THEOS
THEORY AND SIMULATION OF MATERIALS

MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

QUANTUMESPRESSO

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Hubbard interactions from density functional perturbation theory

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Outline

1. Introduction

2. Traditional linear-response method to compute U

3. New method to compute U based on DFPT

4. Conclusions

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DFT+U in a nutshell

In the DFT+U formalism, the total energy is augmented by a corrective Hubbard term

$$E_{\mathrm{DFT}+U} = E_{\mathrm{DFT}} + E_{\mathrm{Hub}}$$

In a simplified rotationally invariant scheme the Hubbard energy reads

$$E_{\mathrm{Hub}} = \frac{1}{2} \sum_{I m_1 m_2} U^I (\delta_{m_1 m_2} - n^I_{m_1 m_2})\, n^I_{m_1 m_2}$$

The occupation matrices are defined as

$$n^I_{m_1 m_2} = \sum_i \langle \psi_i | \varphi^I_{m_1} \rangle \langle \varphi^I_{m_2} | \psi_i \rangle$$

The Kohn-Sham (KS) wavefunctions are obtained by solving the modified KS equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}} + V_{\mathrm{Hub}} \right] |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

where the Hubbard potential is defined as

$$V_{\mathrm{Hub}} = \sum_{I m_1 m_2} U^I \left(\frac{\delta_{m_1 m_2}}{2} - n^I_{m_1 m_2} \right) |\varphi^I_{m_1}\rangle \langle \varphi^I_{m_2}|$$

How to choose U ?

- Determination of U from fitting to the experimental data

- Compute U from first principles

  - Constrained DFT approach

    [*Gunnarsson et al. (1989), Anisimov et al. (1991), Cococcioni et al. (2005)*]

  - Constrained RPA approach (cRPA)

    [*Springer et al. (1998), Aryasetiawan et al. (2004)*]

  - Unrestricted Hartree-Fock approach

    [*Mosey and Carter (2007)*]

  - ACBN0

    [*Agapito, Curtarolo, Buongiorno Nardelli (2015)*]

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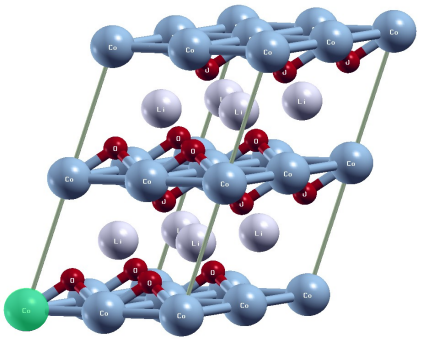
Linear-response calculation of U

The mathematical aspects of such an approach are the following.

The Kohn-Sham equations are modified to include a perturbation of a specific atom:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}} + V_{\mathrm{Hub}} + \alpha_J \sum_m |\varphi_m^J\rangle\langle\varphi_m^J|\right] |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

which leads to changes in occupations of all atoms.



LiCoO2

The interacting and non-interacting response functions are subsequently computed using the finite differences:

$$\chi_{IJ} = \sum_m \frac{\Delta n_{mm}^I}{\Delta \alpha_J} \qquad \chi^\circ_{IJ} = \sum_m \frac{\Delta n^{\circ I}_{mm}}{\Delta \alpha_J}$$

The Hubbard U parameters are defined as

$$U^I = \left(\chi_\circ^{-1} - \chi^{-1}\right)_{II}$$

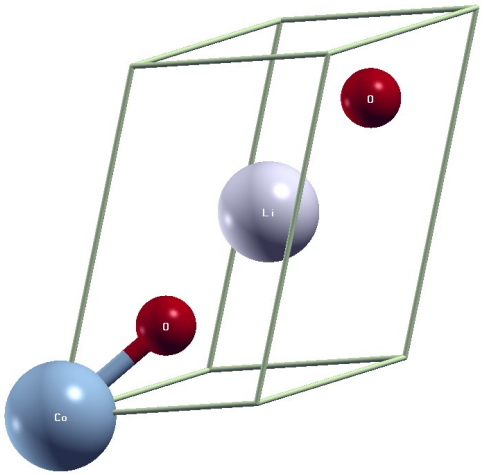
M. Cococcioni and S. de Gironcoli, Phys. Rev. B ***71****, 035105 (2005).*

