First-principles calculation of Hubbard parameter using linear-response theory

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ICTP-MARVEL College, 5 June 2026

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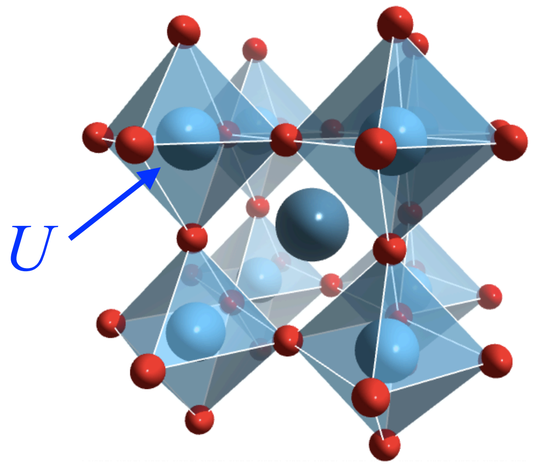
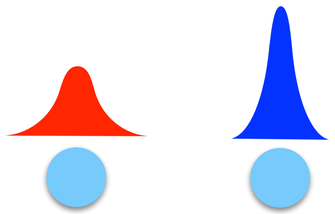
DFT+U(+V)

DFT+*U* : $$E = E_{\mathrm{DFT}} + \frac{1}{2}\sum_{I,\sigma} U^I \,\mathrm{Tr}\left[\left(\mathbf{1} - \mathbf{n}^{I\sigma}\right)\mathbf{n}^{I\sigma}\right] \qquad \left(\mathbf{n}^{I\sigma}\right)_{m_1 m_2} = \sum_i f_i \left\langle \psi_{i\sigma} | \varphi^I_{m_2} \right\rangle \left\langle \varphi^I_{m_1} | \psi_{i\sigma} \right\rangle$$



atomic localisation



DFT DFT+*U*

Dudarev et al., Phys. Rev. B (1998).

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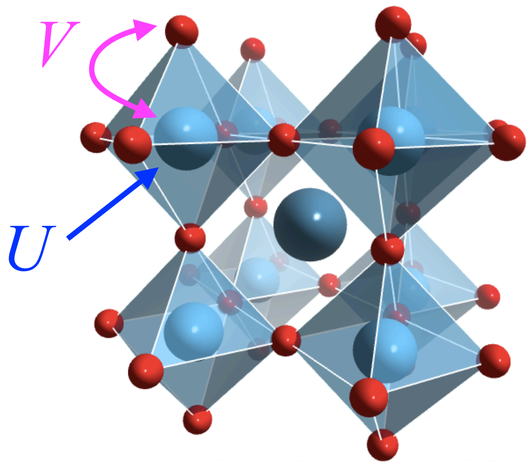
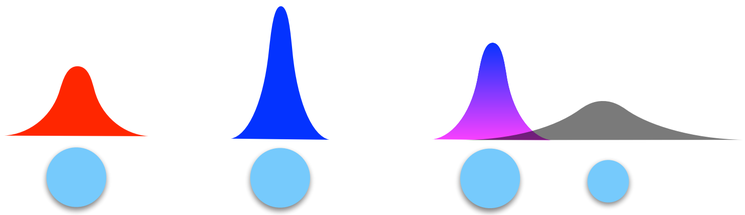
DFT+*U*+*V* : $$E = E_{\mathrm{DFT}} + \frac{1}{2}\sum_{I,\sigma} U^I \,\mathrm{Tr}\left[\left(\mathbf{1} - \mathbf{n}^{I\sigma}\right)\mathbf{n}^{I\sigma}\right] - \frac{1}{2}\sum_{I,J,\sigma} V^{IJ}\,\mathrm{Tr}\left[\mathbf{n}^{IJ\sigma}\mathbf{n}^{JI\sigma}\right]$$



atomic localisation &
inter-atomic hybridisations



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Campo Jr and Cococcioni, J. Phys.: Condens. Matter (2010).

Hubbard parameters and Hubbard projectors

Hubbard parameters and Hubbard projectors

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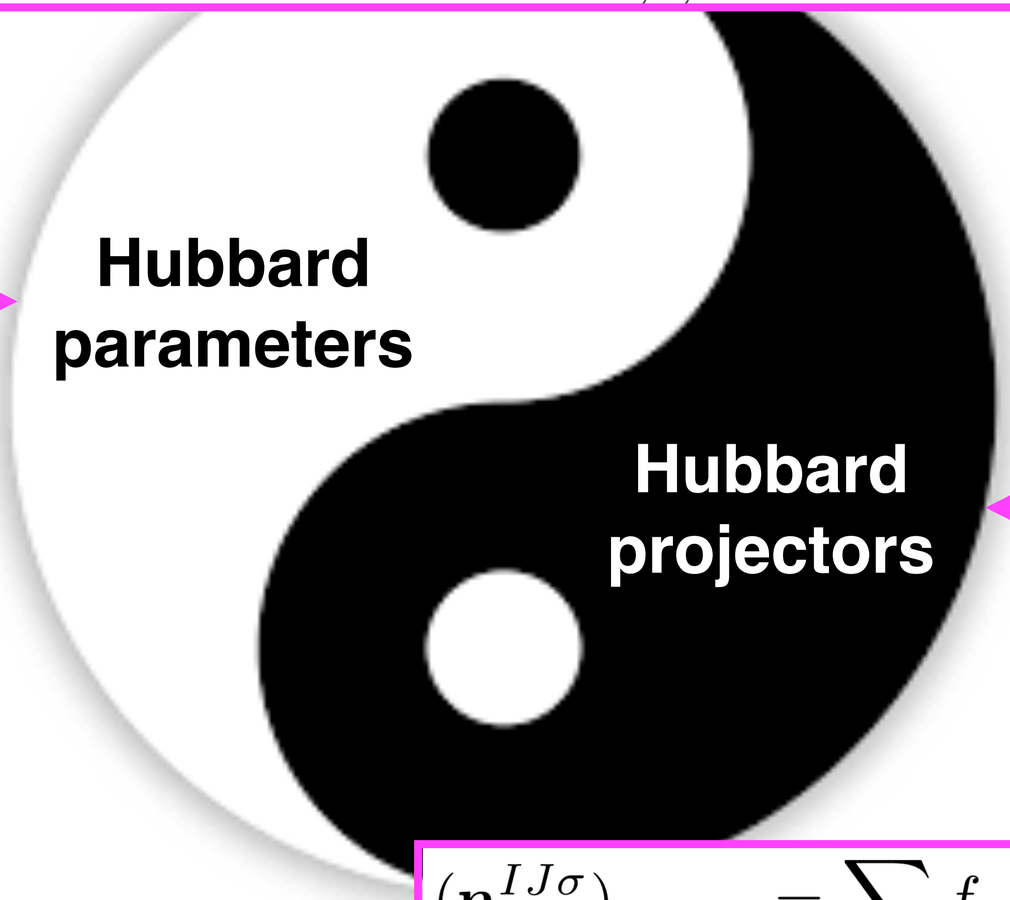

$$(\mathbf{n}^{IJ\sigma})_{m_1 m_2} = \sum_i f_i \,\langle\psi_{i\sigma}|\varphi^J_{m_2}\rangle\langle\varphi^I_{m_1}|\psi_{i\sigma}\rangle$$

How to determine Hubbard parameters?

Strategies

Fitting to experiments	Fitting to other advanced methods	First-principles calculations
magnetic moments	HSE06	Linear response theory (LRT)
band gaps	PBE0	constrained RPA (cRPA)
oxidation enthalpies	GW	Hartree-Fock (ACBN0)

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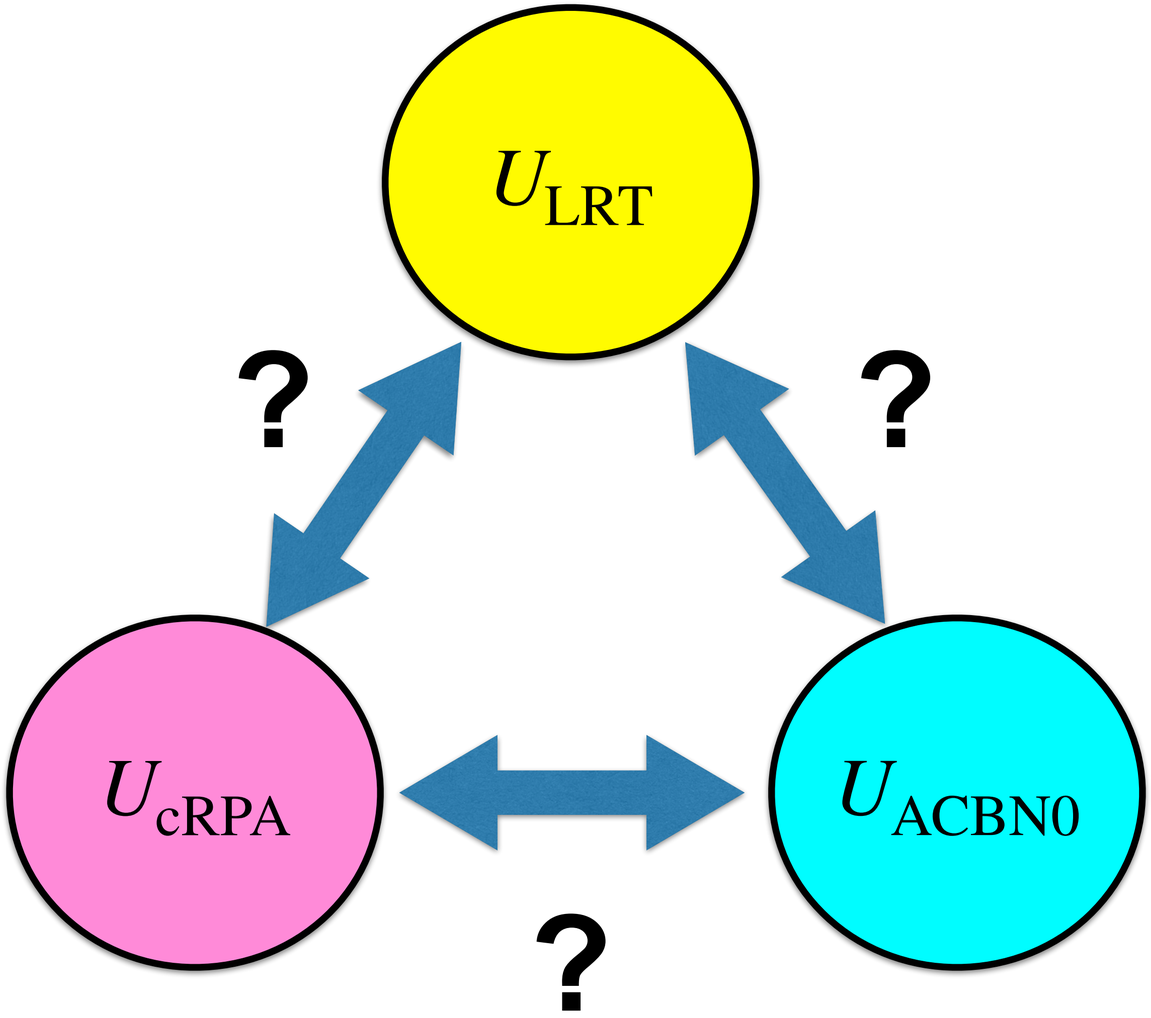
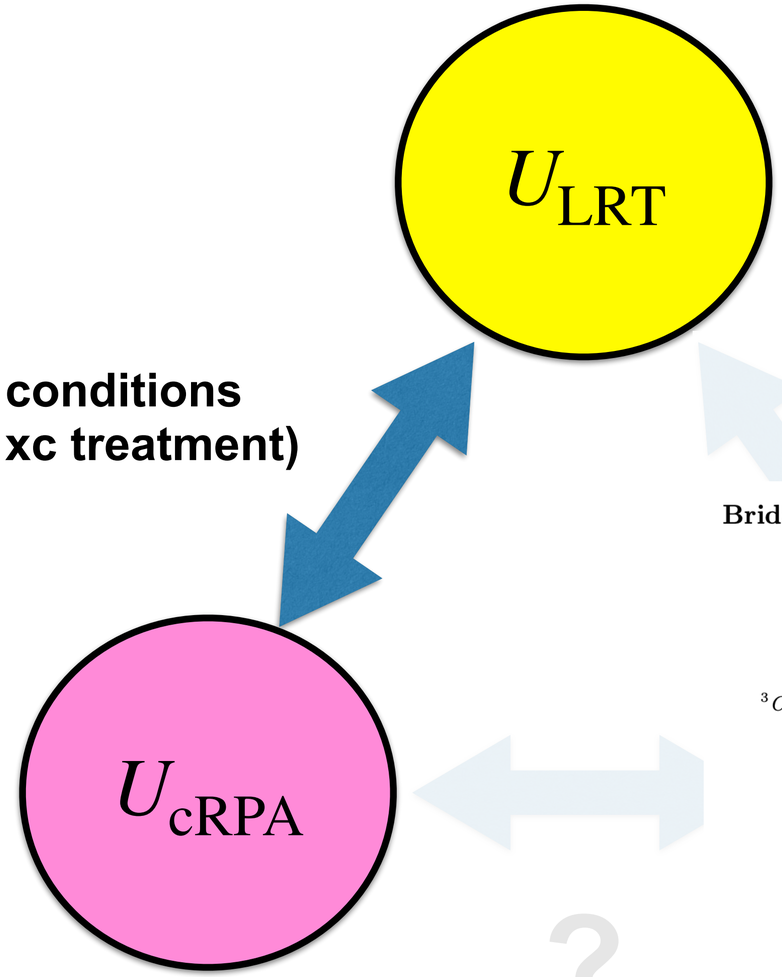
machine learning

Are the U values the same from different methods?



