MARVEL

NATIONAL CENTRE OF COMPETENCE IN RESEARCH

EPFL

THEOS

THEORY AND SIMULATION
OF MATERIALS

First-principles quantum simulations of correlated materials using Hubbard-corrected density-functional (perturbation) theory

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Theory and Simulation of Materials, and NCCR MARVEL,
École Polytechnique Fédérale de Lausanne, Switzerland

Summer School on Advanced Materials and Molecular Modelling (Ljubljana, Slovenia)

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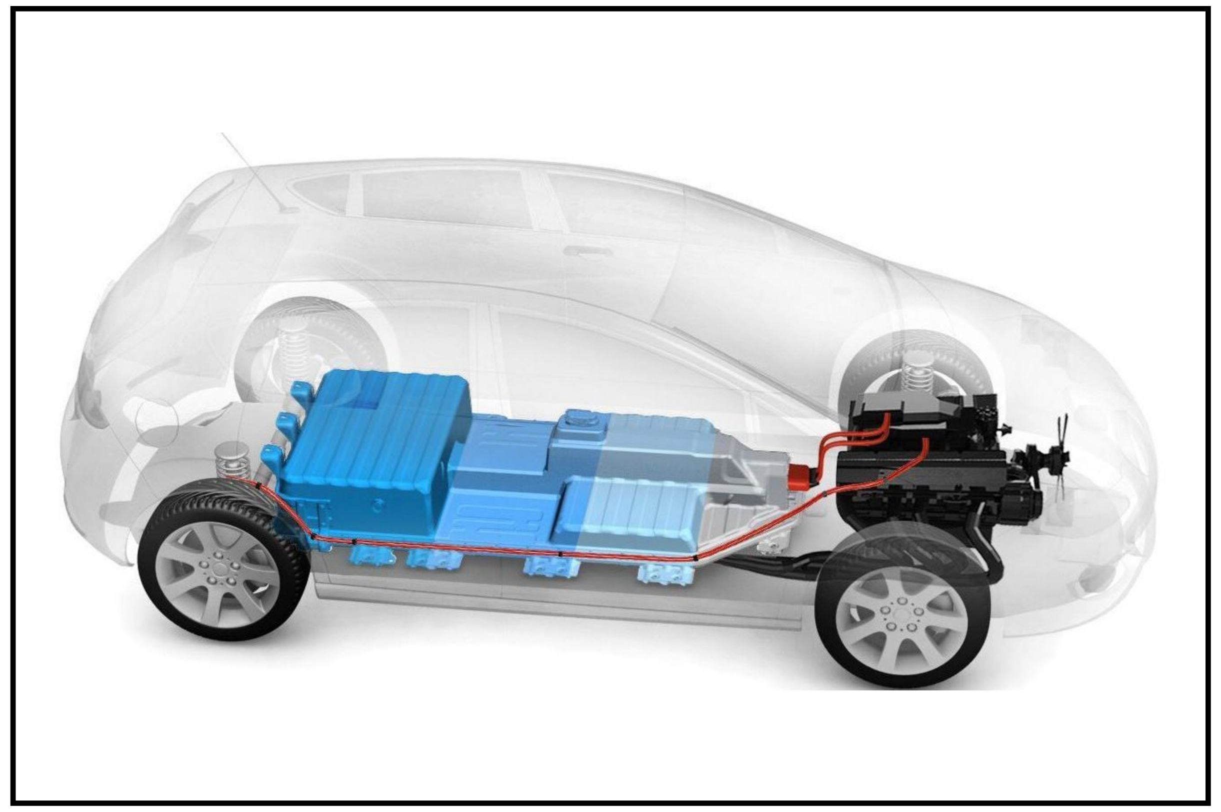
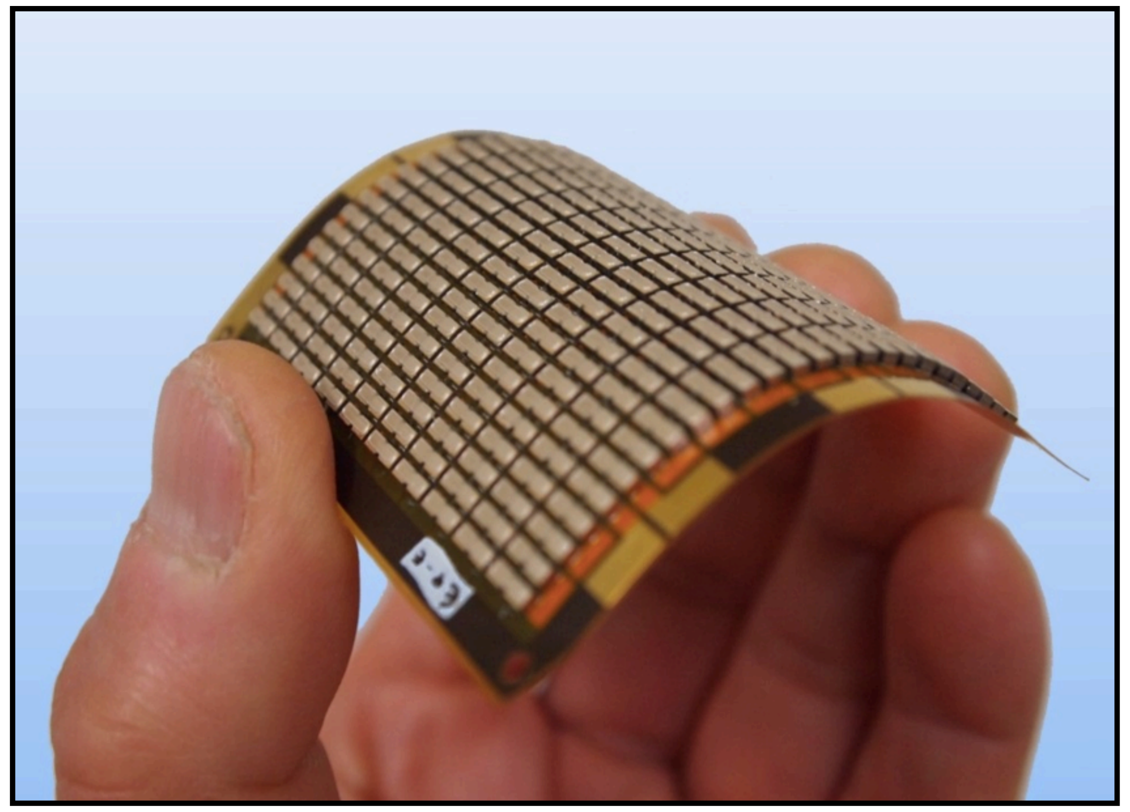
Technological importance of correlated materials

Batteries for e-cars

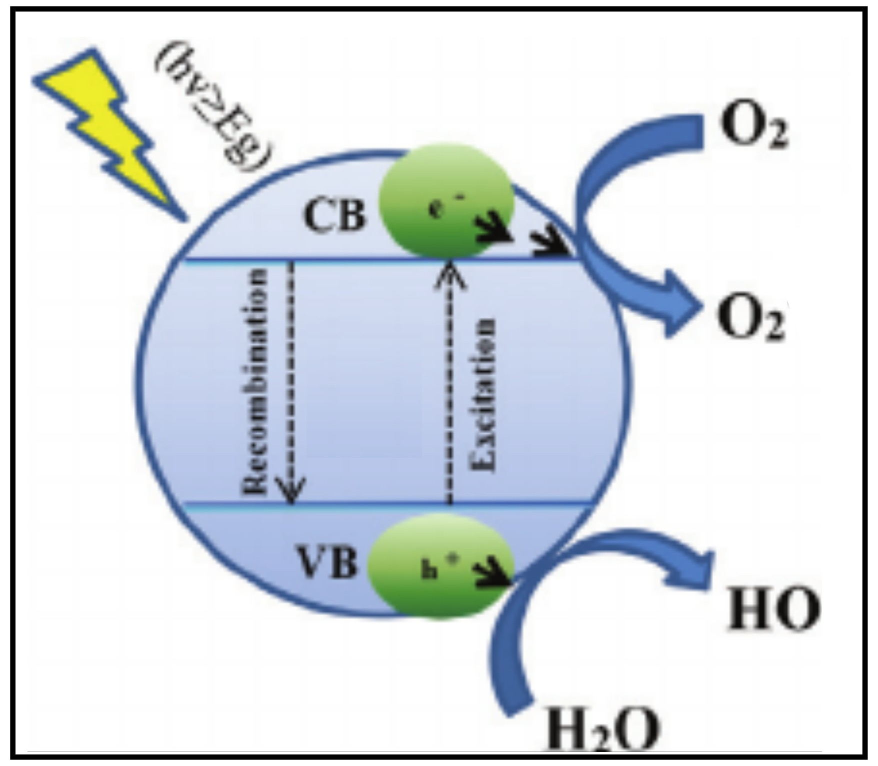


Magnets for generators

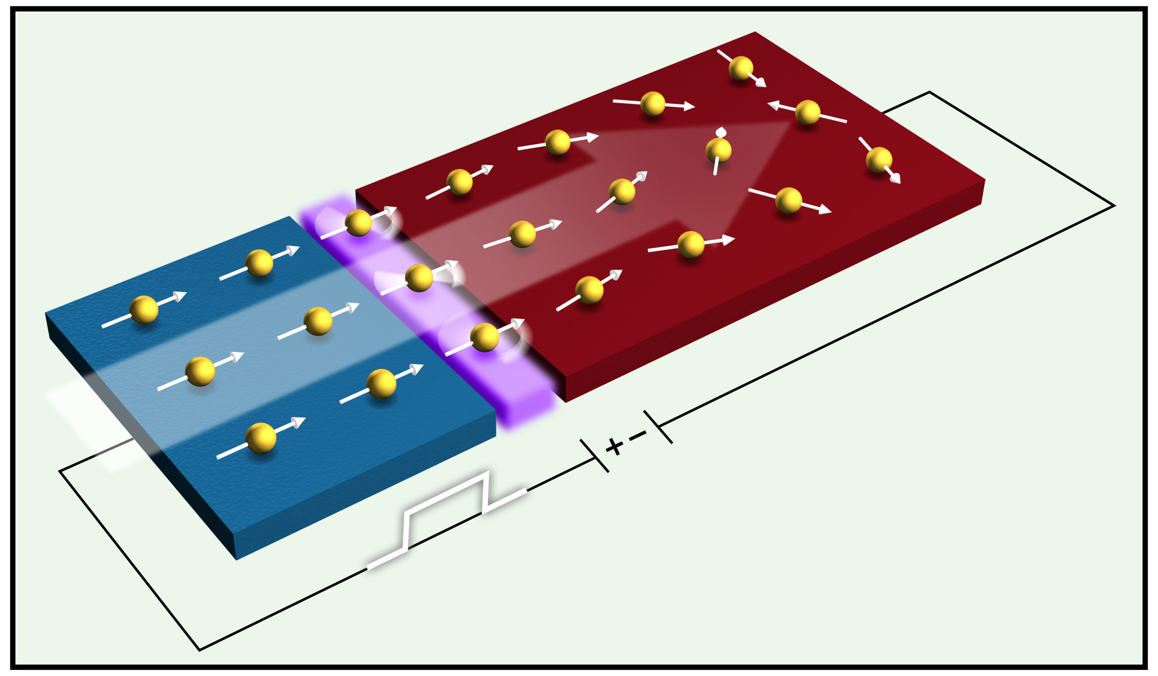
Thermoelectric devices



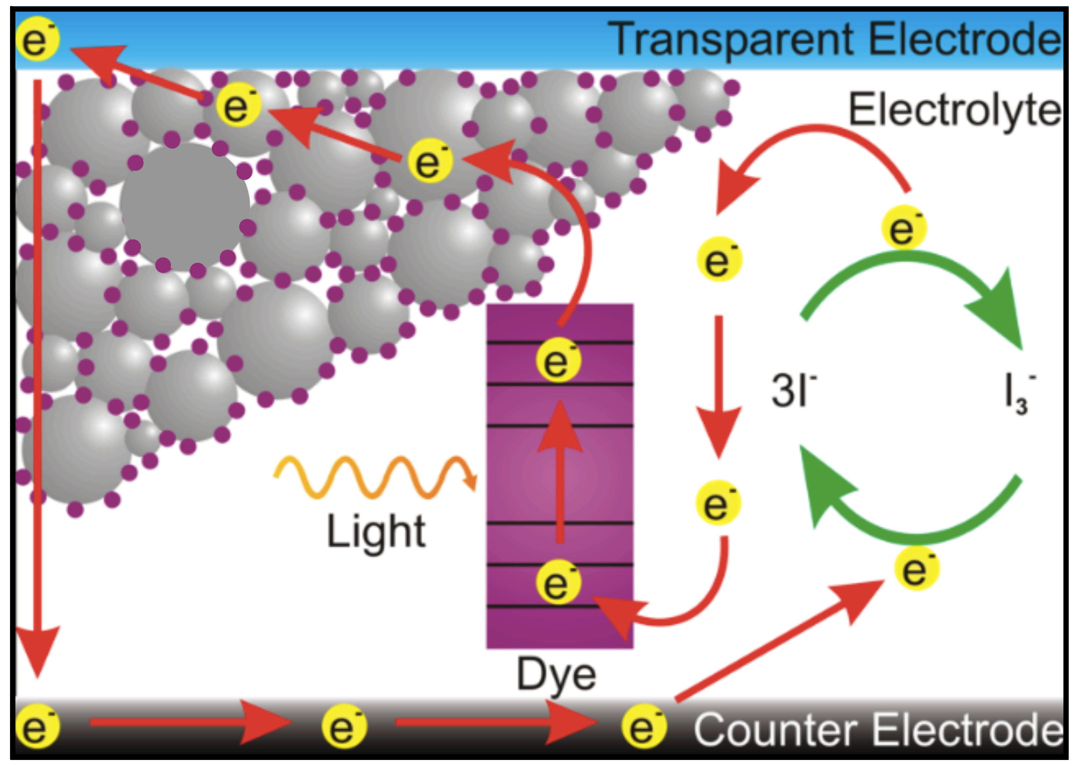
Photocatalysts



Spintronic devices



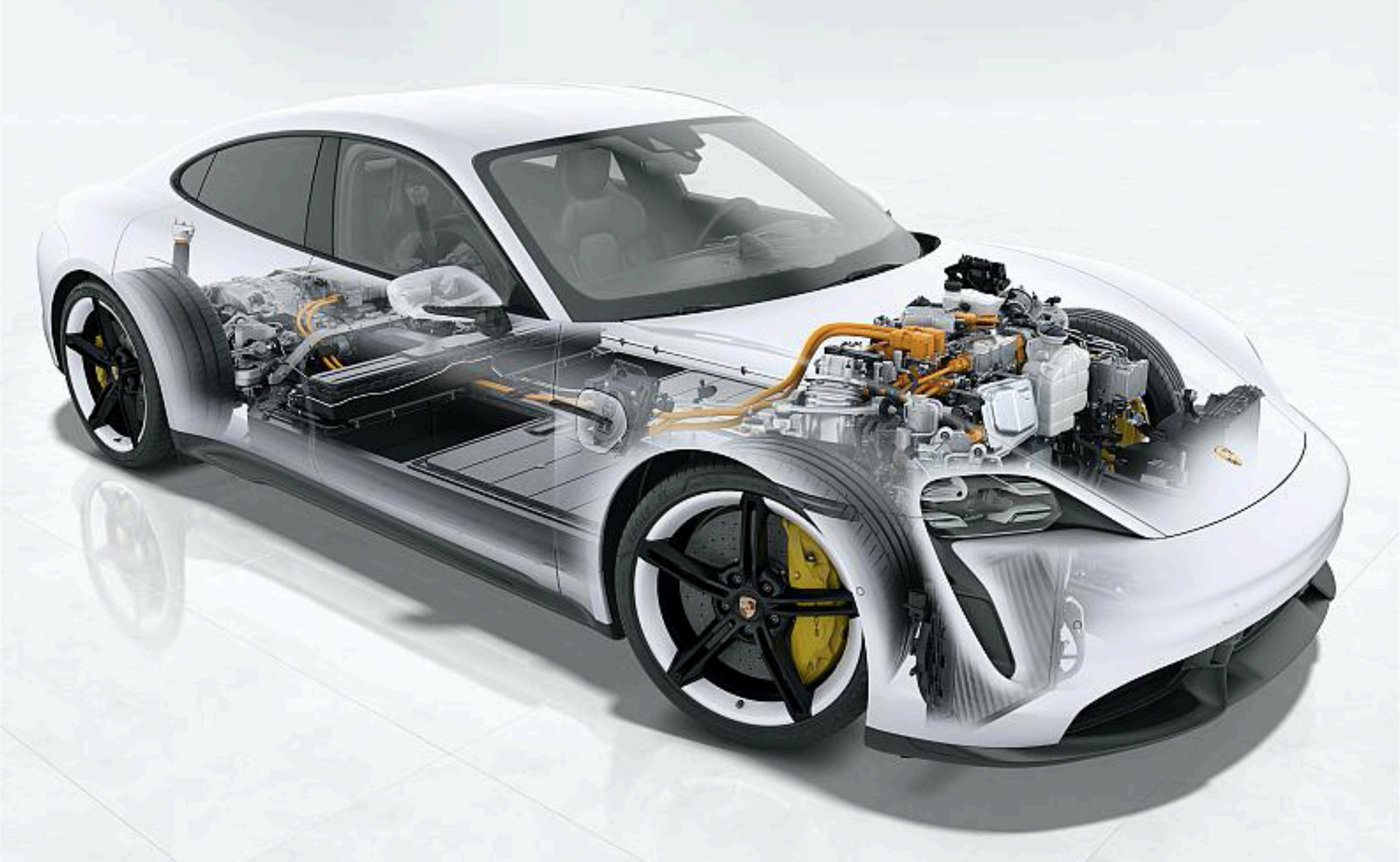
Dye-sensitized solar cells



Full electric vehicles

Mercedes-Benz EQC

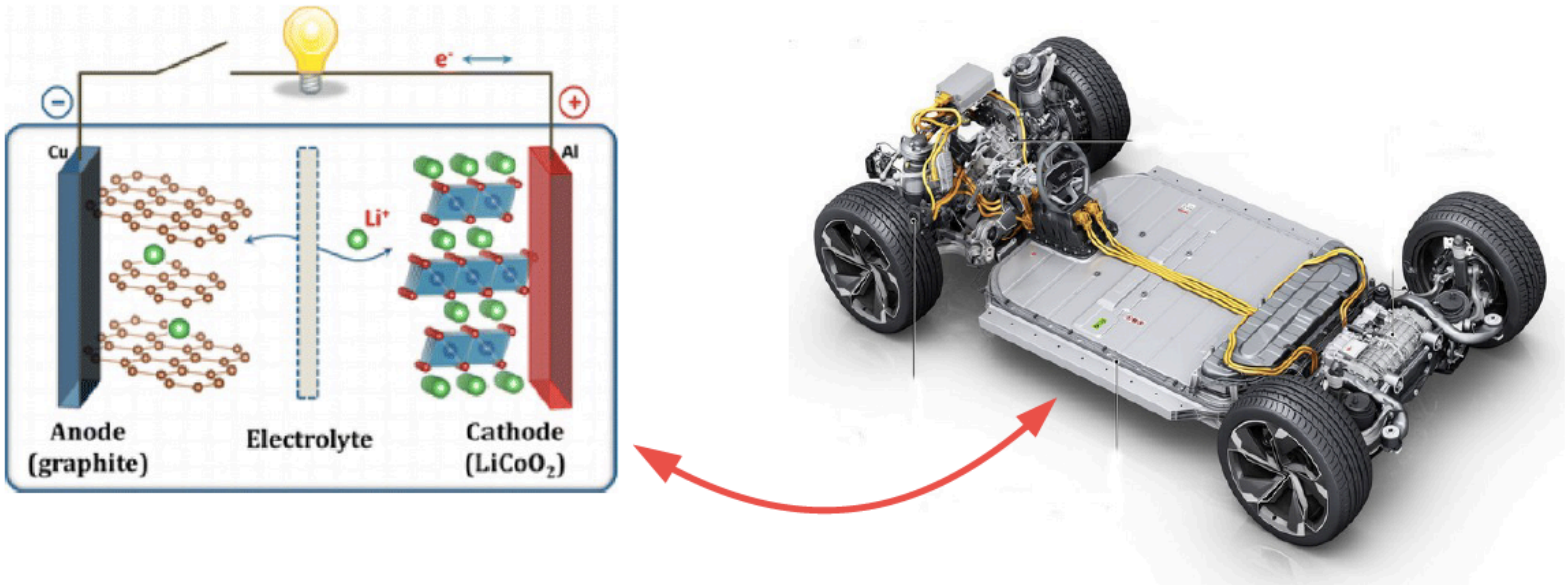
Porsche Taycan



Tesla Model S

- Electric cars replace very rapidly fossil-fuel cars
- The key components of electric cars are batteries
- Batteries should have high power-to-weight ratio, specific energy, capacity, be fast-rechargable, not toxic, and safe

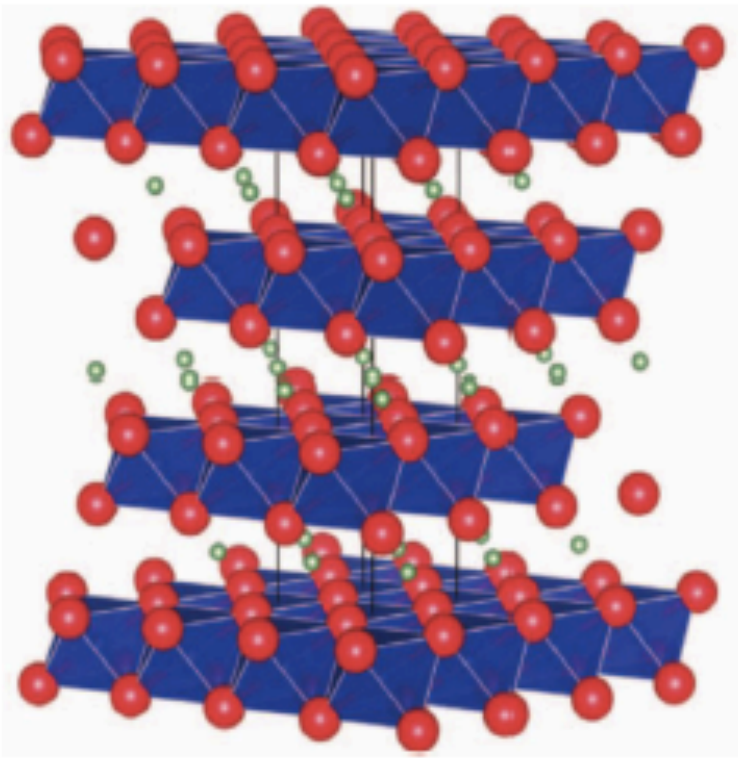
Li-ion batteries



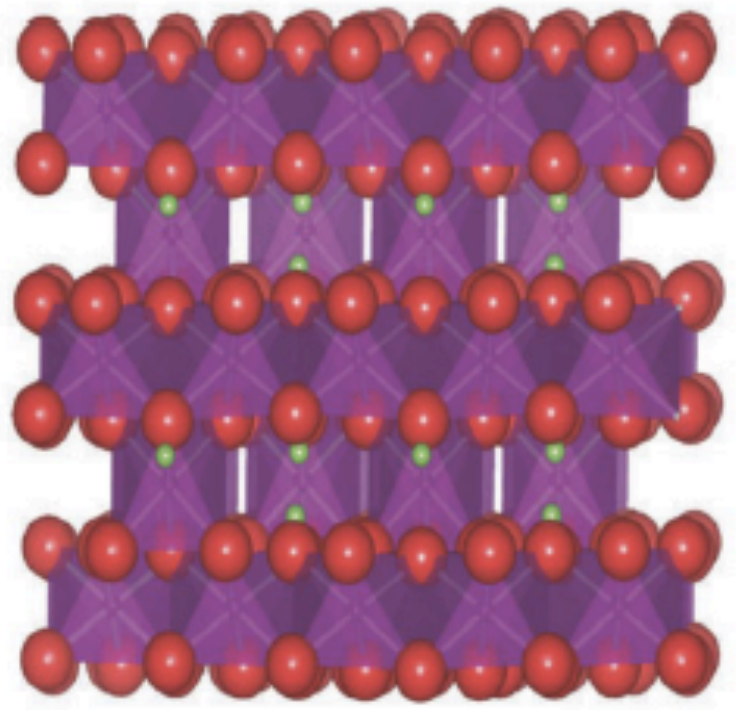
- Traditional Li-ion batteries use $LiCoO_2$ cathode and a graphite anode (high specific energy and 80-90% charge/discharge efficiency)
- Drawbacks of traditional Li-ion batteries:
  Short life cycle, significant degradation with age, fire risk if cherged improperly.
- Search for new more efficient batteries is highly needed

Computer quantum simulations can help to find new battery materials

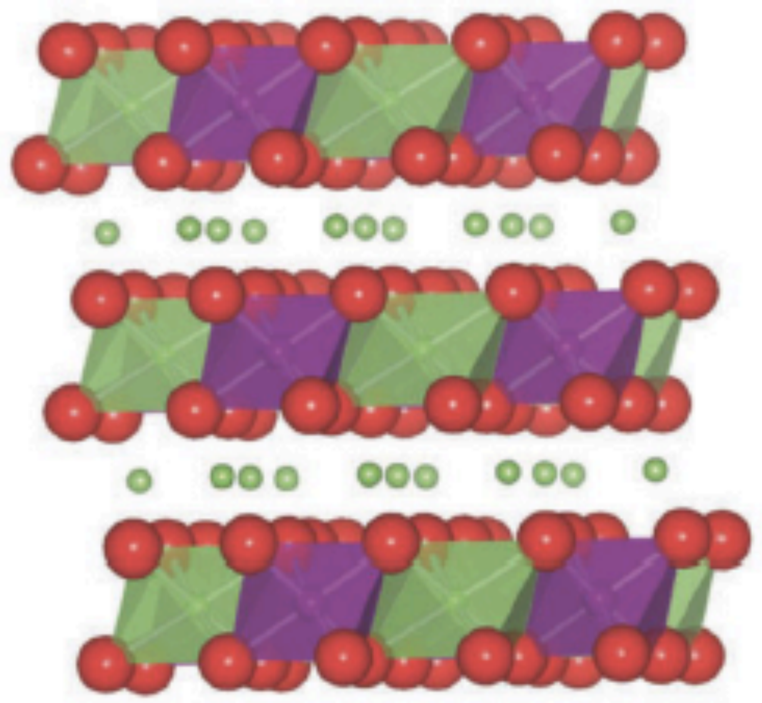
Computational quest for novel correlated materials



