THEOS
THEORY AND SIMULATION OF MATERIALS

MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Hubbard interactions from density functional perturbation theory

Iurii Timrov

Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL),
École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Joint Annual Meeting of SPS and ÖPG

Session: Correlated-Electron Physics in Transition-Metal Oxides

Genève, Switzerland

24 August 2017

Outline

1. Introduction

2. Constrained DFT linear-response method to compute *U*

3. New method to compute *U* based on DFPT

4. Conclusions

Outline

1. Introduction

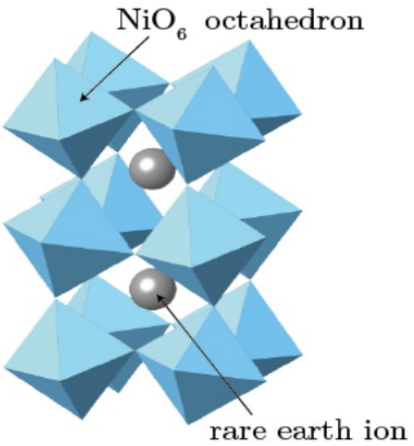
2. Constrained DFT linear-response method to compute *U*

3. New method to compute *U* based on DFPT

4. Conclusions

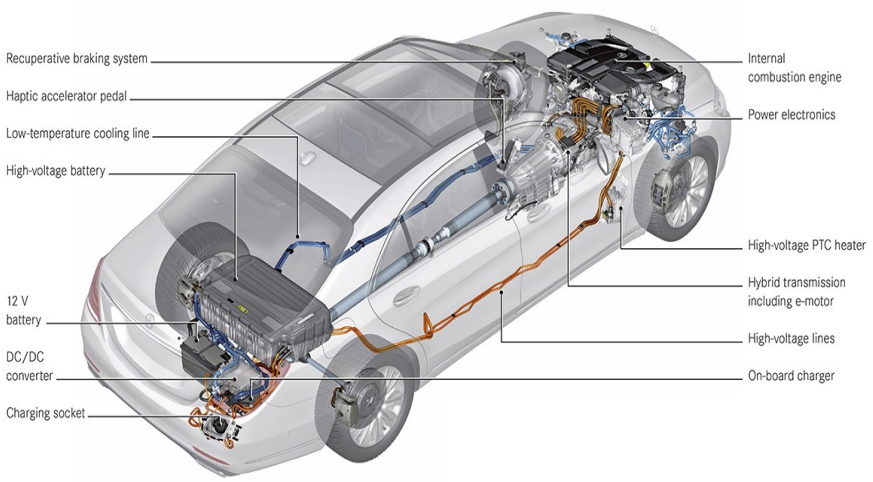
Technological importance of transition-metal compounds (TMCs)

