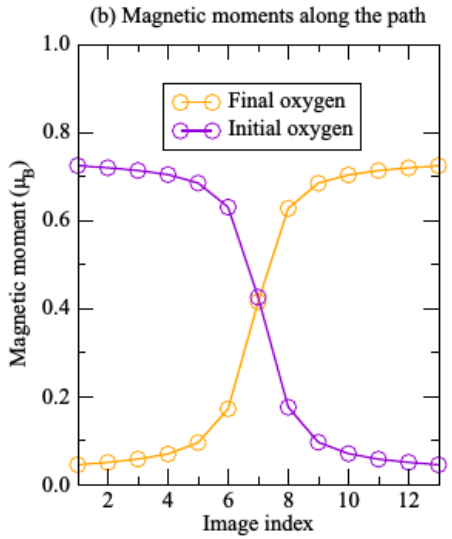
Imposes along the path a linear interpolation between occupation matrices of 1st and last image

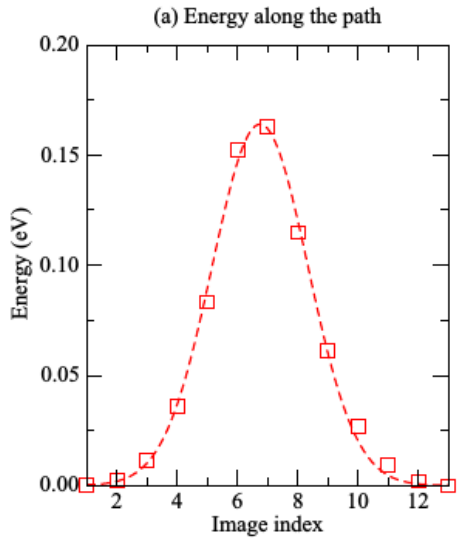
III – Small polaron hopping

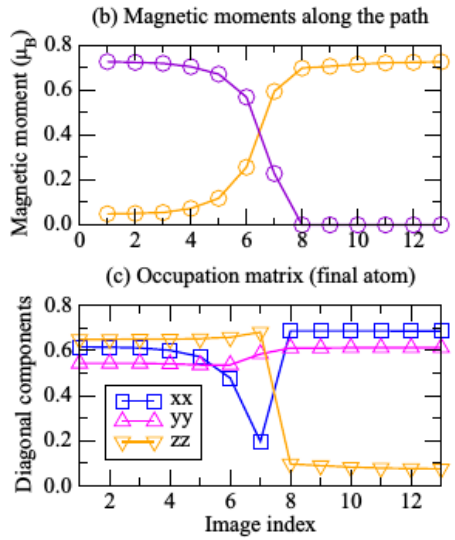
Ex: hole polaron hopping in BaSnO3
Hole = oxygen-type / String Method