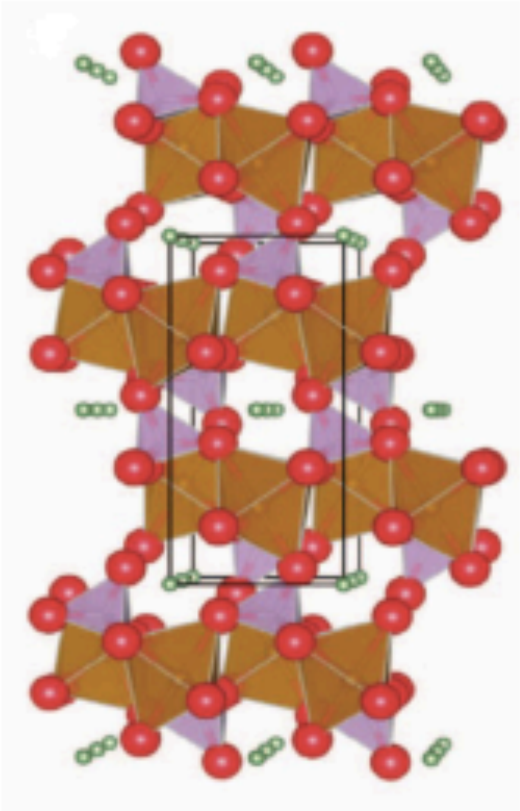
$LiCoO_2$



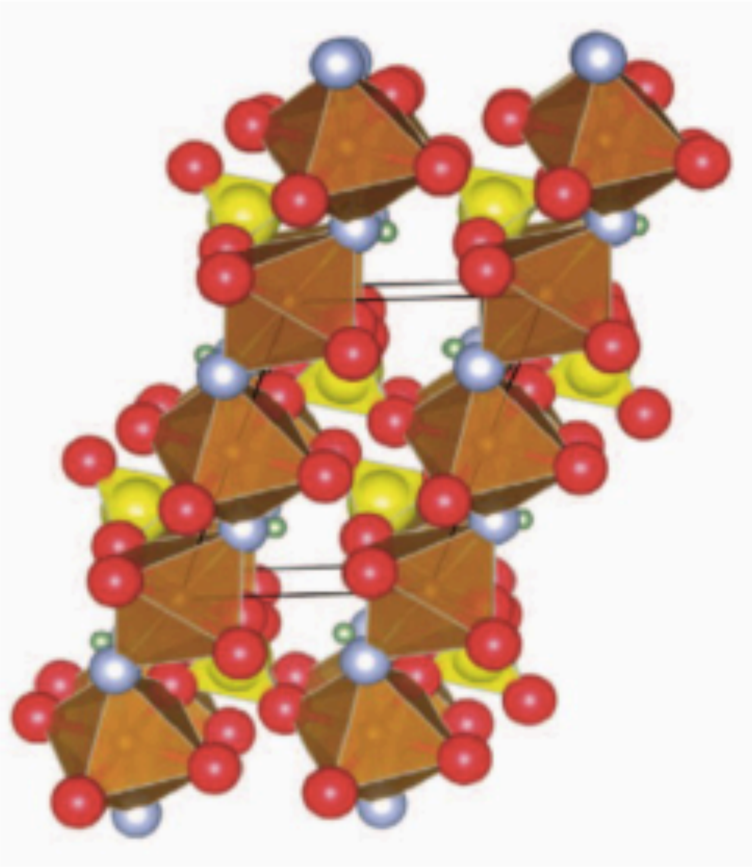
$LiMn_2O_4$



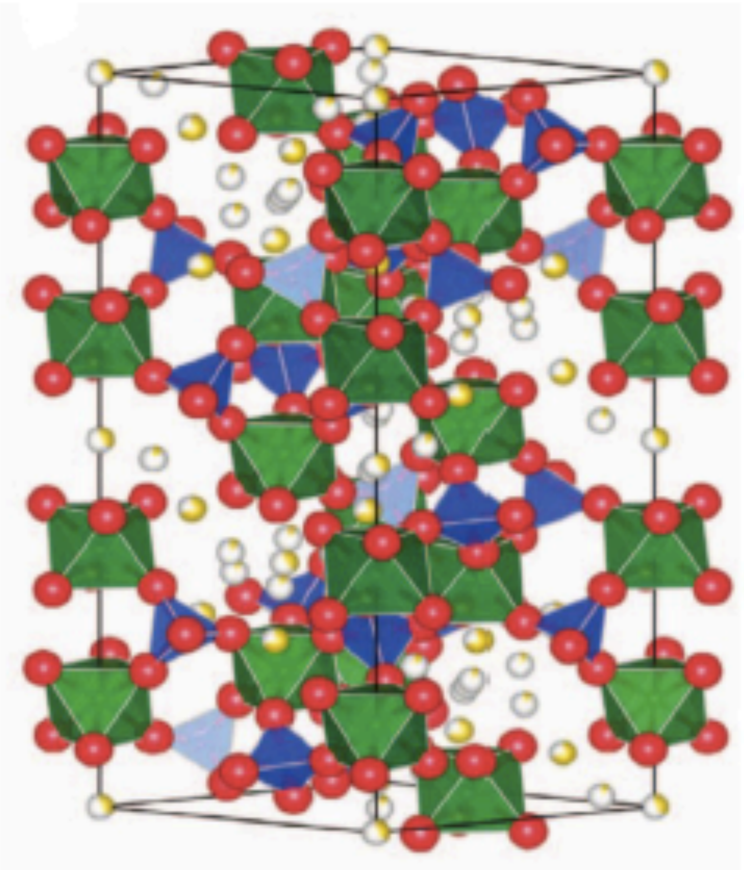
Li_2MnO_3



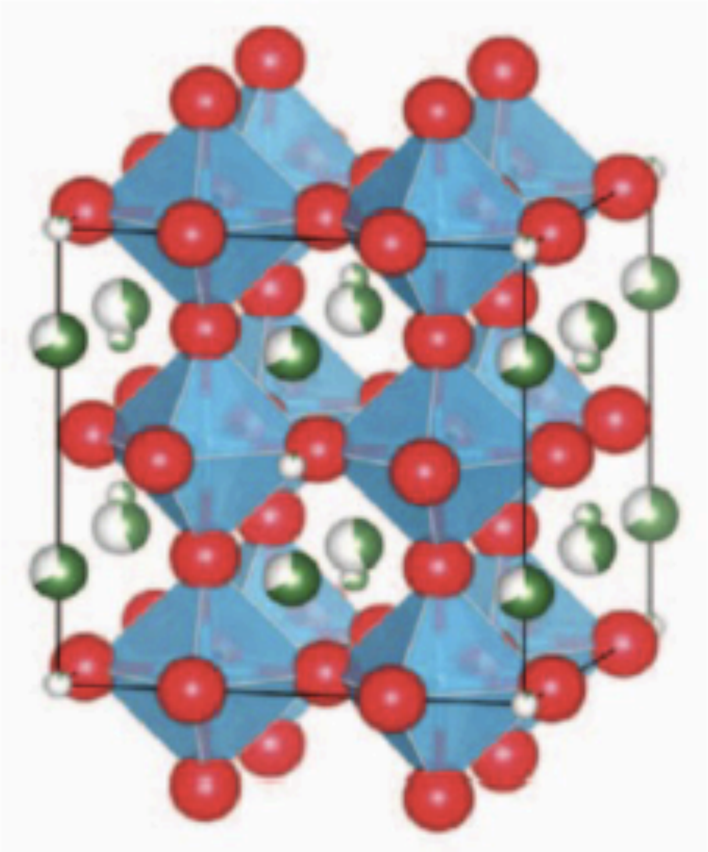
$LiFePO_4$



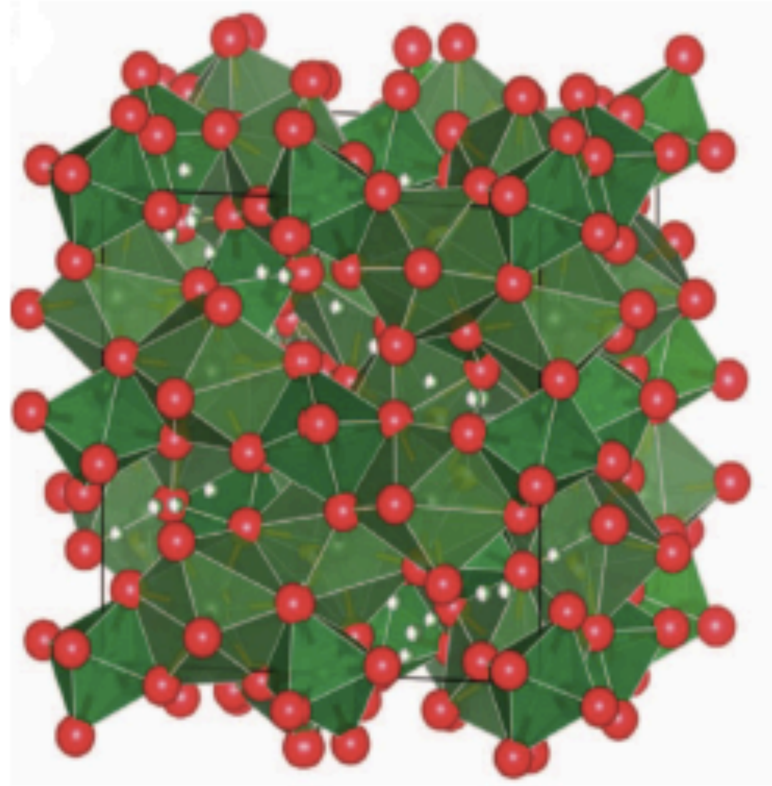
$LiFeSO_4F$



$Na_3Zr_2Si_2PO_{12}$



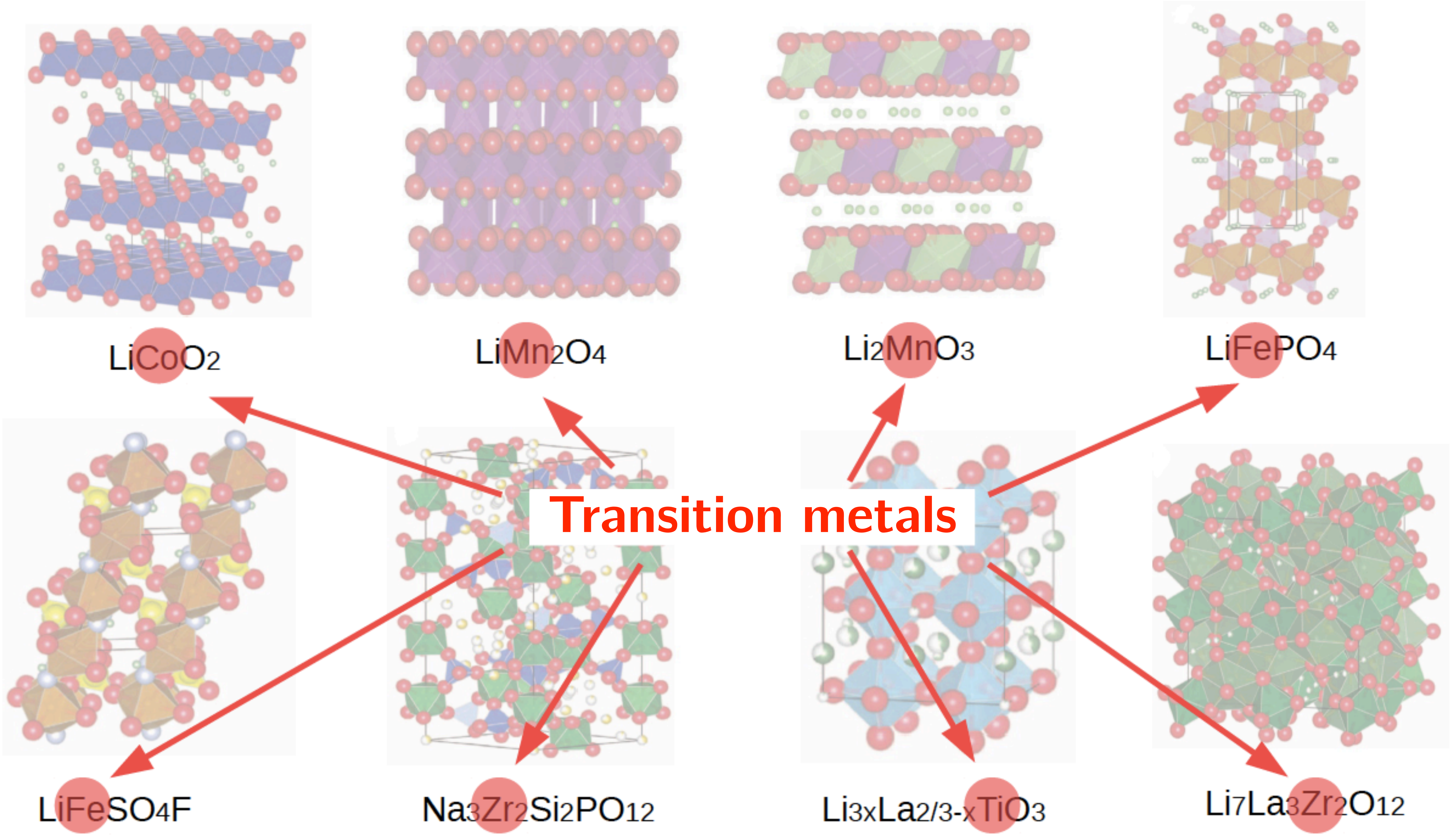
$Li_{3x}La_{2/3-x}TiO_3$



$Li_7La_3Zr_2O_{12}$

Quantum-mechanical atomistic simulations are important for search and discovery of novel materials

Computational quest for novel correlated materials



$LiCoO_2$

$LiMn_2O_4$

Li_2MnO_3

$LiFePO_4$

Transition metals

$LiFeSO_4F$

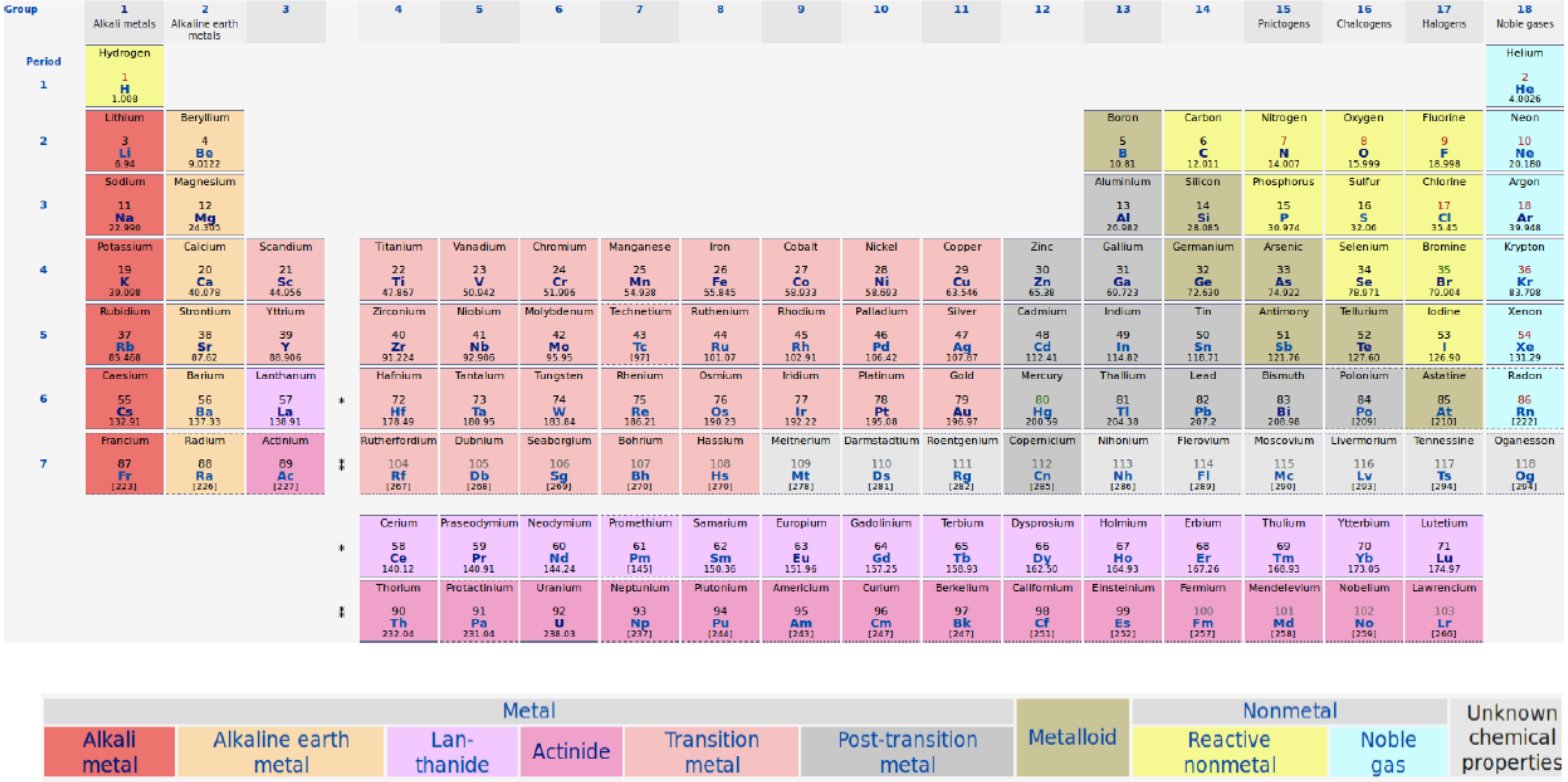
$Na_3Zr_2Si_2PO_{12}$

$Li_{3x}La_{2/3-x}TiO_3$

$Li_7La_3Zr_2O_{12}$

Quantum-mechanical atomistic simulations are important for search and discovery of novel materials

Periodic Table



Group	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	Alkali metals	Alkaline earth metals														Pnictogens	Chalcogens	Halogens	Noble gases
1	Hydrogen 1 H 1.008																		Helium 2 He 4.0026
2	Lithium 3 Li 6.94	Beryllium 4 Be 9.0122												Boron 5 B 10.81	Carbon 6 C 12.011	Nitrogen 7 N 14.007	Oxygen 8 O 15.999	Fluorine 9 F 18.998	Neon 10 Ne 20.180
3	Sodium 11 Na 22.990	Magnesium 12 Mg 24.305												Aluminium 13 Al 26.982	Silicon 14 Si 28.085	Phosphorus 15 P 30.974	Sulfur 16 S 32.06	Chlorine 17 Cl 35.45	Argon 18 Ar 39.948
4	Potassium 19 K 39.098	Calcium 20 Ca 40.078	Scandium 21 Sc 44.956		Titanium 22 Ti 47.867	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.845	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546	Zinc 30 Zn 65.38	Gallium 31 Ga 69.723	Germanium 32 Ge 72.630	Arsenic 33 As 74.922	Selenium 34 Se 78.971	Bromine 35 Br 79.904	Krypton 36 Kr 83.798
5	Rubidium 37 Rb 85.468	Strontium 38 Sr 87.62	Yttrium 39 Y 88.906		Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906	Molybdenum 42 Mo 95.95	Technetium 43 Tc [97]	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 102.91	Palladium 46 Pd 106.42	Silver 47 Ag 107.87	Cadmium 48 Cd 112.41	Indium 49 In 114.82	Tin 50 Sn 118.71	Antimony 51 Sb 121.76	Tellurium 52 Te 127.60	Iodine 53 I 126.90	Xenon 54 Xe 131.29
6	Caesium 55 Cs 132.91	Barium 56 Ba 137.33	Lanthanum 57 La 138.91	*	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.95	Tungsten 74 W 183.84	Rhenium 75 Re 186.21	Osmium 76 Os 190.23	Iridium 77 Ir 192.22	Platinum 78 Pt 195.08	Gold 79 Au 196.97	Mercury 80 Hg 200.59	Thallium 81 Tl 204.38	Lead 82 Pb 207.2	Bismuth 83 Bi 208.98	Polonium 84 Po [209]	Astatine 85 At [210]	Radon 86 Rn [222]
7	Francium 87 Fr [223]	Radium 88 Ra [226]	Actinium 89 Ac [227]	‡	Rutherfordium 104 Rf [267]	Dubnium 105 Db [268]	Seaborgium 106 Sg [269]	Bohrium 107 Bh [270]	Hassium 108 Hs [270]	Meitnerium 109 Mt [278]	Darmstadtium 110 Ds [281]	Roentgenium 111 Rg [282]	Copernicium 112 Cn [285]	Nihonium 113 Nh [286]	Flerovium 114 Fl [289]	Moscovium 115 Mc [290]	Livermorium 116 Lv [293]	Tennessine 117 Ts [294]	Oganesson 118 Og [294]
				*	Cerium 58 Ce 140.12	Praseodymium 59 Pr 140.91	Neodymium 60 Nd 144.24	Promethium 61 Pm [145]	Samarium 62 Sm 150.36	Europium 63 Eu 151.96	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.93	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.93	Erbium 68 Er 167.26	Thulium 69 Tm 168.93	Ytterbium 70 Yb 173.05	Lutetium 71 Lu 174.97	
				‡	Thorium 90 Th 232.04	Protactinium 91 Pa 231.04	Uranium 92 U 238.03	Neptunium 93 Np [237]	Plutonium 94 Pu [244]	Americium 95 Am [243]	Curium 96 Cm [247]	Berkelium 97 Bk [247]	Californium 98 Cf [251]	Einsteinium 99 Es [252]	Fermium 100 Fm [257]	Mendelevium 101 Md [258]	Nobelium 102 No [259]	Lawrencium 103 Lr [266]	

Metal						Metalloid	Nonmetal		Unknown chemical properties
Alkali metal	Alkaline earth metal	Lanthanide	Actinide	Transition metal	Post-transition metal		Reactive nonmetal	Noble gas	

The partly filled *d* electrons in transition metals and the partly filled *f* electrons in the rare earths and actinides series give rise to the characteristic properties of these materials and their compounds.

Outline

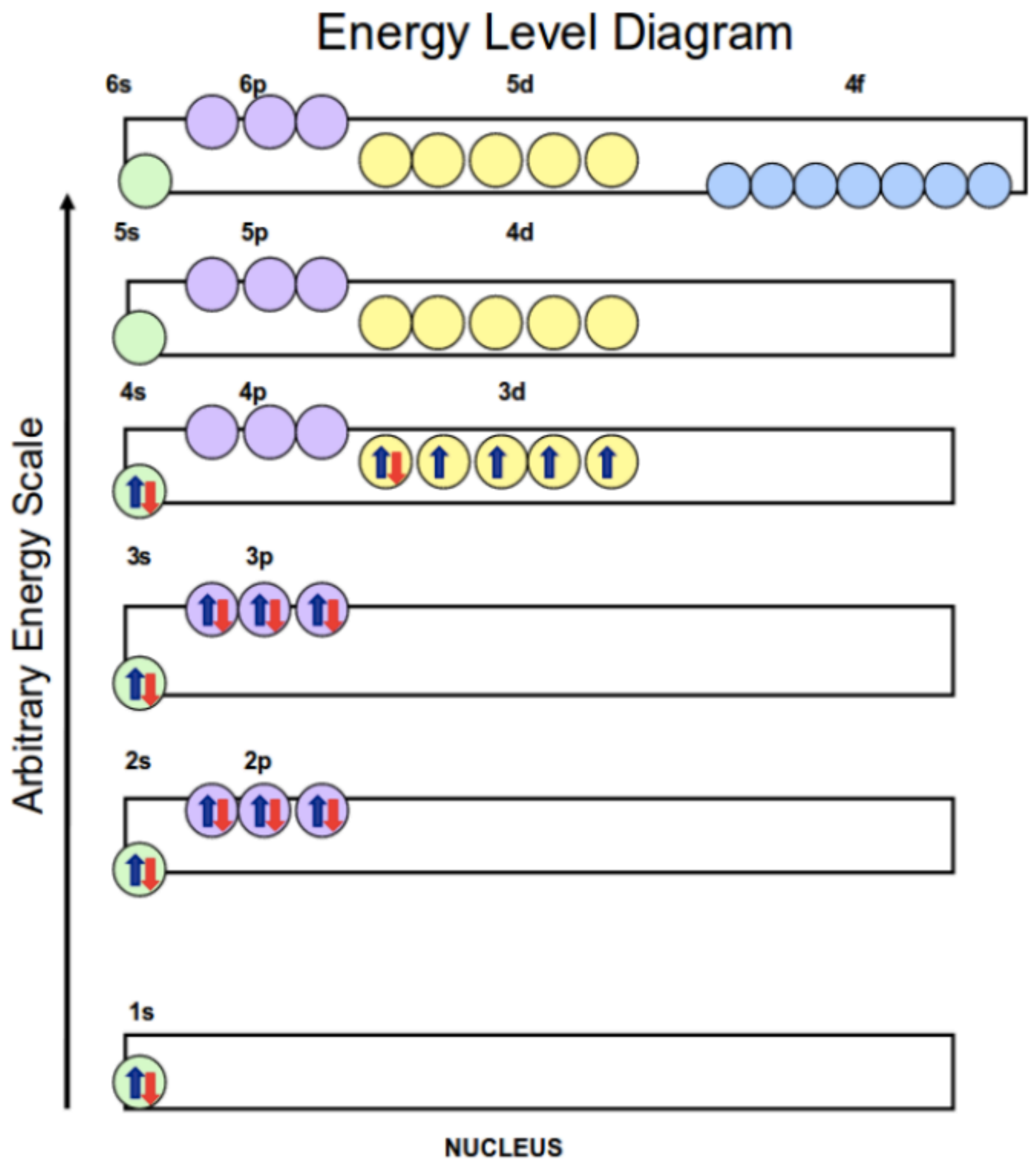
- DFT with (extended) Hubbard functionals

- Calculation of Hubbard parameters from first principles

- Applications: electronic, vibrational, and spectroscopic properties

What is so special about correlated materials?

Electron configuration of Fe atom



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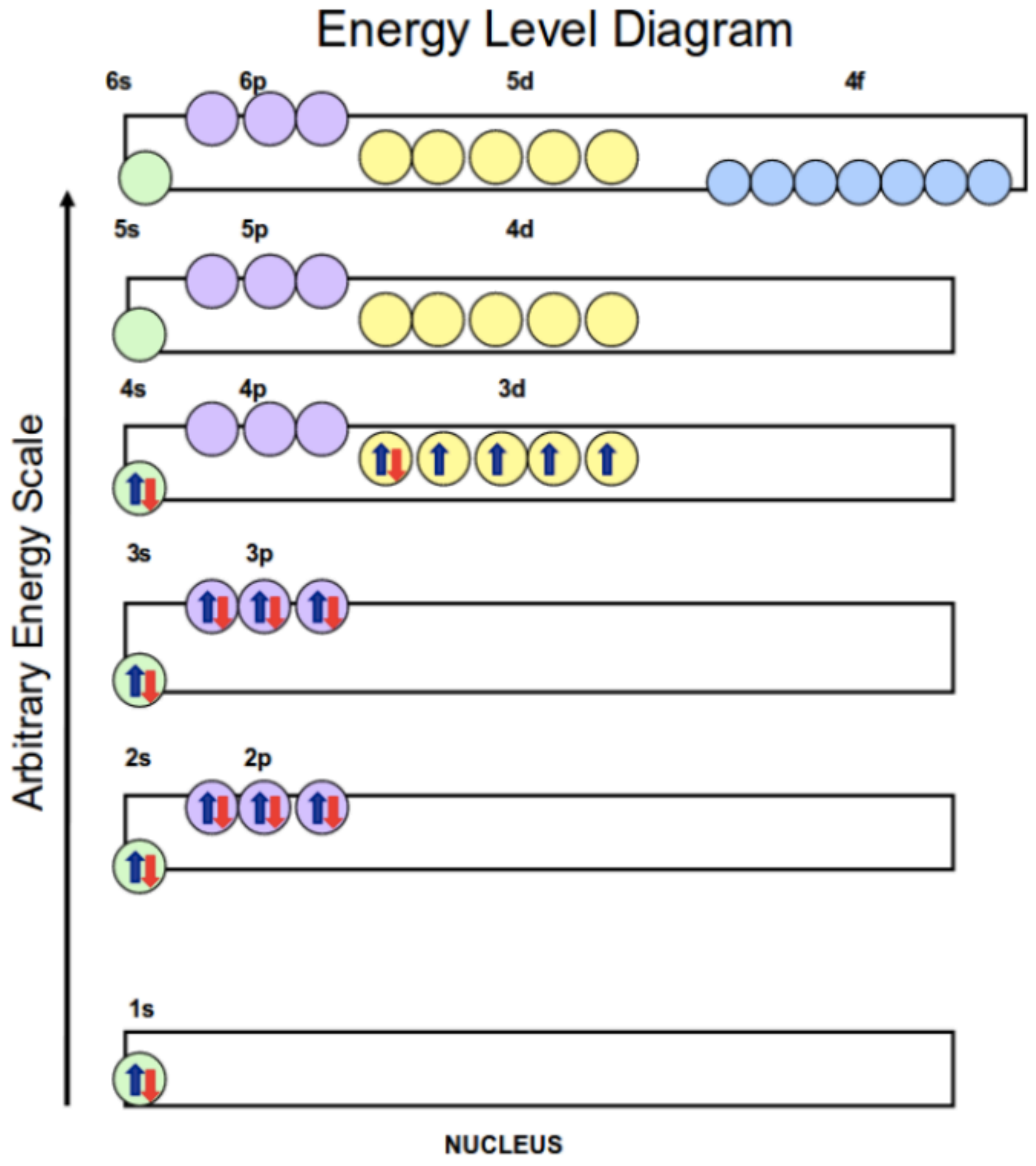
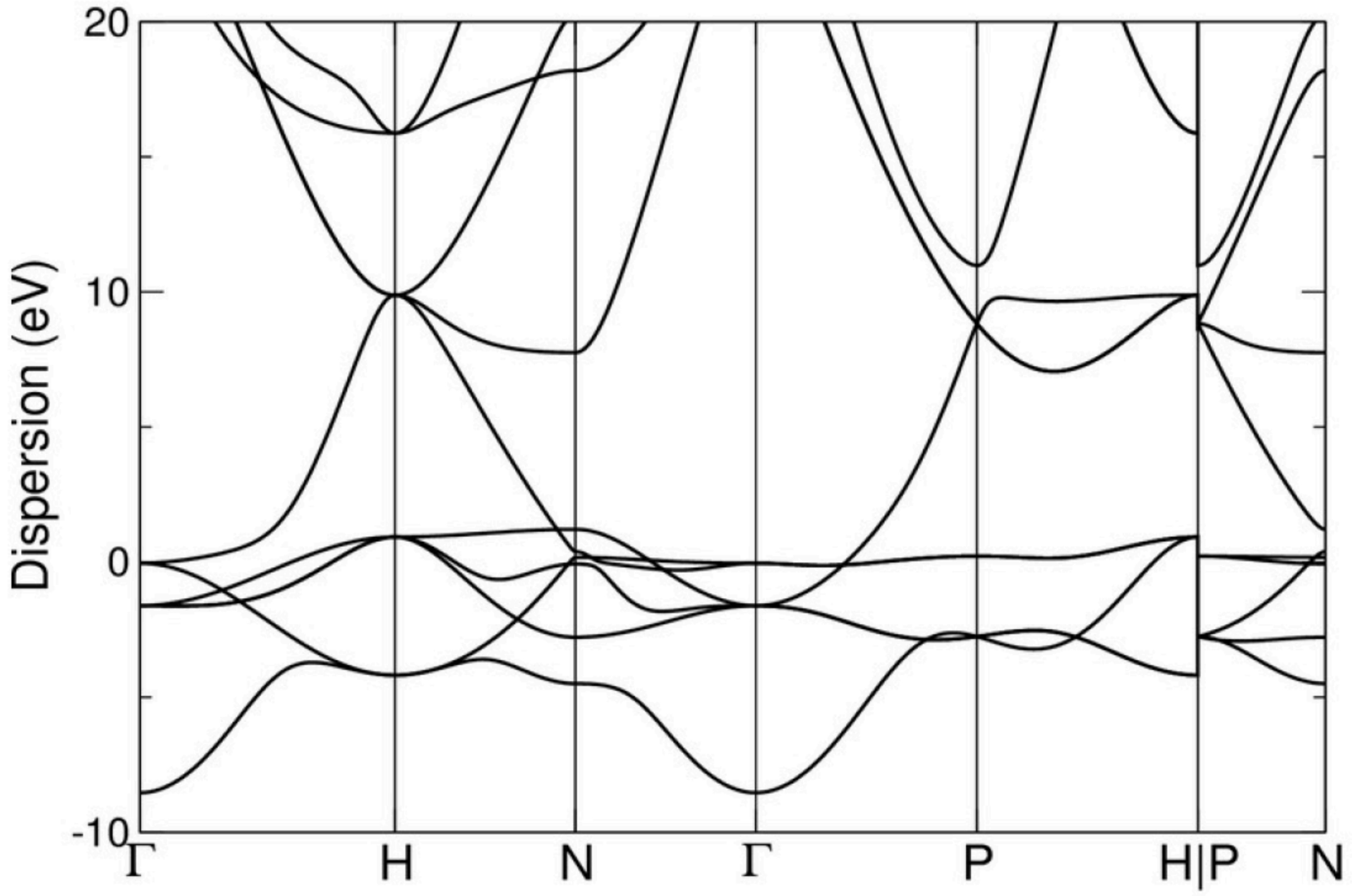


Electron band-structure of Fe solid



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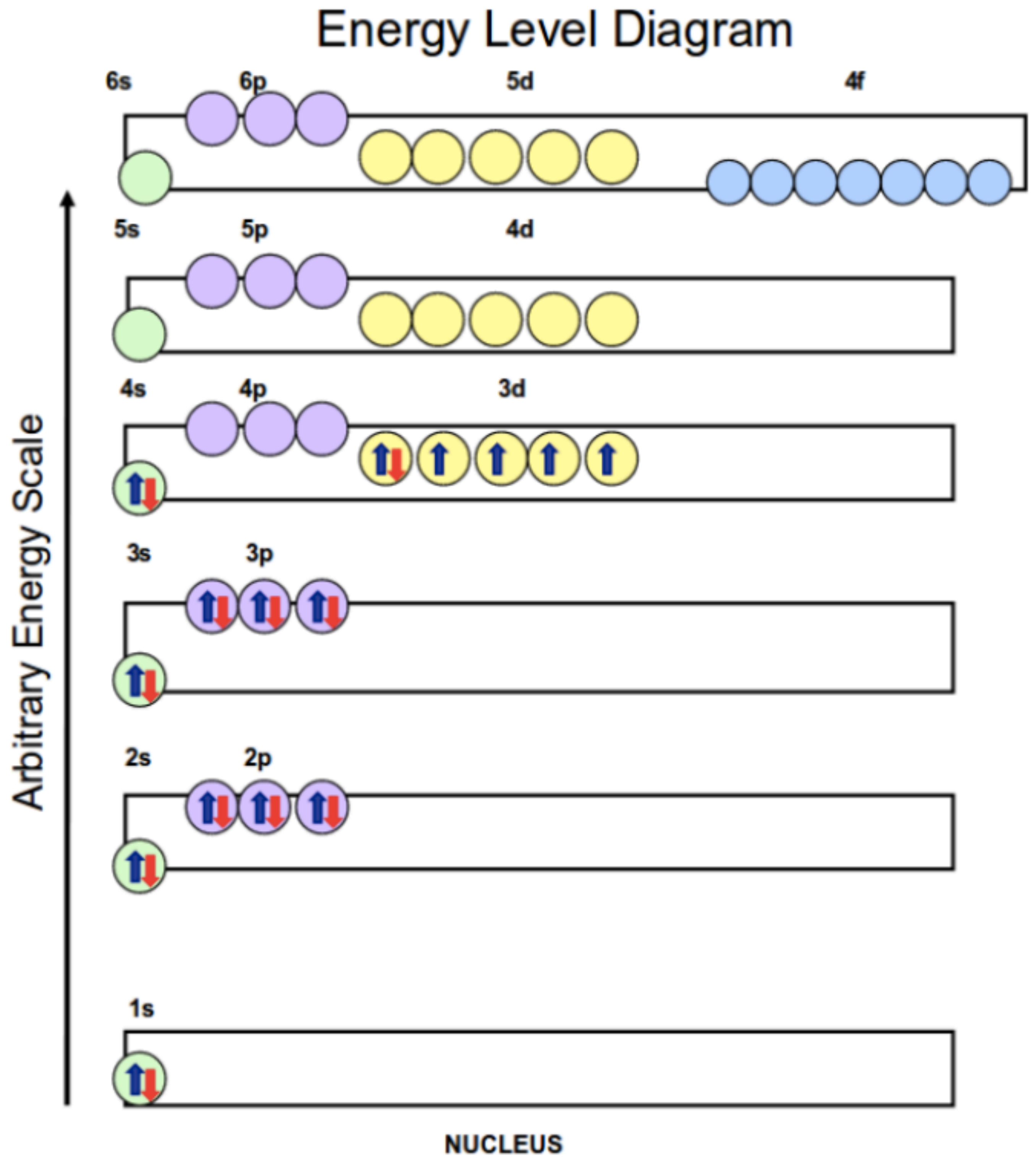