Linear-response calculation of U

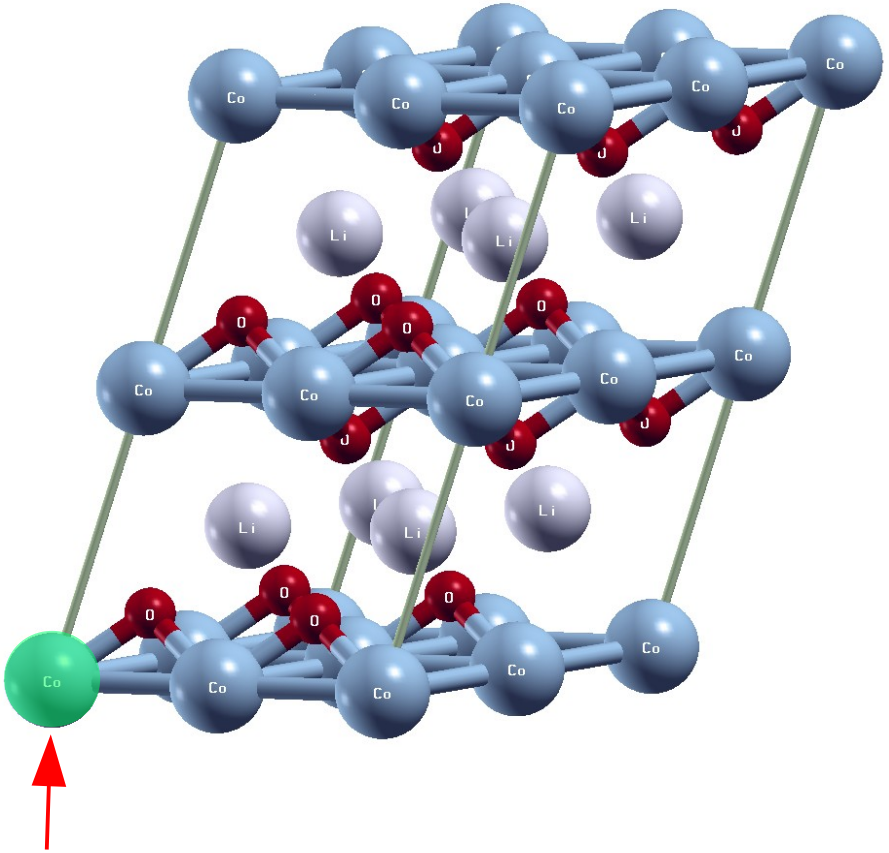
In order to compute the Hubbard U parameters for atoms, we construct a supercell, change slightly the occupations on one atom, and then measure the (linear) response of the system. This procedure must be repeated for all non-equivalent “Hubbard atoms”.

Example: LiCoO2

primitive unit cell



2x2x2 supercell



perturb Co atom & compute the responses of all atoms (including the perturbed atom itself)