Rare-earth nickelates

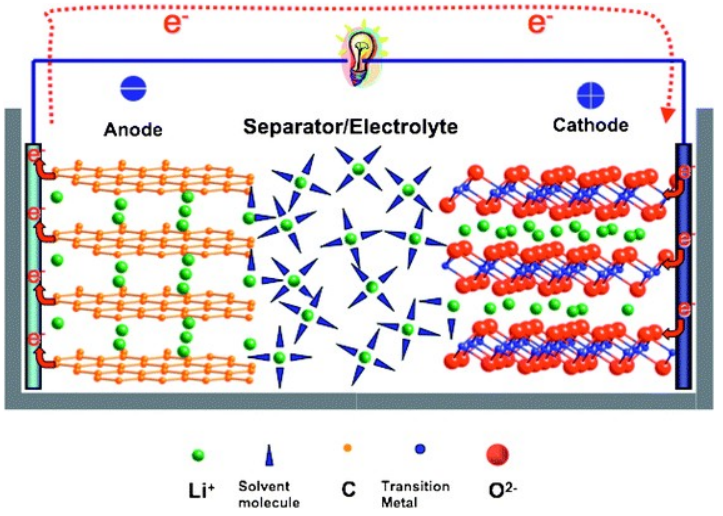


Magnets for generators

Batteries for hybrid cars



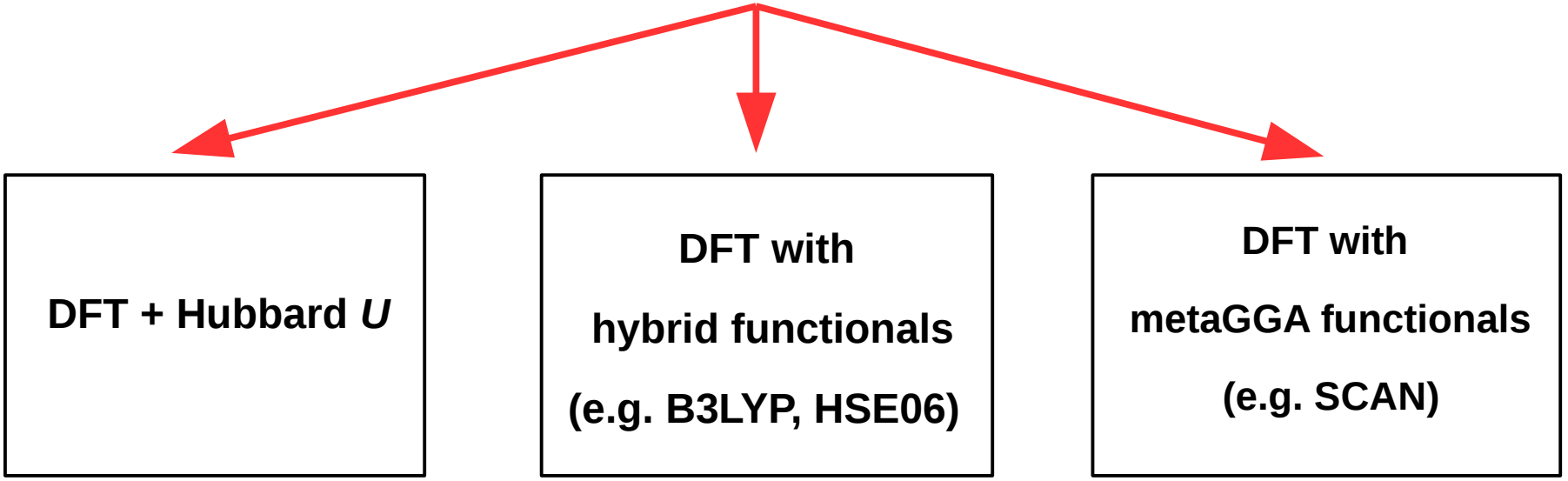
Lithium-ion batteries



Going beyond DFT-LDA (and GGA) to model TMCs

Problem in DFT-LDA (GGA): Overdelocalization of *d*- and *f*-type electrons due to large self-interaction errors

Methods



Anisimov et al., 1991

Becke, 1993
Perdew et al., 1996
Heyd et al., 2006

Perdew et al., 2015

This talk: DFT + *U* → Hubbard *U* is unknown...

DFT + *U* in a nutshell

The DFT total energy is corrected by the Hubbard term:

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

Simplified rotationally invariant scheme [*Dudarev et al., Phys. Rev. B 57, 1505 (1998)*]:

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

Occupation matrices (Plane-Wave-based codes):

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

Modified Kohn-Sham equations:

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

The Hubbard potential:

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

DFT + *U* in a nutshell

The DFT total energy is corrected by the Hubbard term:

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

Simplified rotationally invariant scheme [*Dudarev et al., Phys. Rev. B 57, 1505 (1998)*]:

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

???

Occupation matrices (Plane-Wave-based codes):

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

Modified Kohn-Sham equations:

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

The Hubbard potential:

???

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

Which *U* to use?

- **Empirical *U*** ⇒ fitting to the experimental data (if it is available)

  Drawback: *This approach is not predictive! And it is not fully ab initio!*

- ***Ab initio* calculation of *U***

  - Constrained DFT approach (cDFT)

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

  - Constrained RPA approach (cRPA)

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

  - Hartree-Fock (HF) based approaches (e.g. unrestricted HF, ACBN0)

    [*Mosey & Carter (2007, 2008), Andriotis et al. (2010), Agapito et al. (2015)*]

Drawback: *Many of these approaches are computationally expensive and cumbersome to use and hence new more efficient approaches are desirable.*

Outline

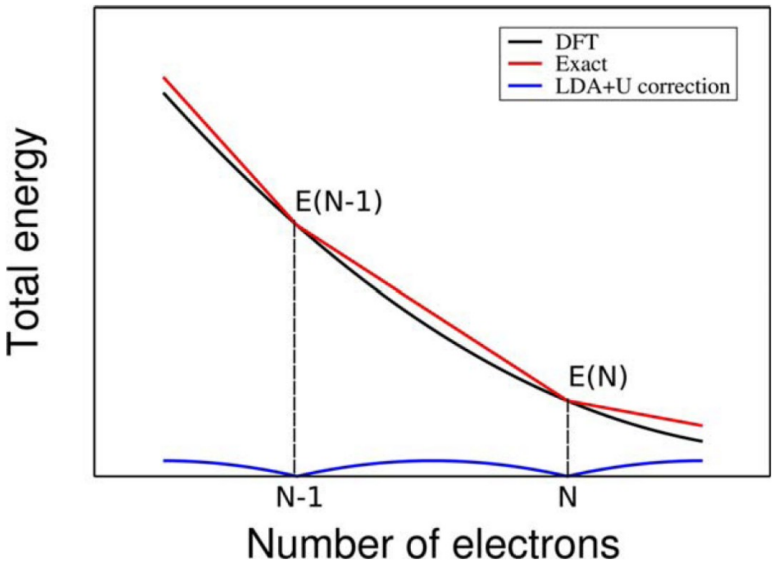
1. Introduction

2. Constrained DFT linear-response method to compute *U*

3. New method to compute *U* based on DFPT

4. Conclusions

Linear-response calculation of U



U is chosen to correct the curvature of the total energy with respect to the occupation of the Hubbard manifold:

$$U^I \equiv \frac{d^2 E_{\mathrm{DFT}}}{dn^2} - \frac{d^2 E^{\circ}_{\mathrm{DFT}}}{dn^2} = \left((\chi^{\circ})^{-1} - \chi^{-1} \right)_{II}$$