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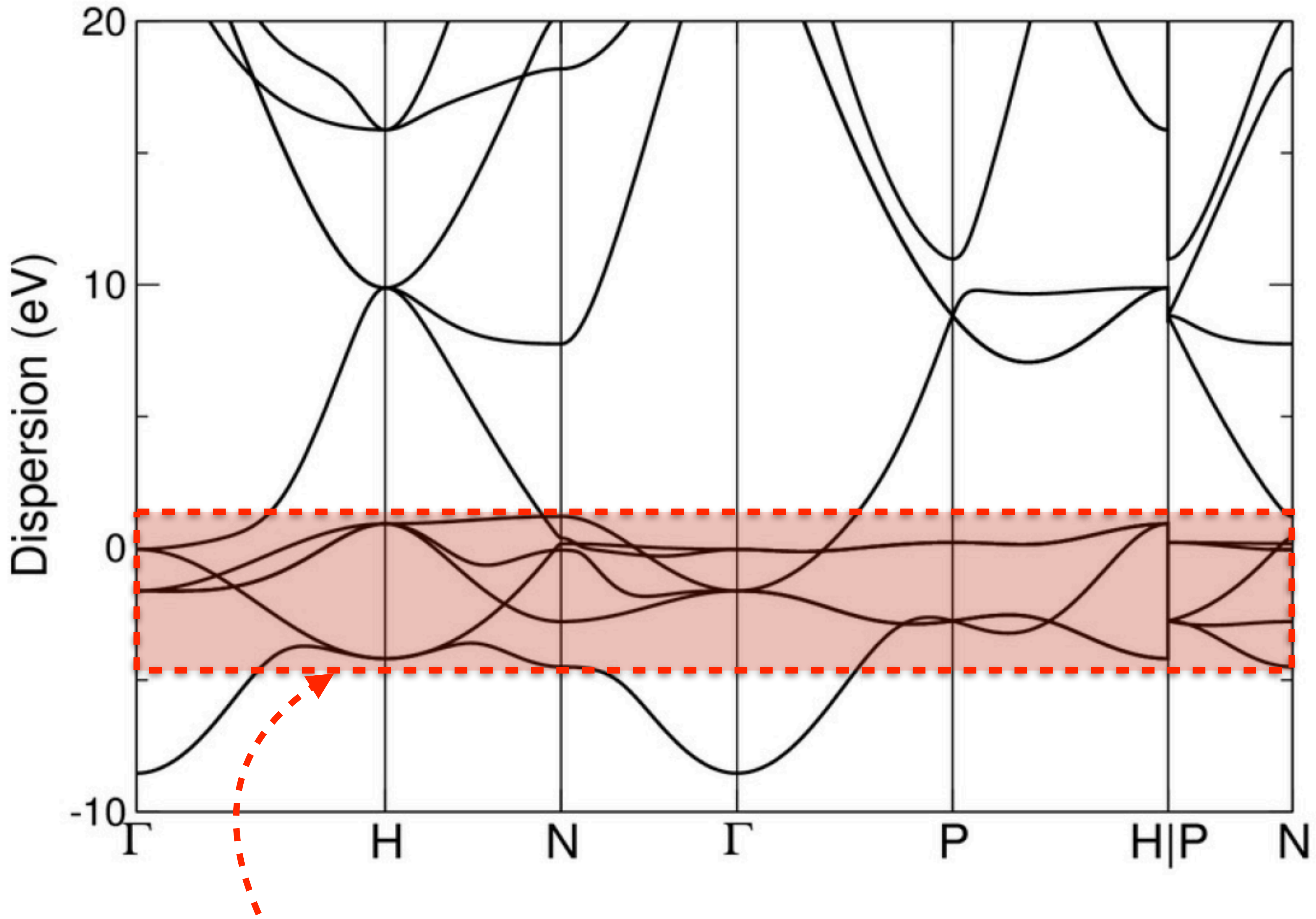

narrow energy bands of *d* character

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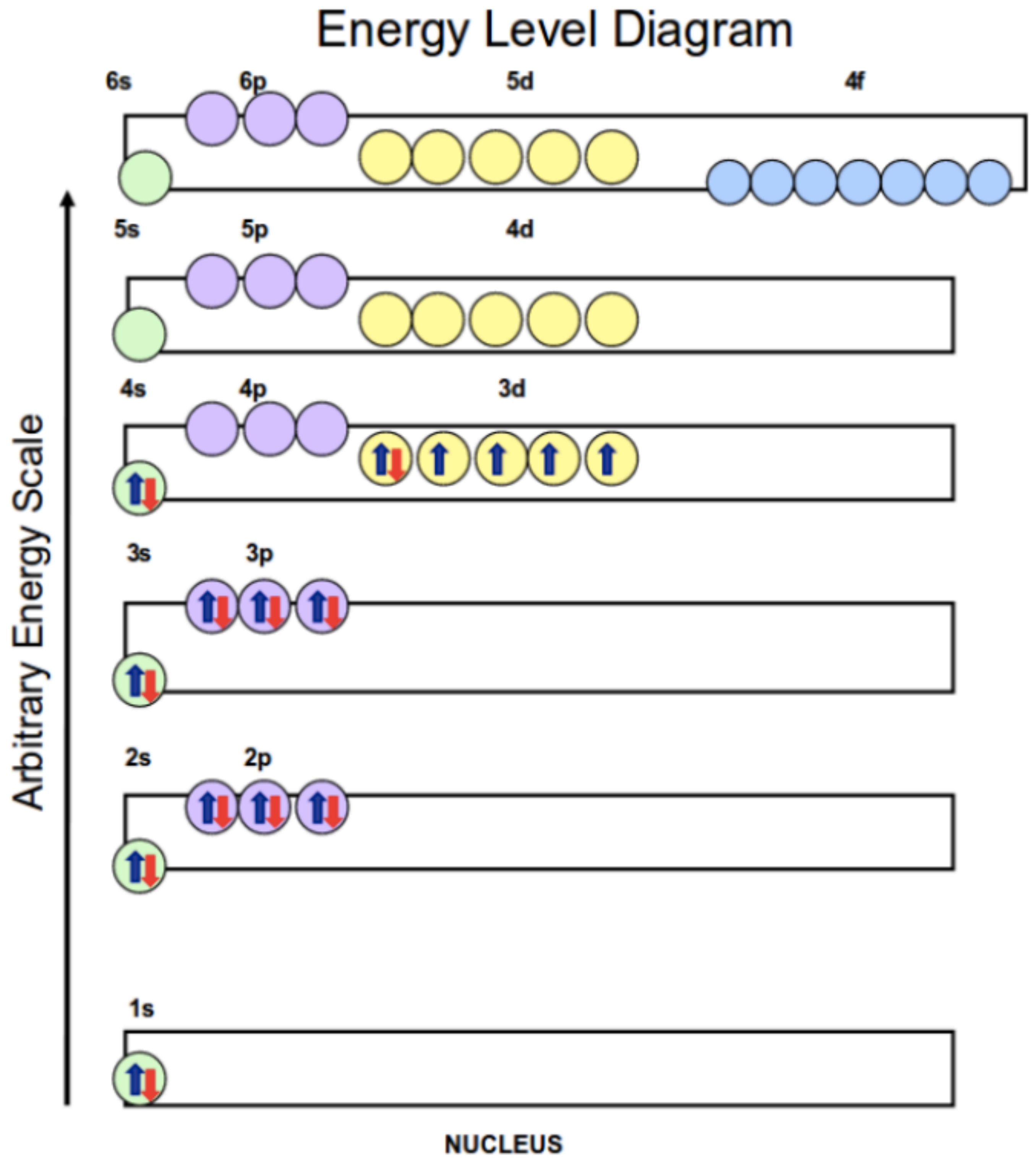

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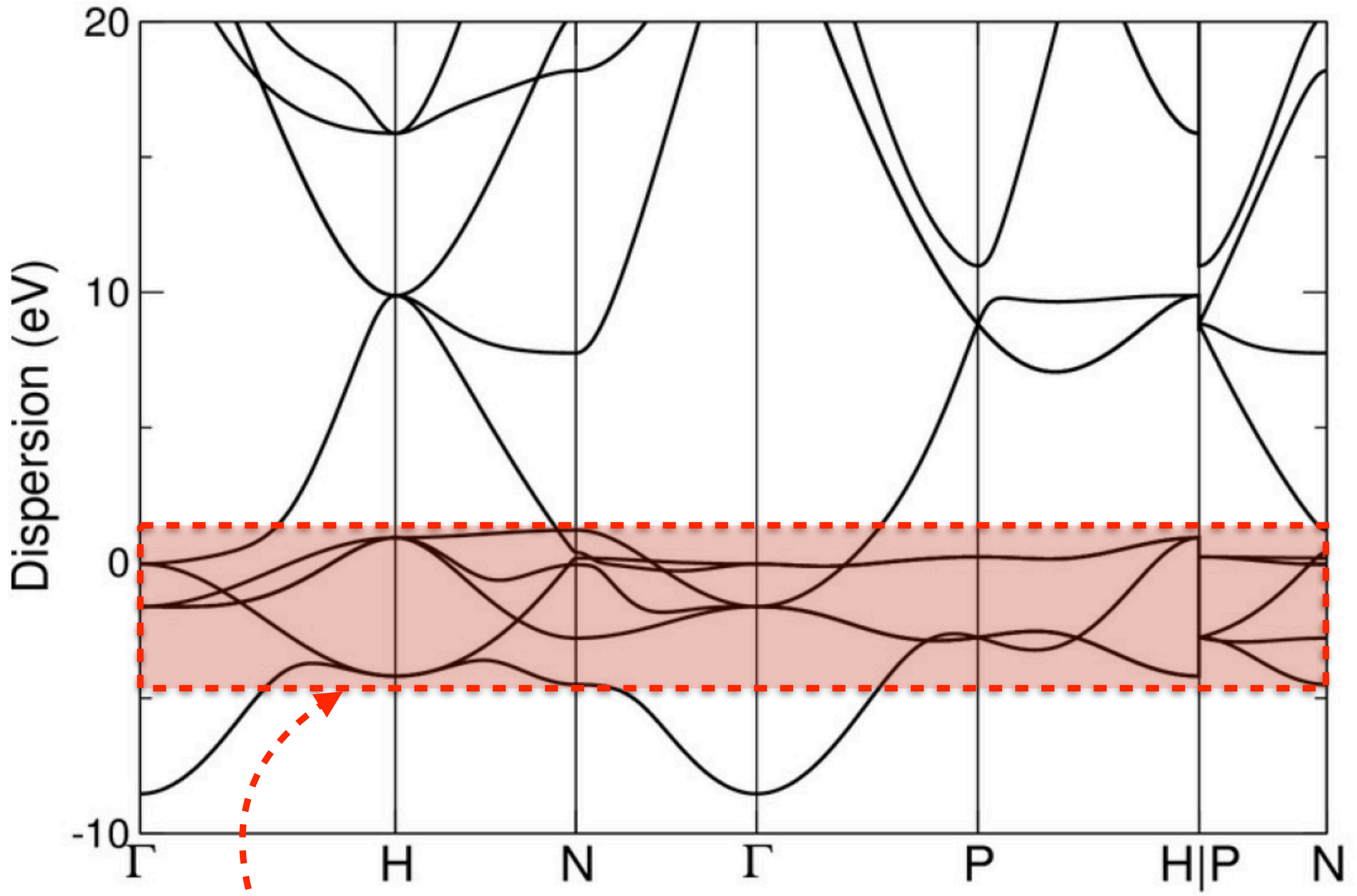

narrow energy bands of *d* character

"It is, in fact found experimentally that the d-electrons of transition metals exhibit behaviour characteristic of both the ordinary band model and the atomic model." [1]

"…it is correlation effects in narrow bands which lead to the atomic behaviour…" [1]

[1] J. Hubbard, Proc. Roy. Soc. London A 276, 238 (1963).

Modelling of correlated materials: what are the challenges?

Density-functional theory (DFT) is one of the most popular methods for modelling of various properties of materials from first-principles: crystal structure, electronic structure, magnetic ordering, etc.

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First and foremost, this is due to large static self-interaction errors (SIE) which are inherent to "standard DFT".

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Going beyond “standard” DFT

Methods

- DFT with metaGGA functionals
  Zhao *et al.*, 2006
  Perdew *et al.*, 2015
- DFT with hybrid functionals
  Becke *et al.*, 1993
  Perdew *et al.*, 1996
- DFT with Hubbard functionals
  Anisimov *et al.*, 1991
  Kulik *et al.*, 2006
- Dynamical mean field theory (DMFT)
  Georges *et al.*, 1996
  Kotliar *et al.*, 2006

Going beyond “standard” DFT

Methods

DFT with metaGGA functionals	DFT with hybrid functionals	DFT with Hubbard functionals	Dynamical mean field theory (DMFT)
Zhao *et al.*, 2006 Perdew *et al.*, 2015	Becke *et al.*, 1993 Perdew *et al.*, 1996 Heyd *et al.*, 2006	Anisimov *et al.*, 1991 Kulik *et al.*, 2006 Himmetoglu*et al.*, 2014	Georges *et al.*, 1996 Kotliar *et al.*, 2006
+ Improves the description of many properties (slightly removes SIE)	+ Improves the description of many properties (partly removes SIE)	+ Removes effectively static self-interactions (material dependent)	+ Includes dynamic correlations (describes metal-insulator transition)
- Worsens the description of itinerant ferromagnets	- Insensitive to material-specific SIE	- At present, dynamical effects are not included	- Access to some observables is challenging
- Numerically unstable, comput. more expensive	- Computationally very expensive	+ Computationally inexpensive	- Computationally very expensive

DFT+U

W. Kohn

DFT

(1964 - 1965)

The Hubbard model

(1963 - 1967)

J. Hubbard

~25 years

DFT+U

V.I. Anisimov, J. Zaanen, O.K. Andersen,
Phys. Rev. B **44**, 943 (1991)

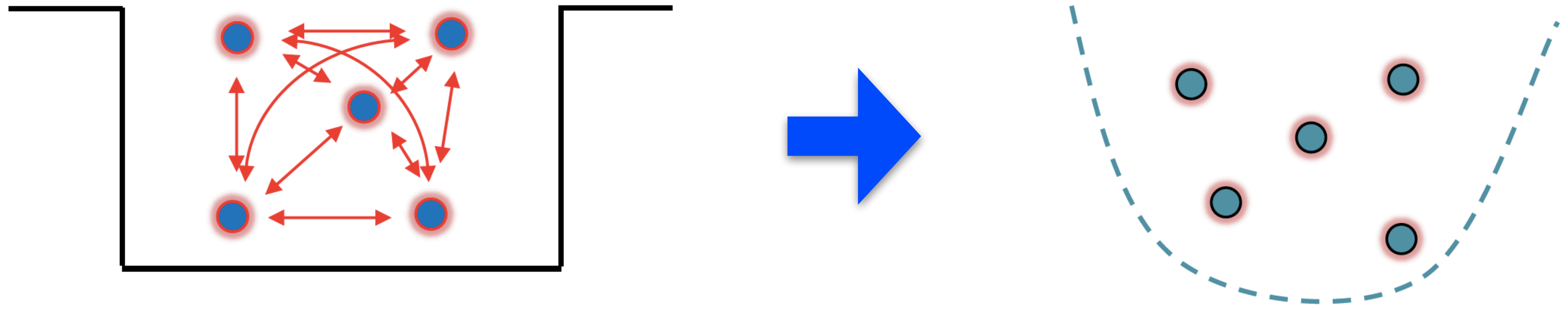
DFT+U

DFT

W. Kohn (1964 - 1965)

The main idea:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \Rightarrow \rho(\mathbf{r})$$



interacting electrons
in the external potential

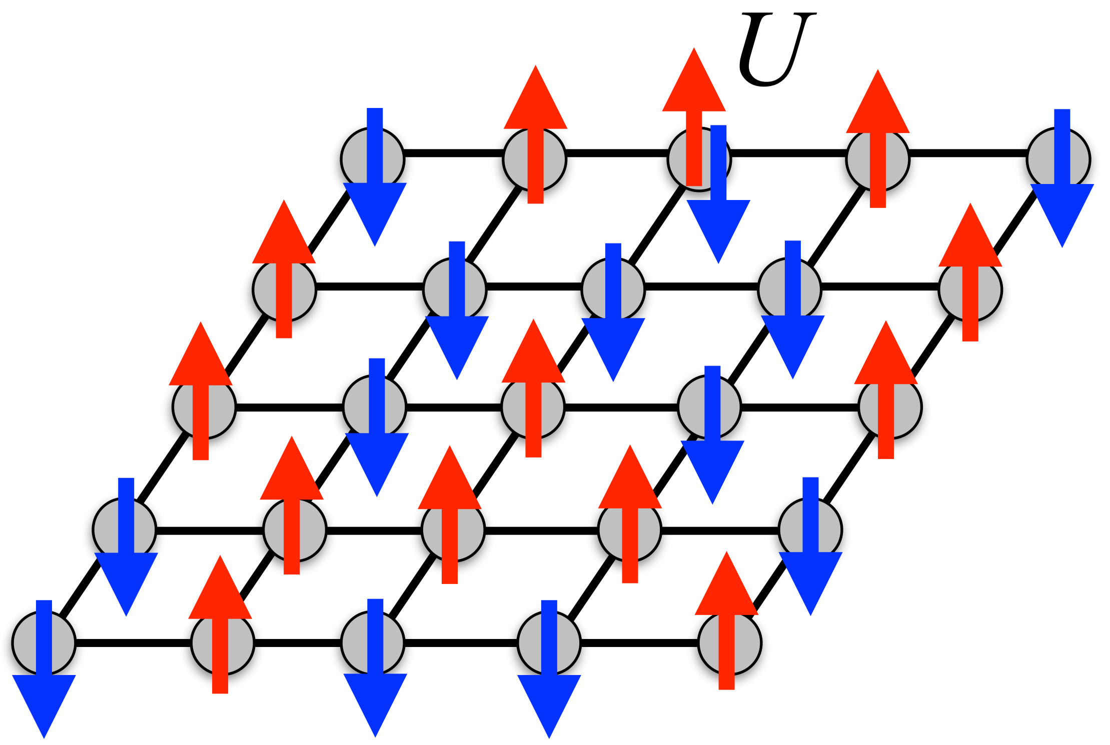
noninteracting electrons
in the effective potential

The Hubbard model

(1963 - 1967) J. Hubbard

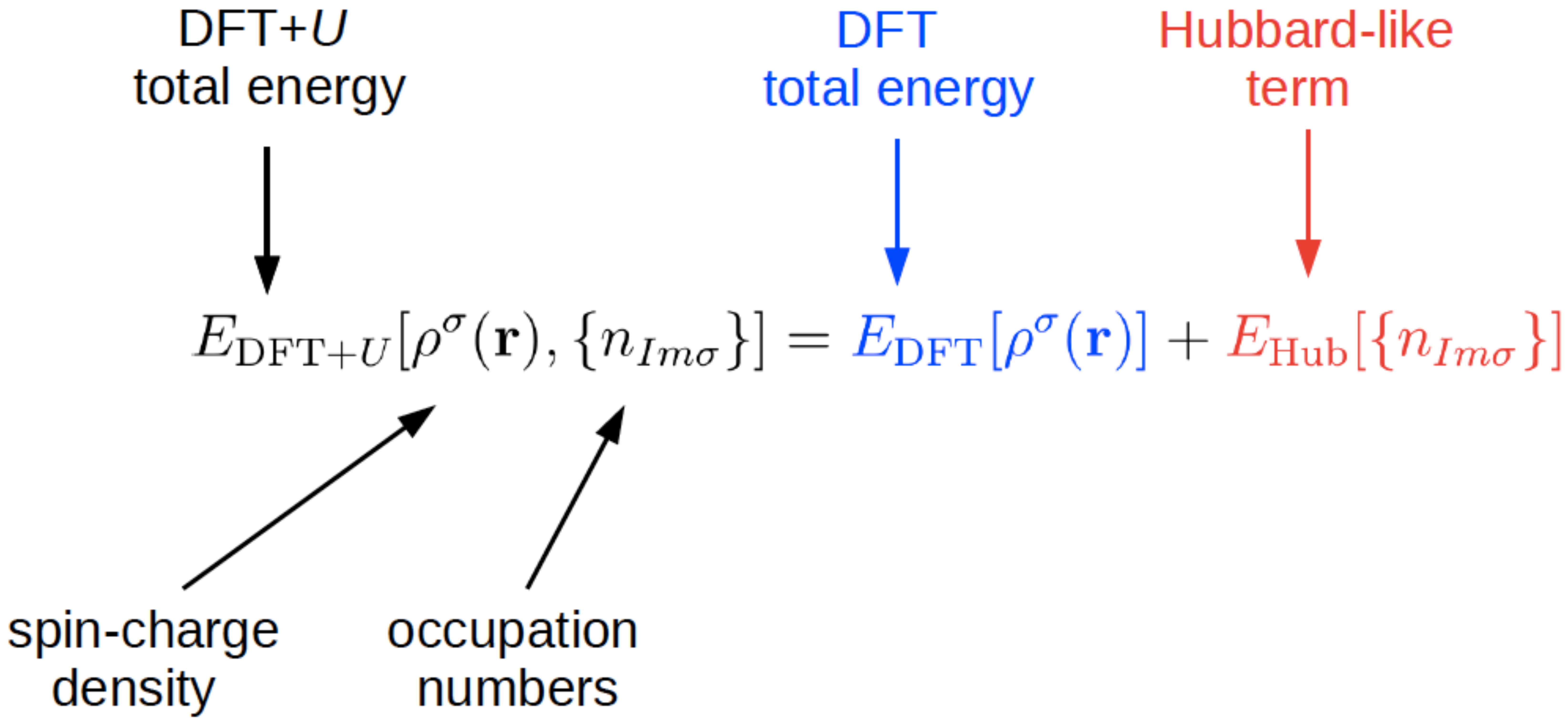
The main idea:

$$\hat{H} = -\sum_{I\neq J,\sigma} t_{IJ}\,\hat{c}^{\dagger}_{I\sigma}\,\hat{c}_{J\sigma} + U\sum_{I}\hat{n}_{I\uparrow}\,\hat{n}_{I\downarrow}$$



DFT+U

DFT total-energy functional is corrected by the Hubbard-like term.



DFT+U total energy

DFT total energy

Hubbard-like term

$$E_{\mathrm{DFT}+U}[\rho^{\sigma}(\mathbf{r}), \{n_{Im\sigma}\}] = E_{\mathrm{DFT}}[\rho^{\sigma}(\mathbf{r})] + E_{\mathrm{Hub}}[\{n_{Im\sigma}\}]$$

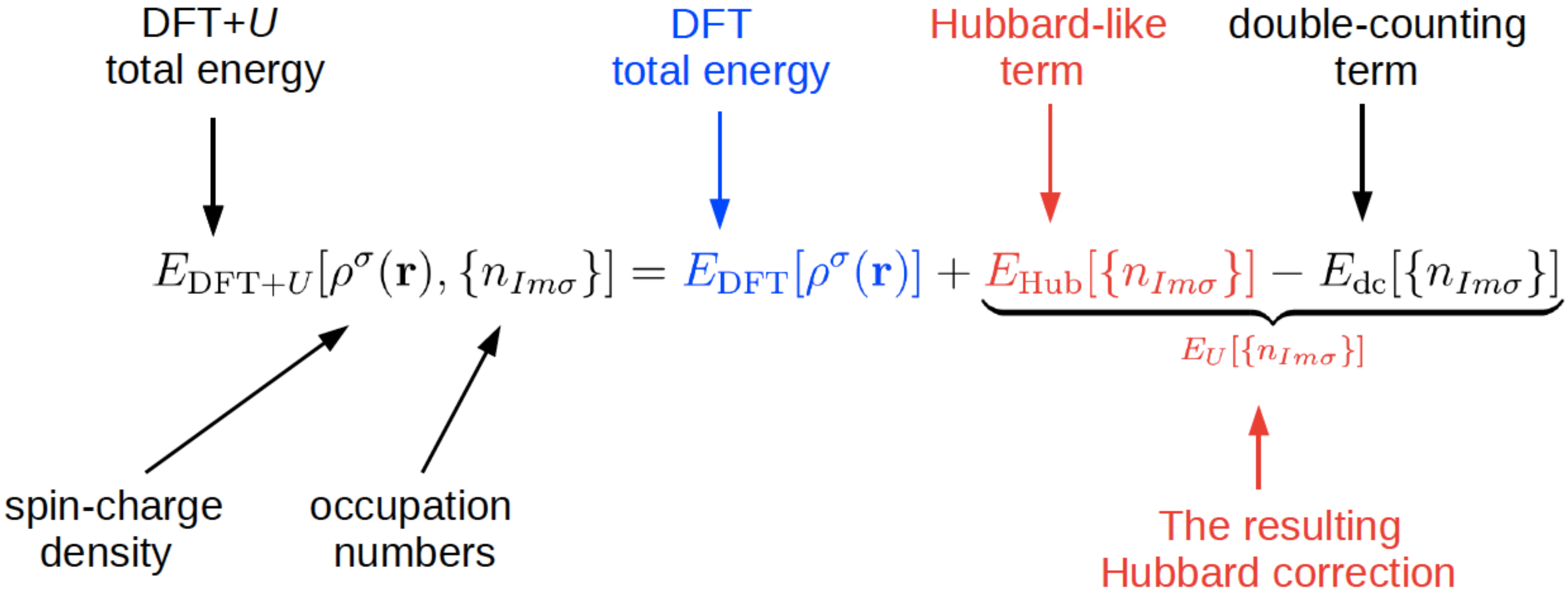
spin-charge density

occupation numbers

DFT+U

DFT total-energy functional is corrected by the Hubbard-like term.

Double-counting problem: subtract a term describing interactions in DFT in some average way.



$$E_{\mathrm{DFT}+U}[\rho^{\sigma}(\mathbf{r}),\{n_{Im\sigma}\}] = E_{\mathrm{DFT}}[\rho^{\sigma}(\mathbf{r})] + \underbrace{E_{\mathrm{Hub}}[\{n_{Im\sigma}\}] - E_{\mathrm{dc}}[\{n_{Im\sigma}\}]}_{E_U[\{n_{Im\sigma}\}]}$$

DFT+U

The DFT+*U* total energy:

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

The Hubbard correction energy:

$$E_U = \frac{1}{2} \sum_{I,m,m',\sigma} \underbrace{\left(U^I - J^I\right)}_{U^I_{\mathrm{eff}}} \left(\delta_{mm'} - n^{I\sigma}_{mm'}\right) n^{I\sigma}_{m'm}$$

effective Hubbard parameter

The occupation matrix:

$$n^{I\sigma}_{mm'} = \sum_{v,\mathbf{k}} f^{\sigma}_{v\mathbf{k}} \langle \psi^{\sigma}_{v\mathbf{k}} | \varphi^{I}_{m'} \rangle \langle \varphi^{I}_{m} | \psi^{\sigma}_{v\mathbf{k}} \rangle$$

v is the band index
$\mathbf{k}$ is the k point in BZ

occupations of
Kohn-Sham levels

Kohn-Sham
wavefunctions

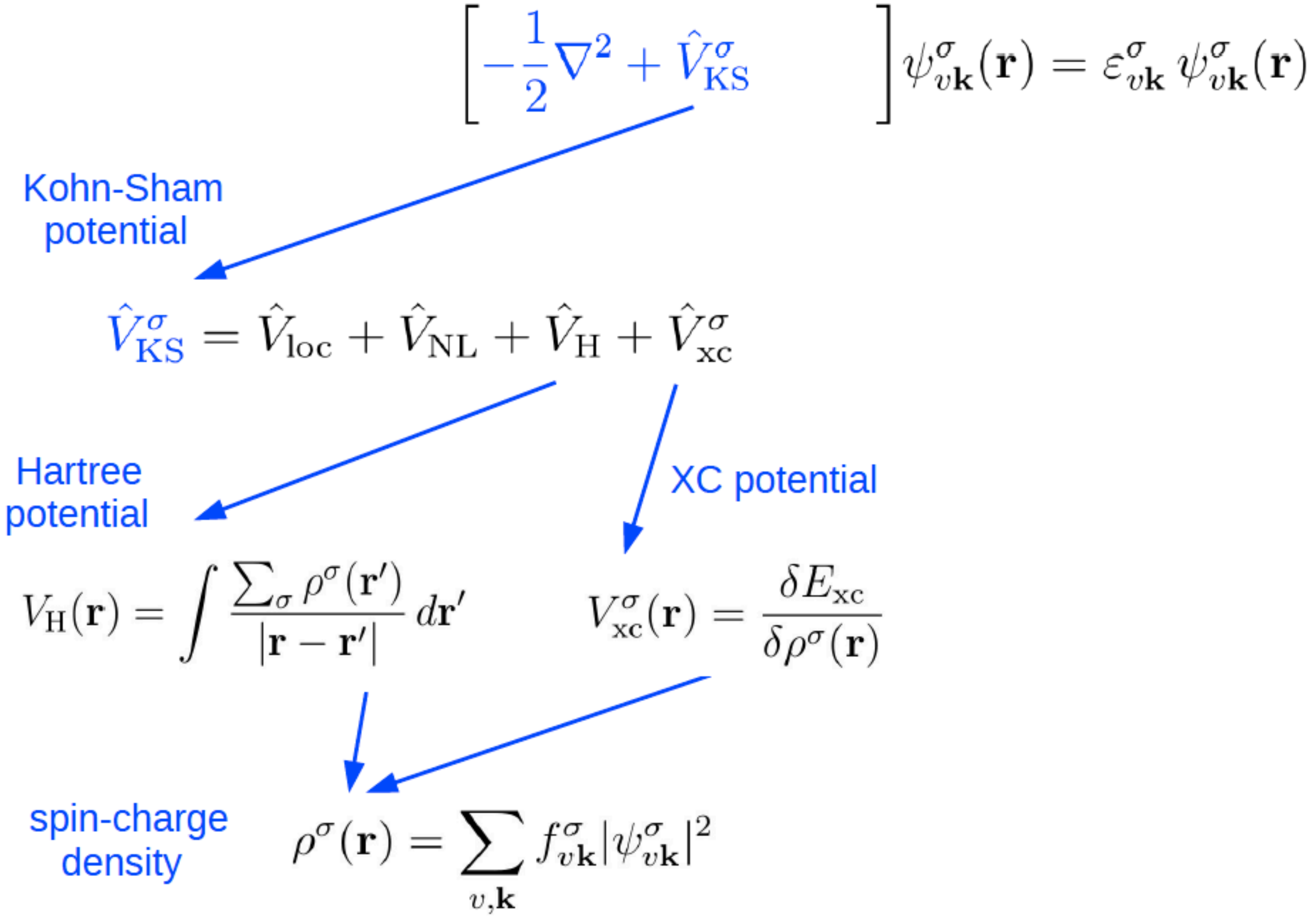
localized orbitals
(e.g. atomic/Wannier)

$$n^I = \sum_{m,\sigma} n^{I\sigma}_{mm}$$

the total occupation of localized states (*d* or *f*) at site *I*

DFT+U

By taking a functional derivative of the DFT+U total-energy functional with respect to the complex-conjugate Kohn-Sham wavefunction, we obtain an expression for the **modified Kohn-Sham equations**:



$$\left[-\frac{1}{2}\nabla^2 + \hat{V}^{\sigma}_{\text{KS}} \qquad\qquad \right]\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r}) = \varepsilon^{\sigma}_{v\mathbf{k}}\,\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r})$$