Linear-response calculation of U

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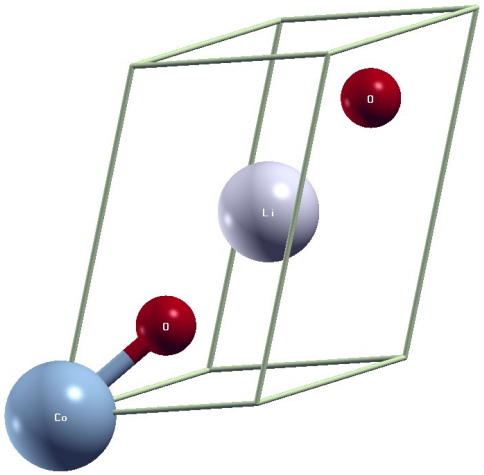
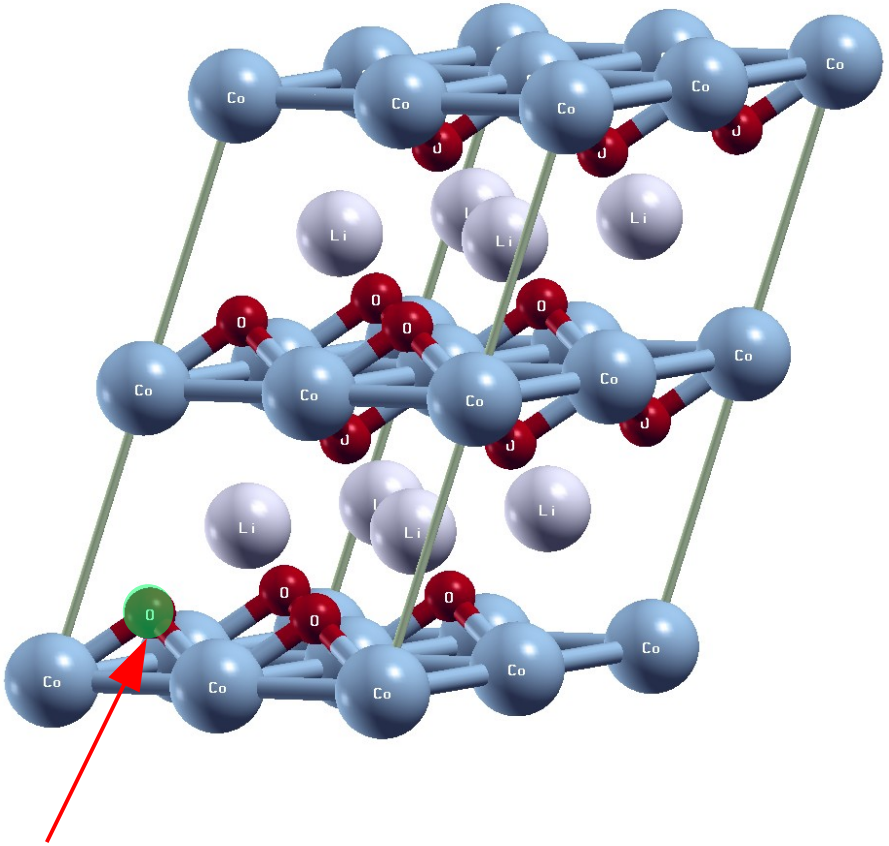


2x2x2 supercell



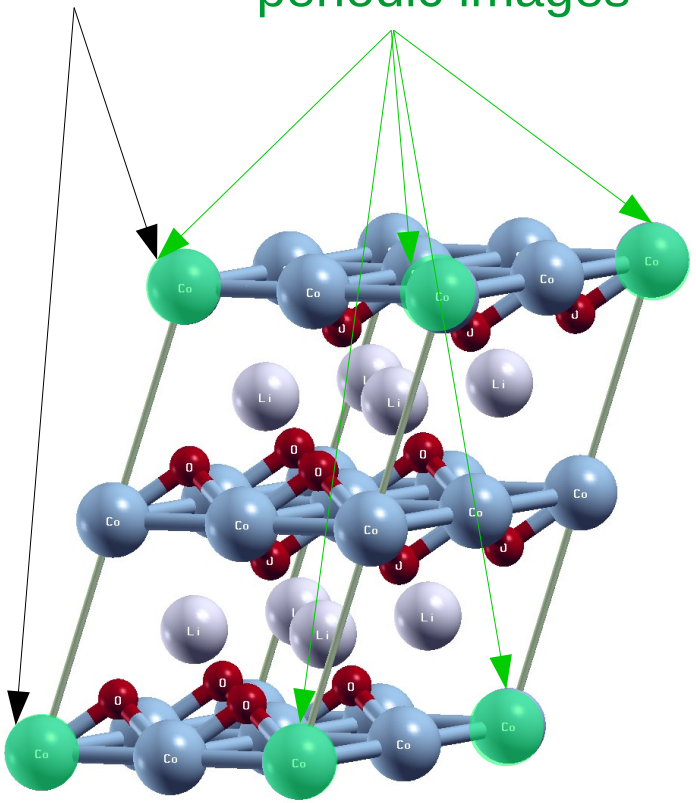
perturb O atom & compute the responses of all atoms (including the perturbed atom itself)