Interacting and non-interacting response matrices:

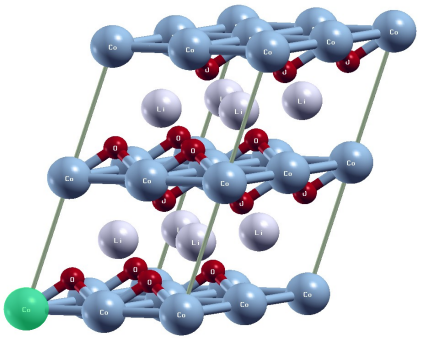
$$\chi_{IJ} = \sum_m \frac{dn^I_{mm}}{d\alpha_J}, \qquad \chi^{\circ}_{IJ} = \sum_m \frac{dn^{\circ I}_{mm}}{d\alpha_J}$$

Linear-response calculation of *U* using cDFT

The Kohn-Sham equations with a perturbing atomic potential:

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

Change of occupation matrices $\Delta n^I_{m_1 m_2}$



Interacting and non-interacting response functions:

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

Hubbard *U* parameters:

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

All derivatives are computed using the finite differences method.

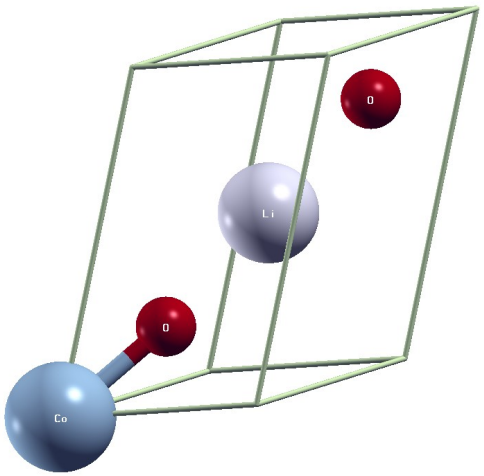
*M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).*

Linear-response calculation of *U* using cDFT

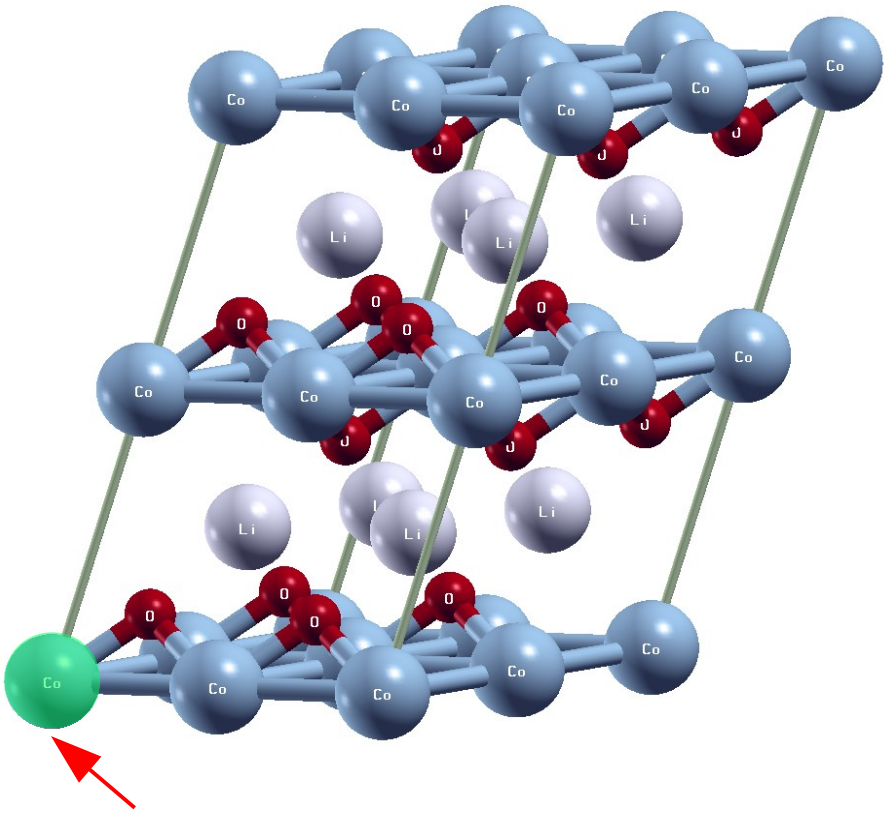
Isolated perturbation → Need of supercells