Kohn-Sham potential

$$\hat{V}^{\sigma}_{\text{KS}} = \hat{V}_{\text{loc}} + \hat{V}_{\text{NL}} + \hat{V}_{\text{H}} + \hat{V}^{\sigma}_{\text{xc}}$$

Hartree potential

XC potential

$$V_{\text{H}}(\mathbf{r}) = \int \frac{\sum_{\sigma}\rho^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' \qquad\qquad V^{\sigma}_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta\rho^{\sigma}(\mathbf{r})}$$

spin-charge density

$$\rho^{\sigma}(\mathbf{r}) = \sum_{v,\mathbf{k}} f^{\sigma}_{v\mathbf{k}}|\psi^{\sigma}_{v\mathbf{k}}|^2$$

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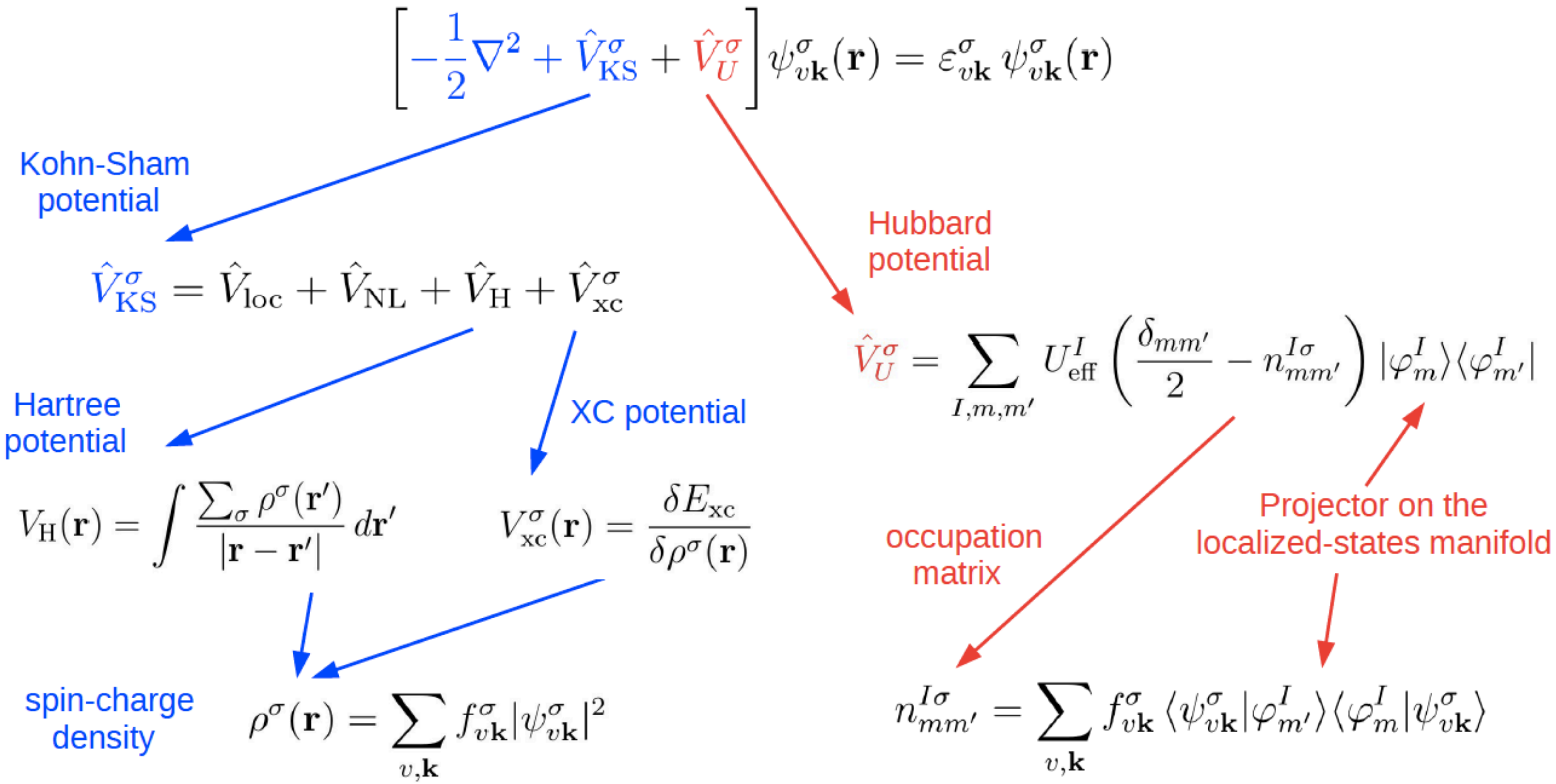


$$\left[-\frac{1}{2}\nabla^2 + \hat{V}^{\sigma}_{\mathrm{KS}} + \hat{V}^{\sigma}_{U}\right]\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r}) = \varepsilon^{\sigma}_{v\mathbf{k}}\,\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r})$$

Kohn-Sham potential

$$\hat{V}^{\sigma}_{\mathrm{KS}} = \hat{V}_{\mathrm{loc}} + \hat{V}_{\mathrm{NL}} + \hat{V}_{\mathrm{H}} + \hat{V}^{\sigma}_{\mathrm{xc}}$$

Hartree potential

$$V_{\mathrm{H}}(\mathbf{r}) = \int \frac{\sum_{\sigma}\rho^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$$

XC potential

$$V^{\sigma}_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta\rho^{\sigma}(\mathbf{r})}$$

spin-charge density

$$\rho^{\sigma}(\mathbf{r}) = \sum_{v,\mathbf{k}} f^{\sigma}_{v\mathbf{k}}|\psi^{\sigma}_{v\mathbf{k}}|^2$$

Hubbard potential

$$\hat{V}^{\sigma}_{U} = \sum_{I,m,m'} U^{I}_{\mathrm{eff}}\left(\frac{\delta_{mm'}}{2} - n^{I\sigma}_{mm'}\right)|\varphi^{I}_{m}\rangle\langle\varphi^{I}_{m'}|$$

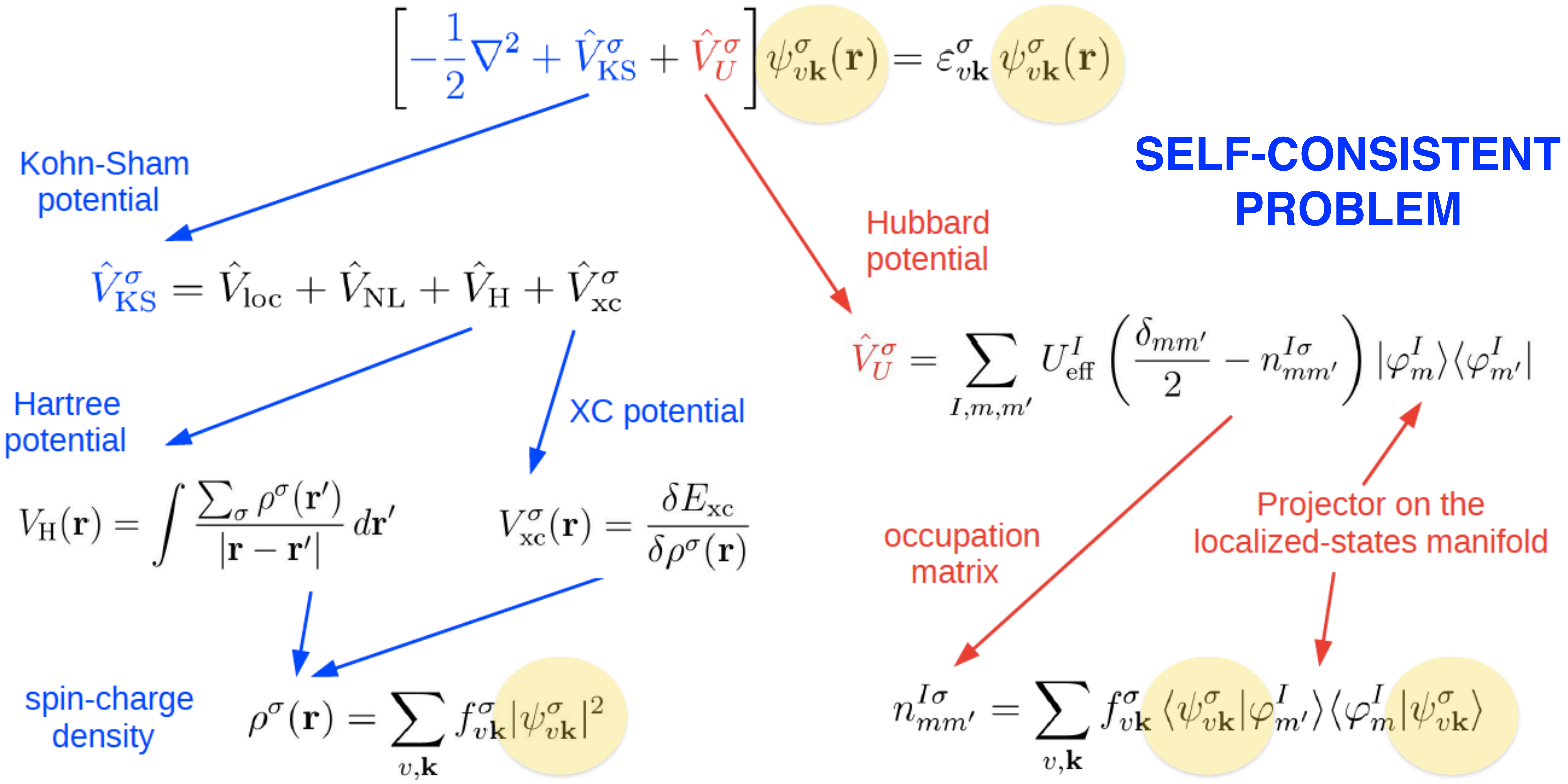
occupation matrix

Projector on the localized-states manifold

$$n^{I\sigma}_{mm'} = \sum_{v,\mathbf{k}} f^{\sigma}_{v\mathbf{k}}\,\langle\psi^{\sigma}_{v\mathbf{k}}|\varphi^{I}_{m'}\rangle\langle\varphi^{I}_{m}|\psi^{\sigma}_{v\mathbf{k}}\rangle$$

DFT+U

By taking a functional derivative of the DFT+U total-energy functional with respect to the complex-conjugate Kohn-Sham wavefunction, we obtain an expression for the **modified Kohn-Sham equations**:



$$\left[-\frac{1}{2}\nabla^2 + \hat{V}^\sigma_{\mathrm{KS}} + \hat{V}^\sigma_U\right]\psi^\sigma_{v\mathbf{k}}(\mathbf{r}) = \varepsilon^\sigma_{v\mathbf{k}}\,\psi^\sigma_{v\mathbf{k}}(\mathbf{r})$$

SELF-CONSISTENT PROBLEM

Kohn-Sham potential

$$\hat{V}^\sigma_{\mathrm{KS}} = \hat{V}_{\mathrm{loc}} + \hat{V}_{\mathrm{NL}} + \hat{V}_{\mathrm{H}} + \hat{V}^\sigma_{\mathrm{xc}}$$

Hartree potential

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occupation matrix

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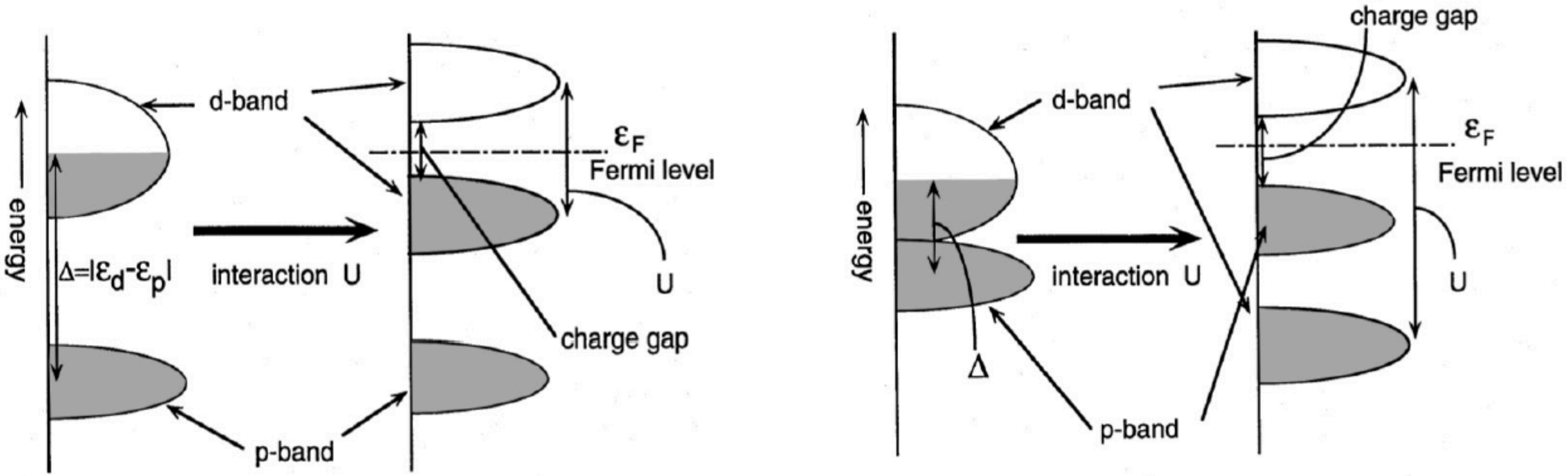
Metallic vs insulating ground state

In some correlated materials, DFT predicts a metallic ground state, while DFT+U predicts an insulating one.

The insulating ground state is due to strong Coulomb electron-electron interactions between *d* electrons.



(a) Mott-Hubbard Insulator

(b) Charge Transfer Insulator

M. Imada *et al.*, Rev. Mod. Phys. **70**, 1039 (1998).

DFT+U+V

In correlated materials with covalent interactions DFT+U and DMFT does not work very well!

Not only on-site Hubbard U is needed, but also inter-site Hubbard V should be included to describe hybridizations of orbitals centered on neighbouring sites.

V.L. Campo Jr. *et al.*, J. Phys.: Condens. Matter **22**, 055602 (2010).

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

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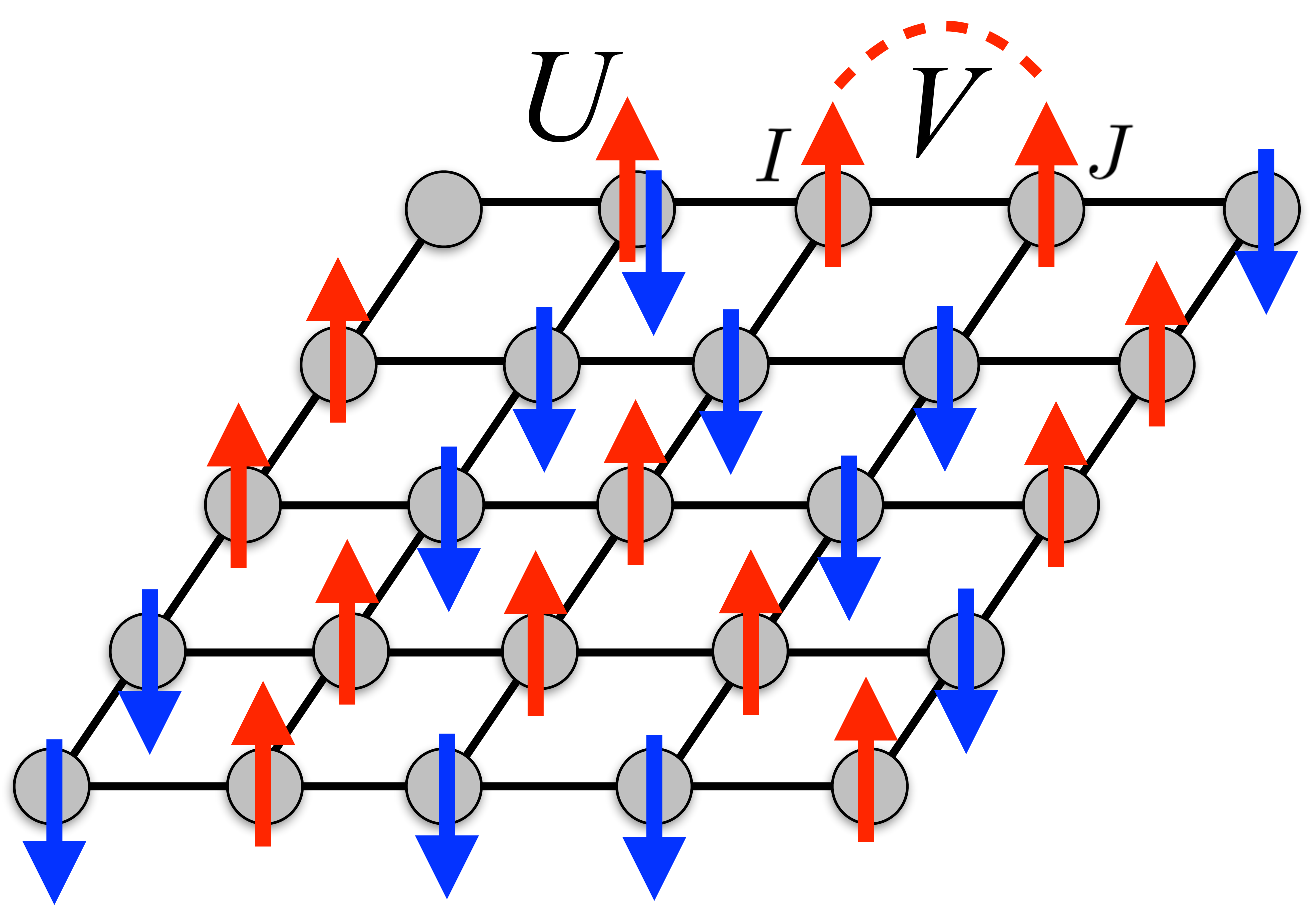
The DFT+U+V total energy: $E_{\mathrm{DFT}+U+V} = E_{\mathrm{DFT}} + E_{U+V}$

$$E_{U+V} = \frac{1}{2} \sum_{I,m,m',\sigma} \underbrace{\left(U^I - J^I\right)}_{U^I_{\mathrm{eff}}} \left(\delta_{mm'} - n^{I\sigma}_{mm'}\right) n^{I\sigma}_{m'm} - \frac{1}{2} \sum_{I\neq J,m,m',\sigma} V^{IJ}\, n^{IJ\sigma}_{mm'}\, n^{JI\sigma}_{m'm}$$



The generalized occupation matrix:

$$n^{IJ\sigma}_{mm'} = \sum_{v,\mathbf{k}} f^{\sigma}_{v\mathbf{k}} \langle \psi^{\sigma}_{v\mathbf{k}} | \varphi^{J}_{m'} \rangle \langle \varphi^{I}_{m} | \psi^{\sigma}_{v\mathbf{k}} \rangle$$

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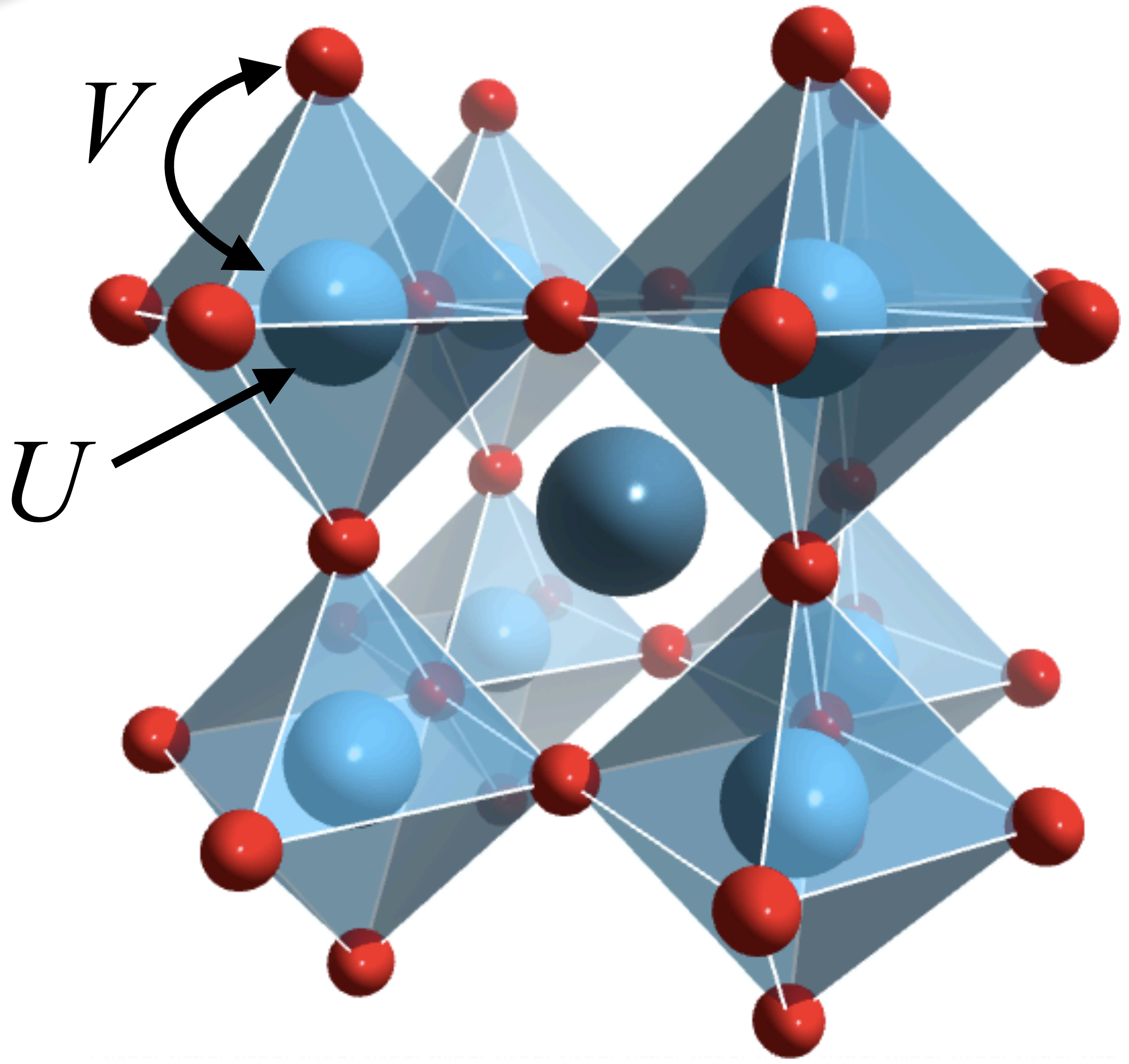

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V.L. Campo Jr. *et al.*, J. Phys.: Condens. Matter **22**, 055602 (2010).

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

The main question of the DFT+U and DFT+U+V methods:

What values of the Hubbard U&V parameters to use?

Which $U\&V$ to use?

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

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

Which $U\&V$ to use?

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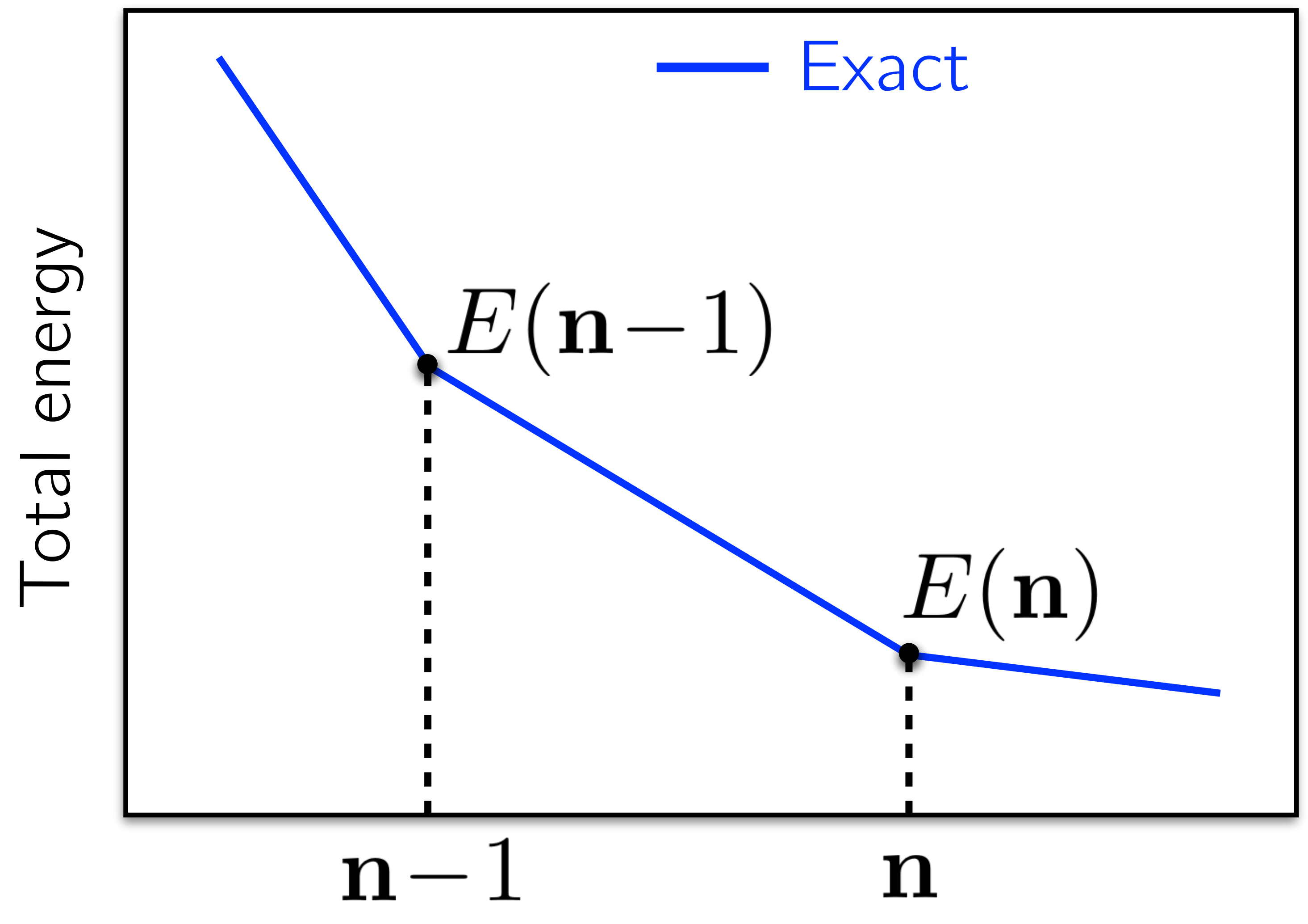
Drawback: *This approach is not predictive! And it is not fully ab initio!*

- ***Ab initio***
  - 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 quite expensive and cumbersome to use*

Linear-response calculation of U using cDFT



J. P. Perdew, R. G. Parr, M. Levy, J. L. Balduz, Jr.,
Phys. Rev. Lett. 49, 1691 (1982)

"Density-Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy"

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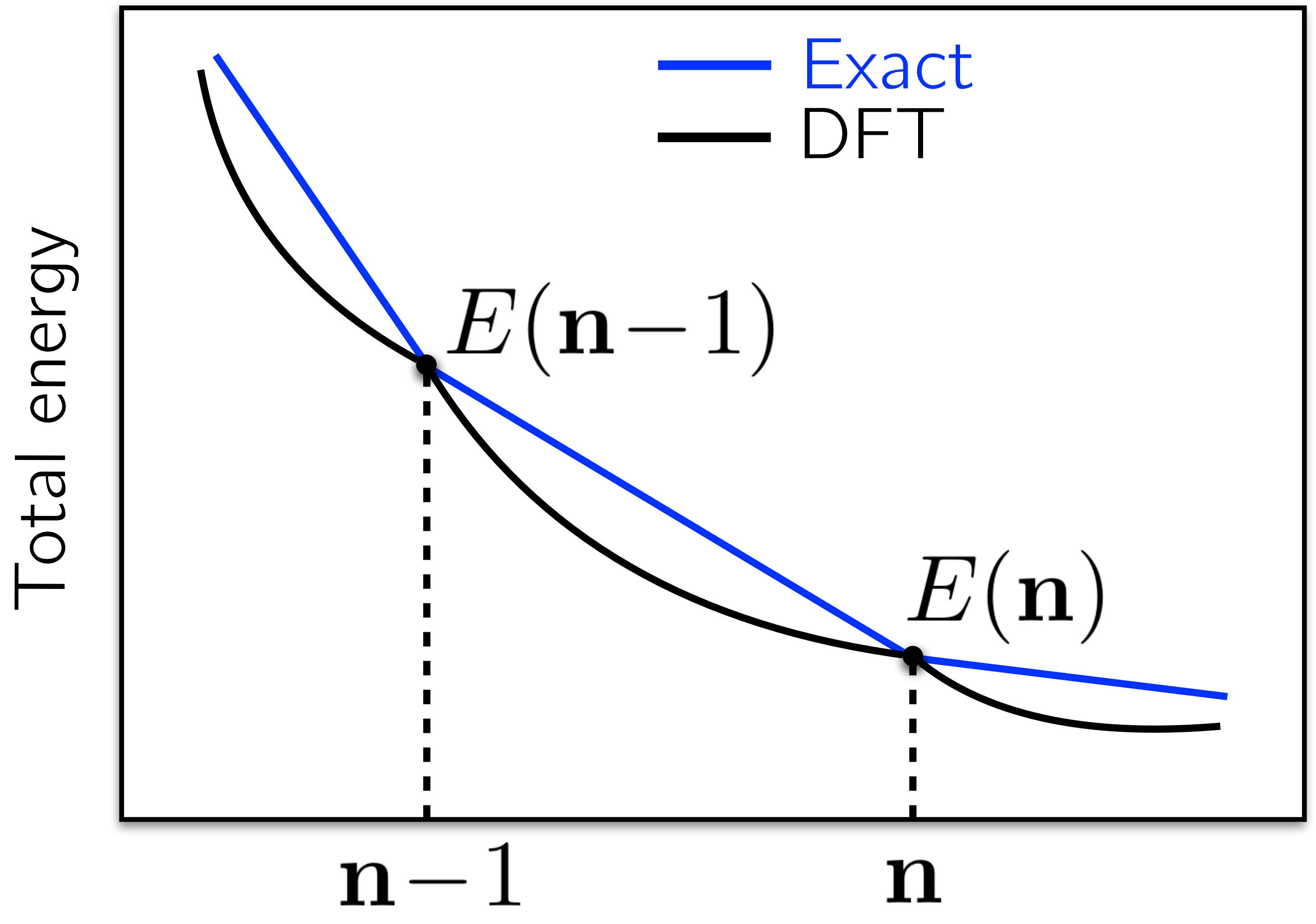