Linear-response calculation of U

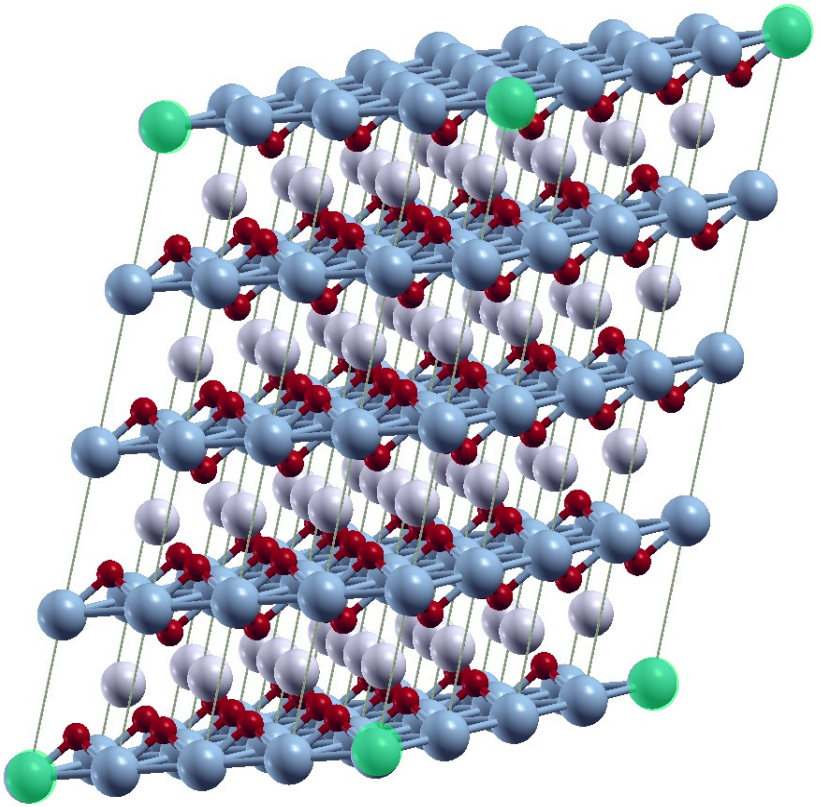
The supercell must be large enough in order to get rid of spurious interactions of the perturbed atom with its periodic image (since we are using periodic boundary conditions).