Are the U values the same from different methods?



Yes, under certain conditions (coarse graining and xc treatment)

accepted to PRL

Bridging constrained random-phase approximation and linear response theory for computing Hubbard parameters

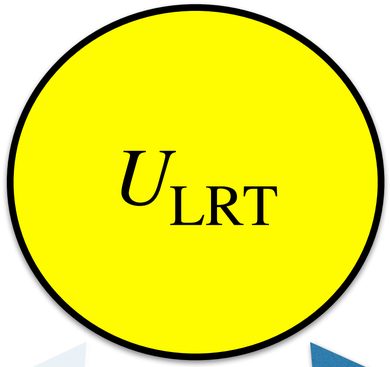
Alberto Carta,[1,2,*] Iurii Timrov,[2,†] Sophie Beck,[3] and Claude Ederer[1,‡]

[1] *Materials Theory, ETH Zürich, Wolfgang-Pauli-Strasse 27, 8093 Zürich, Switzerland*
[2] *PSI Center for Scientific Computing, Theory, and Data, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*
[3] *Center for Computational Quantum Physics, Flatiron Institute, 162 5th Avenue, New York, NY 10010, USA*

(Dated: December 24, 2025)

The predictive accuracy of popular extensions to density-functional theory (DFT) such as DFT+U and DFT plus dynamical mean-field theory (DFT+DMFT) hinges on using realistic values for the screened Coulomb interaction U. Here, we present a systematic comparison of the two most widely used approaches to compute this parameter, *i.e.* linear response theory (LRT) and the constrained random-phase approximation (cRPA), using a unified framework based on the use of maximally localized Wannier functions. We show that the U in LRT and cRPA can differ as much as 30%. We demonstrate that this discrepancy arises from two main differences: neglecting the response of the exchange-correlation potential in cRPA and additional excitation channels in LRT. By taking these differences into account, we can achieve near perfect agreement between the two techniques. Moreover, we show that in cases with strong hybridization between interacting and screening subspaces, the application of cRPA becomes ambiguous and can lead to unrealistically small U values, while LRT remains well-behaved. Our work formally connects both methods, sheds light on their strengths and limitations, and emphasizes the importance of using a consistent set of Wannier orbitals to ensure transferability of U values between different implementations.

Are the U values the same from different methods?



Similar for partially filled states
and
Very different for nearly empty
or fully filled states

npj | computational materials **(in press)**

Article | Open access | Published: 16 May 2026

Comparing Hubbard parameters from linear-response theory and a Hartree-Fock-based approach

Wooil Yang, Iurii Timrov ✉, Francesco Aquilante & Young-Woo Son ✉

npj Computational Materials (2026) | Cite this article

Hubbard parameters are not universal

Computed Hubbard parameters depend on:

- **Type of Hubbard projector functions** (e.g. atomic, Wannier, etc.)

$$(\mathbf{n}^{I\sigma})_{m_1 m_2} = \sum_i f_i \langle \psi_{i\sigma} | \varphi^I_{m_2} \rangle \langle \varphi^I_{m_1} | \psi_{i\sigma} \rangle$$

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- **Pseudopotential and the oxidation state**

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- **Pseudopotential and the oxidation state**

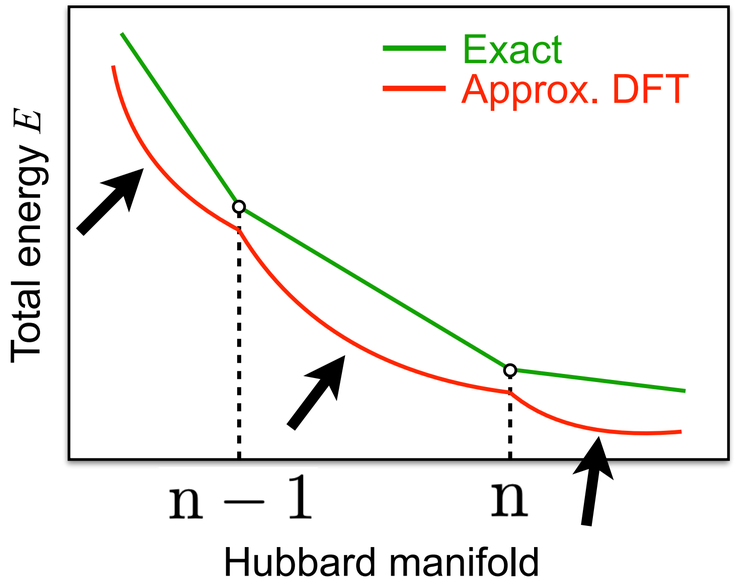
- **Exchange-correlation functional** (e.g. LDA, GGA, etc.)

- **Self-consistency** (i.e. either “one-shot” or self-consistent)

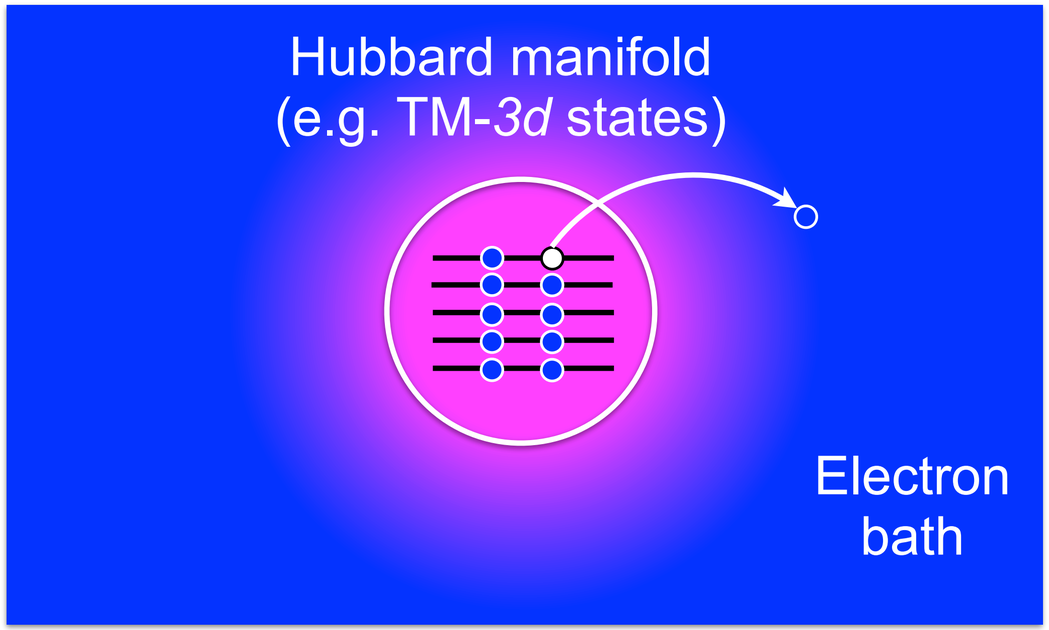
Hubbard U from linear response theory (LRT)

$$E = E_{\mathrm{DFT}} + \frac{1}{2} U \,\mathrm{Tr}\left[(\mathbf{1} - \mathbf{n})\,\mathbf{n}\right]$$

Heuristic statement: Energy changes in a linear fashion when moving electrons from the Hubbard manifold to the rest of the system.



Cococcioni and de Gironcoli, Phys. Rev. B (2005).



Definition of Hubbard *U:*

$$\frac{d^2 E}{d\mathrm{n}^2} = 0 \quad \Rightarrow \quad U = \frac{d^2 E_{\mathrm{DFT}}}{d\mathrm{n}^2}$$

Linear response theory (LRT)

Legendre transformation and minimization of the total energy w.r.t spin-charge density ρ_σ :

$$E(\{\lambda^I\}) = \min_{\rho_\sigma} \left\{ E_{\mathrm{DFT}}[\rho_\sigma] + \sum_I \lambda^I n^I \right\}$$

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Compute the 1st and 2nd derivatives:

$$\frac{d\bar{E}}{dn^I} = -\lambda^I \qquad \frac{d^2\bar{E}}{d(n^I)^2} = -\frac{d\lambda^I}{dn^I} = -(\chi^{-1})_{II}$$

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The Hubbard *U* parameter is defined as:

$$U^I = [-(\chi^{-1})_{II}] - [-(\chi_0^{-1})_{II}] = (\chi_0^{-1} - \chi^{-1})_{II}$$

not related to e-e interactions

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$$U^I = [-(\chi^{-1})_{II}] - [-(\chi_0^{-1})_{II}] = (\chi_0^{-1} - \chi^{-1})_{II} \quad \Leftrightarrow \quad \chi = \chi_0 + \chi_0 U \chi$$

Dyson equation:

not related to e-e interactions

Cococcioni and de Gironcoli, Phys. Rev. B (2005).

LRT using supercells and finite differences

Modified Kohn-Sham equations:

$$\left(\hat{H}_\sigma + \lambda^J \hat{V}^J_{\mathrm{pert}}\right)|\psi_{v\mathbf{k}\sigma}\rangle = \varepsilon_{v\mathbf{k}\sigma}|\psi_{v\mathbf{k}\sigma}\rangle$$

Perturbing potential:

$$\hat{V}^J_{\mathrm{pert}} = \sum_m |\varphi^J_m\rangle\langle\varphi^J_m|$$

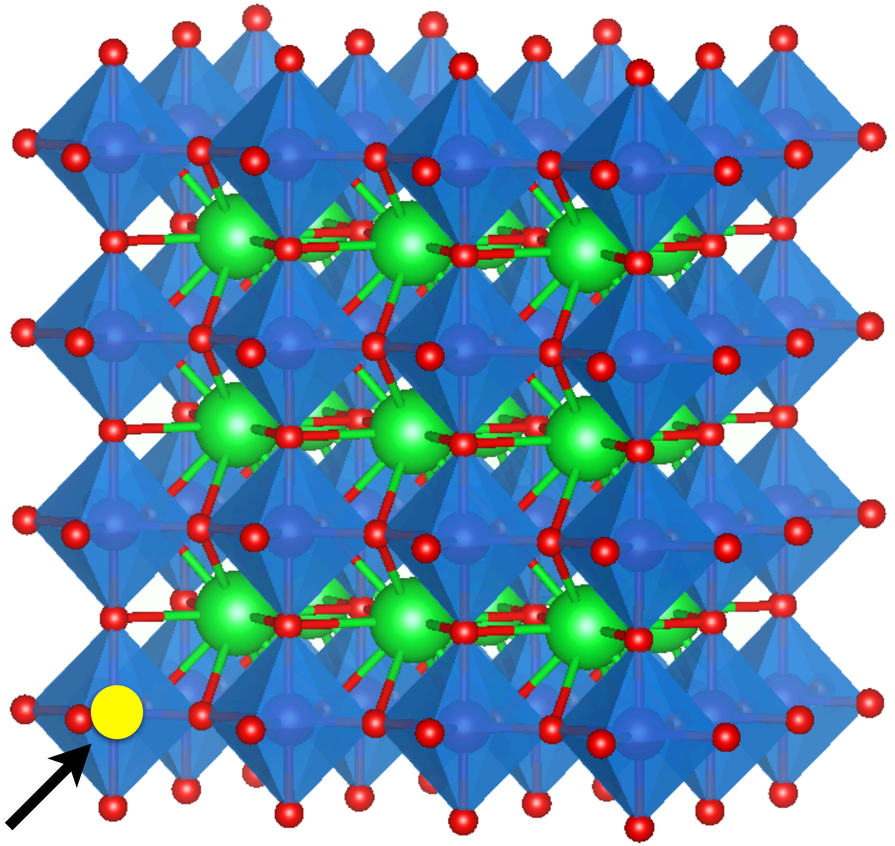
Response matrices
(numerical derivative using finite differences)

$$\chi_{IJ} = \frac{\Delta n^I}{\Delta \lambda^J}$$

Hubbard parameters:

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II} \quad V^{IJ} = (\chi_0^{-1} - \chi^{-1})_{IJ}$$

Cococcioni and de Gironcoli, Phys. Rev. B (2005).