primitive unit cell

LiCoO2



2x2x2 supercell



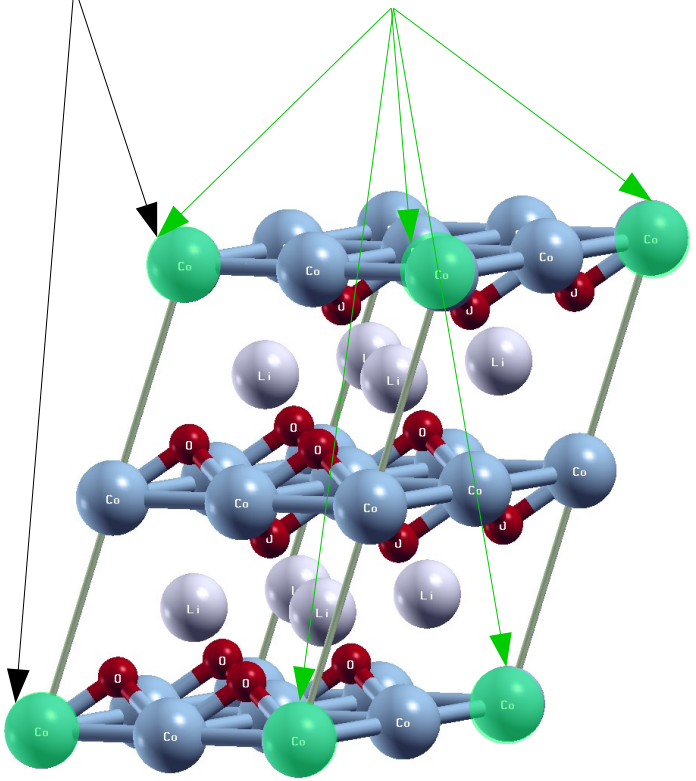
perturb an atom & compute the responses of all atoms (including the perturbed atom itself)

Linear-response calculation of *U* using cDFT

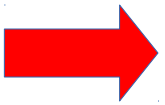
Hubbard *U* must be converged with respect to the supercell size!

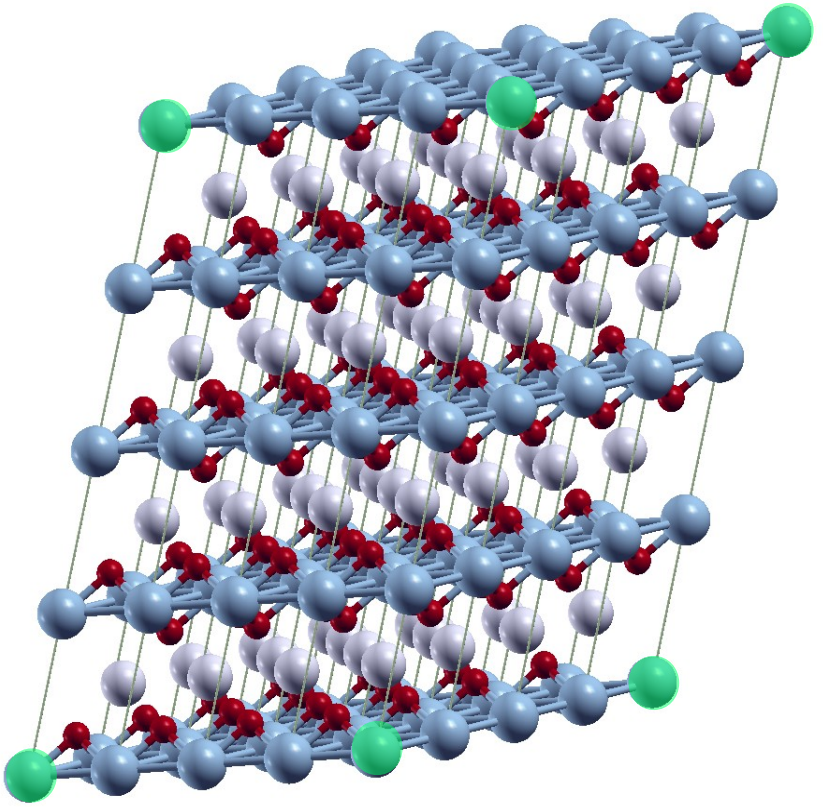
spurious interaction

periodic images



increase more





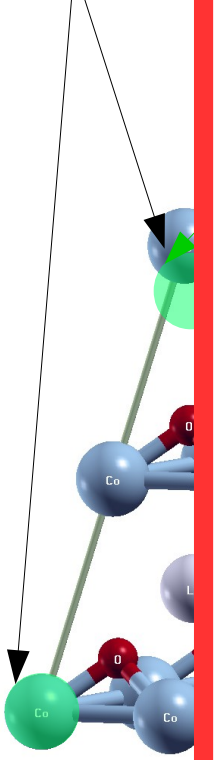
2x2x2 supercell

4x4x4 supercell

Linear-response calculation of *U* using cDFT

Hubbard *U* must be converged with respect to the supercell size!