spurious interaction

periodic images



increase more



2x2x2 supercell

4x4x4 supercell

Linear-response calculation of U

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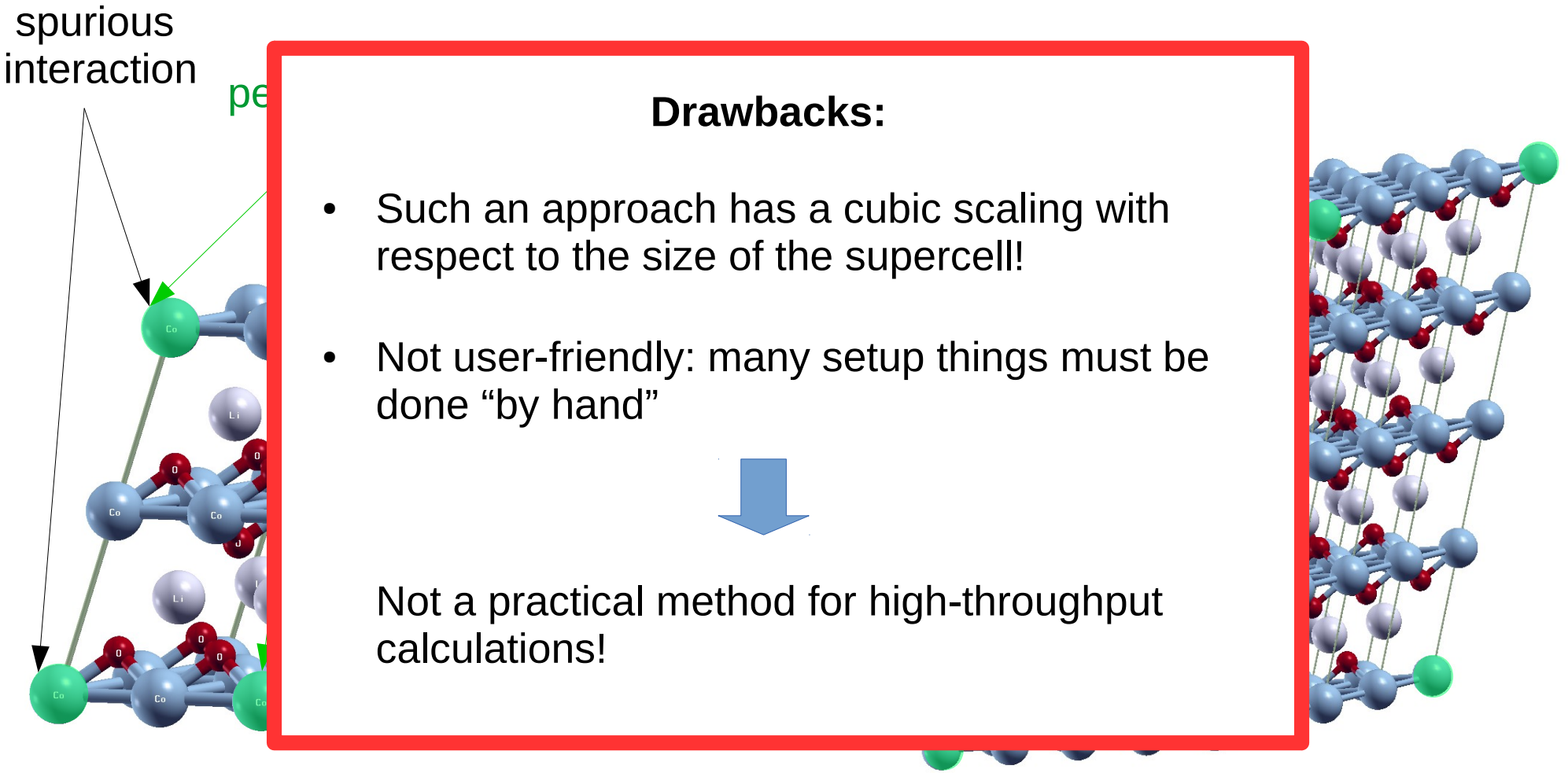

Drawbacks:

- Such an approach has a cubic scaling with respect to the size of the supercell!
- Not user-friendly: many setup things must be done “by hand”

Not a practical method for high-throughput calculations!

2x2x2 supercell

4x4x4 supercell

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Motivation

- We do not want to use supercells (cubic scaling)!

  ➔ Instead we want to use primitive unit cells with **k** points and **q** points (to mimic supercells) like in PHonon (DFPT)

- We do not want to use the finite differences method!

  ➔ Instead we want to compute the derivatives of quantities (response functions) directly like in PHonon (DFPT)

- We do not want to bother with the computational setup!

  ➔ Instead we want to have a user-friendly and automated way of computing U

U from density functional perturbation theory

The linear-response Kohn-Sham equations within DFPT read:

$$\left[-\frac{1}{2}\nabla^2 + V_{\rm KS} - \varepsilon_{i,\mathbf{k}}\right]\left|\frac{d\psi_{i,\mathbf{k}}}{d\alpha_{J,\mathbf{R}_J}}\right\rangle = -\left[\frac{dV_{\rm KS}}{d\alpha_{J,\mathbf{R}_J}} + \sum_m |\varphi_m^{J,\mathbf{R}_J}\rangle\langle\varphi_m^{J,\mathbf{R}_J}|\right]|\psi_{i,\mathbf{k}}\rangle$$

ground-state KS potential

response KS wavefunction

response KS potential

perturbation

Response occupation matrix is

$$\frac{dn_{m_1,m_2}^{I,\mathbf{R}_I}}{d\alpha_{J,\mathbf{R}_J}} = \sum_i \sum_{\mathbf{k}} \left[\langle\psi_{i,\mathbf{k}}|\varphi_{m_2}^{I,\mathbf{R}_I}\rangle\left\langle\varphi_{m_1}^{I,\mathbf{R}_I}\left|\frac{d\psi_{i,\mathbf{k}}}{d\alpha_{J,\mathbf{R}_J}}\right.\right\rangle + \left\langle\frac{d\psi_{i,\mathbf{k}}}{d\alpha_{J,\mathbf{R}_J}}\right|\varphi_{m_2}^{I,\mathbf{R}_I}\left.\right\rangle\langle\varphi_{m_1}^{I,\mathbf{R}_I}|\psi_{i,\mathbf{k}}\rangle\right]$$