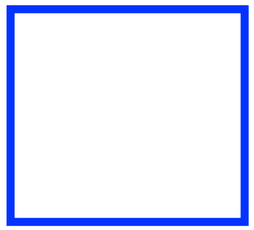


Perturbed atom

- Computationally expensive
- Possible convergence issues when using large supercells
- Quite cumbersome to use

Link between primitive unit cells and supercells

primitive unit cell



$\boldsymbol{a}_i$

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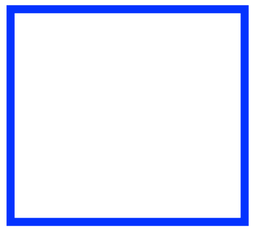
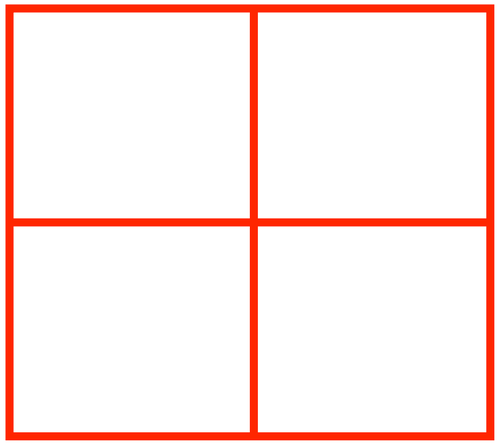


$\boldsymbol{a}_i$

supercell: $L_1 \times L_2 \times L_3$



$$\boldsymbol{A}_i = L_i \, \boldsymbol{a}_i$$

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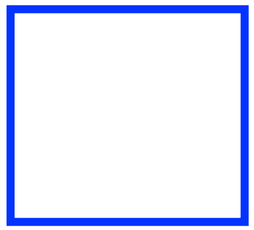

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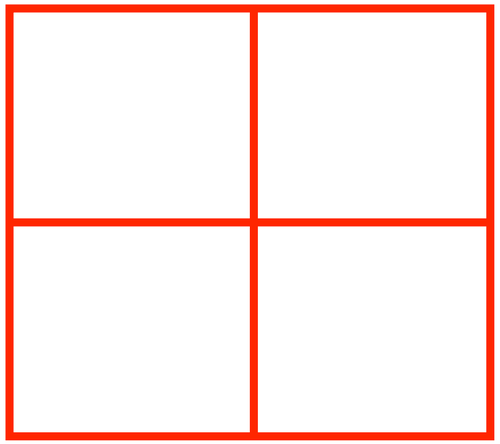

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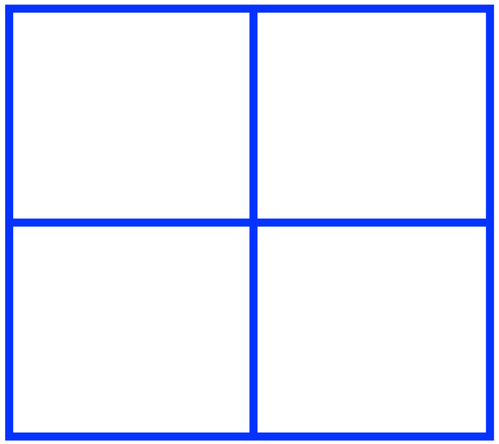
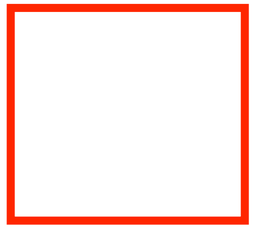
Brillouin zone



$\boldsymbol{b}_i$

Brillouin zone



$$\boldsymbol{B}_i = \frac{\boldsymbol{b}_i}{L_i}$$

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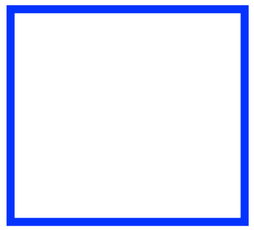
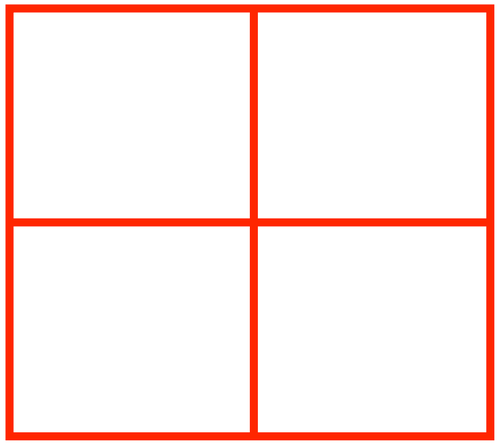


$\boldsymbol{a}_i$

supercell: $L_1 \times L_2 \times L_3$



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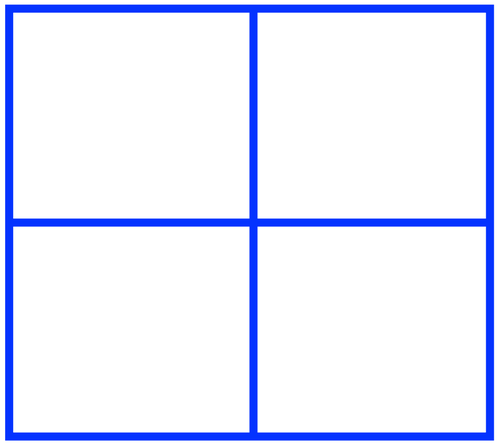
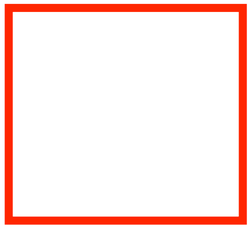


$\boldsymbol{b}_i$

Generic resiprocal lattice vector:

$\mathbf{g}_{k'l'm'} = k'\boldsymbol{b}_1 + l'\boldsymbol{b}_2 + m'\boldsymbol{b}_3$

Brillouin zone



$$\boldsymbol{B}_i = \frac{\boldsymbol{b}_i}{L_i}$$

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$$\mathbf{G}_{klm} = \frac{k}{L_1}\boldsymbol{b}_1 + \frac{l}{L_2}\boldsymbol{b}_2 + \frac{m}{L_3}\boldsymbol{b}_3$$

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$$k = k' L_1 + \bar{k},$$

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quotients

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remainders

Link between primitive unit cells and supercells

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$$\mathbf{G}_{klm} = \mathbf{g}_{k'l'm'} + \mathbf{q}_{\bar{k}\bar{l}\bar{m}}$$

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quotients

remainders

$$\mathbf{g}_{k'l'm'} = k'\boldsymbol{b}_1 + l'\boldsymbol{b}_2 + m'\boldsymbol{b}_3$$

$$\mathbf{q}_{\bar{k}\bar{l}\bar{m}} = \frac{\bar{k}}{L_1}\boldsymbol{b}_1 + \frac{\bar{l}}{L_2}\boldsymbol{b}_2 + \frac{\bar{m}}{L_3}\boldsymbol{b}_3$$

Link between primitive unit cells and supercells

Fourier expansion of the perturbing localized potential in a supercell:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}\, V(\mathbf{G})$$

$$\equiv \sum_{klm} e^{i\mathbf{G}_{klm}\cdot\mathbf{r}}\, V(\mathbf{G}_{klm})$$

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$$\equiv \sum_{klm} e^{i\mathbf{G}_{klm}\cdot\mathbf{r}}\, V(\mathbf{G}_{klm})$$

We can rewrite this potential as a sum of monochromatic perturbations ($\mathbf{G} = \mathbf{g} + \mathbf{q}$):

$$V(\mathbf{r}) = \sum_{\bar{k}\bar{l}\bar{m}} \sum_{k'l'm'} e^{i(\mathbf{g}_{k'l'm'} + \mathbf{q}_{\bar{k}\bar{l}\bar{m}})\cdot\mathbf{r}}\, V(\mathbf{g}_{k'l'm'} + \mathbf{q}_{\bar{k}\bar{l}\bar{m}})$$

$$\equiv \sum_{\mathbf{q}} \sum_{\mathbf{g}} e^{i(\mathbf{g}+\mathbf{q})\cdot\mathbf{r}}\, V(\mathbf{g}+\mathbf{q})$$

$$= \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\, \bar{V}_{\mathbf{q}}(\mathbf{r}).$$

$$\bar{V}_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{r}}\, V(\mathbf{g}+\mathbf{q})$$

LRT: from supercells to primitive unit cells

Modified Kohn-Sham equations:

$$\left(\hat{H}_\sigma + \lambda^J \hat{V}^J_{\text{pert}}\right)|\psi_{v\mathbf{k}\sigma}\rangle = \varepsilon_{v\mathbf{k}\sigma}|\psi_{v\mathbf{k}\sigma}\rangle$$

Perturbing potential:

$$\hat{V}^J_{\text{pert}} = \sum_m |\varphi^J_m\rangle\langle\varphi^J_m|$$

Perturbation theory to 1st order:

$$(\hat{H}^\circ_\sigma - \varepsilon^\circ_{v\mathbf{k}\sigma})\left|\frac{d\psi_{v\mathbf{k}\sigma}}{d\lambda^J}\right\rangle$$

$$= -\left(\frac{d\hat{V}_{\text{Hxc},\sigma}}{d\lambda^J} - \frac{d\varepsilon_{v\mathbf{k}\sigma}}{d\lambda^J} + \hat{V}^J_{\text{pert}}\right)|\psi^\circ_{v\mathbf{k}\sigma}\rangle$$

Timrov, Marzari, and Cococcioni, Phys. Rev. B (2018) & (2021).

LRT: from supercells to primitive unit cells

Modified Kohn-Sham equations:

$$\left(\hat{H}_\sigma + \lambda^J \hat{V}^J_{\text{pert}}\right)|\psi_{v\mathbf{k}\sigma}\rangle = \varepsilon_{v\mathbf{k}\sigma}|\psi_{v\mathbf{k}\sigma}\rangle$$

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Potential in a supercell can be decomposed into a sum over **q** points for a primitive cell:

$$V(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\,\bar{V}_{\mathbf{q}}(\mathbf{r})$$

Timrov, Marzari, and Cococcioni, Phys. Rev. B (2018) & (2021).

LRT: from supercells to primitive unit cells

Modified Kohn-Sham equations:

$$\left(\hat{H}_\sigma + \lambda^J \hat{V}^J_{\text{pert}}\right)|\psi_{v\mathbf{k}\sigma}\rangle = \varepsilon_{v\mathbf{k}\sigma}|\psi_{v\mathbf{k}\sigma}\rangle$$

Perturbing potential:

$$\hat{V}^J_{\text{pert}} = \sum_m |\varphi^J_m\rangle\langle\varphi^J_m|$$

Response matrices
(numerical derivative using finite differences)

$$\chi_{IJ} = \frac{\Delta n^I}{\Delta\lambda^J}$$

Hubbard parameters:

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II} \quad V^{IJ} = (\chi_0^{-1} - \chi^{-1})_{IJ}$$

Perturbation theory to 1st order:

$$(\hat{H}^\circ_\sigma - \varepsilon^\circ_{v\mathbf{k}\sigma})\left|\frac{d\psi_{v\mathbf{k}\sigma}}{d\lambda^J}\right\rangle = -\left(\frac{d\hat{V}_{\text{Hxc},\sigma}}{d\lambda^J} - \frac{d\varepsilon_{v\mathbf{k}\sigma}}{d\lambda^J} + \hat{V}^J_{\text{pert}}\right)|\psi^\circ_{v\mathbf{k}\sigma}\rangle$$

Potential in a supercell can be decomposed into a sum over **q** points for a primitive cell:

$$V(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\,\bar{V}_{\mathbf{q}}(\mathbf{r})$$

Response occupation matrices
(from the iterative solution of the eq. above)

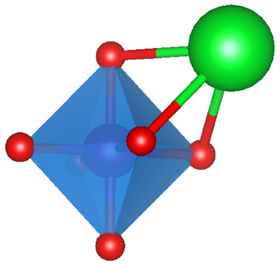
$$\frac{dn^{sl\sigma}_{m_1m_2}}{d\lambda^{s'l'}} = \frac{1}{N_{\mathbf{q}}}\sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})}\,\Delta^{s'}_{\mathbf{q}}\bar{n}^{s\,\sigma}_{m_1m_2}$$

Timrov, Marzari, and Cococcioni, Phys. Rev. B (2018) & (2021).

LRT: from supercells to primitive unit cells

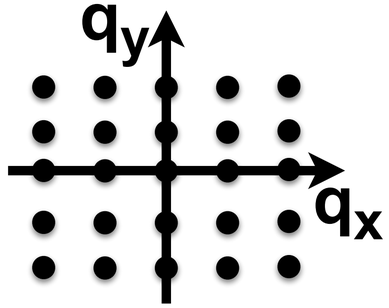
Density-functional perturbation theory (DFPT)

primitive cell



+

monochromatic perturbations



- Computationally much less expensive
- Easier convergence
- User-friendly and autonomous

Inspired by DFPT for phonons:

Baroni, de Gironcoli, Dal Corso, Giannozzi, RMP (2001).