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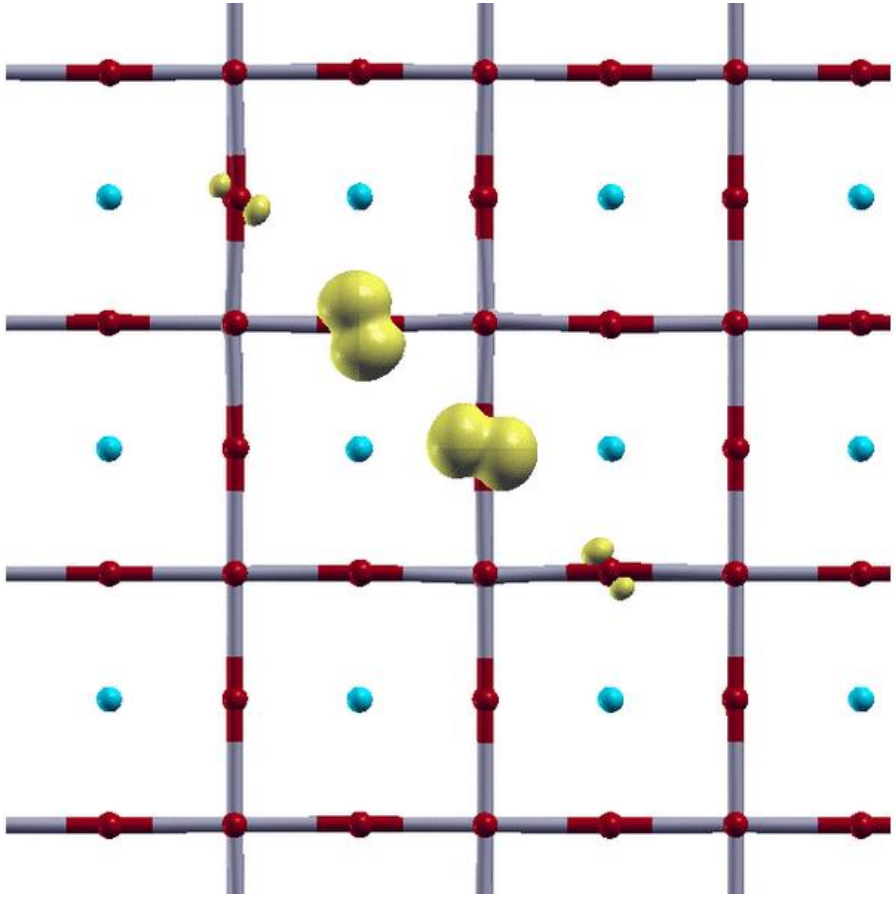
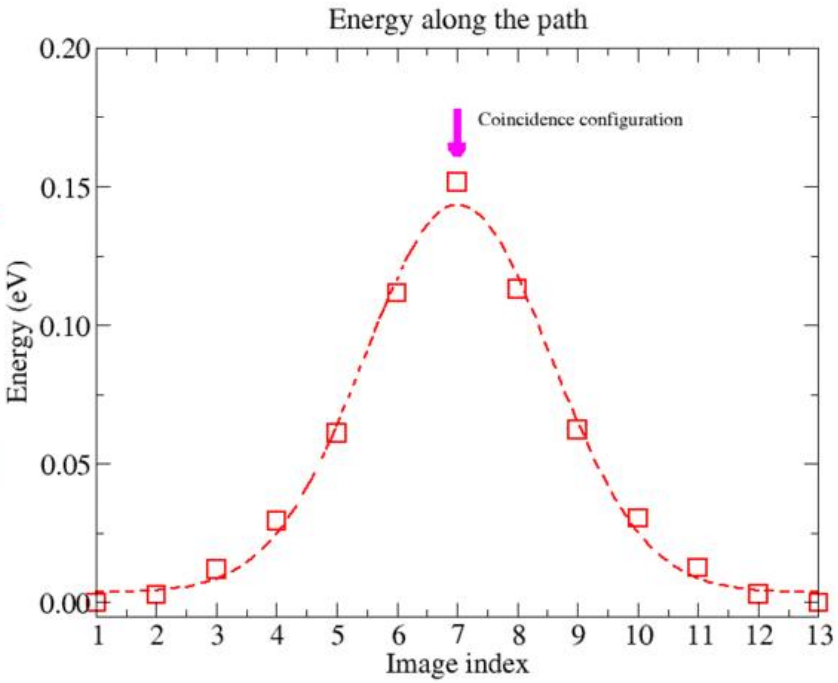
“Simple hopping” mechanism:





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Conclusion

- ABINIT offers functionalities to simulate efficiently small polarons:

  Occupation matrices of correlated orbitals (DFT+U)

- Allows to simulate polaron on given atom, in given orbital, with a systematic procedure

- Allows to find the most stable quantum state for a polaron

- Allows to compute hopping path

Acknowledgments

B. Amadon, G. Dezanneau, C. Paillard, B. Dkhil

Thank you for your attention