Response functions are

$$\chi_{IJ}^{\circ\mathbf{R}_I,\mathbf{R}_J} = \sum_m \left(\frac{dn_{mm}^{I,\mathbf{R}_I}}{d\alpha_{J,\mathbf{R}_J}}\right)_{iter=1} \qquad \chi_{IJ}^{\mathbf{R}_I,\mathbf{R}_J} = \sum_m \frac{dn_{mm}^{I,\mathbf{R}_I}}{d\alpha_{J,\mathbf{R}_J}}$$

$$U_{IJ} = \left(\chi_{IJ}^{\circ\mathbf{R}_I,\mathbf{R}_J}\right)^{-1} - \left(\chi_{IJ}^{\mathbf{R}_I,\mathbf{R}_J}\right)^{-1}$$

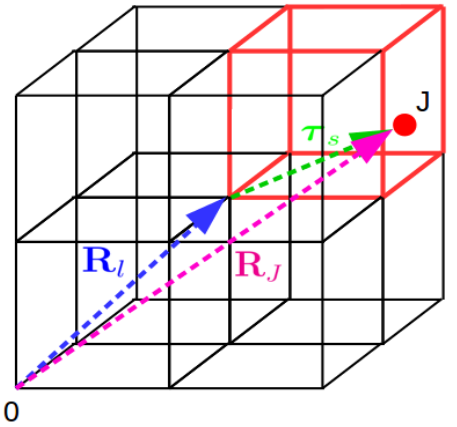
From supercells to primitive cells: use of q points grid

The response KS wavefunctions of a supercell can be represented as a sum of the response KS wavefunctions of a primitive unit cell at different wavevectors **q**.

$$\frac{d\psi_{i,\mathbf{k}}(\mathbf{r})}{d\alpha_{s,\mathbf{R}_l}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{R}_l} \, \Delta^s_{\mathbf{q}} \psi_{i,\mathbf{k}}(\mathbf{r}) \quad \Longleftrightarrow \quad \Delta^s_{\mathbf{q}} \psi_{i,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_l} e^{i\mathbf{q}\cdot\mathbf{R}_l} \, \frac{d\psi_{i,\mathbf{k}}(\mathbf{r})}{d\alpha_{s,\mathbf{R}_l}}$$

This allows us to rewrite the response occupation matrix as

$$\frac{dn^{s',\mathbf{R}'_l}_{m_1,m_2}}{d\alpha_{s,\mathbf{R}_l}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}'_l - \mathbf{R}_l)} \, \Delta^s_{\mathbf{q}} n^{s'}_{m_1,m_2}$$



2x2x2 supercell

where for every **q** vector we have

$$\Delta^s_{\mathbf{q}} n^{s'}_{m_1,m_2} = \frac{1}{N} \sum_i \sum_{\mathbf{k}} \left[\langle u_{i,\mathbf{k}} | \phi^{s'}_{m_1,\mathbf{k}} \rangle \langle \phi^{s'}_{m_2,\mathbf{k}+\mathbf{q}} | \Delta^s_{\mathbf{q}} u_{i,\mathbf{k}} \rangle + \langle u_{i,\mathbf{k}} | \phi^{s'}_{m_2,\mathbf{k}} \rangle \langle \phi^{s'}_{m_1,\mathbf{k}+\mathbf{q}} | \Delta^s_{\mathbf{q}} u_{i,\mathbf{k}} \rangle \right]$$

Implementation

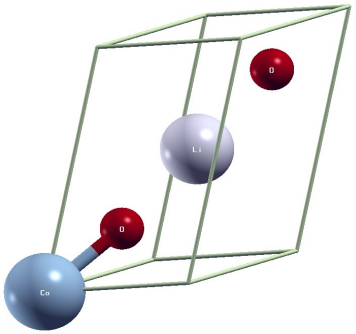
The new method is implemented in the development version of **Quantum ESPRESSO**.