Timrov, Marzari, and Cococcioni, Phys. Rev. B (2018) & (2021).

Perturbation theory to 1st order:

$$(\hat{H}^{\circ}_{\sigma} - \varepsilon^{\circ}_{v\mathbf{k}\sigma}) \left| \frac{d\psi_{v\mathbf{k}\sigma}}{d\lambda^J} \right\rangle$$

$$= -\left(\frac{d\hat{V}_{\mathrm{Hxc},\sigma}}{d\lambda^J} - \frac{d\varepsilon_{v\mathbf{k}\sigma}}{d\lambda^J} + \hat{V}^J_{\mathrm{pert}} \right) |\psi^{\circ}_{v\mathbf{k}\sigma}\rangle$$

Potential in a supercell can be decomposed into a sum over **q** points for a primitive cell:

$$V(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\, \bar{V}_{\mathbf{q}}(\mathbf{r})$$

Response occupation matrices (from the iterative solution of the eq. above)

$$\frac{dn^{sl\sigma}_{m_1 m_2}}{d\lambda^{s'l'}} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})}\, \Delta^{s'}_{\mathbf{q}} \bar{n}^{s\,\sigma}_{m_1 m_2}$$

Hubbard parameters from DFPT

PHYSICAL REVIEW B **98**, 085127 (2018)

Hubbard parameters from density-functional perturbation theory

Iurii Timrov, Nicola Marzari, and Matteo Cococcioni
Theory and Simulation of Materials (THEOS) and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

(Received 4 May 2018; revised manuscript received 27 July 2018; published 16 August 2018)

Computer Physics Communications 279 (2022) 108455

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www.elsevier.com/locate/cpc

HP – A code for the calculation of Hubbard parameters using density-functional perturbation theory ☆,☆☆

Iurii Timrov [a,*], Nicola Marzari [a,b], Matteo Cococcioni [c]

PHYSICAL REVIEW B **103**, 045141 (2021)

Self-consistent Hubbard parameters from density-functional perturbation theory in the ultrasoft and projector-augmented wave formulations

Iurii Timrov [1,*] Nicola Marzari [1] and Matteo Cococcioni [2]
[1] *Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*
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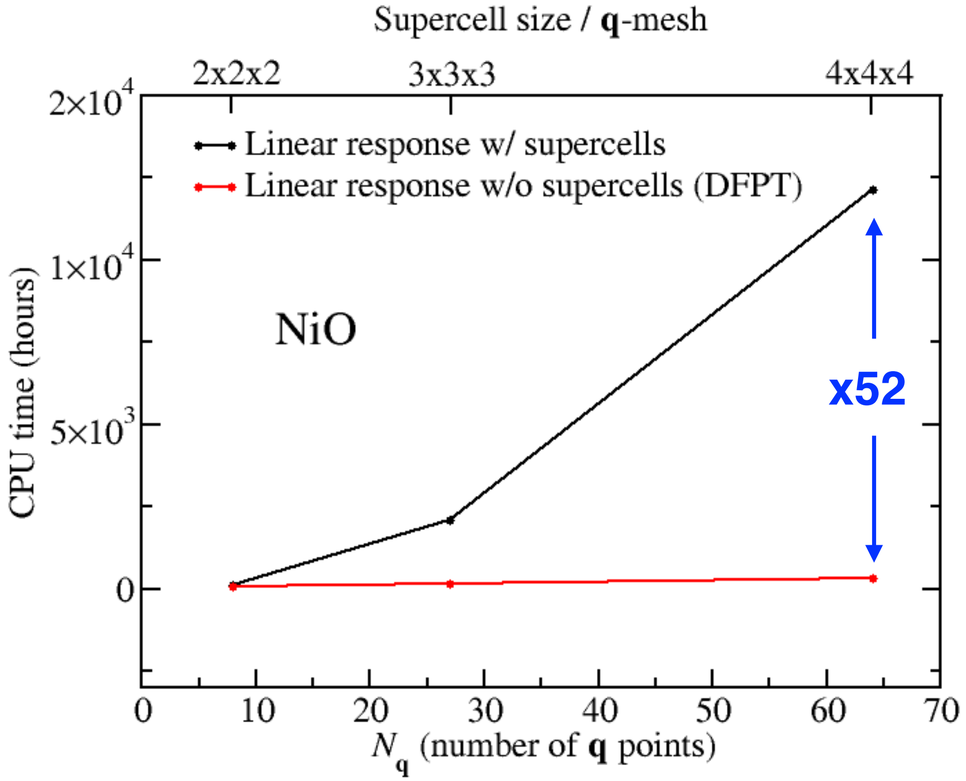
(Received 6 November 2020; accepted 14 January 2021; published 29 January 2021)

QUANTUMESPRESSO

Numerical comparison of U from LRT and DFPT

Scaling

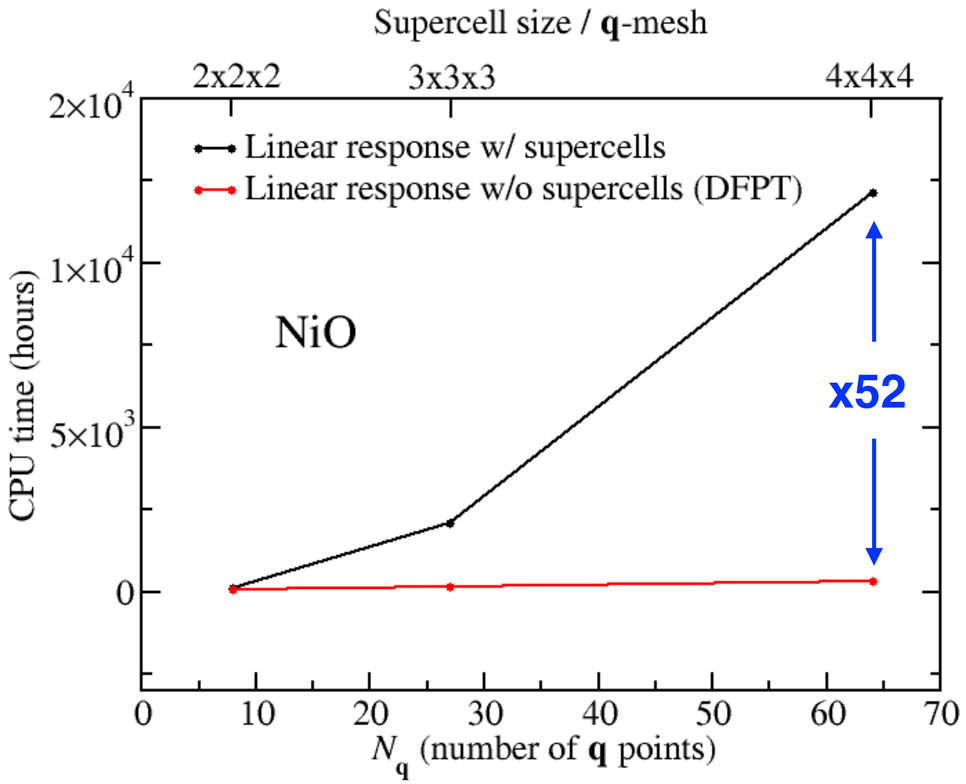


Symmetry → Reduction of $N_{\mathbf{q}}$ in DFPT
(no equivalence in the SC approach)

Timrov, Marzari, and Cococcioni, Phys. Rev. B (2018) & (2021).

Numerical comparison of U from LRT and DFPT

Scaling



Benchmark of the equivalence between the two approaches

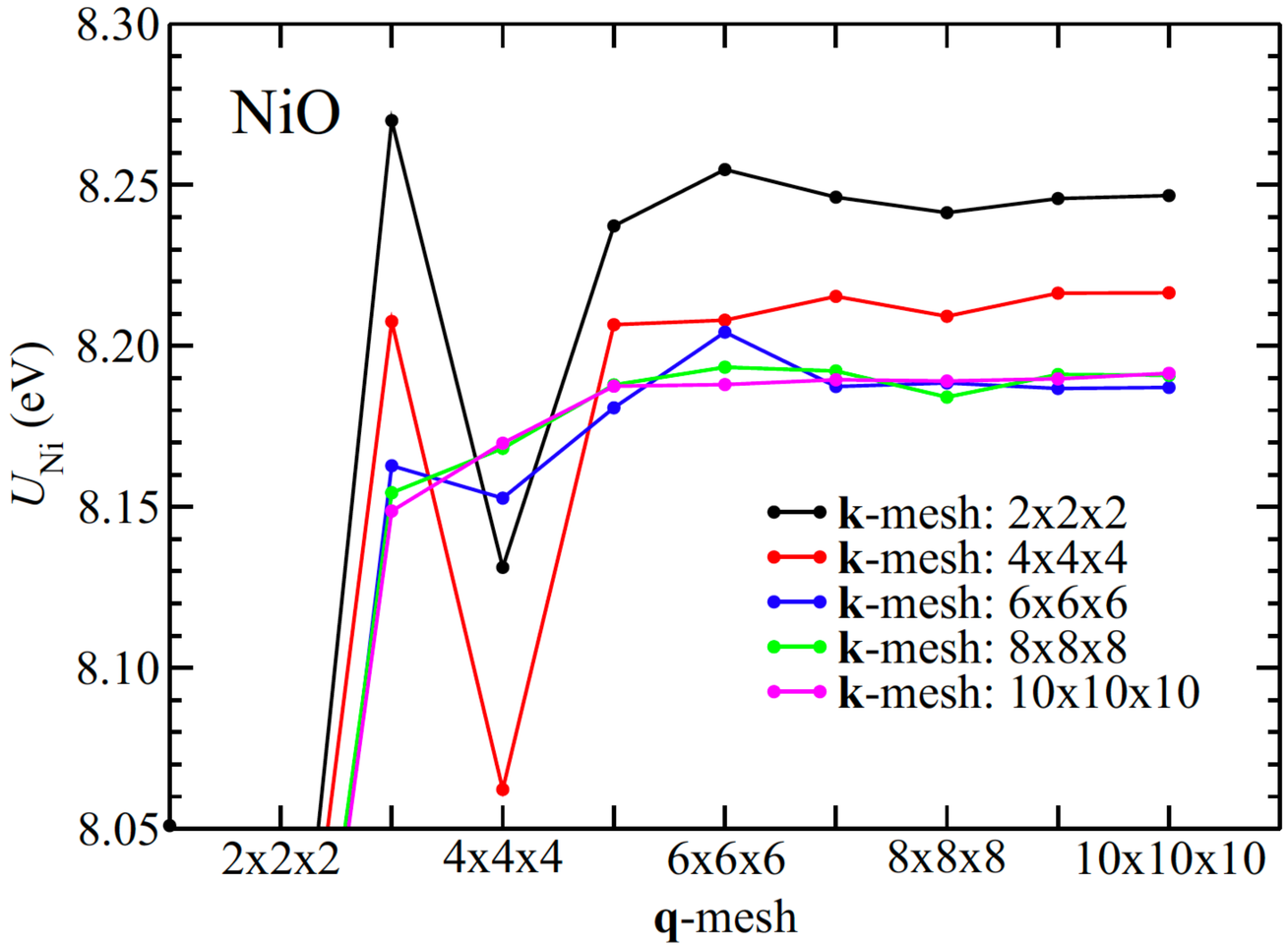
Method	**k**-mesh	SC-size/**q**-mesh	U(Ni-d)
LR-SC	6 × 6 × 6	2 × 2 × 2	7.895
DFPT	12 × 12 × 12		7.900
LR-SC	4 × 4 × 4	3 × 3 × 3	8.146
DFPT	12 × 12 × 12		8.149
LR-SC	3 × 3 × 3	4 × 4 × 4	8.168
DFPT	12 × 12 × 12		8.172

Symmetry → Reduction of $N_{\mathbf{q}}$ in DFPT
(no equivalence in the SC approach)

Exact matching
(modulo the numerical noise)

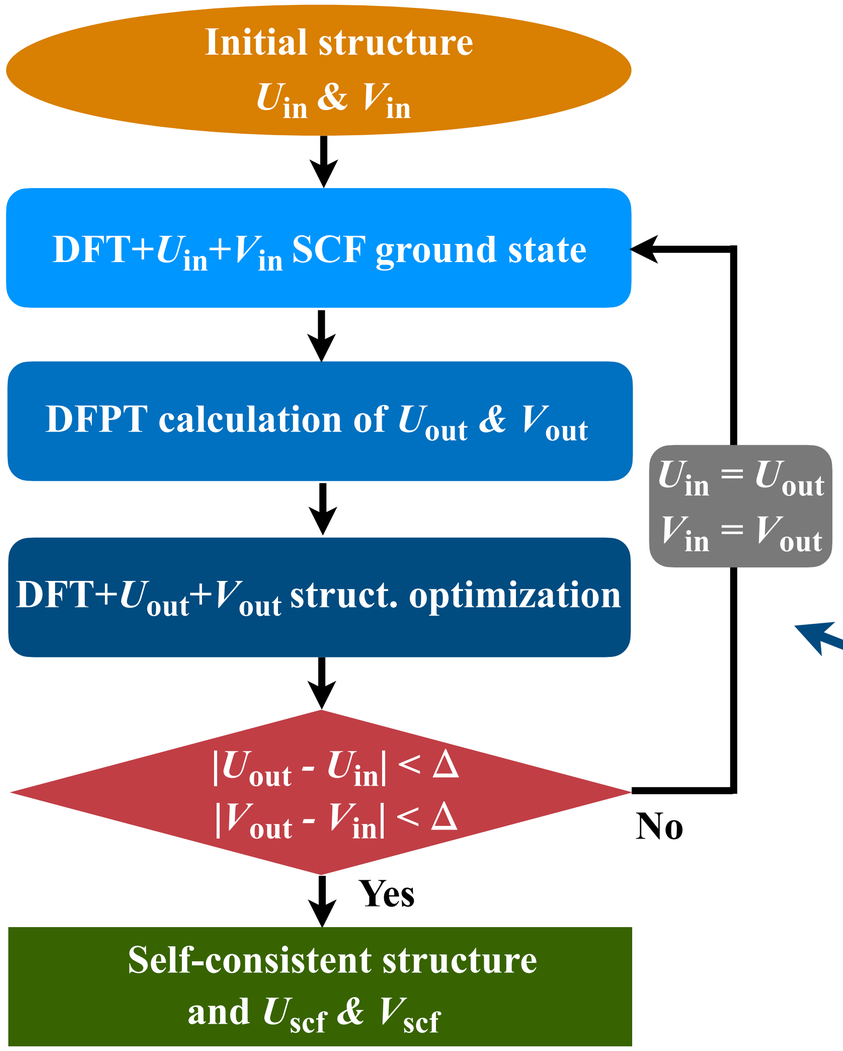
Timrov, Marzari, and Cococcioni, Phys. Rev. B (2018) & (2021).