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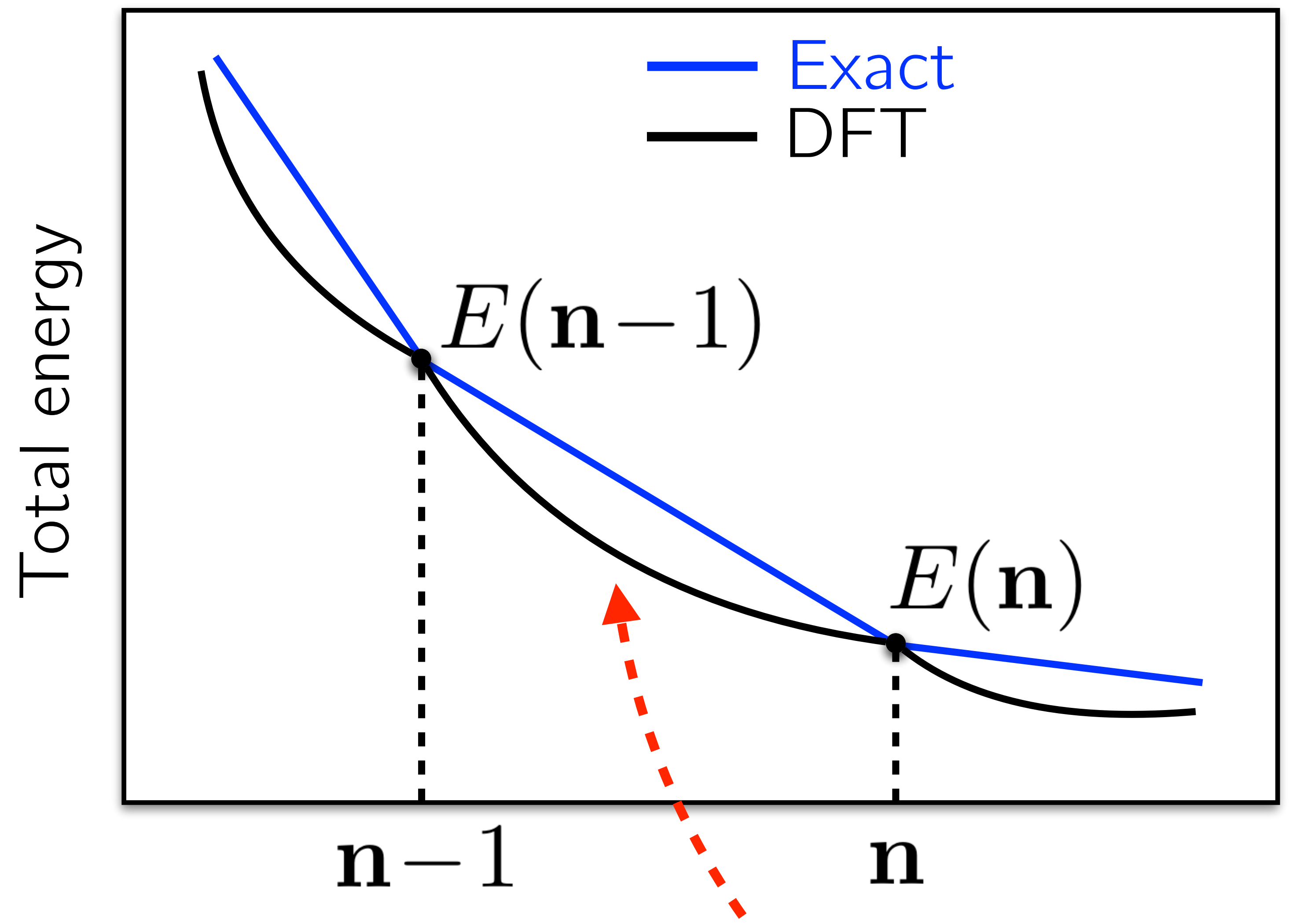

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“Density-Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy”

Approximate DFT deviates from the exact piece-wise linearity due to self-interactions

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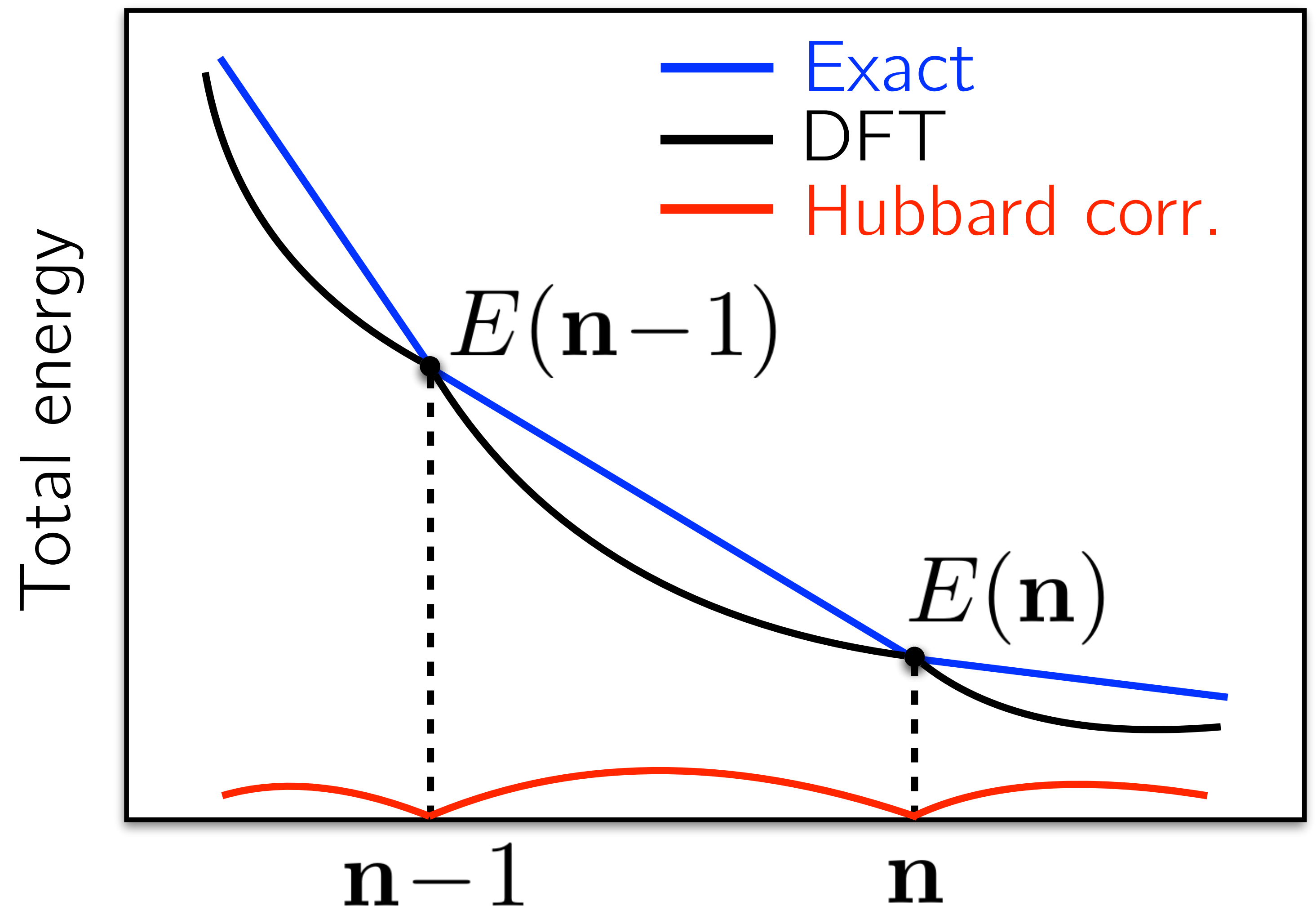
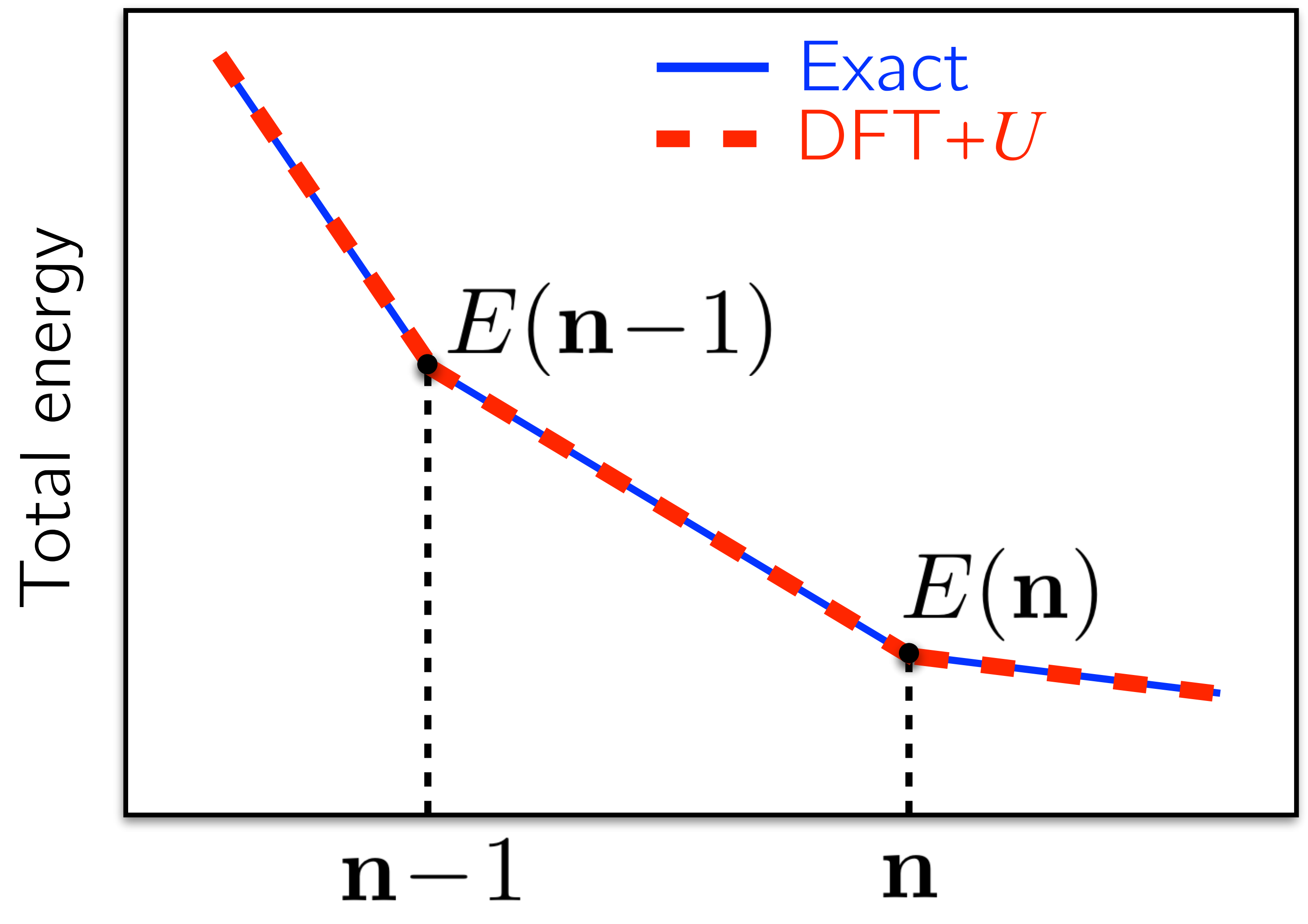


$$E_U = \sum_{I,\sigma} \frac{U^I_{\text{eff}}}{2} \operatorname{Tr}\left[(\mathbf{1} - \mathbf{n}^{I\sigma})\mathbf{n}^{I\sigma}\right]$$

add linearity & remove quadraticity

Linear-response calculation of U using cDFT



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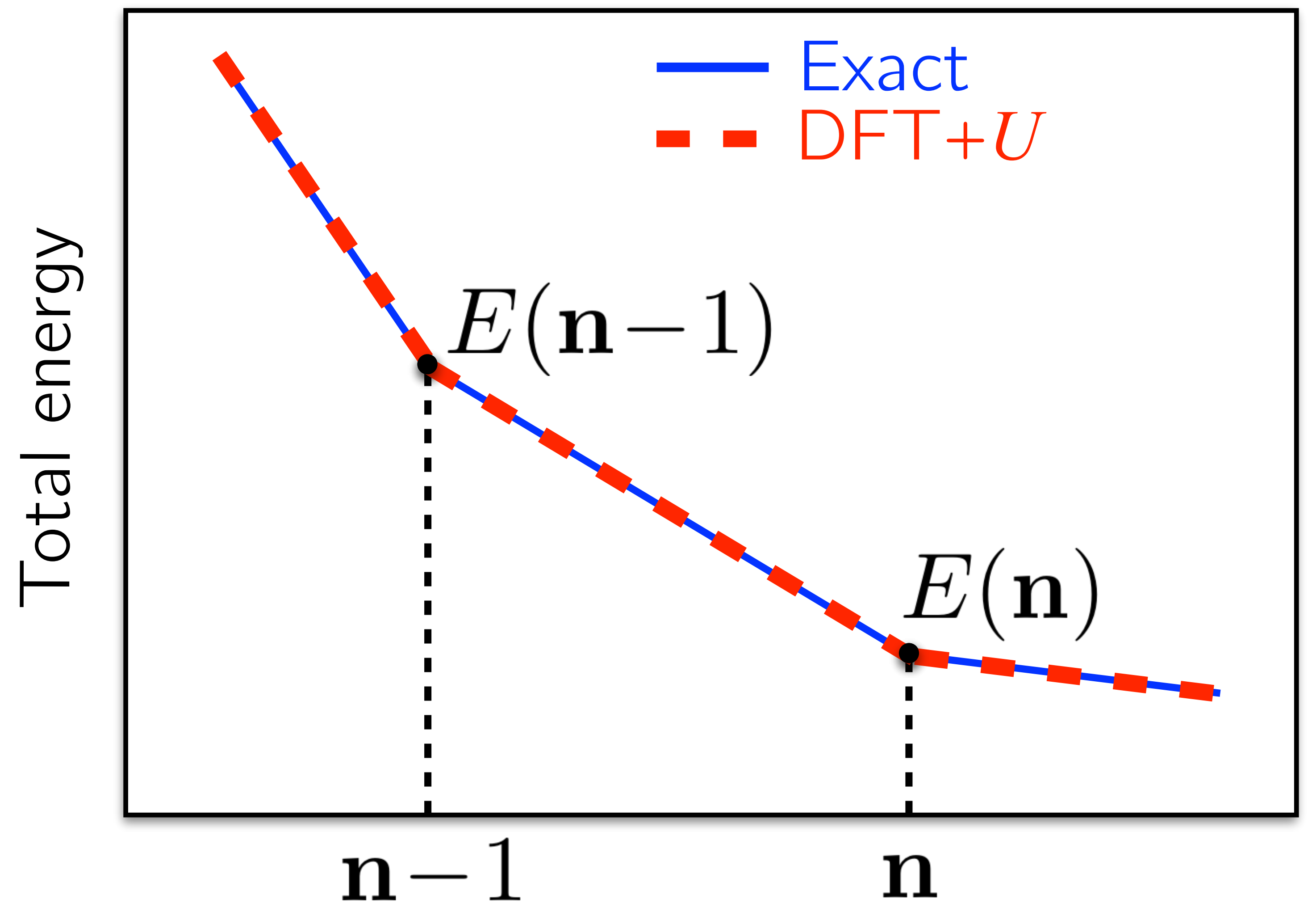

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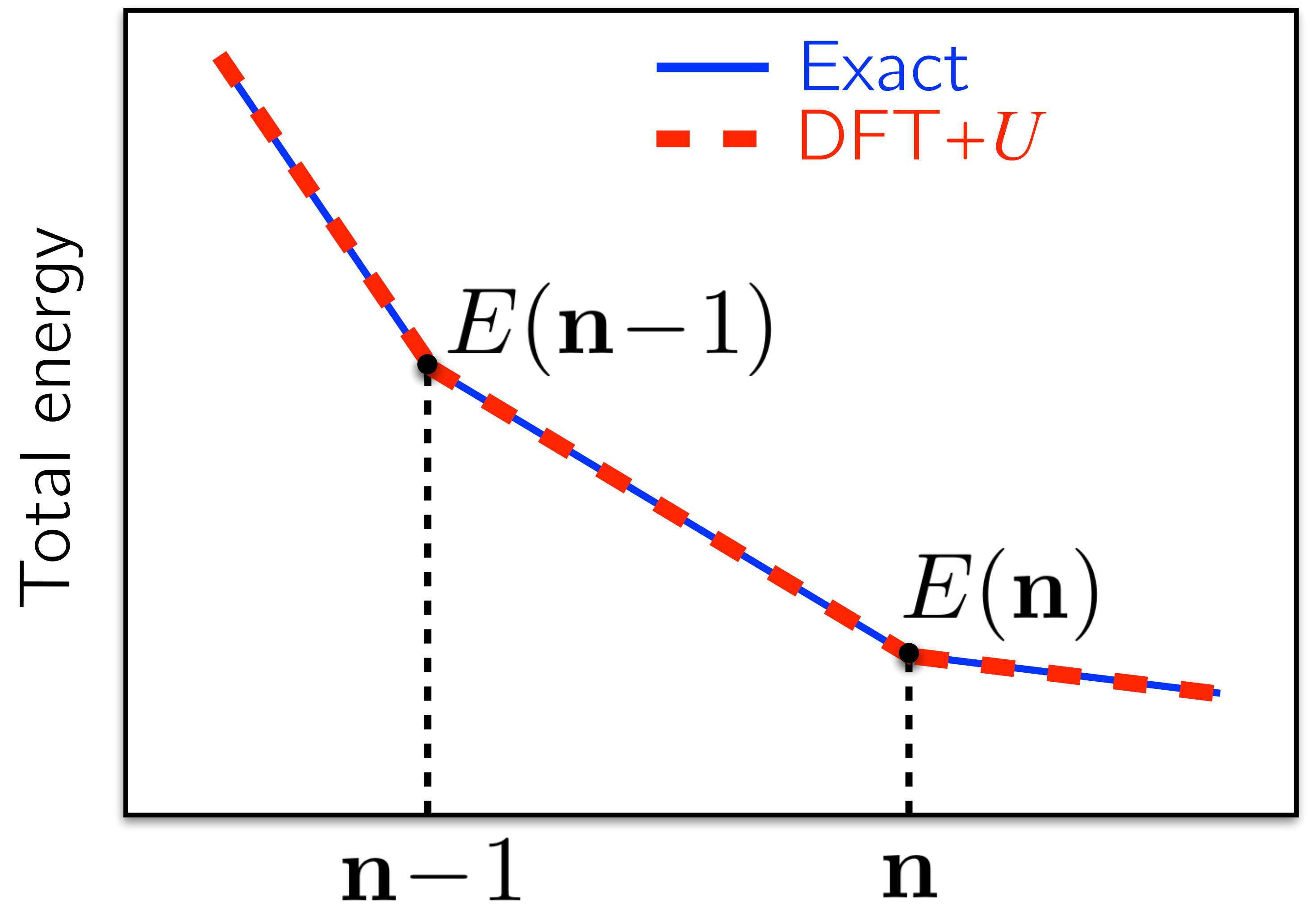
So how do we define Hubbard U based on this knowledge?

Linear-response calculation of U using cDFT



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Hubbard U parameter is computed as a second derivative of the DFT total energy wrt number of electrons in the Hubbard manifold (e.g. the *d* shell of a transition metal atom).

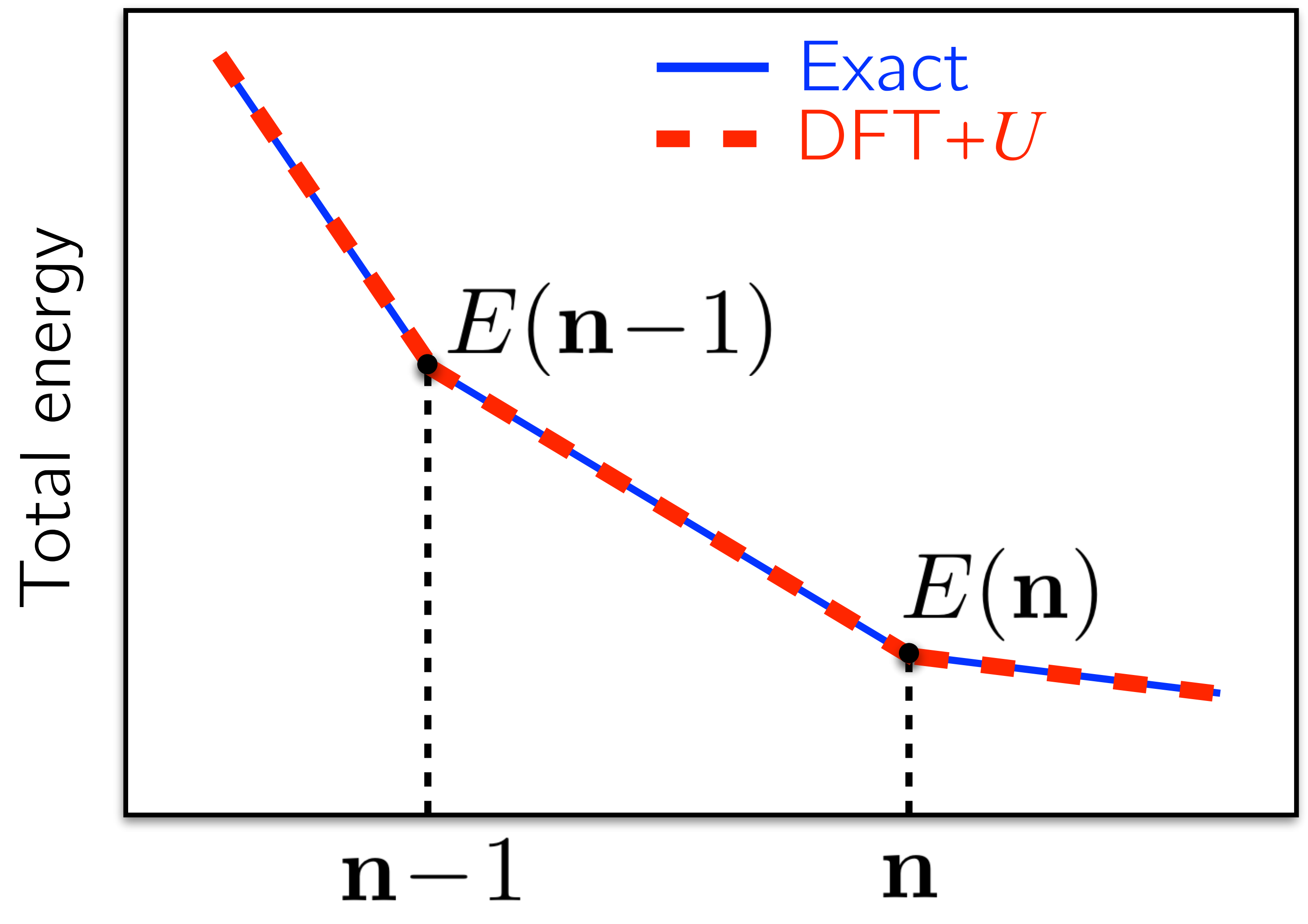
$$U^I_{\text{eff}} = \frac{d^2 E_{\text{DFT}}}{d(n^I)^2} - \frac{d^2 E^0_{\text{DFT}}}{d(n^I)^2}$$

self-consistent term

bare (non-interacting) term

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

Linear-response calculation of U using cDFT



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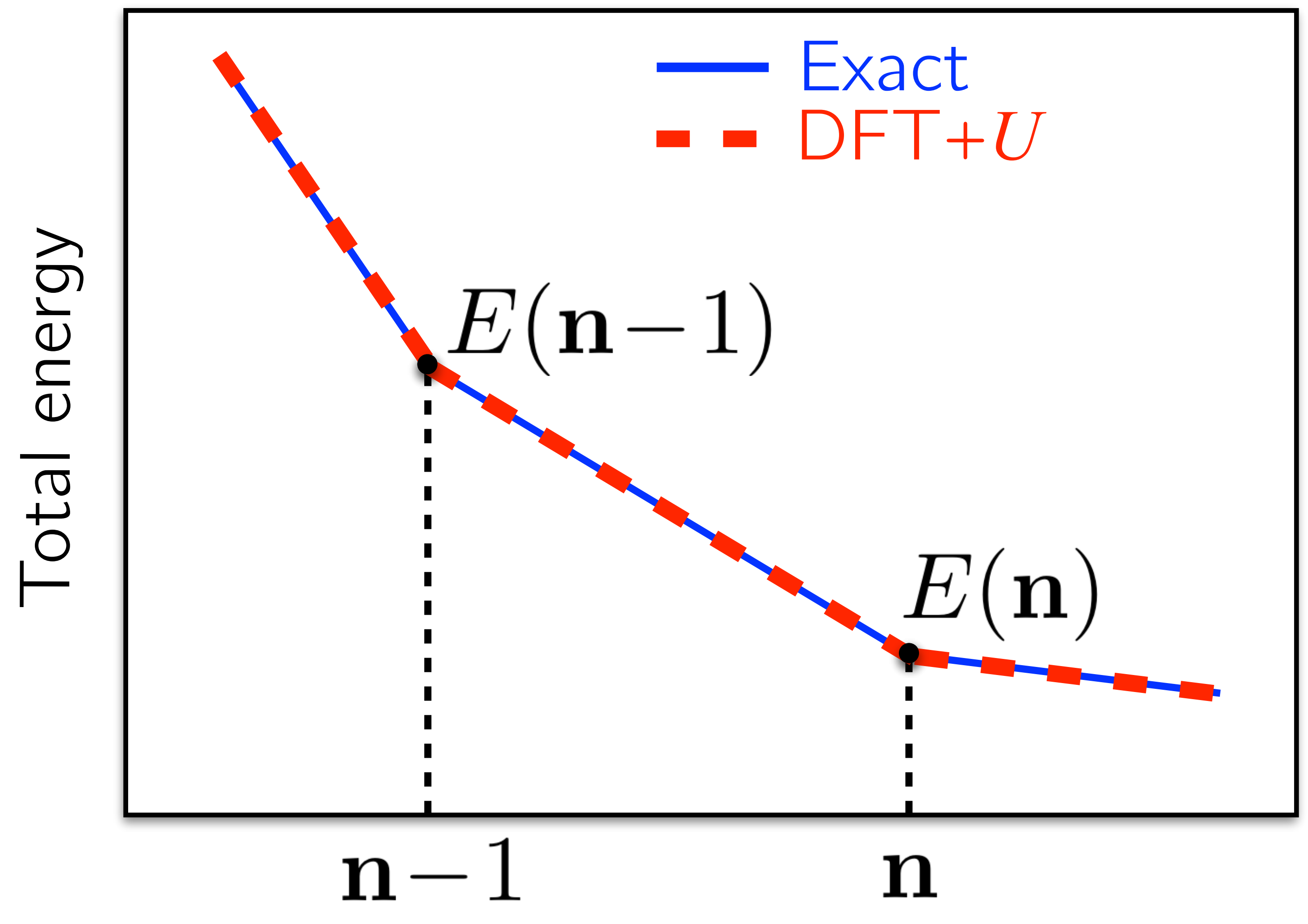

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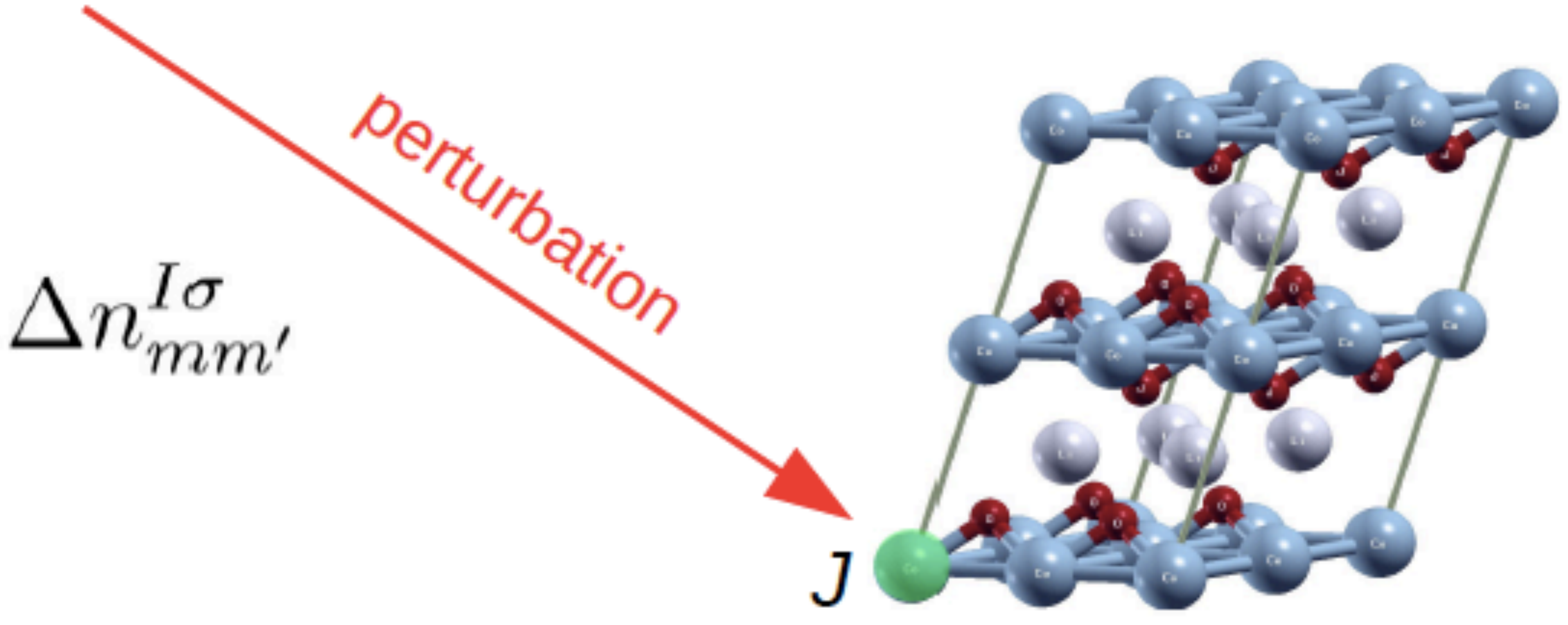
Calculation of U: practicalities (old way)

The Kohn-Sham equations with a perturbing atomic potential:

$$\left[-\frac{1}{2}\nabla^2 + \hat{V}^{\sigma}_{\mathrm{KS}} + \hat{V}^{\sigma}_{U} + \alpha_J \sum_m |\varphi^J_m\rangle\langle\varphi^J_m| \right] \psi^{\sigma}_{v\mathbf{k}}(\mathbf{r}) = \varepsilon^{\sigma}_{v\mathbf{k}}\, \psi^{\sigma}_{v\mathbf{k}}(\mathbf{r})$$



Evaluate the change in occupation matrices: $\Delta n^{I\sigma}_{mm'}$

Compute the interacting and non-interacting response matrices:

$$\chi_{IJ} = \sum_{m,\sigma} \frac{\Delta n^{I\sigma}_{mm}}{\Delta \alpha_J}, \qquad \chi^0_{IJ} = \sum_{m,\sigma} \frac{\Delta n^{0\,I\sigma}_{mm}}{\Delta \alpha_J}$$

- supercells
- finite differences

On-site Hubbard U_{eff} parameters (diagonal matrix elements):

$$U^I_{\mathrm{eff}} = \left((\chi^0)^{-1} - \chi^{-1} \right)_{II}$$

α_J is the amplitude of the perturbation of the J-th atom

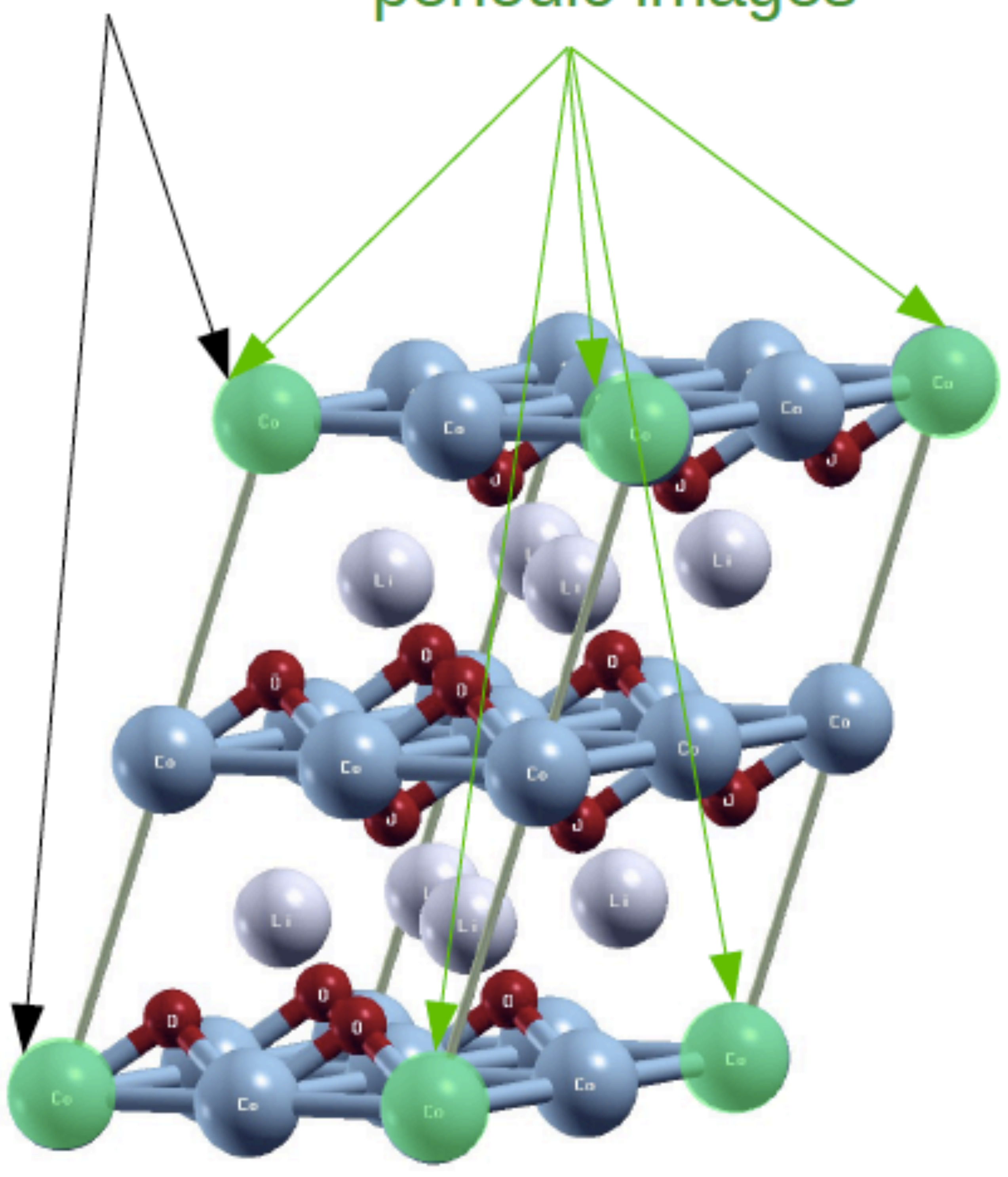
All derivatives are computed using finite differences.