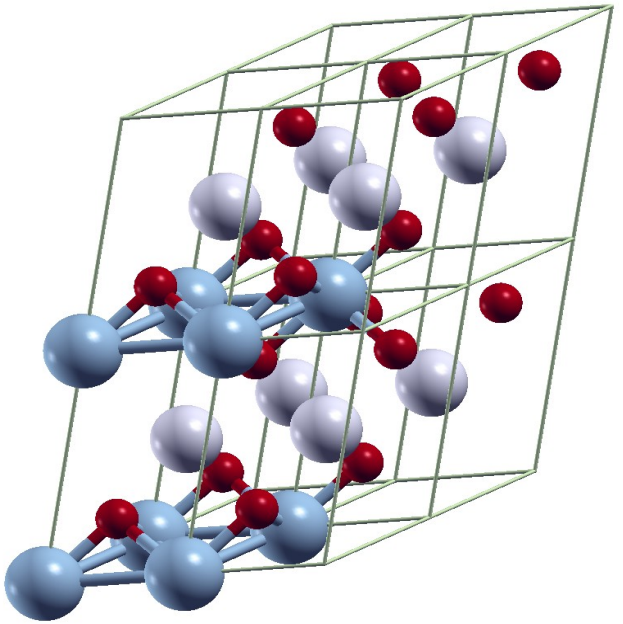
Currently it can be used:

- With norm-conserving as well as with ultra-soft pseudopotentials
- For insulators as well as for metals
- For spin-unpolarized as well as for spin-polarized systems
- Using symmetry
- Using parallelization over plane waves and **k** points
- For uniform (symmetry allowed) and non-uniform (symmetry not allowed) **q** point grids

Testing: DFPT vs constrained-DFT

Example: LiCoO2





primitive unit cell (4 atoms)

k points grid: 2x2x2

q points grid: 2x2x2

2x2x2 supercell (32 atoms)