Convergence of U with respect to k and q points meshes within DFPT



The converged *U* value is ~8.18 eV.

Self-consistent workflow for computing U and V

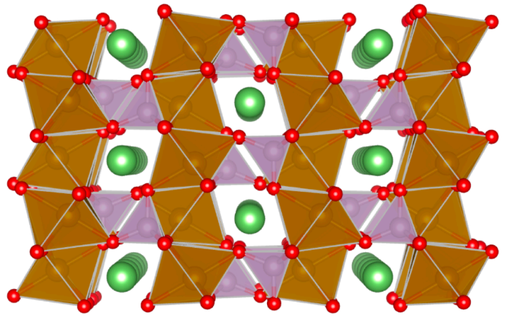


Calculation of Hubbard parameters

$$U^I = \left(\frac{d^2 E_{\mathrm{DFT}}}{d\mathbf{n}^2} - \frac{d^2 E^{\circ}_{\mathrm{DFT}}}{d\mathbf{n}^2} \right)_{II}$$

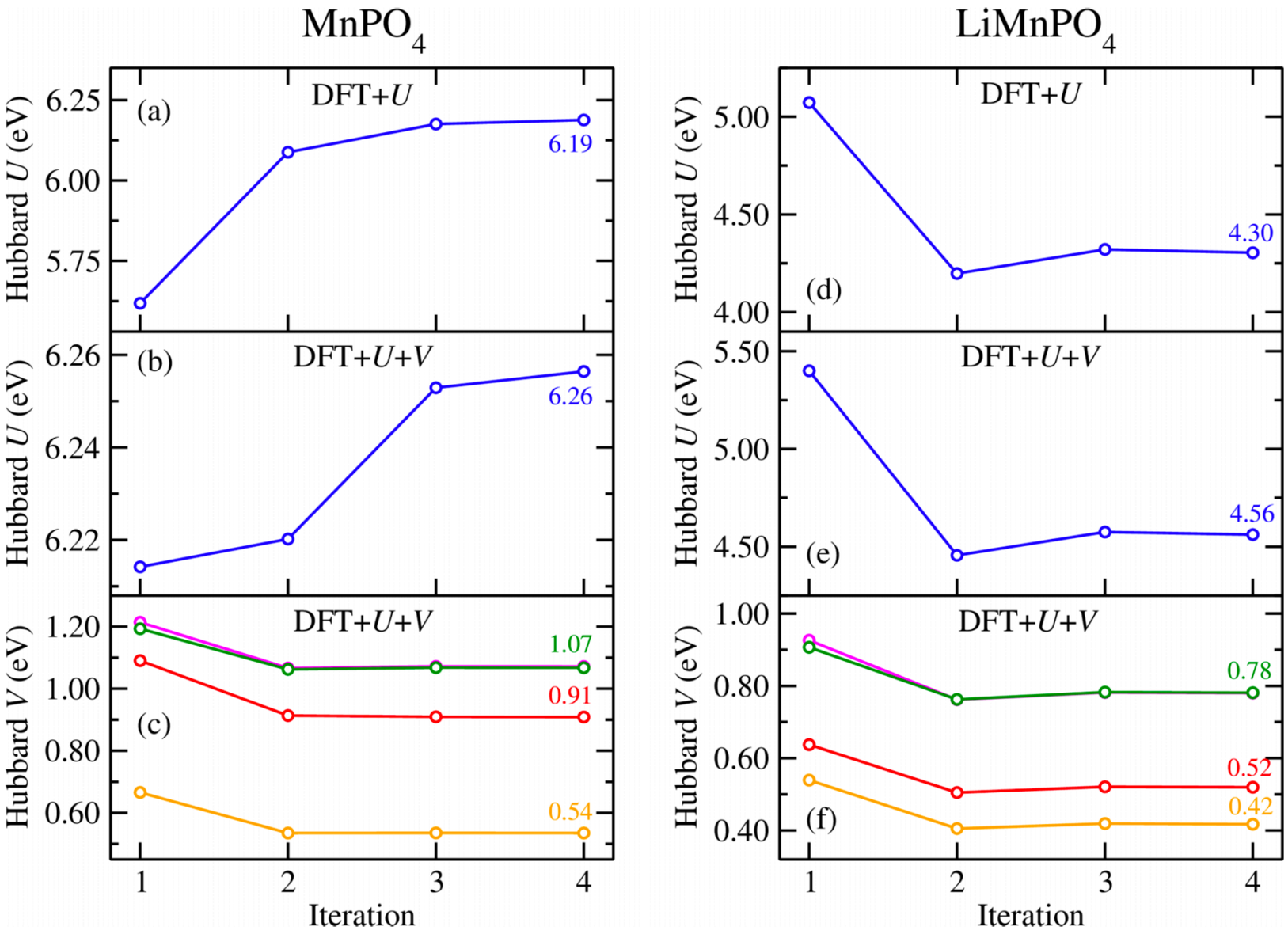
$$V^{IJ} = \left(\frac{d^2 E_{\mathrm{DFT}}}{d\mathbf{n}^2} - \frac{d^2 E^{\circ}_{\mathrm{DFT}}}{d\mathbf{n}^2} \right)_{IJ}$$

Structural optimisation



Timrov, Marzari, and Cococcioni, Phys. Rev. B (2021).

Self-consistent Hubbard parameters



Types of Hubbard projector functions

1. Nonorthogonalized atomic orbitals (NAO)

$$\phi^I_{m_1}(\mathbf{r}-\mathbf{R}_I)$$ (contained in pseudopotentials)

2. Orthogonalized atomic orbitals (OAO)

$$\tilde{\phi}^I_{m_1}(\mathbf{r}-\mathbf{R}_I) = \sum_{Jm_2} \left(\hat{O}^{-\frac{1}{2}}\right)^{JI}_{m_2 m_1} \phi^J_{m_2}(\mathbf{r}-\mathbf{R}_J)$$

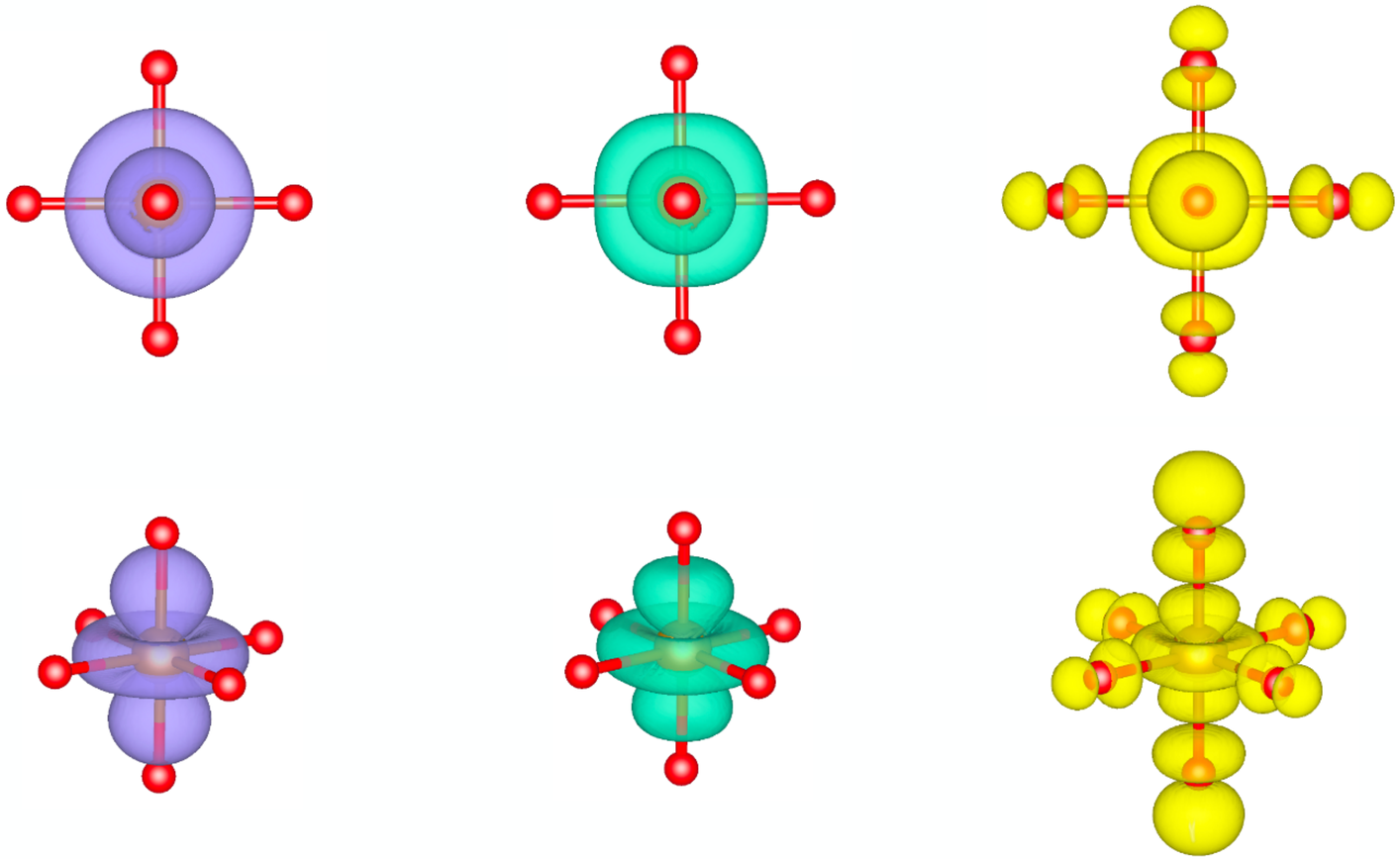
$$\left(\hat{O}\right)^{IJ}_{m_1 m_2} = \langle \phi^I_{m_1} | \phi^J_{m_2} \rangle$$

3. Maximally localized Wannier functions (MLWF)

$$w^I_{m_1}(\mathbf{r}-\mathbf{R}_I) = \frac{1}{\sqrt{N_{\mathbf{k}}}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_I} \sum_{n}^{N_{\mathrm{KSbands}}} U^{(\mathbf{k})}_{nm_1}\, \psi_{n\mathbf{k}}(\mathbf{r})$$

Types of Hubbard projector functions (for FeO)

NAO **OAO** **MLWFs (frontier)**



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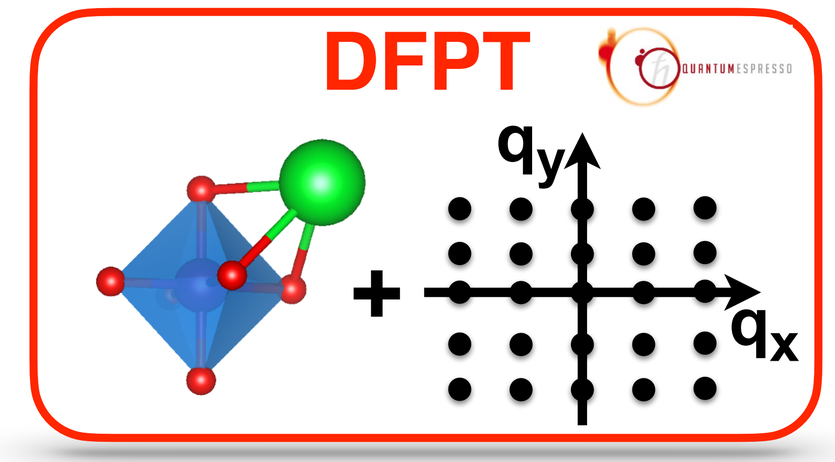