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

Note: $\hat{V}^{\sigma}_{U}$ is fixed!

Calculation of U: practicalities (old way)

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).

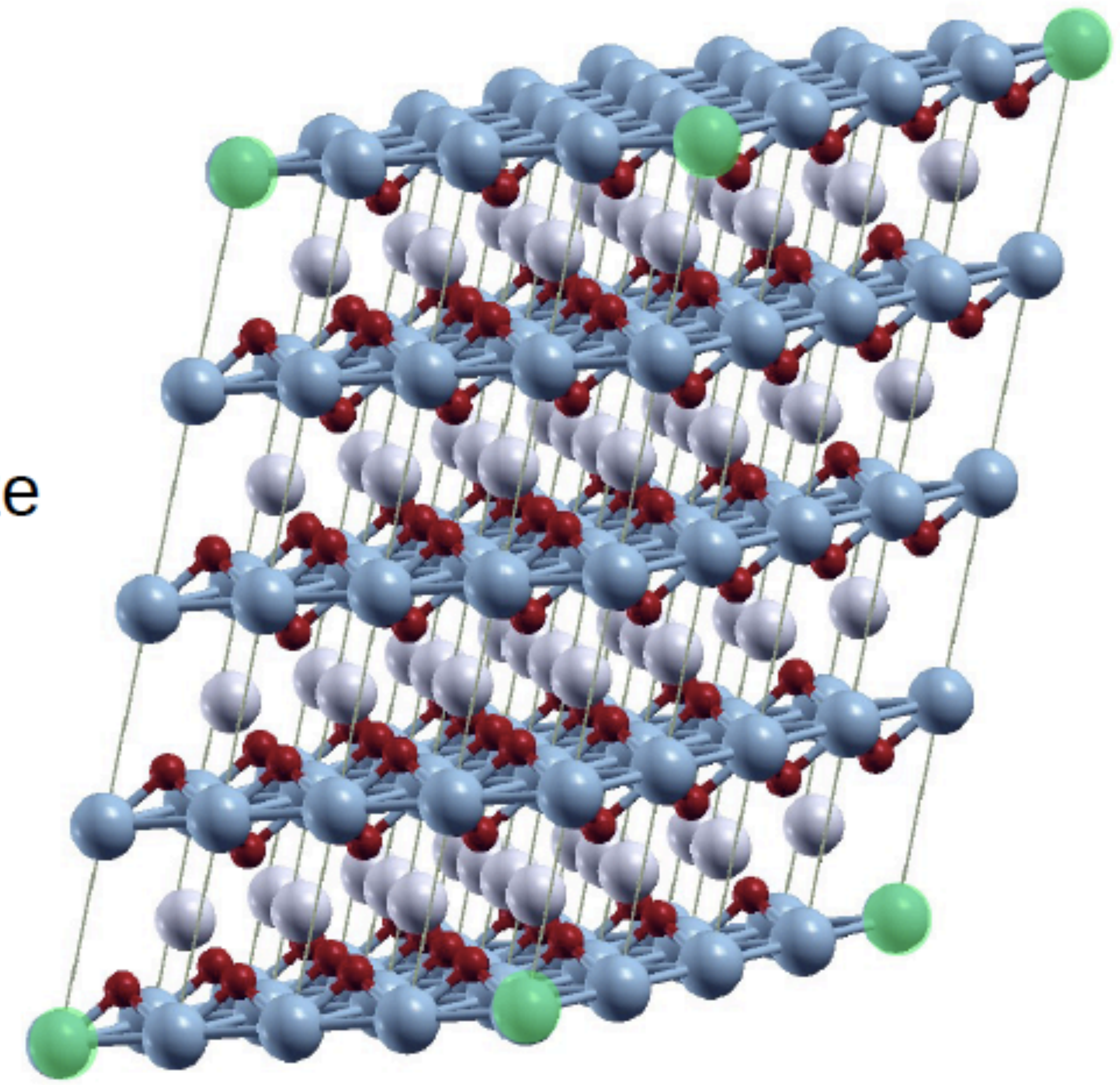


spurious interaction

periodic images

2x2x2 supercell

increase the size

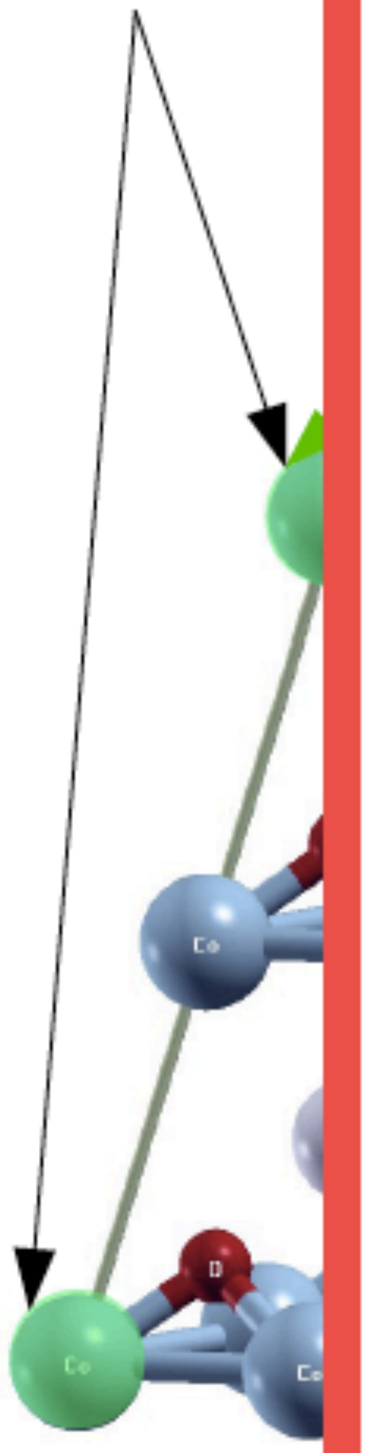


4x4x4 supercell

Calculation of U: practicalities (old way)

The sup ne
perturbe litions).

spurious
interaction



Drawbacks:

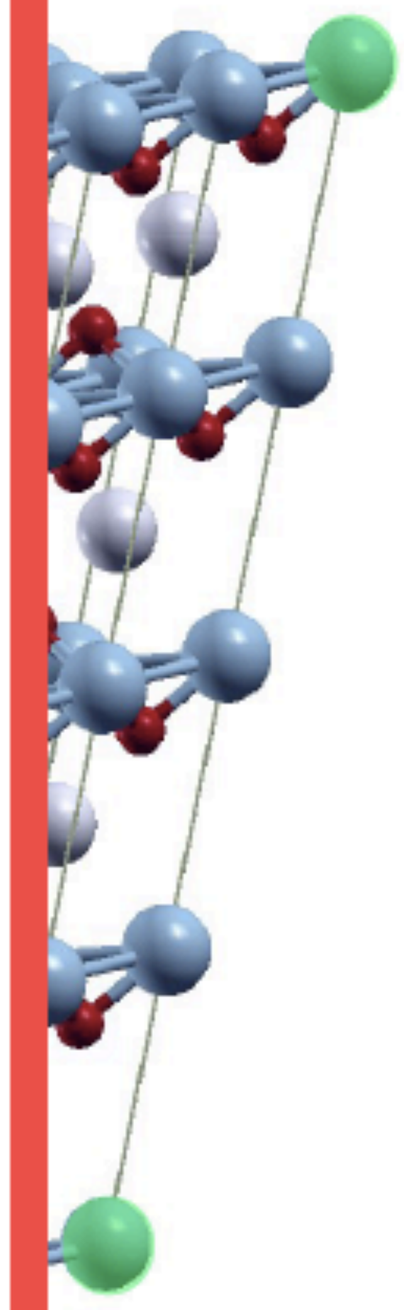
- Supercells are needed → high computational cost (cubic scaling)
- Finite differences → limited accuracy of *U*
- Post-processing is cumbersome in practice

↓

Not a practical method for applications and/or high-throughput calculations!

Limitation: cDFT cannot be applied to closed-shell systems (i.e. when *d/f* states are fully occupied and are lying deeply below the Fermi level).

K. Yu and E.A. Carter, J. Chem. Phys. ***140****, 121105 (2014).*

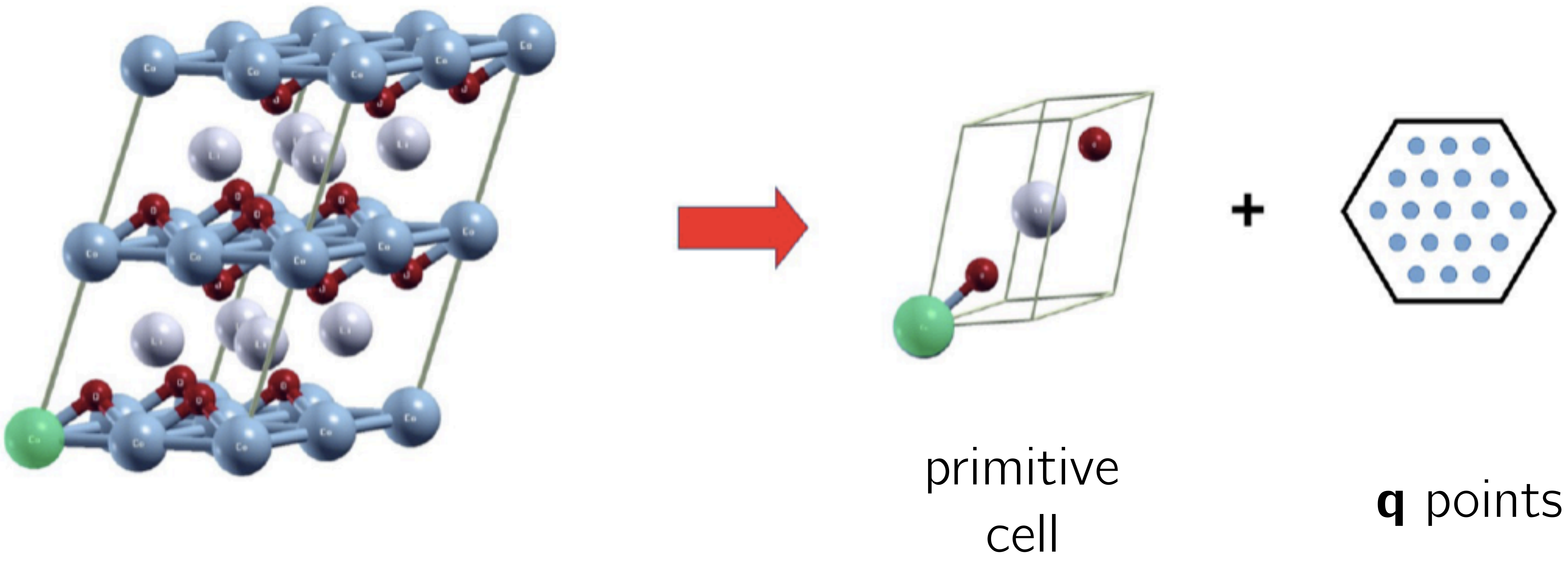


2x2x2 supercell

4x4x4 supercell

Calculation of U using density-functional perturbation theory

Main idea: Recasting of an isolated perturbation in a supercell as a sum of monochromatic perturbations in a primitive cell in reciprocal space using density-functional perturbation theory (DFPT).



Fast, automatic, efficient, accurate method to compute U from first principles.

I. Timrov, N. Marzari, and M. Cococcioni, Phys. Rev. B **98**, 085127 (2018).

Calculation of U using density-functional perturbation theory

The Kohn-Sham (KS) equations with a perturbing atomic potential:

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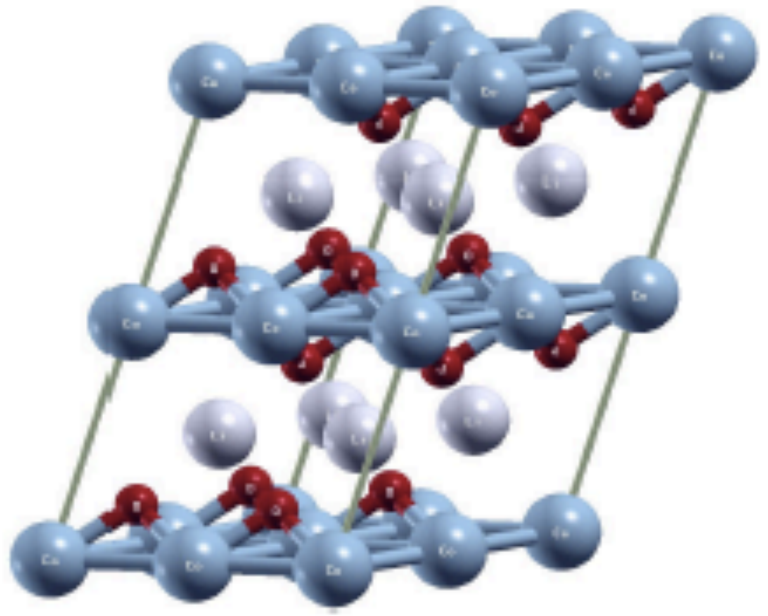
↑

small perturbation

↓



supercell

We can use perturbation theory up to 1st order (**linear response**): wavefunctions, density, occupation matrices, potentials, energies.

Taylor series in α_J:

$$\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r}) = \psi^{\sigma\,\circ}_{v\mathbf{k}}(\mathbf{r}) + \alpha_J \frac{d\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r})}{d\alpha_J} + \ldots \qquad \varepsilon^{\sigma}_{v\mathbf{k}} = \varepsilon^{\sigma\,\circ}_{v\mathbf{k}} + \alpha_J \frac{d\varepsilon^{\sigma}_{v\mathbf{k}}}{d\alpha_J} + \ldots$$

$$\rho^{\sigma}(\mathbf{r}) = \rho^{\sigma\,\circ}(\mathbf{r}) + \alpha_J \frac{d\rho^{\sigma}(\mathbf{r})}{d\alpha_J} + \ldots \qquad \hat{V}^{\sigma}_{\mathrm{KS}} = \hat{V}^{\sigma\,\circ}_{\mathrm{KS}} + \alpha_J \frac{d\hat{V}^{\sigma}_{\mathrm{Hxc}}}{d\alpha_J} + \ldots$$

$$n^{I\sigma}_{mm'} = n^{I\sigma\,\circ}_{mm'} + \alpha_J \frac{dn^{I\sigma}_{mm'}}{d\alpha_J} + \ldots \qquad \hat{V}^{\sigma}_{U} = \hat{V}^{\sigma\,\circ}_{U} + \alpha_J \xcancel{\frac{d\hat{V}^{\sigma}_{U}}{d\alpha_J}} + \ldots$$

Calculation of U using density-functional perturbation theory

After using Taylor series for various quantities with respect to α_J, we can write the equations for the 1st order quantities (linear-response quantities):

$$\left[-\frac{1}{2}\nabla^2 + \hat{V}^{\sigma\,\circ}_{\rm KS} + \hat{V}^{\sigma\,\circ}_{U} - \varepsilon^{\sigma\,\circ}_{v\mathbf{k}}\right] \frac{d\psi^{\sigma}_{v\mathbf{k}}(\mathbf{r})}{d\alpha_J} = -\left[\frac{d\hat{V}^{\sigma}_{\rm Hxc}}{d\alpha_J} - \frac{d\varepsilon^{\sigma}_{v\mathbf{k}}}{d\alpha_J} + \sum_m |\varphi^J_m\rangle\langle\varphi^J_m|\right] \psi^{\sigma\,\circ}_{v\mathbf{k}}(\mathbf{r})$$

response KS wavefunctions

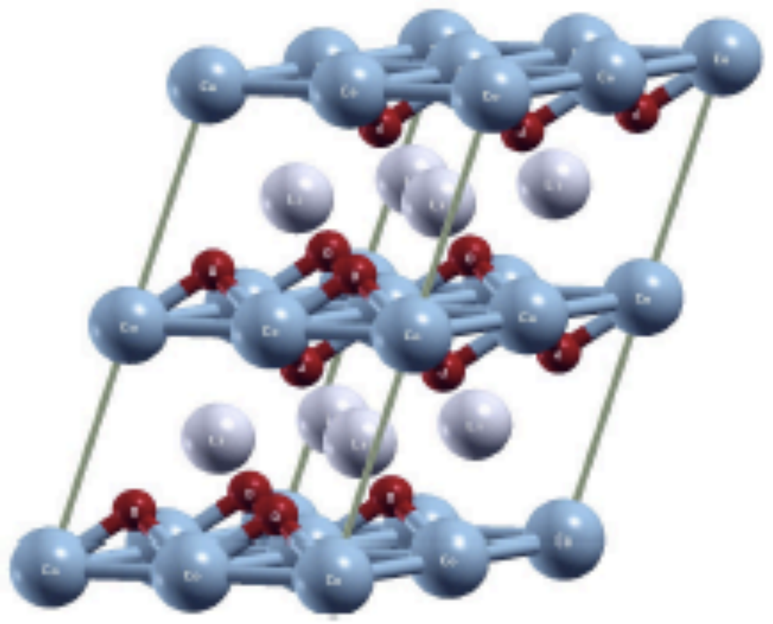
response Hxc potential

response KS energies

perturbation

Note:

- The parameter α_J is no longer present in the equations;
- Now there is no need in numerical derivatives (no finite differences).
- This equation is still formulated for supercells;
- This equation is expensive to solve for large supercells;
- For the sake of simplicity we consider here insulators (i.e. occupations $f^{\sigma}_{v\mathbf{k}}$ are 0 or 1);



supercell

Calculation of U using density-functional perturbation theory

The DFPT approach to compute U is implemented in Quantum ESPRESSO:

The HP code

(Hubbard Parameters)

The HP code contains:

- 9 examples
- documentation

If you have questions, ask them on the pw_forum.

But first read the posting guidelines:

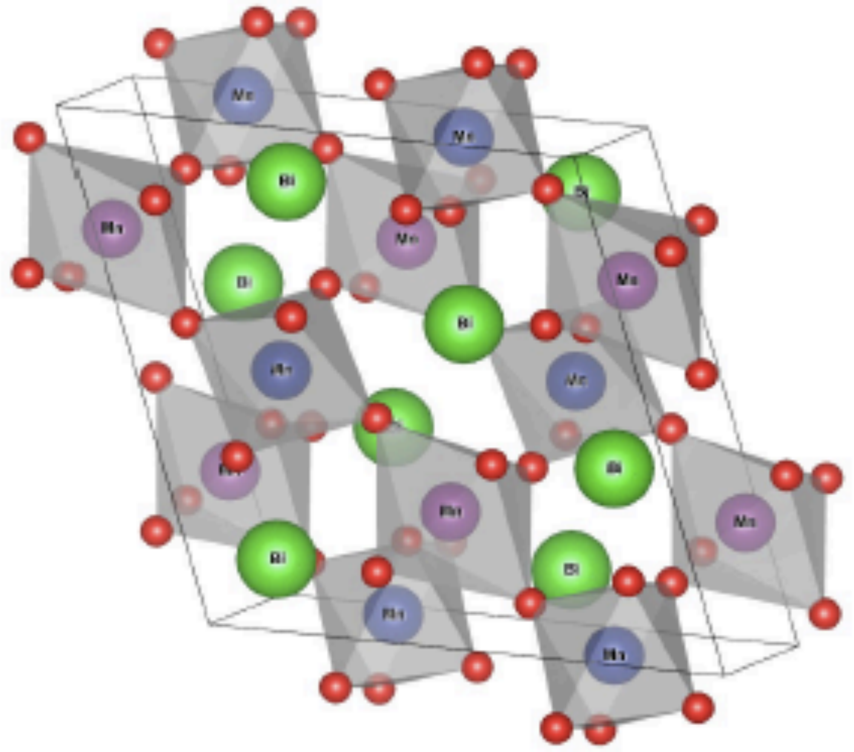
https://www.quantum-espresso.org/forum

There is a hands-on on how to use the HP code:

https://agenda.ethernet.edu.et/event/33/

Applications

I. Electronic structure of $BiMnO_3$



Monoclinic cell

(40 atoms)

Ferromagnetic ordering

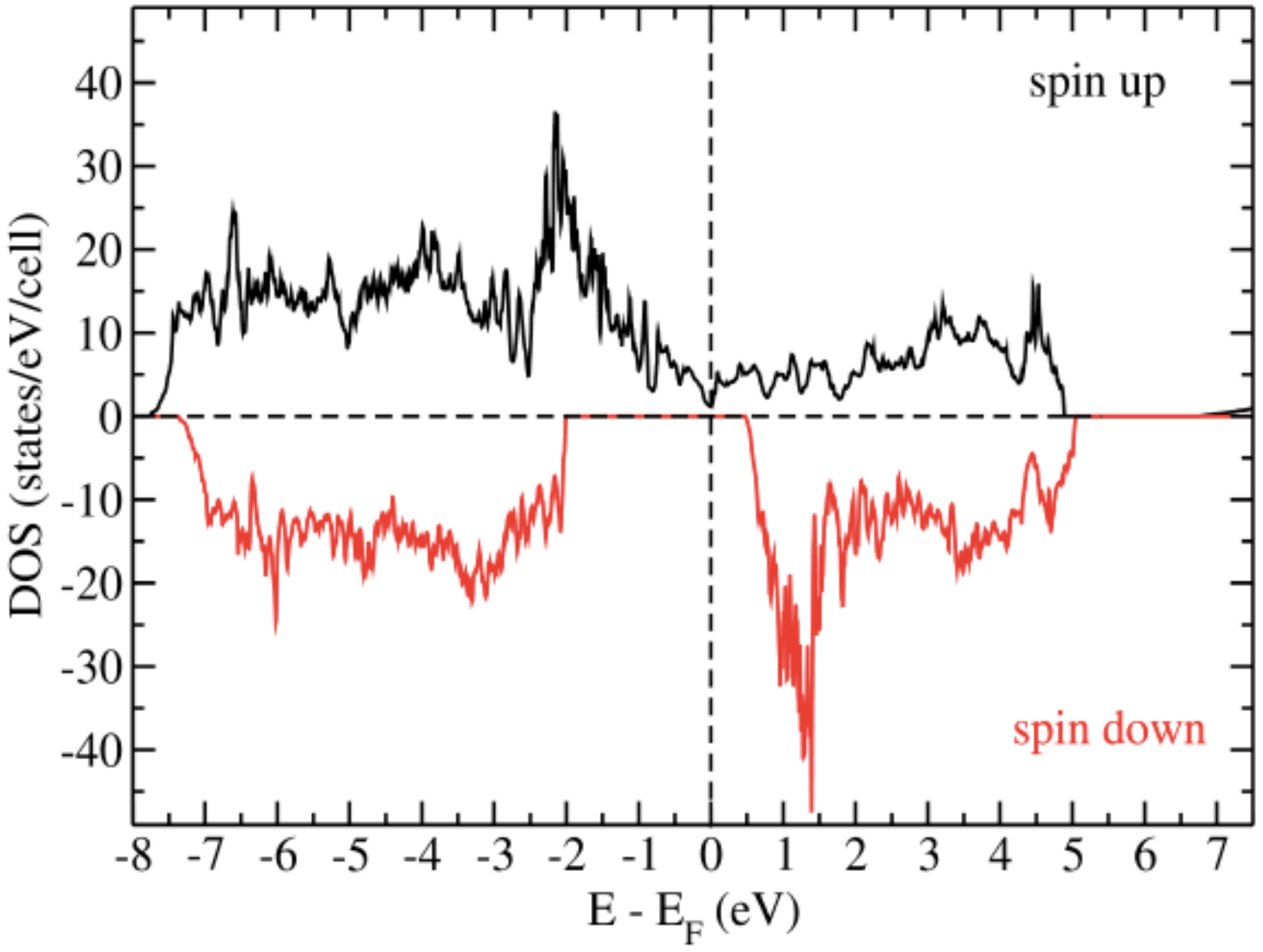
DFT → metallic (wrong)

DFT+*U* → insulating (correct)

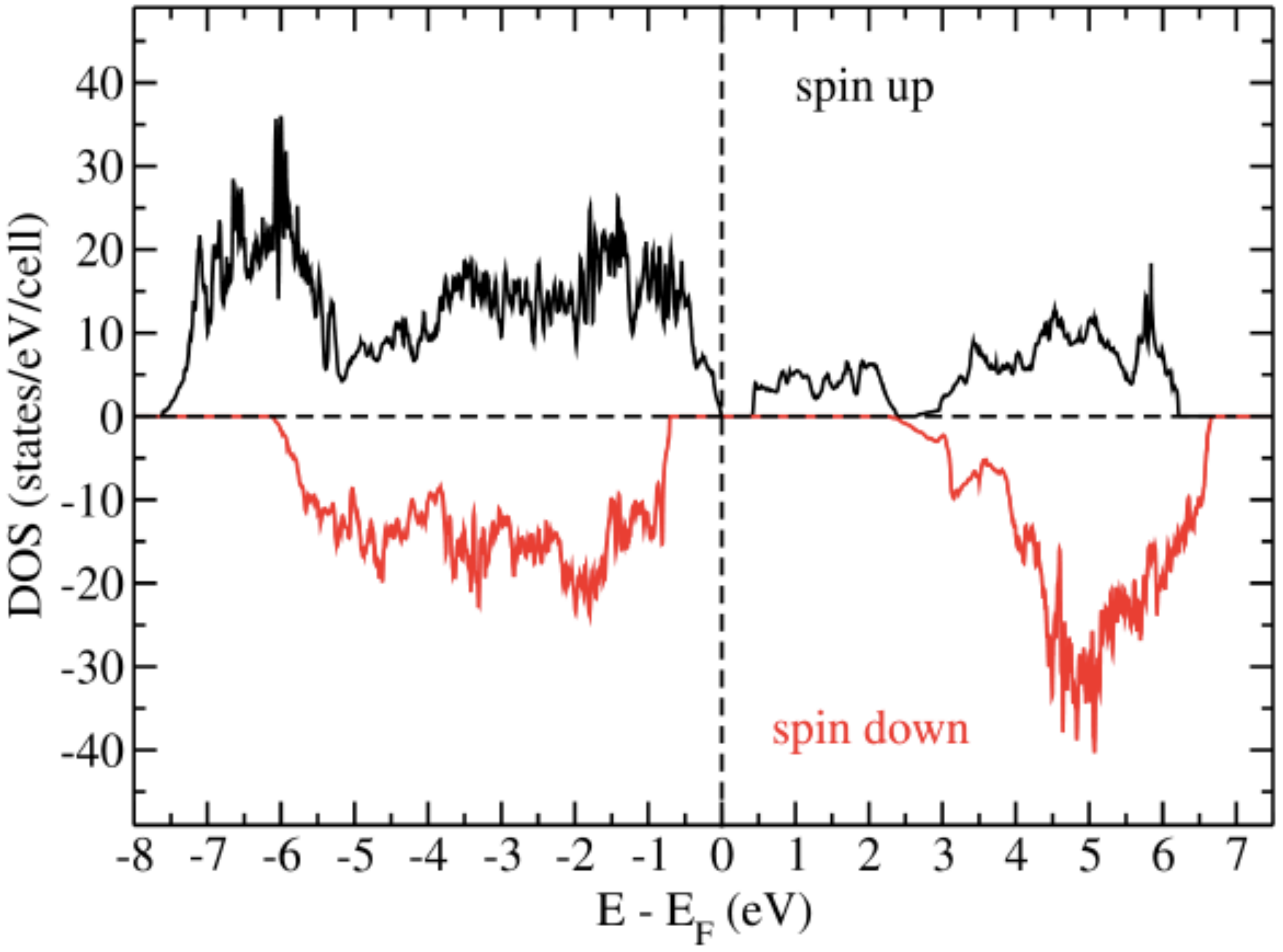
Hubbard $U_{\rm eff}$ = 6.3 (eV) for the 3*d* states of Mn

$E_{\rm GAP}^{\rm DFT+U} = 0.4\,(\rm eV)$ $E_{\rm GAP}^{expt} = 0.9 - 1.1\,(\rm eV)$