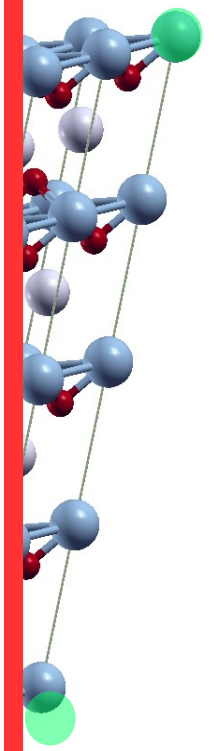
spurious interaction



Drawbacks:

- Supercells are needed → high computational cost (cubic scaling)
- Finite differences → limited accuracy of *U*
- Post-processing is cumbersome in practice

Not a practical method for high-throughput calculations!



2x2x2 supercell

4x4x4 supercell

Outline

1. Introduction

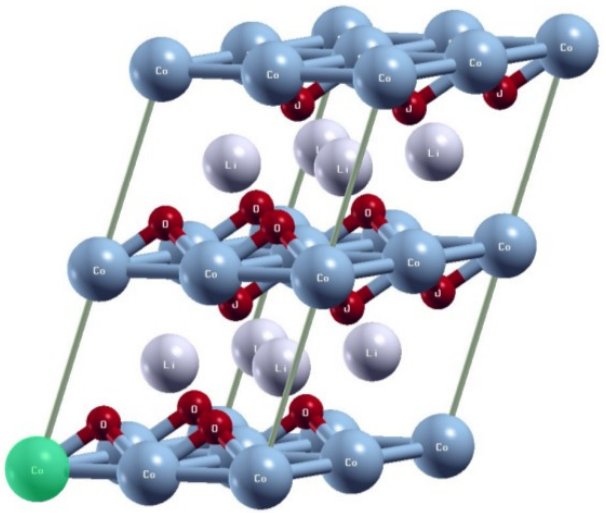
2. Constrained DFT linear-response method to compute *U*

3. New method to compute *U* based on DFPT

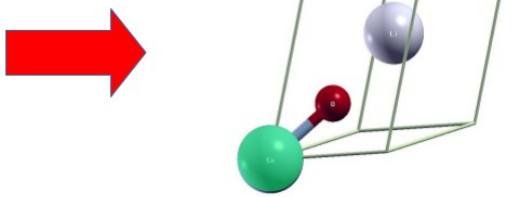
4. Conclusions

General idea

Recasting of the Gamma point perturbation in a supercell as a sum of monochromatic perturbations in a primitive cell using density functional perturbation theory (DFPT).

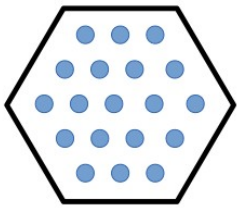


Supercell + Gamma point



Primitive cell

+



q points sampling of Brillouin zone

I. Timrov, M. Cococcioni and N. Marzari, in preparation.

U from DFPT

Linear response occupation matrices:

$$\frac{dn^I_{m_1 m_2}}{d\alpha_J} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_I - \mathbf{R}_J)} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}}^{N_{\mathbf{k}}} \sum_{i}^{N_{\mathrm{v}}} \Big[\langle u_{i,\mathbf{k}} | \varphi^I_{m_1,\mathbf{k}} \rangle \langle \varphi^I_{m_2,\mathbf{k}+\mathbf{q}} | \Delta^J_{\mathbf{q}} u_{i,\mathbf{k}} \rangle + (m_1 \leftrightarrow m_2) \Big]$$

U from DFPT

Linear response occupation matrices:

$$\frac{dn^I_{m_1 m_2}}{d\alpha_J} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_I - \mathbf{R}_J)} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}}^{N_{\mathbf{k}}} \sum_{i}^{N_{\mathrm{v}}} \left[\langle u_{i,\mathbf{k}} | \varphi^I_{m_1,\mathbf{k}} \rangle \langle \varphi^I_{m_2,\mathbf{k}+\mathbf{q}} | \Delta^J_{\mathbf{q}} u_{i,\mathbf{k}} \rangle + (m_1 \leftrightarrow m_2) \right]$$

Solution of linear response Kohn-Sham equations (for every **q**):

$$\left[\frac{(-i\nabla + \mathbf{k} + \mathbf{q})^2}{2} + V^{\mathbf{k}+\mathbf{q}}_{\mathrm{KS}} - \varepsilon_{i,\mathbf{k}} \right] |\Delta^J_{\mathbf{q}} u_{i,\mathbf{k}}\rangle = -\left[\Delta^J_{\mathbf{q}} V^{\mathbf{k}+\mathbf{q}}_{\mathrm{KS}} + \sum_m |\varphi^J_{m,\mathbf{k}+\mathbf{q}}\rangle \langle \varphi^J_{m,\mathbf{k}}| \right] |u_{i,\mathbf{k}}\rangle$$