U_{atomic}
V_{atomic}

$\neq$

U_{ortho}
V_{ortho}

Types of Hubbard projector functions

1. Nonorthogonalized atomic orbitals (NAO)

$$\phi^I_{m_1}(\mathbf{r}-\mathbf{R}_I)$$ (contained in pseudopotentials)

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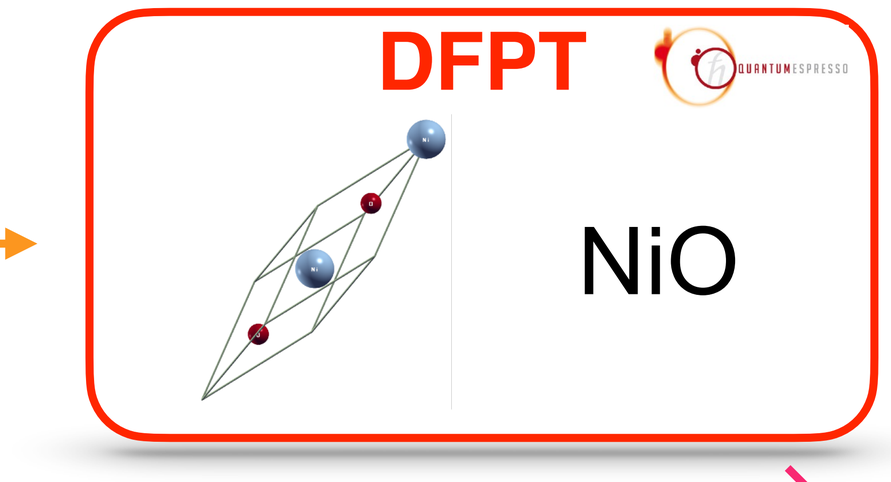


U=6.76
V=1.25

≠

U=7.43
V=0.37

Types of Hubbard projector functions

1. Nonorthogonalized atomic orbitals

$\phi^I_{m_1}(\mathbf{r} - \mathbf{R}$

2. Orthogo

$\tilde{\phi}^I_{m_1}(\mathbf{r} -$

3. Maxima

$$w^I_{m_1}(\mathbf{r} - \mathbf{R}_I) = \frac{1}{\sqrt{N_\mathbf{k}}} \sum_\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}_I} \sum_n U^{(\mathbf{k})}_{nm_1} \psi_{n\mathbf{k}}(\mathbf{r})$$

It is crucial to keep consistency between Hubbard parameters and Hubbard projectors!

U=6.76
V=1.25

≠

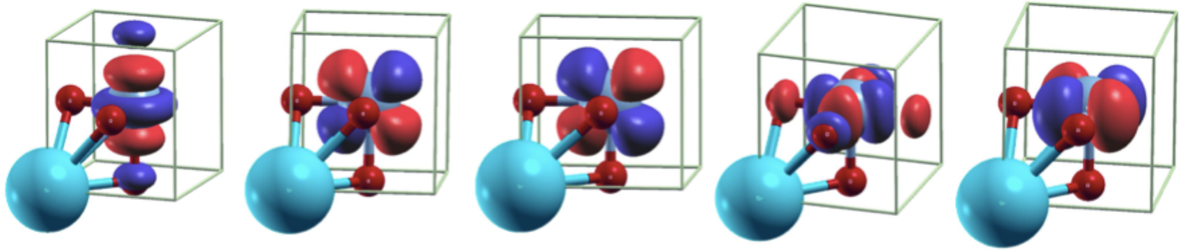
U=7.43
V=0.37

DFT+U with Wannier functions as projectors

WANNIER90

QUANTUMESPRESSO

$$\bar{w}^{I}_{m,\mathbf{k}}(\mathbf{r}) = \sum_{n}^{N_{\mathrm{KSbands}}} U^{(\mathbf{k})}_{nm}\, u_{n\mathbf{k}}(\mathbf{r})$$

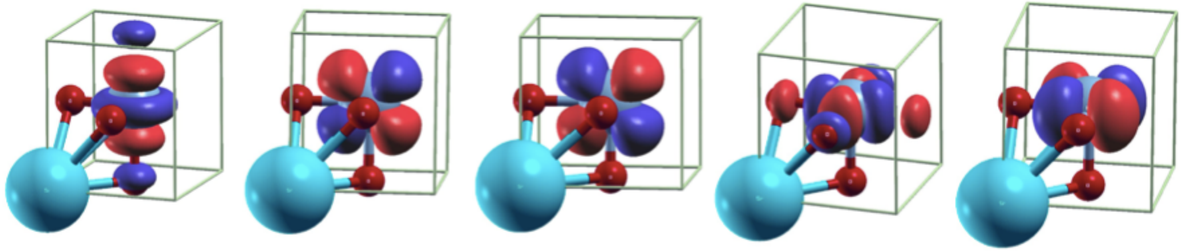


DFT+U with Wannier functions as projectors

WANNIER90

QUANTUMESPRESSO

$$\bar{w}^I_{m,\mathbf{k}}(\mathbf{r}) = \sum_{n}^{N_{\mathrm{KSbands}}} U^{(\mathbf{k})}_{nm}\, u_{n\mathbf{k}}(\mathbf{r})$$

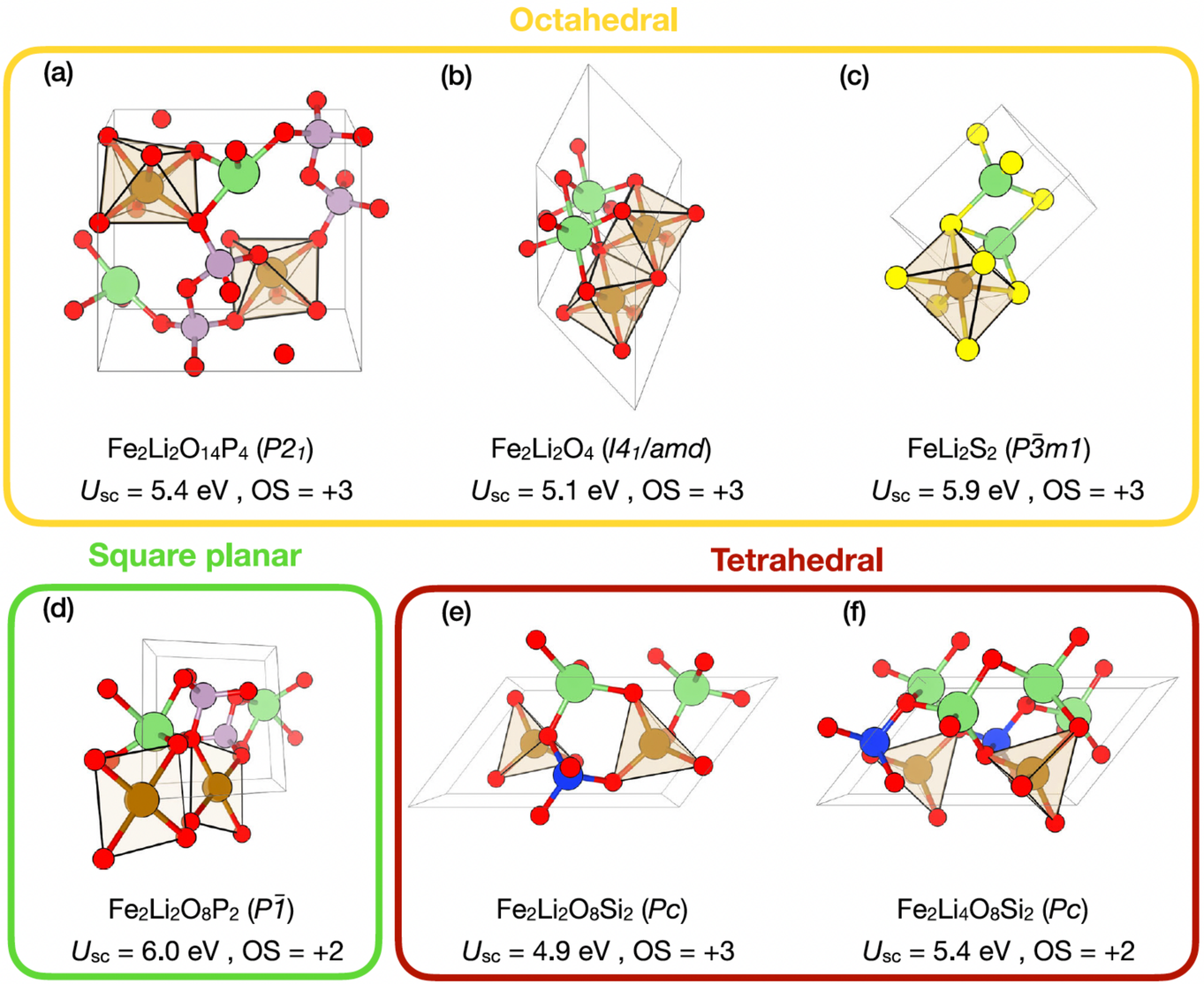


$$n^I_{m_1 m_2} = \frac{1}{N_{\mathbf{k}}} \sum_{v\mathbf{k}} \langle u_{v\mathbf{k}} | \bar{w}^I_{m_2,\mathbf{k}} \rangle \langle \bar{w}^I_{m_1,\mathbf{k}} | u_{v\mathbf{k}} \rangle$$

→ DFT+*U*

Carta, Timrov, Mlkvik, Hampel, Ederer, Phys. Rev. Res.(2025).

Hubbard parameters depend on many factors

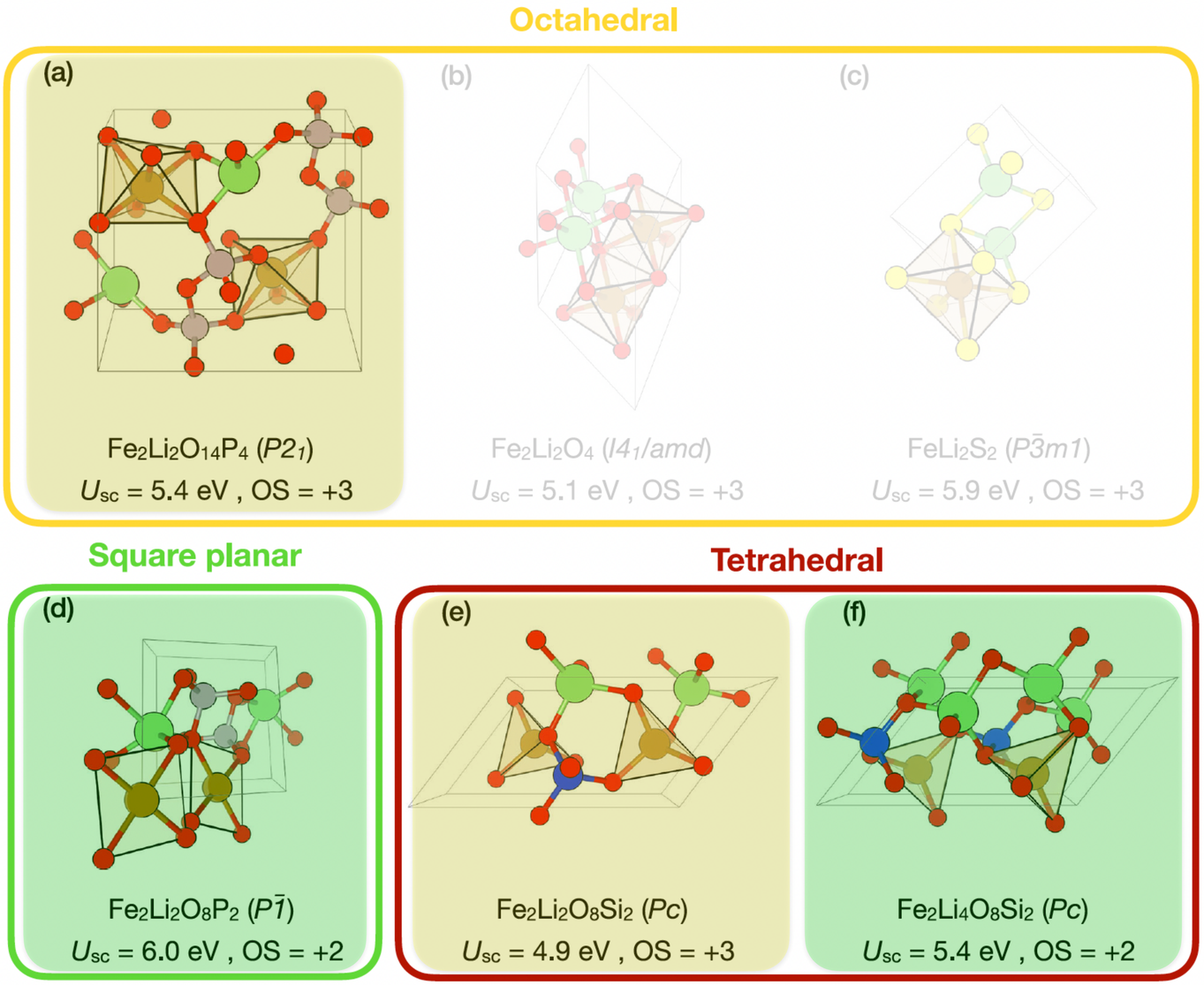


Self-consistent calculations of
Hubbard parameters for
115 Li-containing materials using
the AiiDA-Hubbard workflow