DFT



DFT+*U*



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

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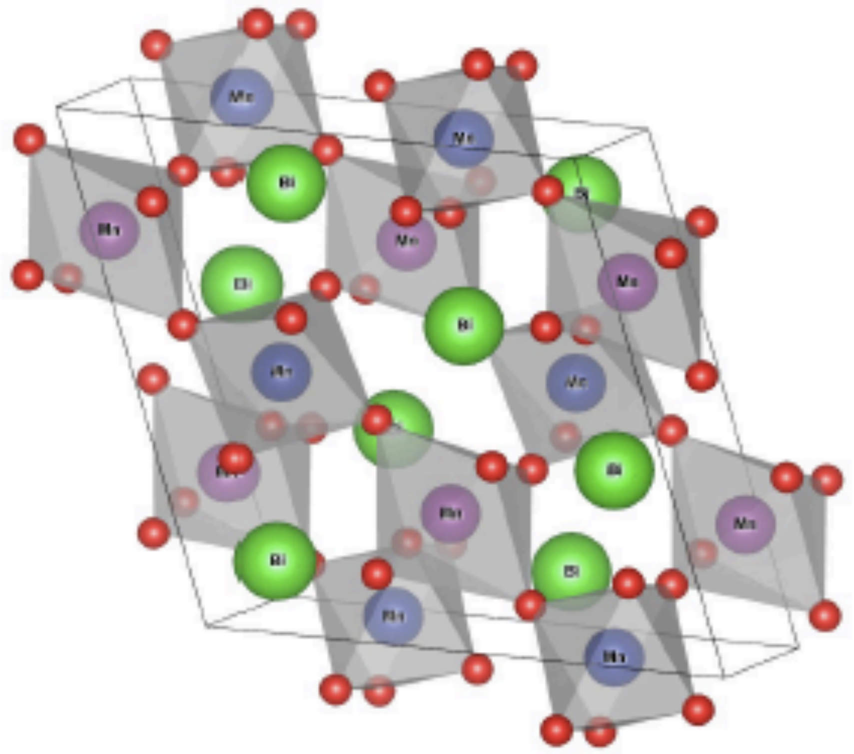

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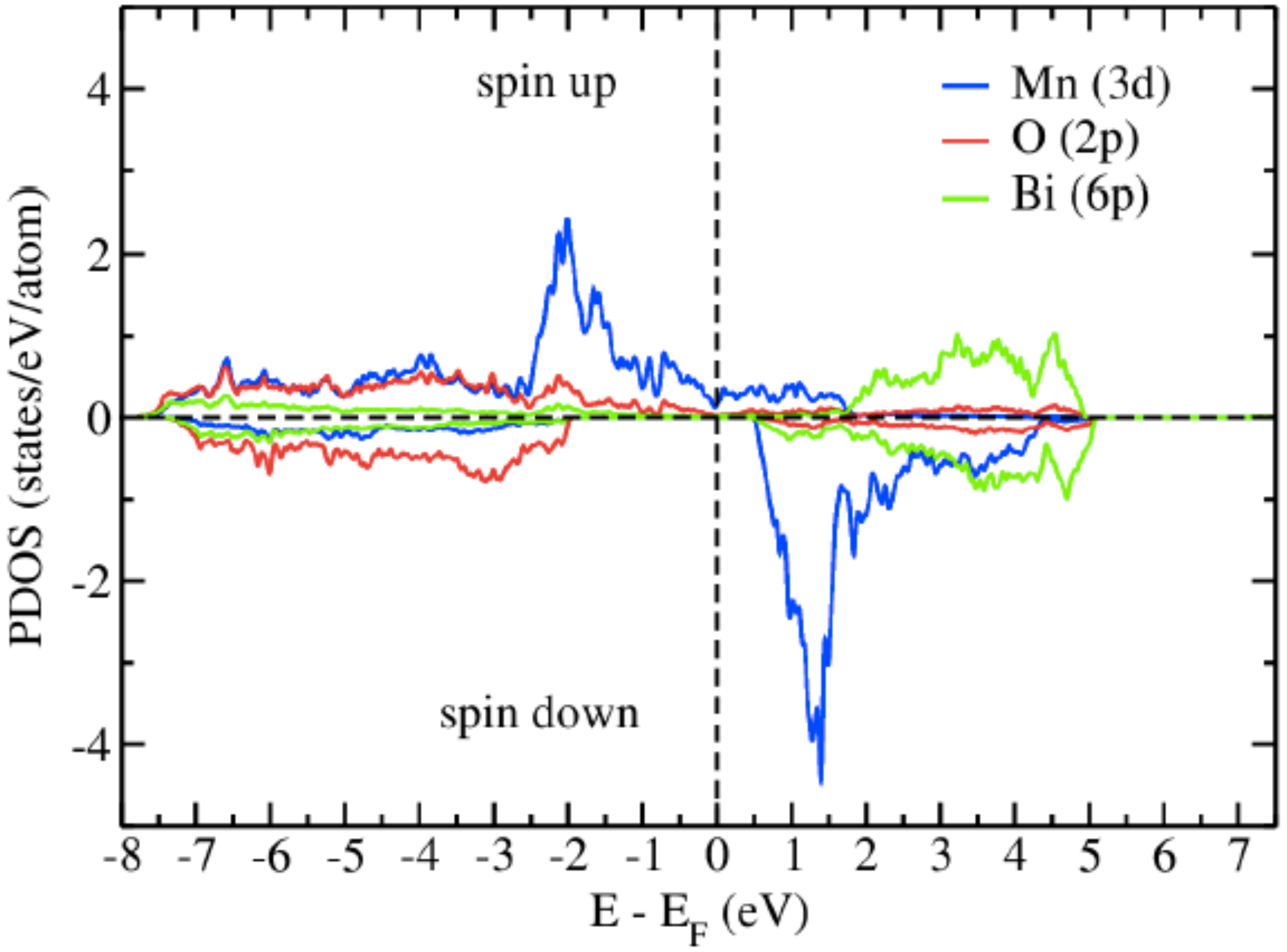
Hubbard U_{eff} = 6.3 (eV) for the 3*d* states of Mn

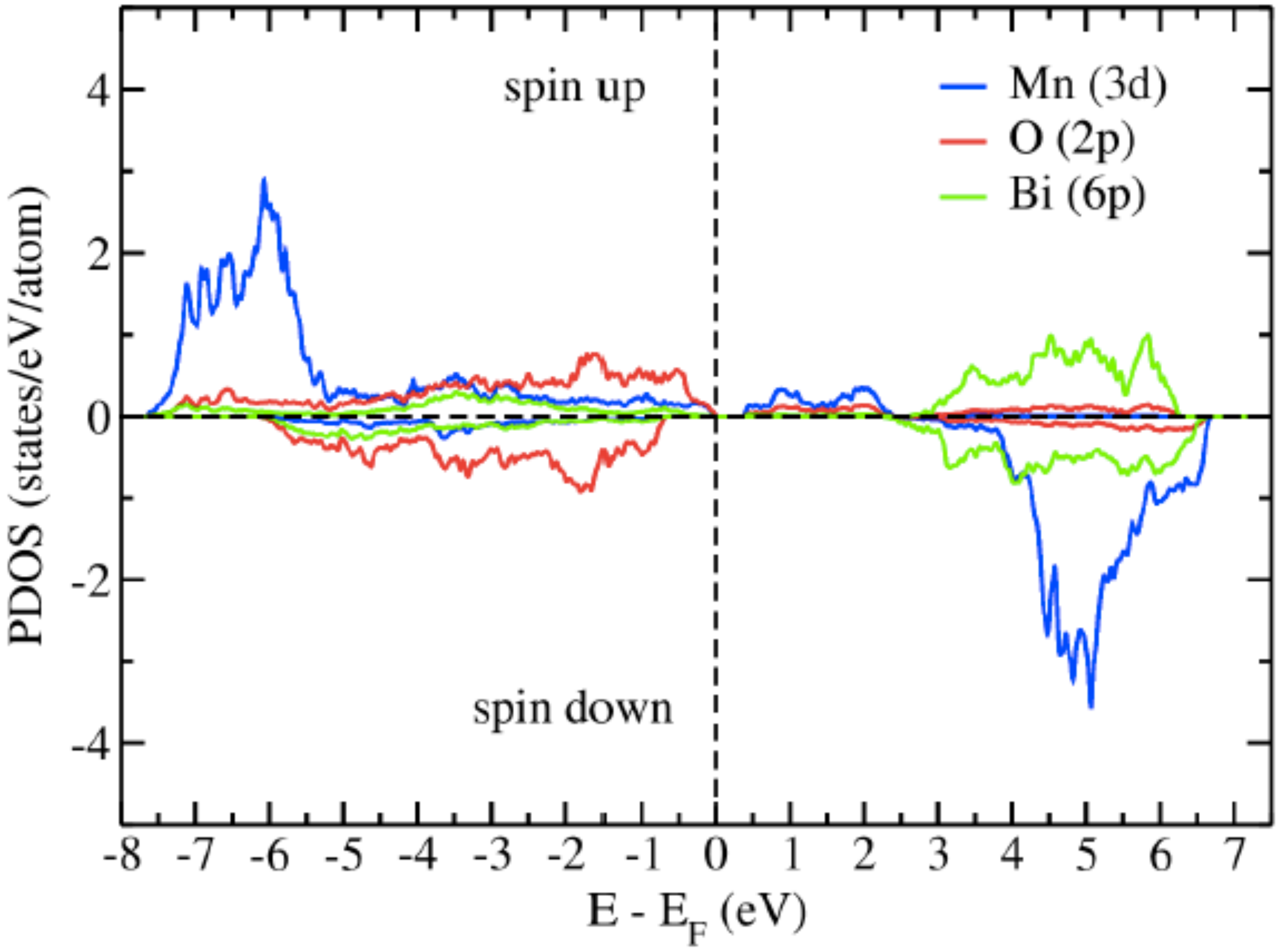
$$E_{\mathrm{GAP}}^{\mathrm{DFT}+U}=0.4\,(\mathrm{eV}) \qquad E_{\mathrm{GAP}}^{expt}=0.9-1.1\,(\mathrm{eV})$$

Metal

DFT



DFT+*U*

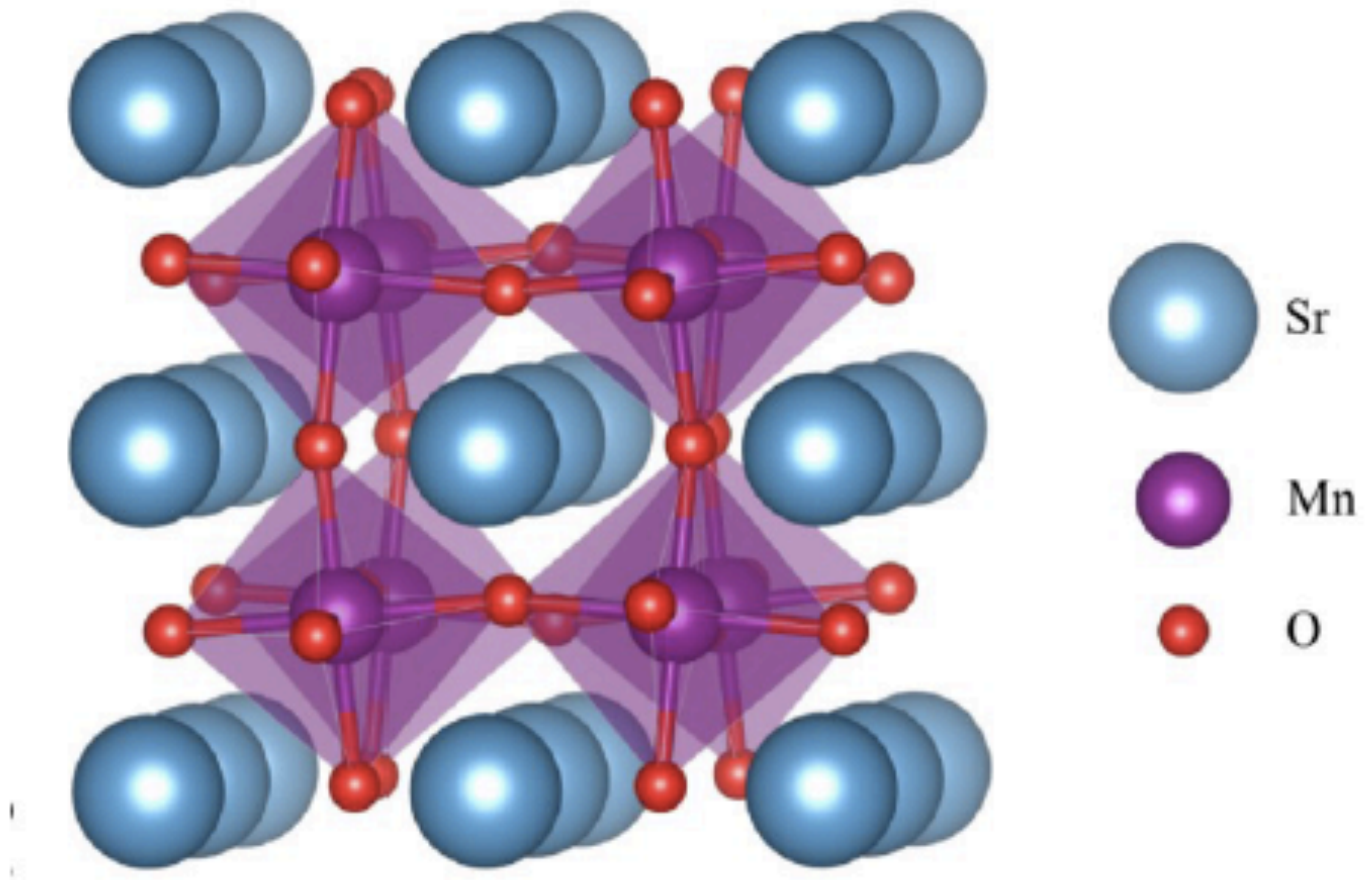


Charge-transfer insulator

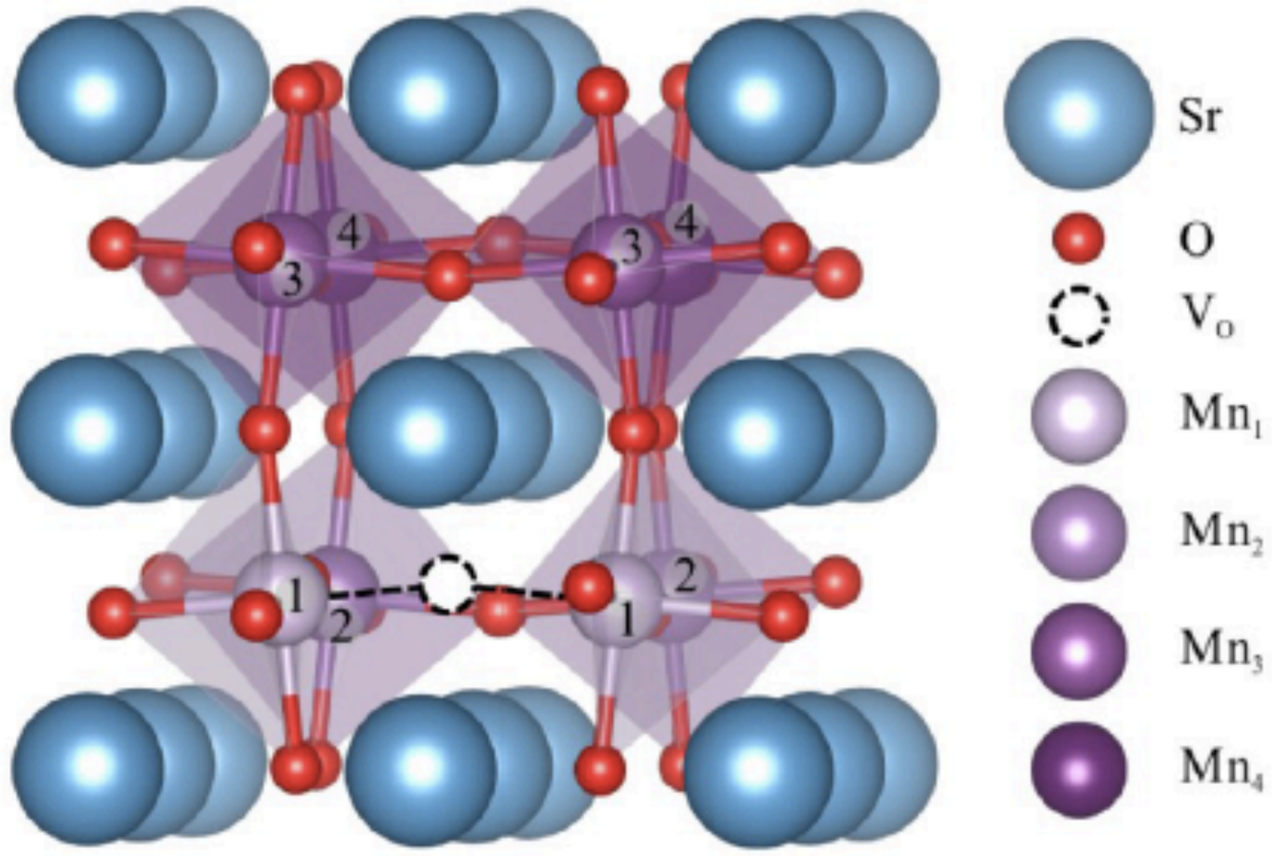
I. Timrov, N. Marzari, and M. Cococcioni, in preparation.

II.Formation energies of $SrMnO_3$

Stoichiometric SrMnO3



Defective SrMnO3



C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, Phys. Rev. B **99**, 094102 (2019).

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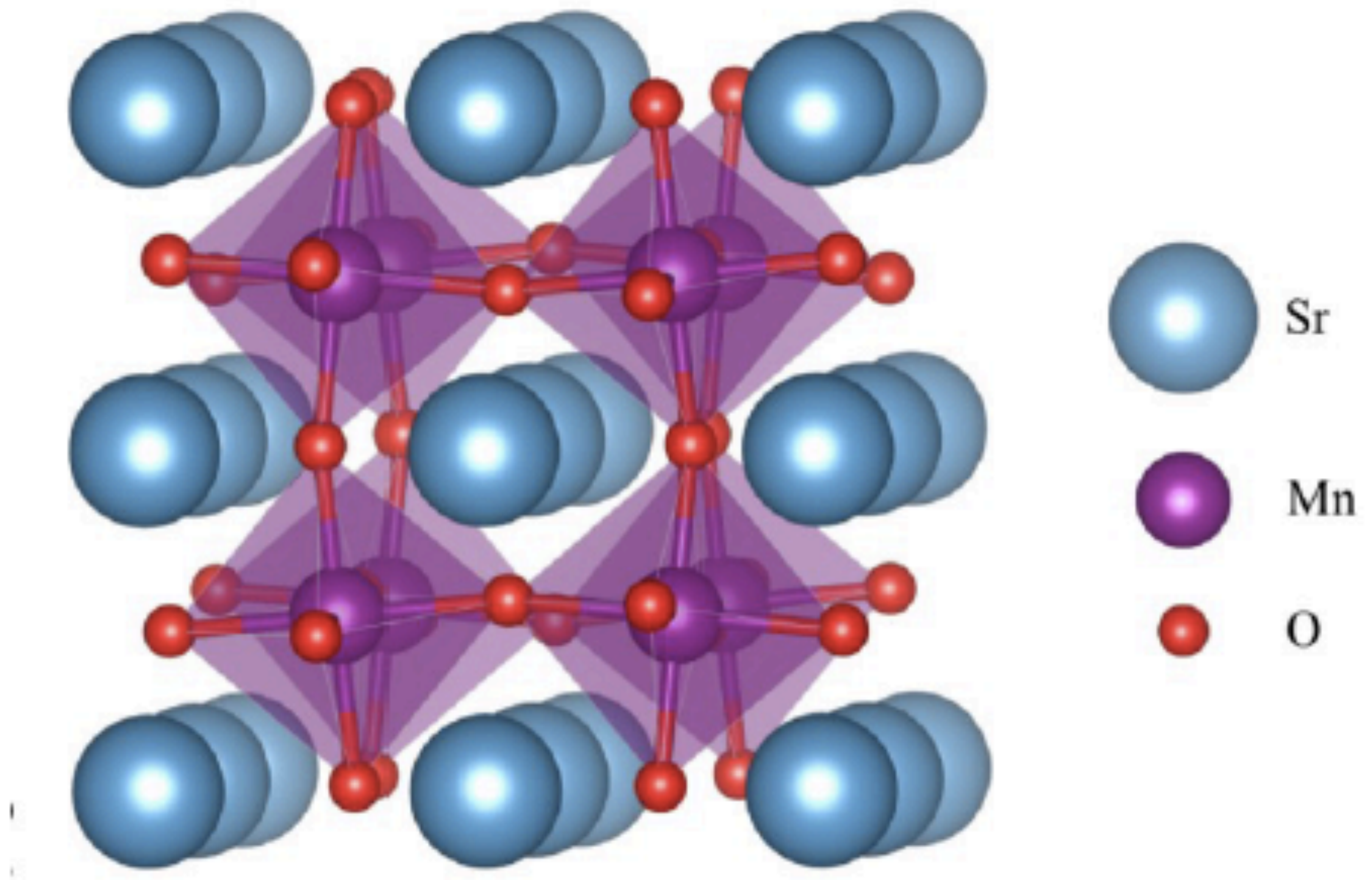
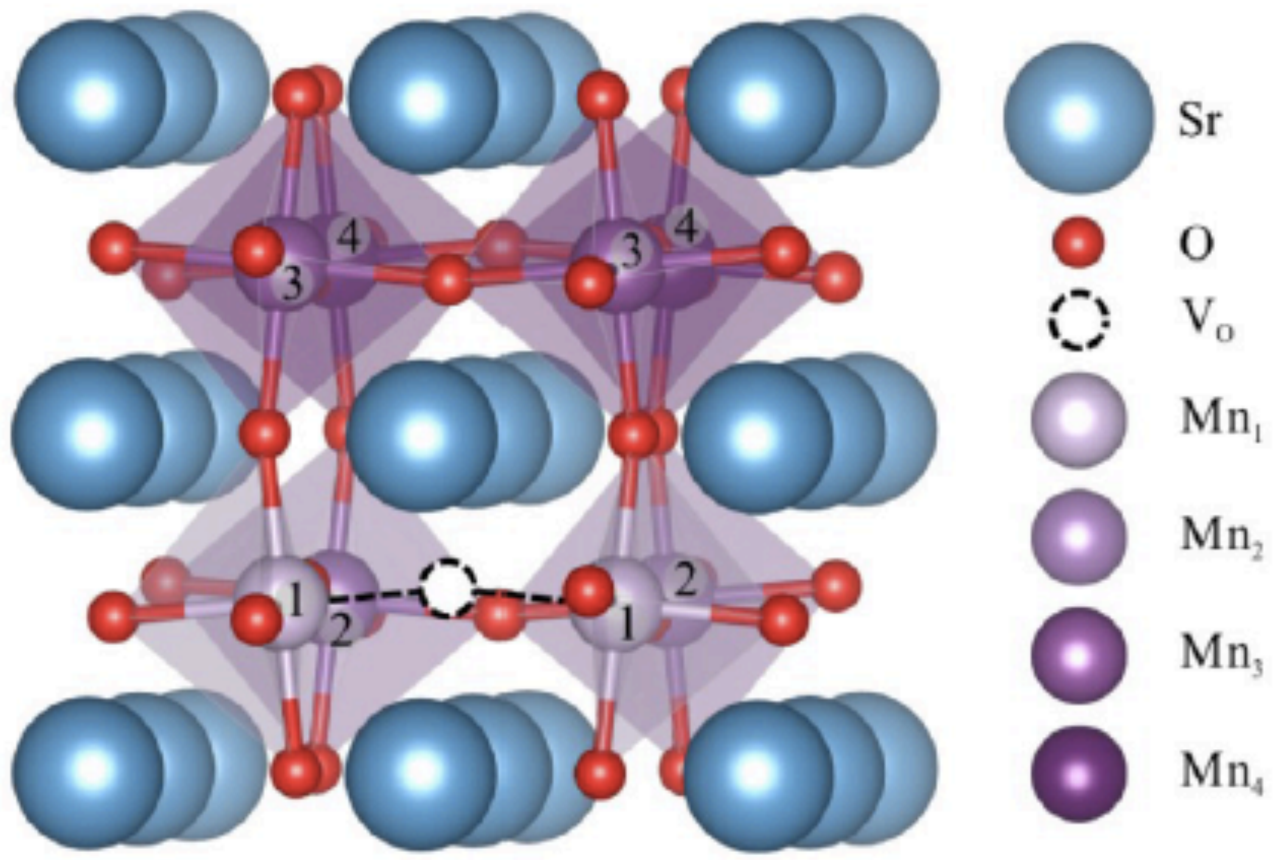
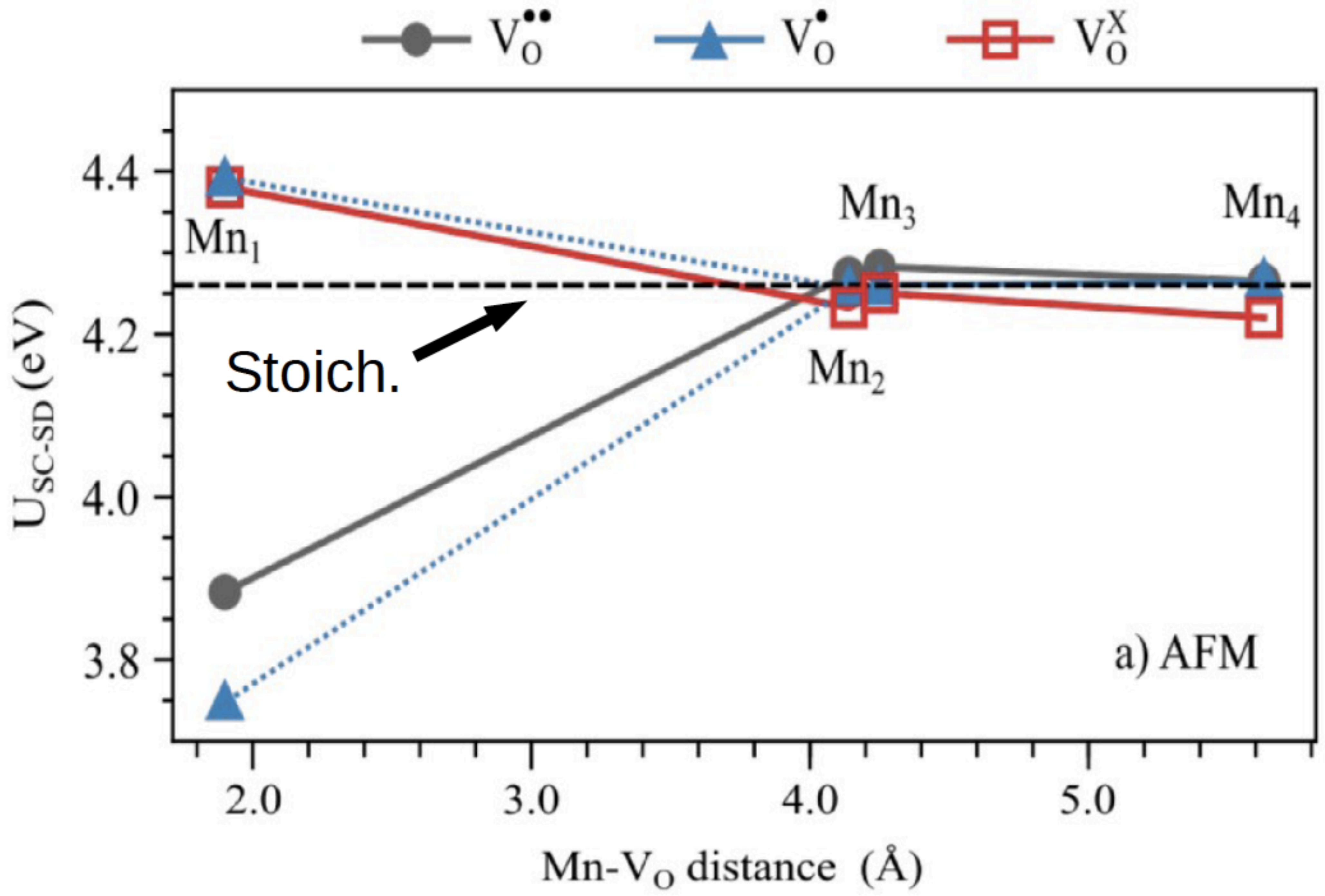


Defective SrMnO3





In a perfect crystal U_{eff} is global, i.e. the same for all Mn atoms.

In a crystal with defects (oxygen vacancies) U_{eff} is different for different Mn atoms depending on the distance from the defect.

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, Phys. Rev. B **99**, 094102 (2019).

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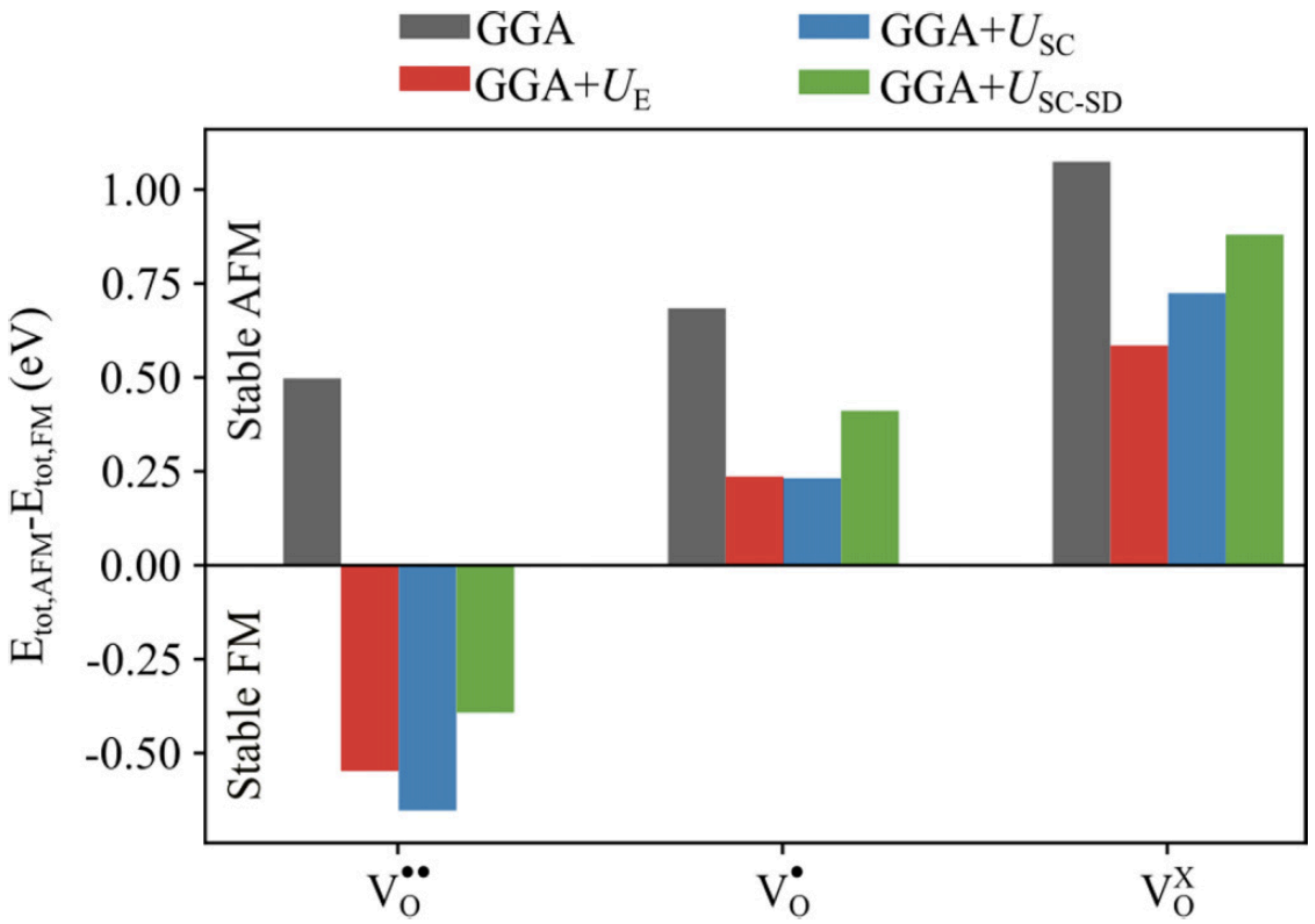

Total-energy differences between defective cells with AFM and FM ordering

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, Phys. Rev. B **99**, 094102 (2019).