k = 0

Testing: DFPT vs constrained-DFT

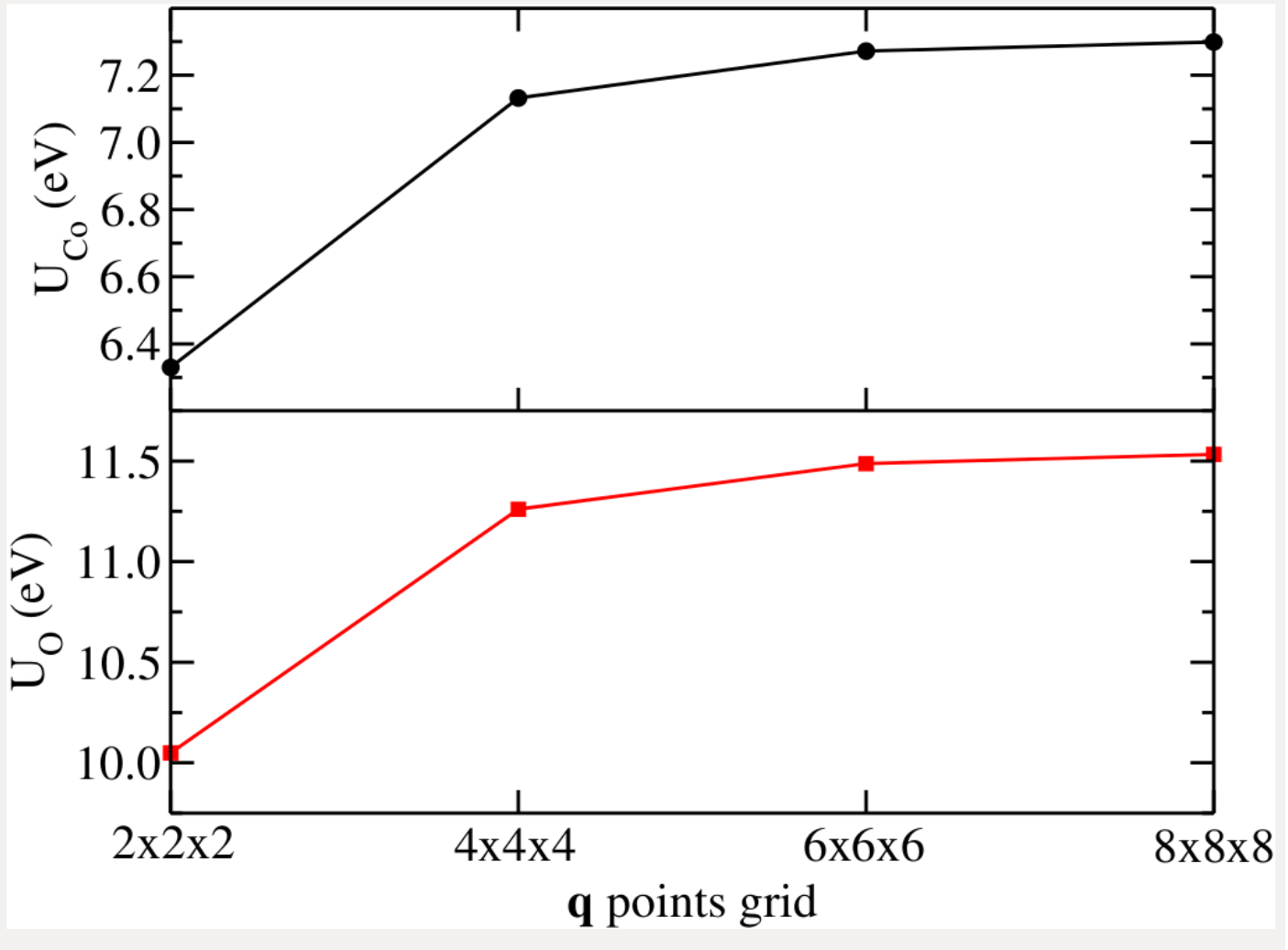
System	Type	Constrained-DFT	DFPT
LiCoO2	insulator non-magnetic	U (Co) = 6.406 (eV) U (O) = 12.538 (eV)	U (Co) = 6.404 (eV) U (O) = 12.534 (eV)
NiO	insulator magnetic	U (Ni) = 5.295 (eV) U (O) = 18.980 (eV)	U (Ni) = 5.298 (eV) U (O) = 18.985 (eV)
Ag	metal non-magnetic	U (Ag) = 53.815 (eV)	U (Ag) = 53.812 (eV)
Ni	metal magnetic	U (Ni) = 5.787 (eV)	U (Ni) = 5.787 (eV)

These value of U are not converged! This is just a check between two methods.

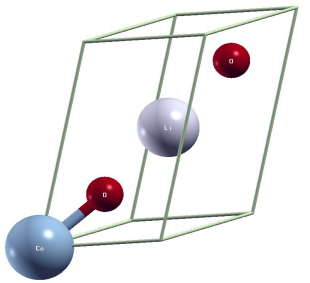
The agreement between two methods is excellent!

Convergence

The convergence procedure with respect to the density of the **q** points grid is very straightforward and fully automated, which is not the case when using the supercell approach.



LiCoO2



k points grid: 6x6x6

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Conclusions

The new method has several advantages over the traditional linear-response method:

- It scales linearly with the number of **q** points, which is much better than cubic scaling of a supercell;
- It is easy to perform convergence tests of U with respect to the size of the **q** points grid;
- It is possible to control the accuracy of U by converging the response functions to a threshold specified by the user, which is not possible with the finite differences;
- It is user-friendly and automated, which allows us to perform highthroughput calculations for thousands of materials.

Future work

- Currently the code is implemented in Quantum ESPRESSO 5.0.2.
  Port the code to the latest version of QE (make dependencies on **LR_Modules**).
- Further methodological developments:
  - more generic perturbations, which would allow us to avoid inversions of response matrices;
  - possibility to treat closed-shell systems and compute magnetic interactions.

Thank you for your attention!