AiiDA

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

Hubbard parameters depend on many factors



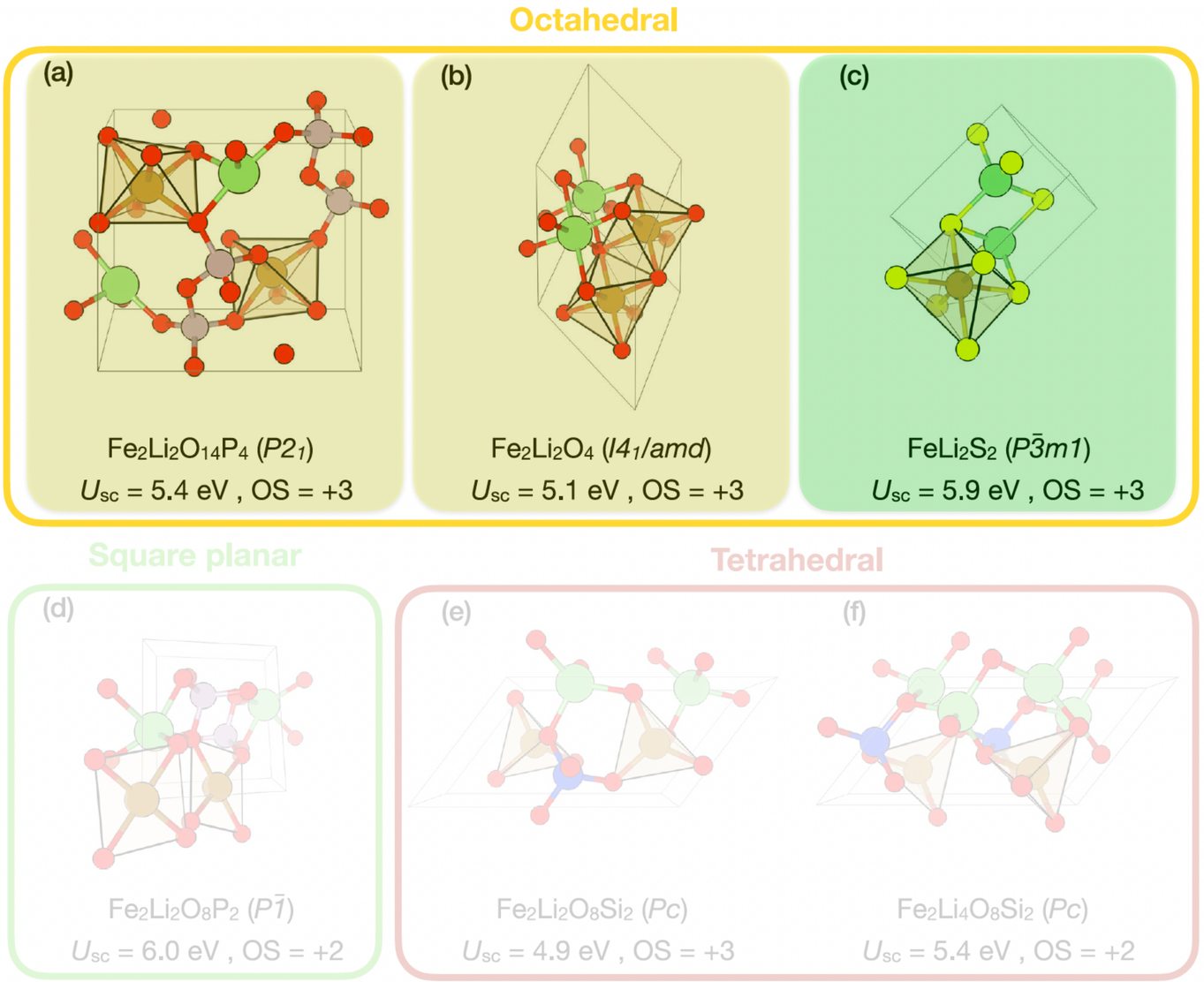
1. *U* dependence on coordination geometry

- Fe pairs (a,e) and (d,f):
  - Same oxidation state
  - Same oxygen ligand field (O)
  - Different coordination geometries

$\Delta U \approx 0.5$ - 0.6 eV

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

Hubbard parameters depend on many factors



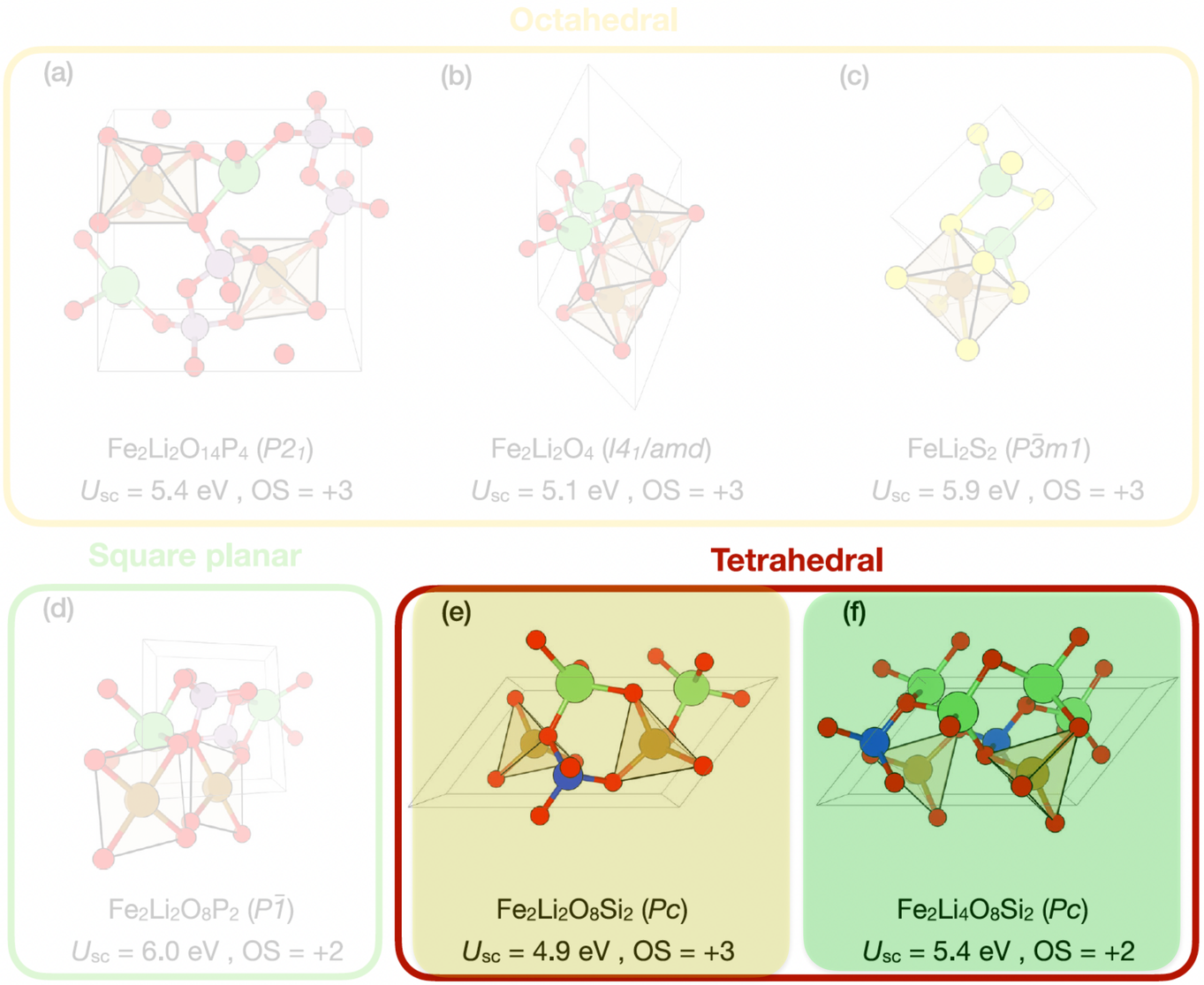
2. *U* dependence on ligand species

- Fe sites (a,b) vs (c):
  - Same oxidation state
  - Same octahedral coordination
  - Different ligands (O vs S)

$\Delta U \approx 0.5 - 0.8$ eV

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

Hubbard parameters depend on many factors



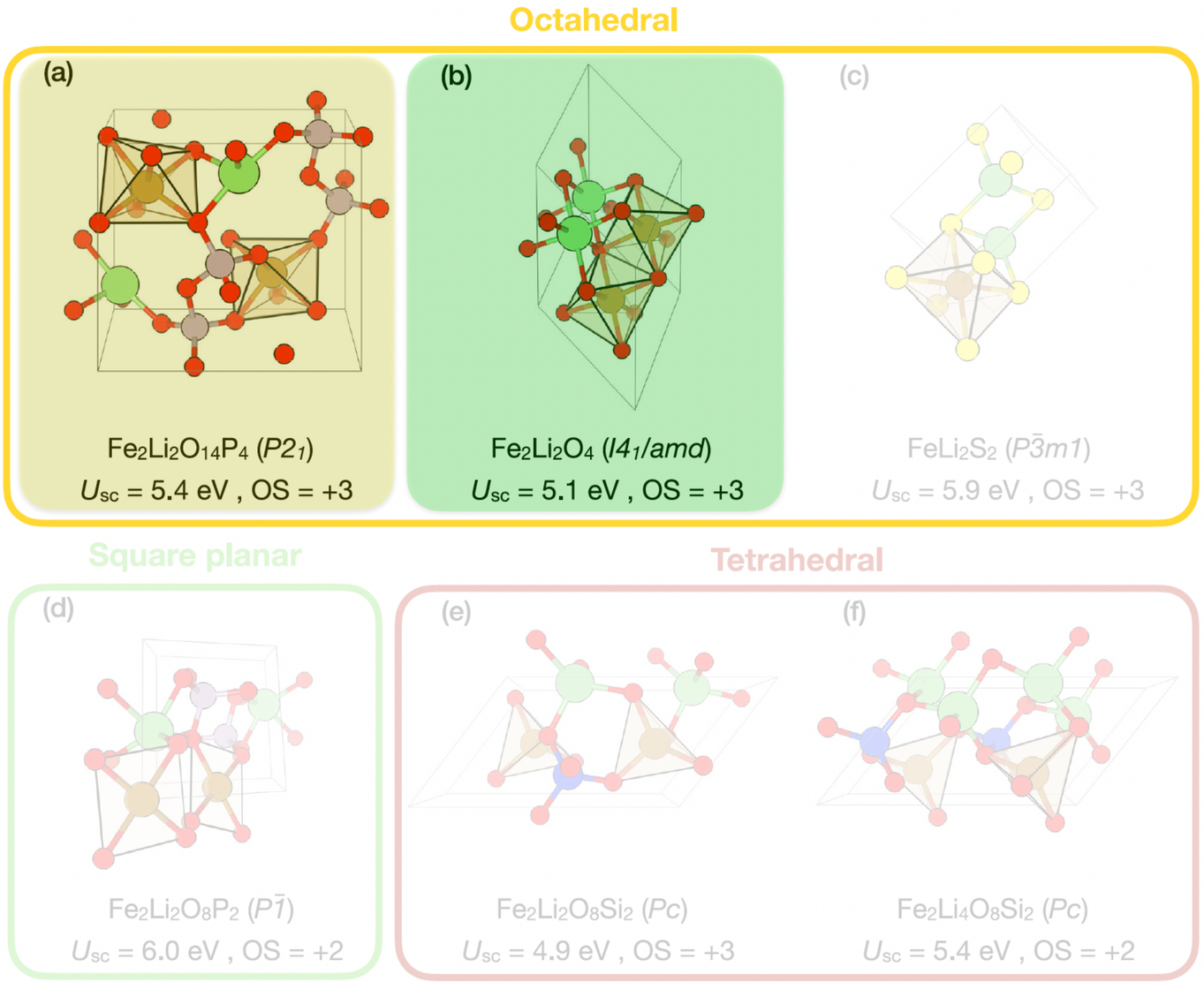
3. *U* dependence on oxidation state

- Fe sites (e) vs (f):
  - Same tetrahedral coordination
  - Same oxygen ligand field (O)
  - Different oxidation state (due to different amount of Li)