U from DFPT

Linear response occupation matrices:

$$\frac{dn^I_{m_1 m_2}}{d\alpha_J} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_I - \mathbf{R}_J)} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}}^{N_{\mathbf{k}}} \sum_{i}^{N_{\mathrm{v}}} \left[\langle u_{i,\mathbf{k}} | \varphi^I_{m_1,\mathbf{k}} \rangle \langle \varphi^I_{m_2,\mathbf{k}+\mathbf{q}} | \Delta^J_{\mathbf{q}} u_{i,\mathbf{k}} \rangle + (m_1 \leftrightarrow m_2) \right]$$

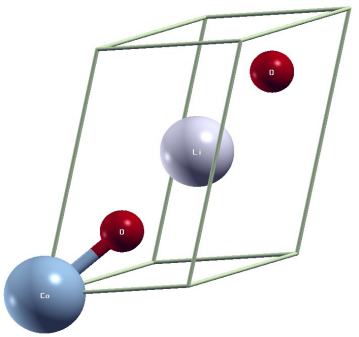
Solution of linear response Kohn-Sham equations (for every **q**):

$$\left[\frac{(-i\nabla + \mathbf{k} + \mathbf{q})^2}{2} + V^{\mathbf{k}+\mathbf{q}}_{\mathrm{KS}} - \varepsilon_{i,\mathbf{k}} \right] |\Delta^J_{\mathbf{q}} u_{i,\mathbf{k}}\rangle = -\left[\Delta^J_{\mathbf{q}} V^{\mathbf{k}+\mathbf{q}}_{\mathrm{KS}} + \sum_m |\varphi^J_{m,\mathbf{k}+\mathbf{q}}\rangle\langle\varphi^J_{m,\mathbf{k}}| \right] |u_{i,\mathbf{k}}\rangle$$

Advantages:

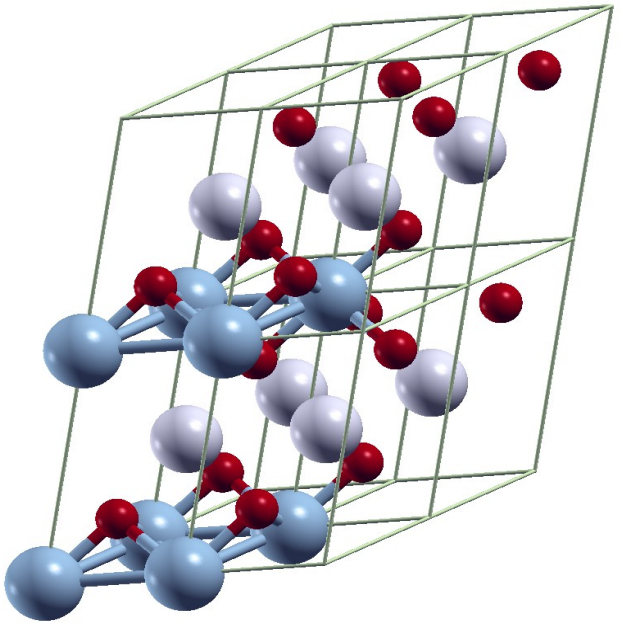
- No need for supercells or finite differences;
- Linear scaling with respect to the number of **q** points;
- Higher control of accuracy in calculation of *U*;
- User-friendly and automated ⇒ high-throughput calculations.

Testing: DFPT vs cDFT



LiCoO2

equivalent



primitive unit cell (4 atoms)

k points grid: 2x2x2

q points grid: 2x2x2

2x2x2 supercell (32 atoms)

k = 0

q = 0

Testing: DFPT vs cDFT

$LiCoO_2$

	1x1x1	2x2x2	3x3x3	4x4x4
DFPT	*U*=8.367	*U*=7.734	*U*=7.541	*U*=7.559
cDFT	*U*=8.367	*U*=7.732	*U*=7.539	*U*=7.555

Cu_2O

	1x1x1	2x2x2	3x3x3	4x4x4
DFPT	*U*=8.819	*U*=10.994	*U*=11.300	*U*=11.299
cDFT	*U*=8.821	*U*=10.992	*U*=11.298	*U*=11.295