$\Delta U \approx 0.5$ eV

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

Hubbard parameters depend on many factors



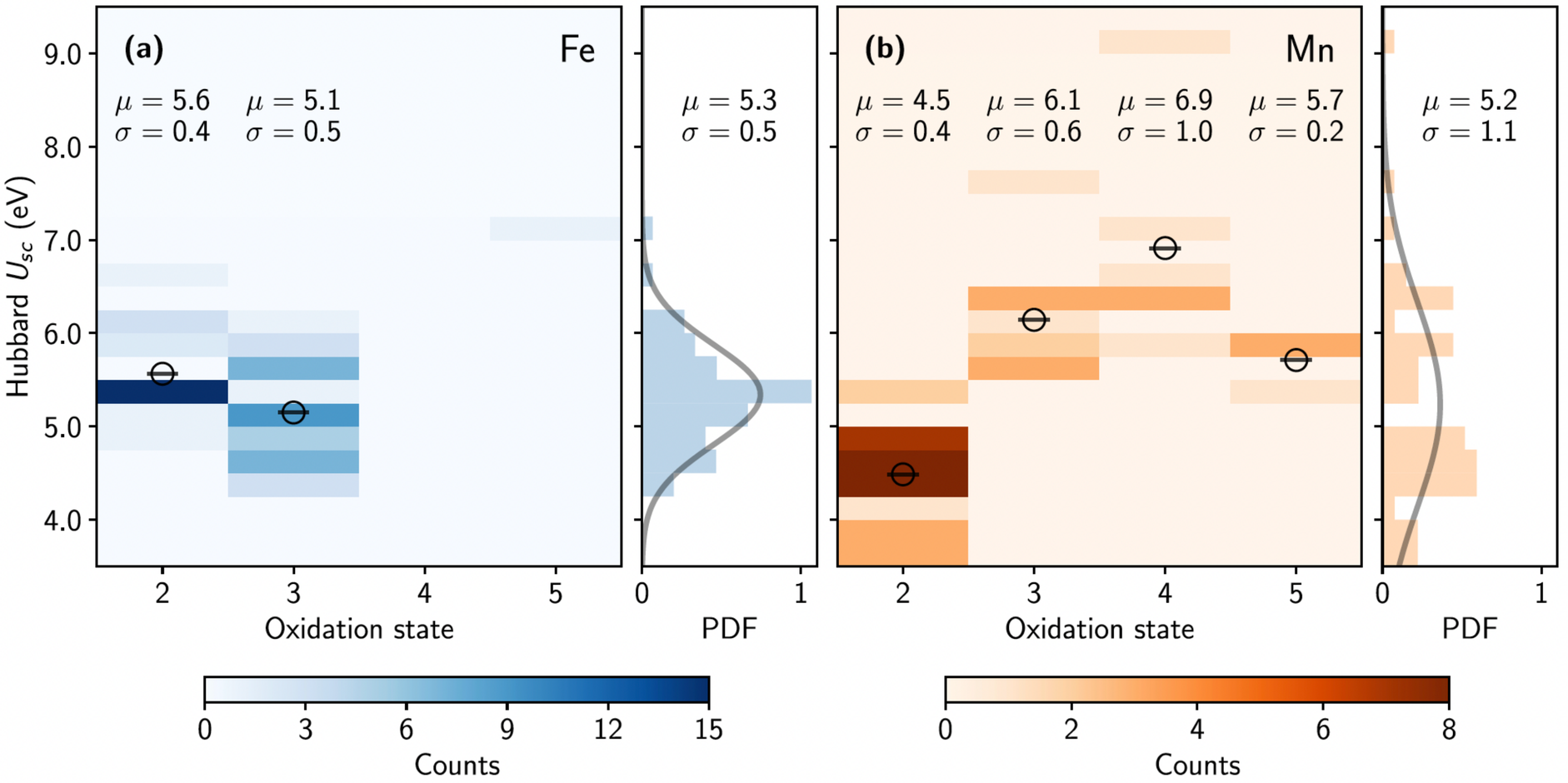
4. *U* dependence on local distortions

- Fe sites (a) vs (b):
  - Same octahedral coordination
  - Same oxygen ligand field (O)
  - Same oxidation state

$\Delta U \approx 0.3$ eV
(due to changes in electronic screening)

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

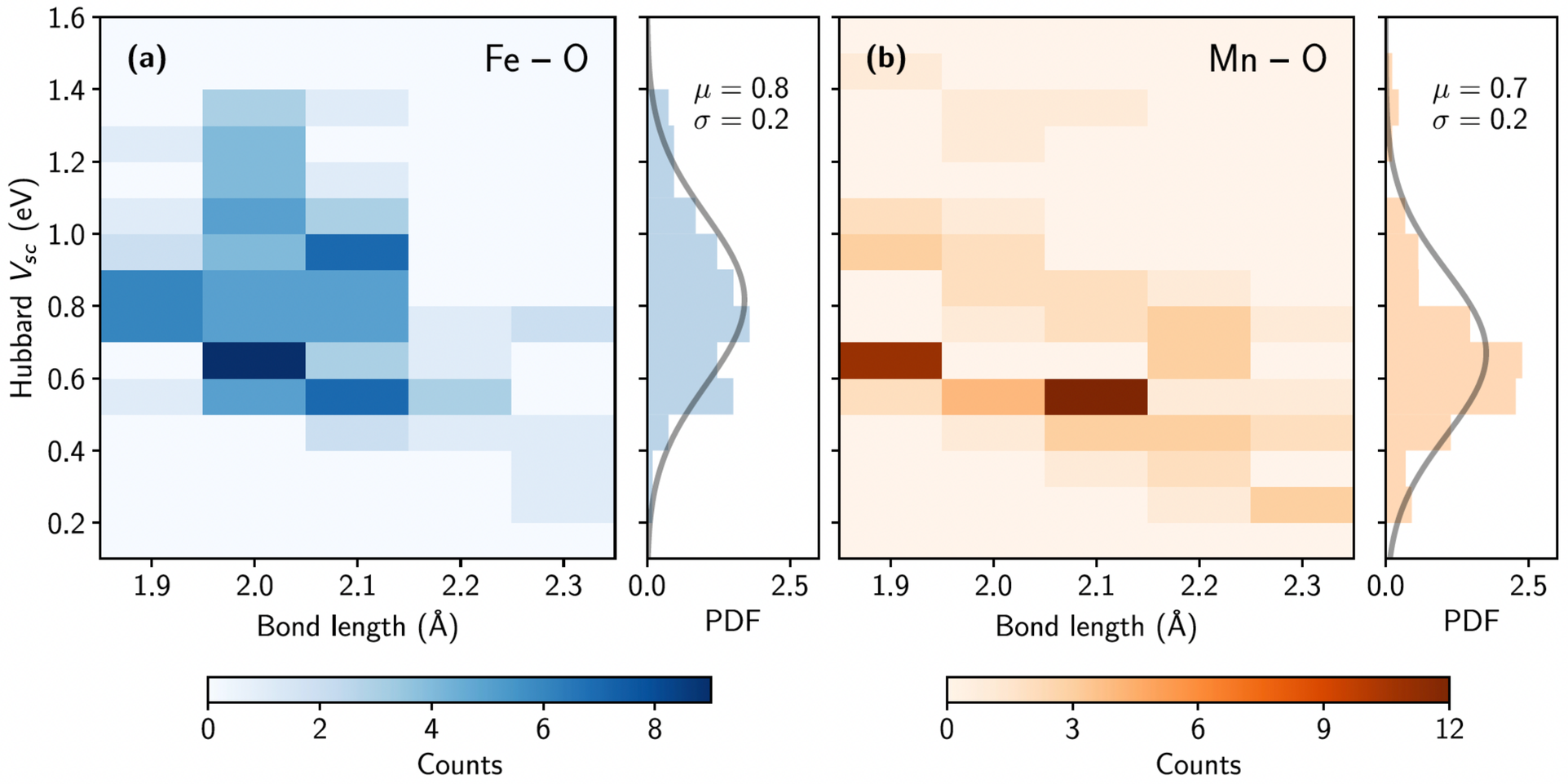
Distribution of Hubbard U for Fe(3d) and Mn(3d)



Hubbard *U* is not a universal (global) parameter! It depends on many factors (OS, coordination, ligands, etc.)

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

Distribution of Hubbard V for Fe/Mn-ligand

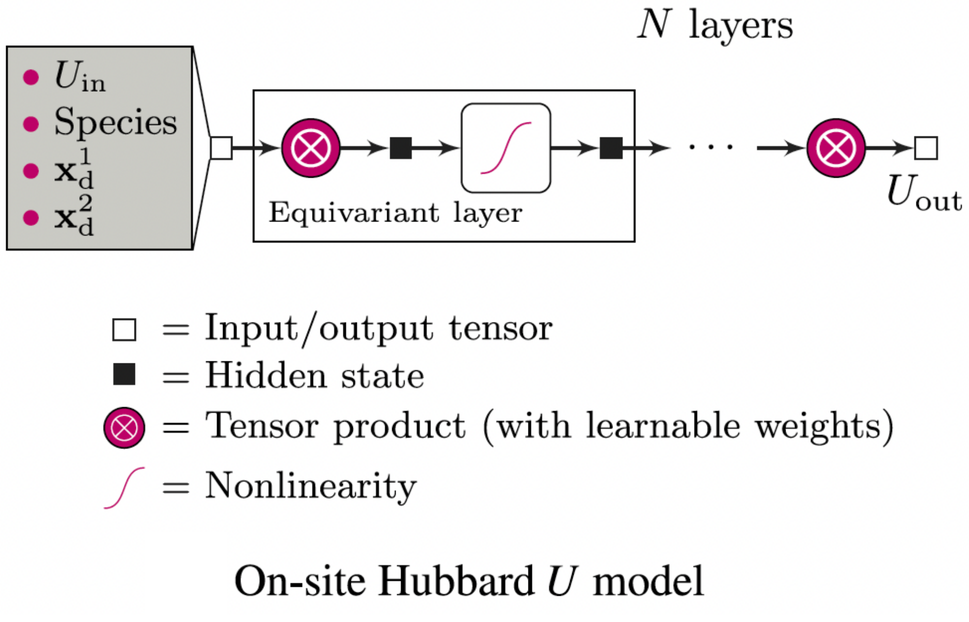


The inter-site Hubbard *V* decreases as the interatomic distance increases

Bastonero, Malica, Macke, Bercx, Huber, Timrov, Marzari, npj Comput. Mater. (2025).

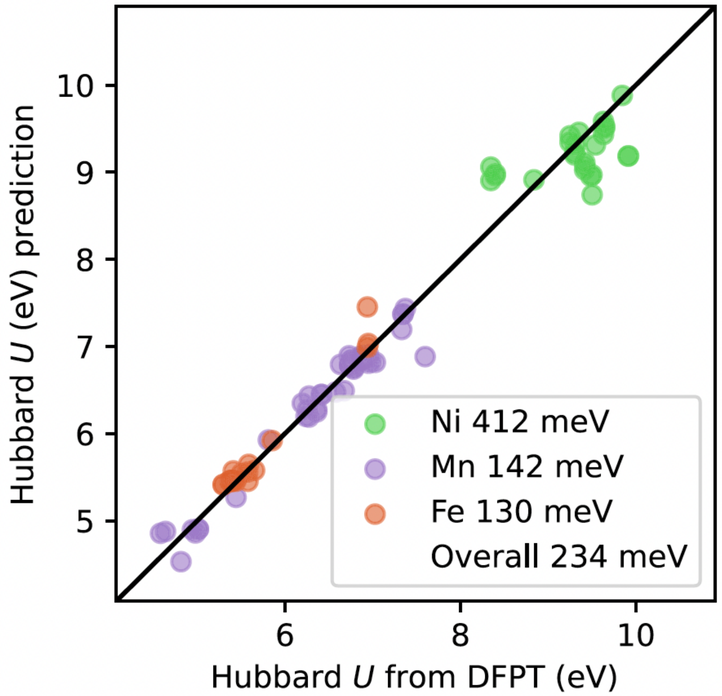
Machine learning Hubbard parameters

Equivariant neural network



On-site Hubbard U model

ML Hubbard *U*



Using the DFT+*U* occupation matrix as the main descriptor of the ML model and DFPT *U* values as the training data, we machine-learn Hubbard parameters to accelerate Li-ion battery research

Uhrin, Zadoks, Binci, Marzari, Timrov, npj Comput. Mater. (2025).

Take-home messages

- DFT+*U* and DFT+*U*+*V* are accurate and computationally efficient approaches to model transition-metal and rare-earth compounds
- Hubbard parameters are not universal
- Hubbard parameters can be computed from first-principles using linear-response theory
- Linear response without supercells: DFPT comes to the rescue
- Hubbard parameters depend on Hubbard projectors