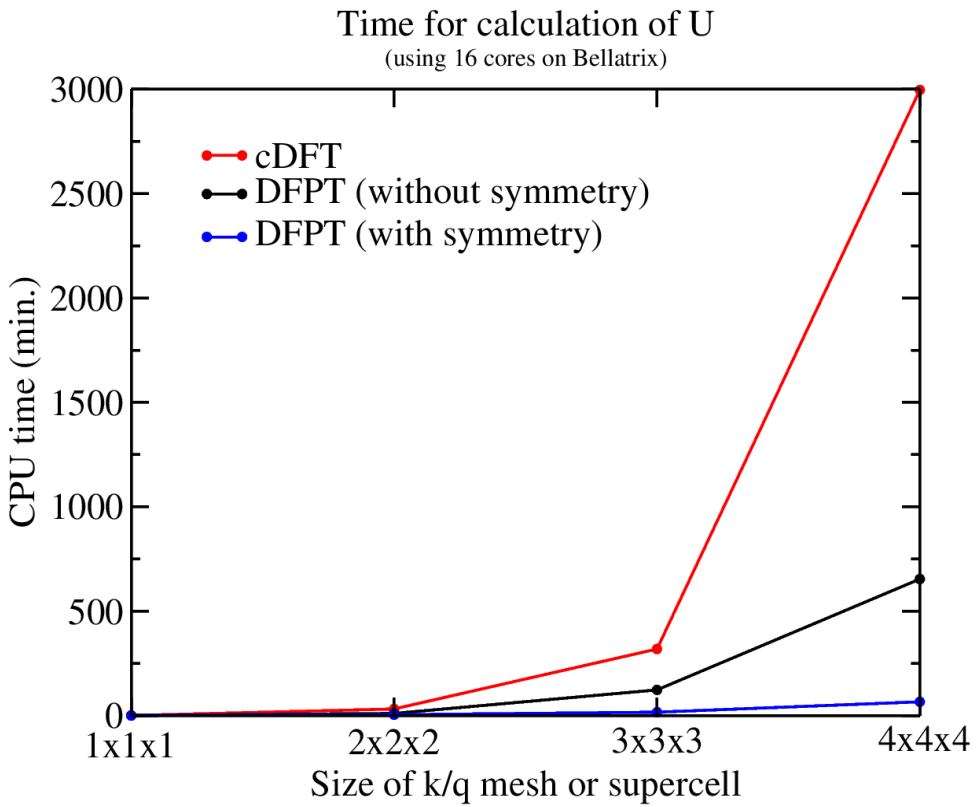
NiO

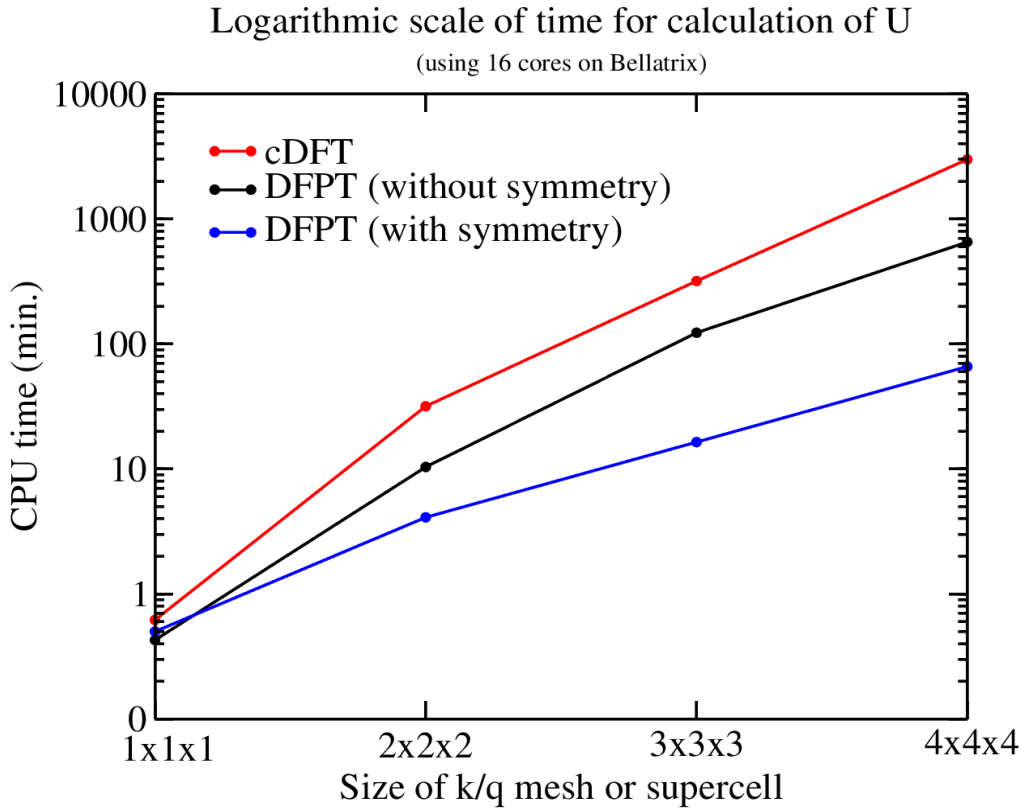
	1x1x1	2x2x2	3x3x3	4x4x4
DFPT	*U*=10.087	*U*=7.938	*U*=8.139	*U*=8.062
cDFT	*U*=10.087	*U*=7.938	*U*=8.137	*U*=8.061

The agreement between the two methods is excellent!

Scaling: DFPT vs cDFT

Test case: $LiCoO_2$

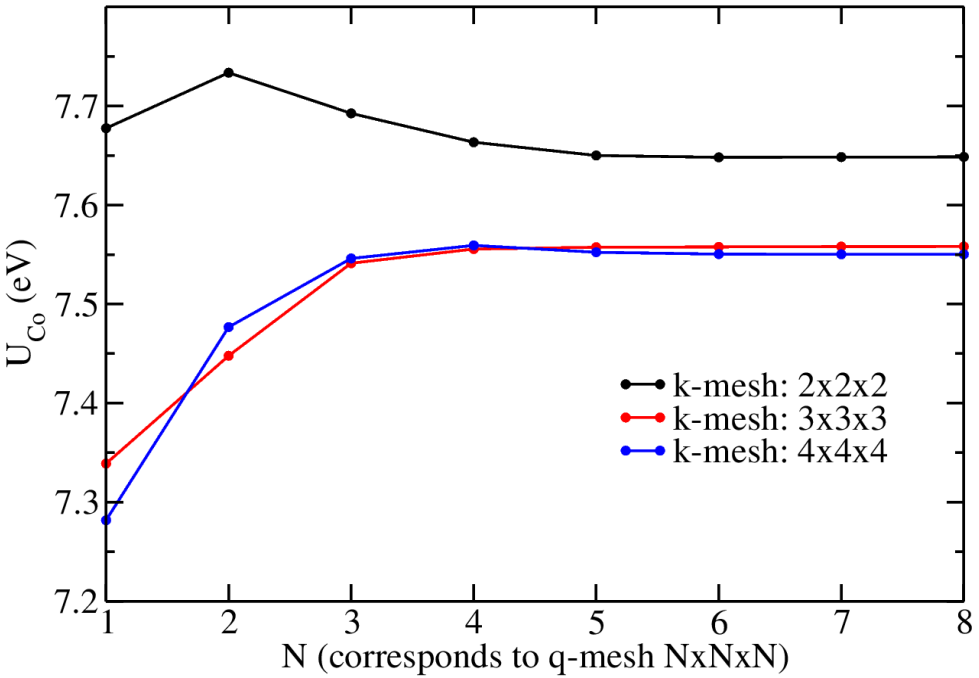


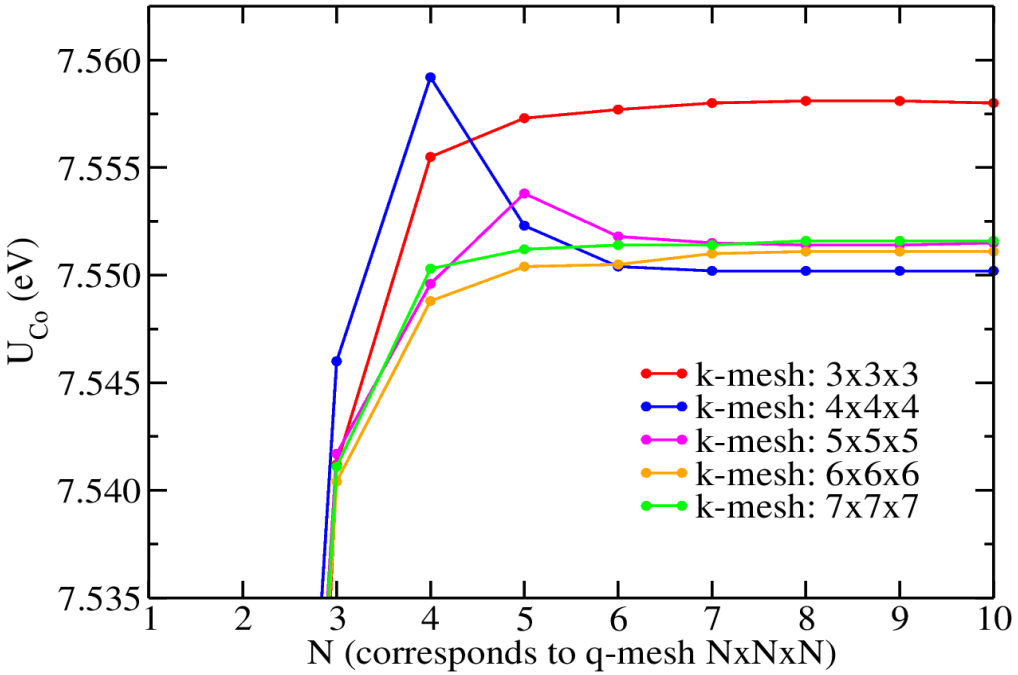


$LiCoO_2$: Convergence of *U* wrt k and q points

k-mesh ⇒ ground-state properties (e.g. charge density)

q-mesh ⇒ monochromatic perturbations





U = 7.55 (eV) with the accuracy 0.01 (eV).

This accuracy is achieved with the k-mesh 5x5x5 and q-mesh 4x4x4.

Conclusions

Calculation of *U* from DFPT:

- No need of supercells and finite differences;
- Monochromatic perturbations → linear scaling with the number of **q** points;
- Easy and convenient convergence tests of *U* with respect to **q** points;
- Higher control on accuracy of *U*;
- Improved user-friendliness and automation: suitability for high-throughput calculations.

Thanks to

Matteo Cococcioni

Nicola Marzari

… and you for your attention!