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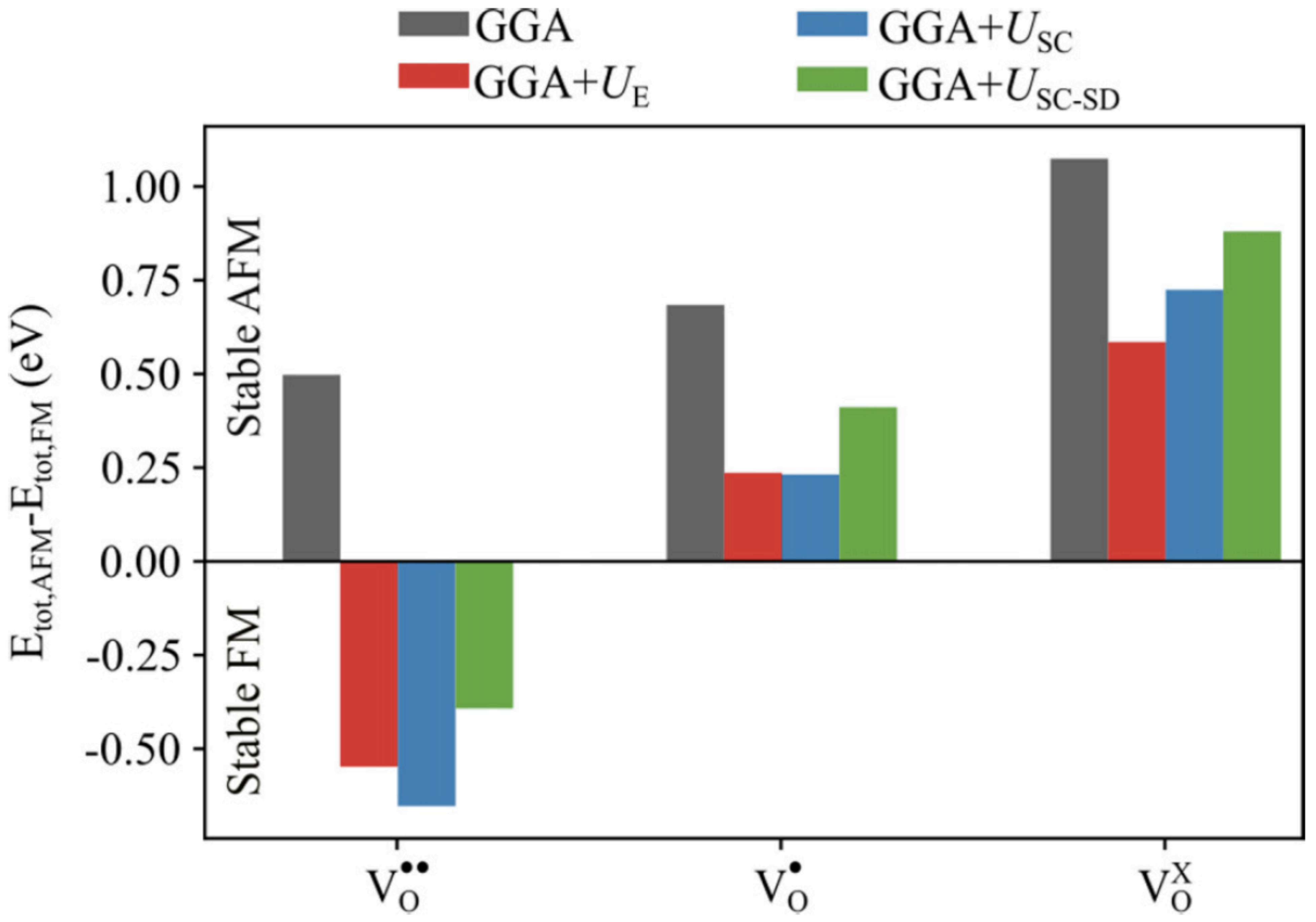

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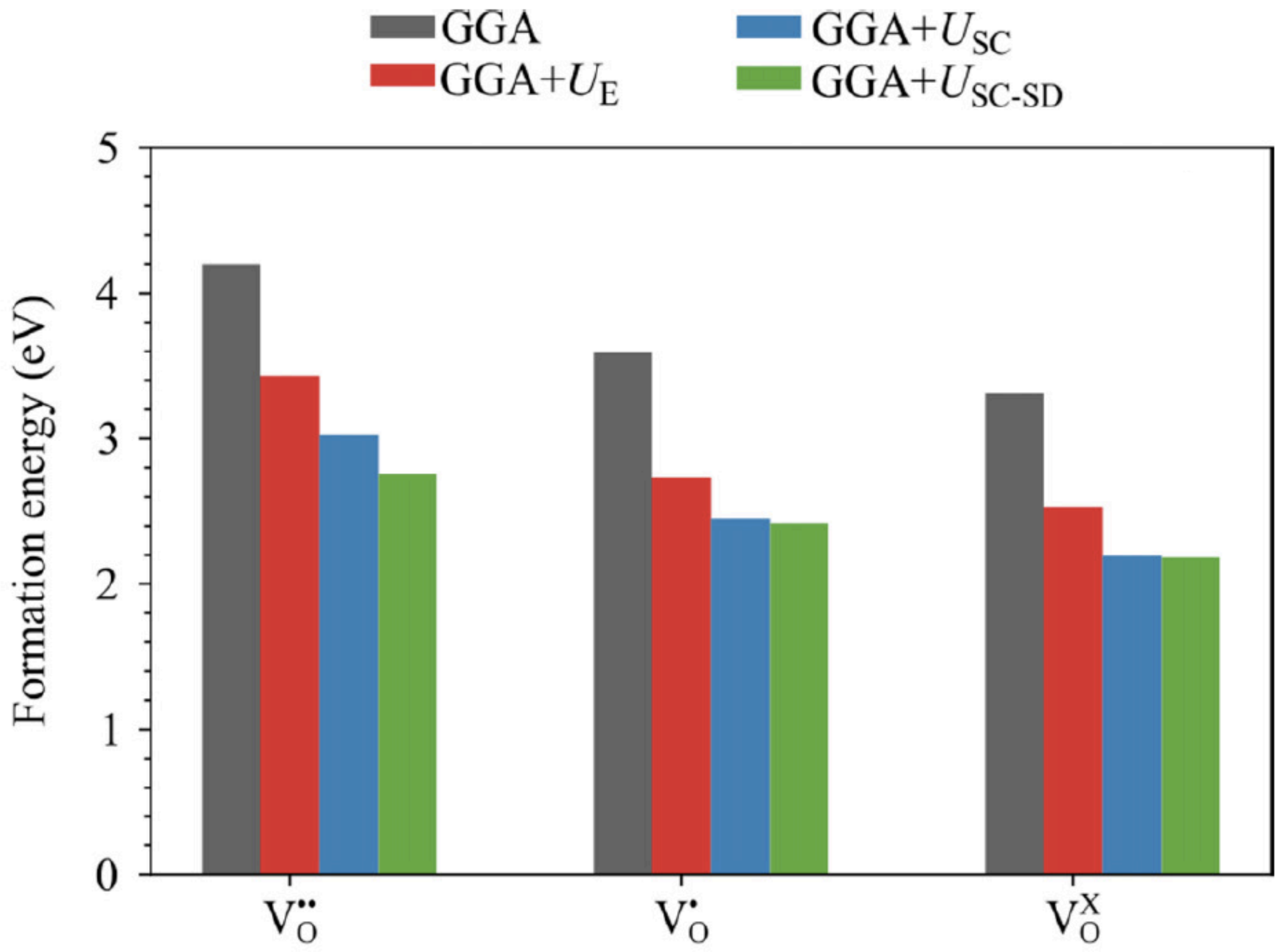

Formation energy for three types of defects for the AFM ordering

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, Phys. Rev. B **99**, 094102 (2019).

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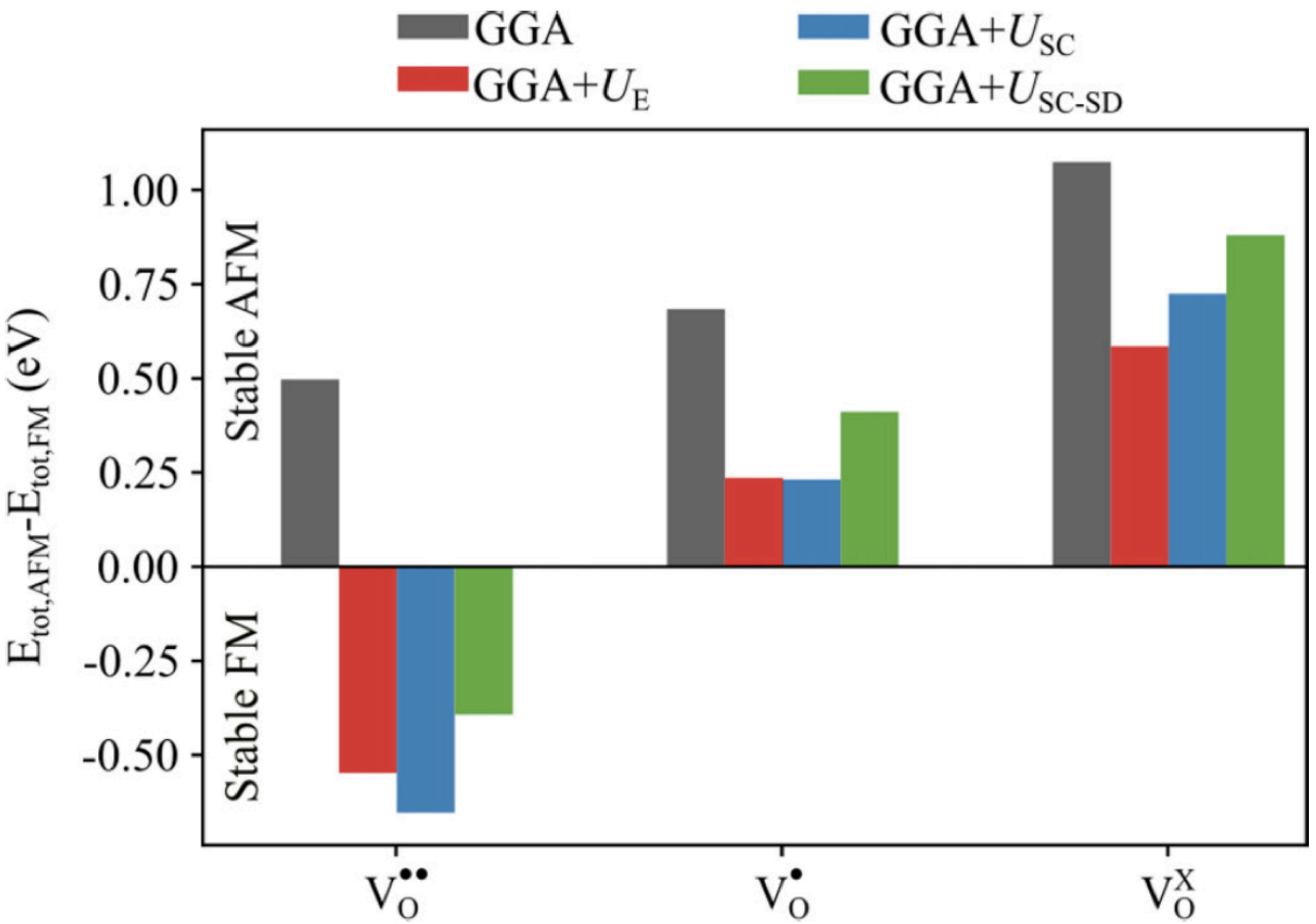
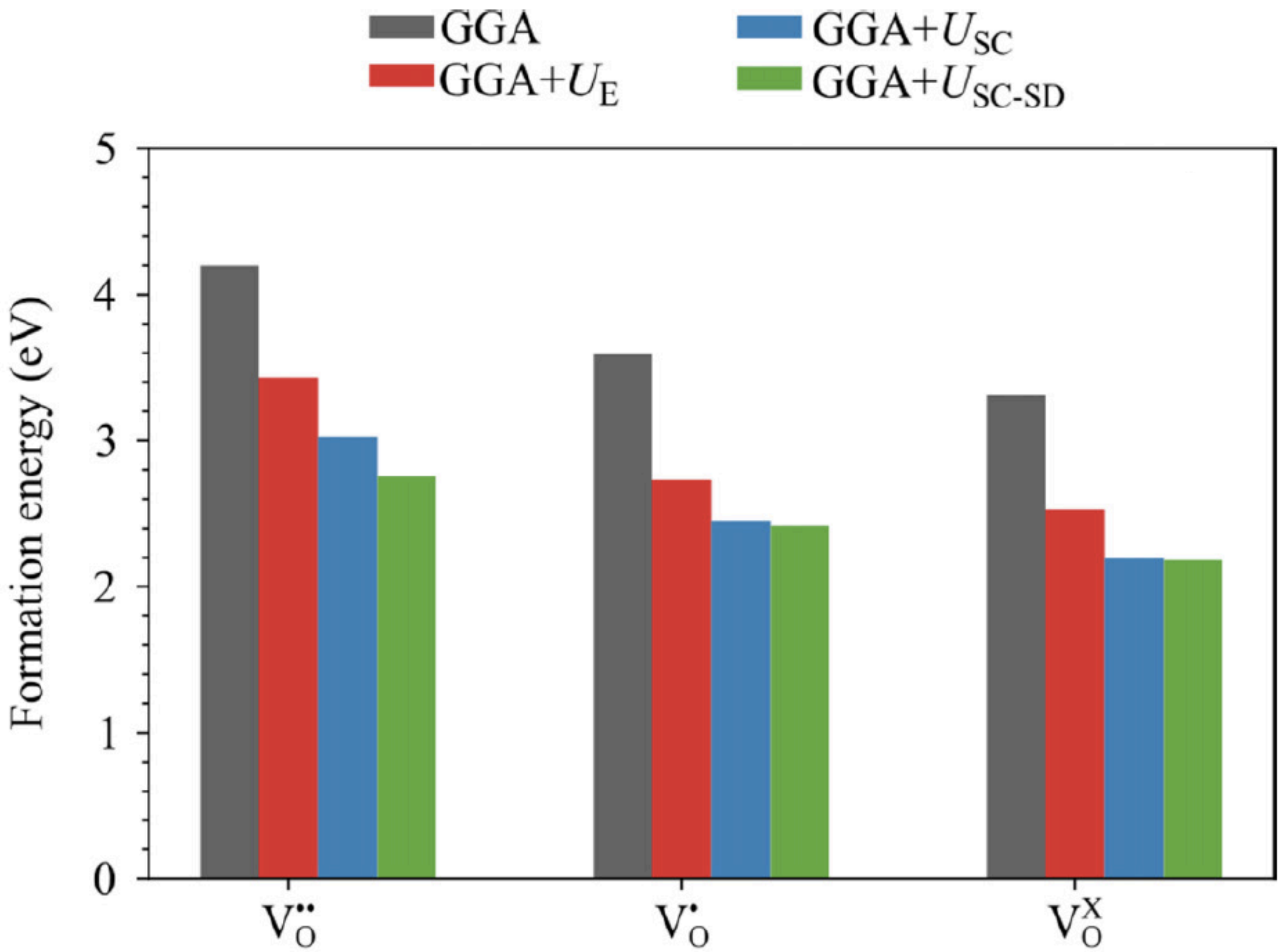


Total-energy differences between defective cells with AFM and FM ordering

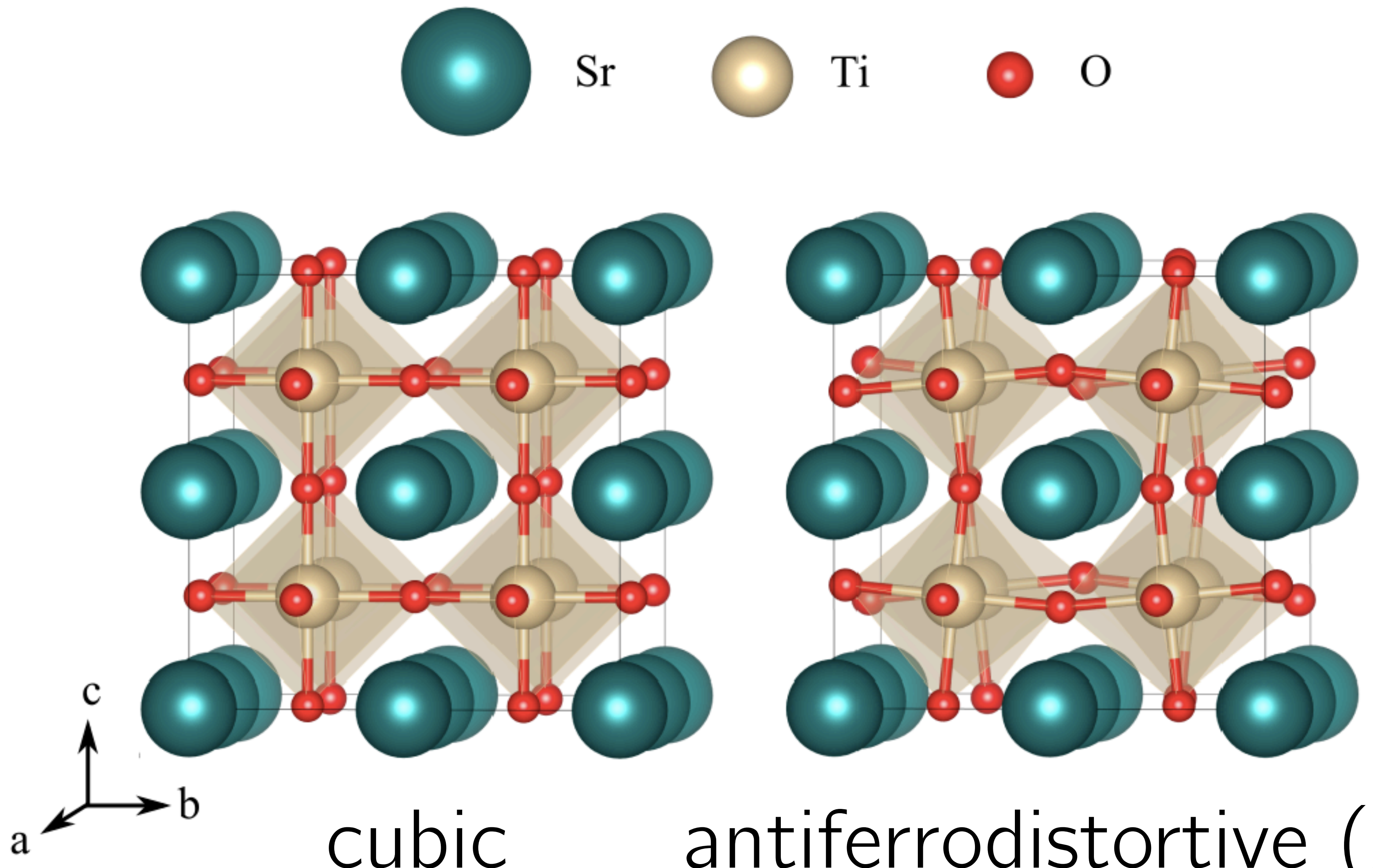


Formation energy for three types of defects for the AFM ordering

Changes in the total-energy differences and in the formation energy reflect the strong dependence on the value of the Hubbard U_{eff} parameter.

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, Phys. Rev. B **99**, 094102 (2019).

III. Formation energies of $SrTiO_3$

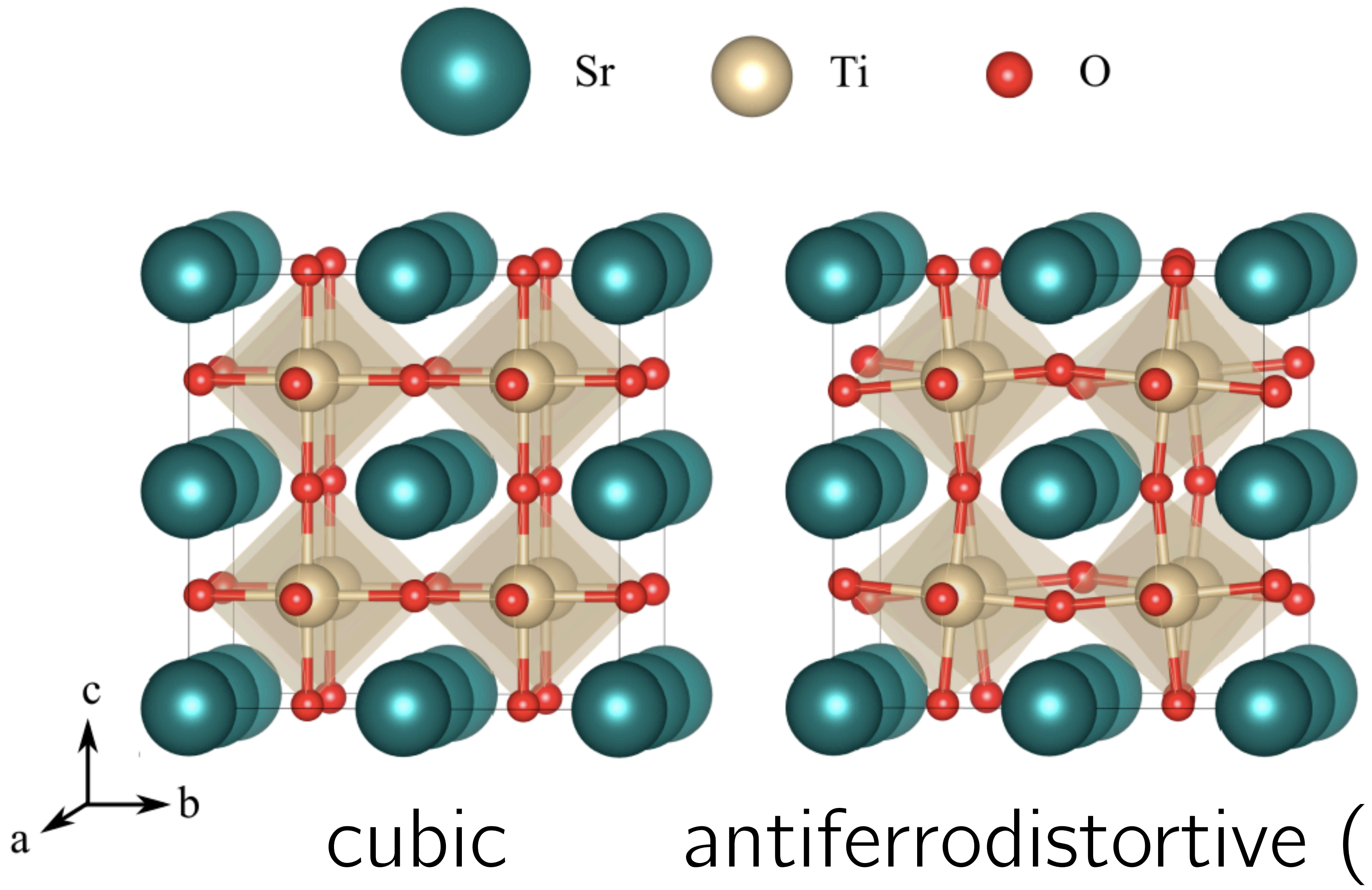


cubic structure

antiferrodistortive (AFD) structure

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, in preparation.

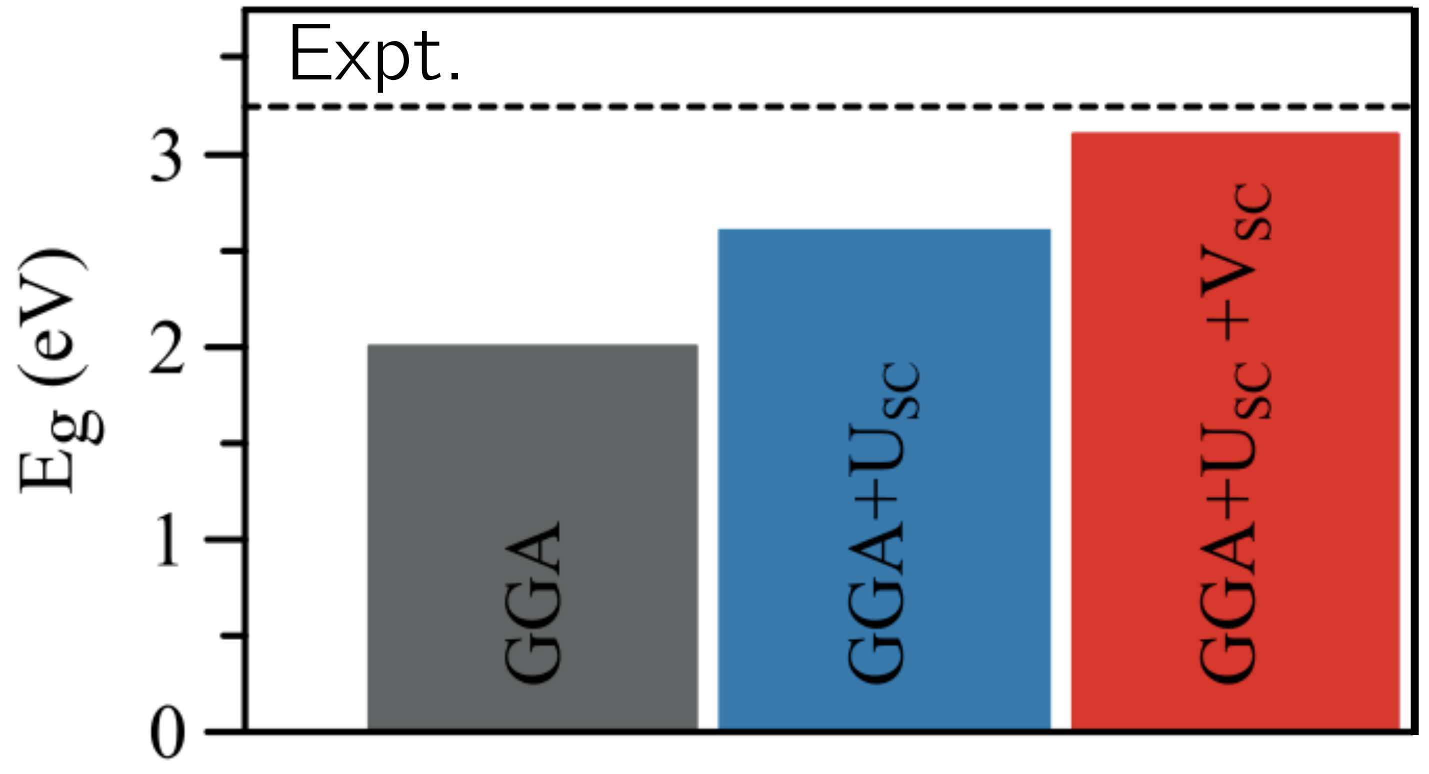
III. Formation energies of $SrTiO_3$

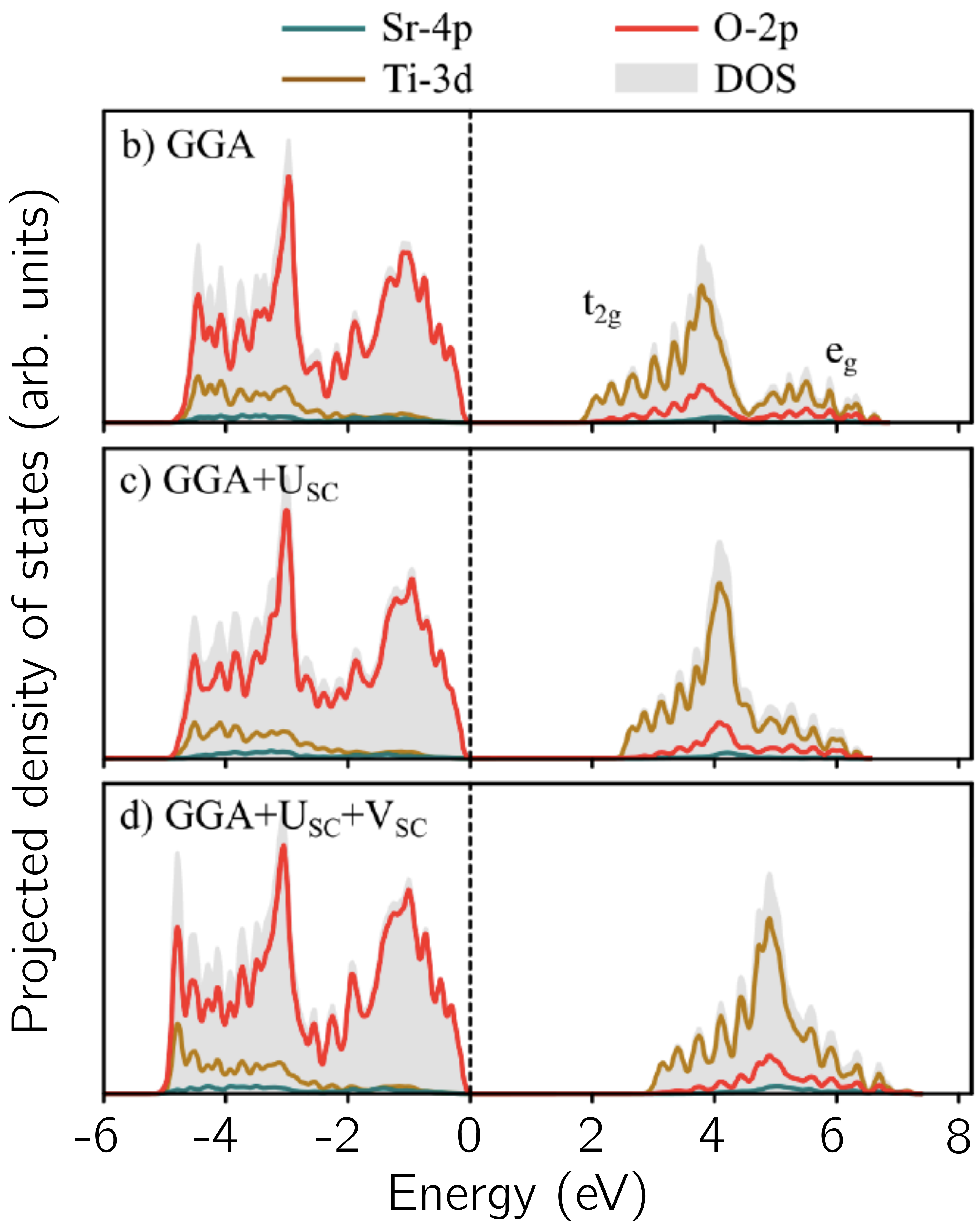


cubic structure

antiferrodistortive (AFD) structure

Band gap for the AFD structure





C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, in preparation.

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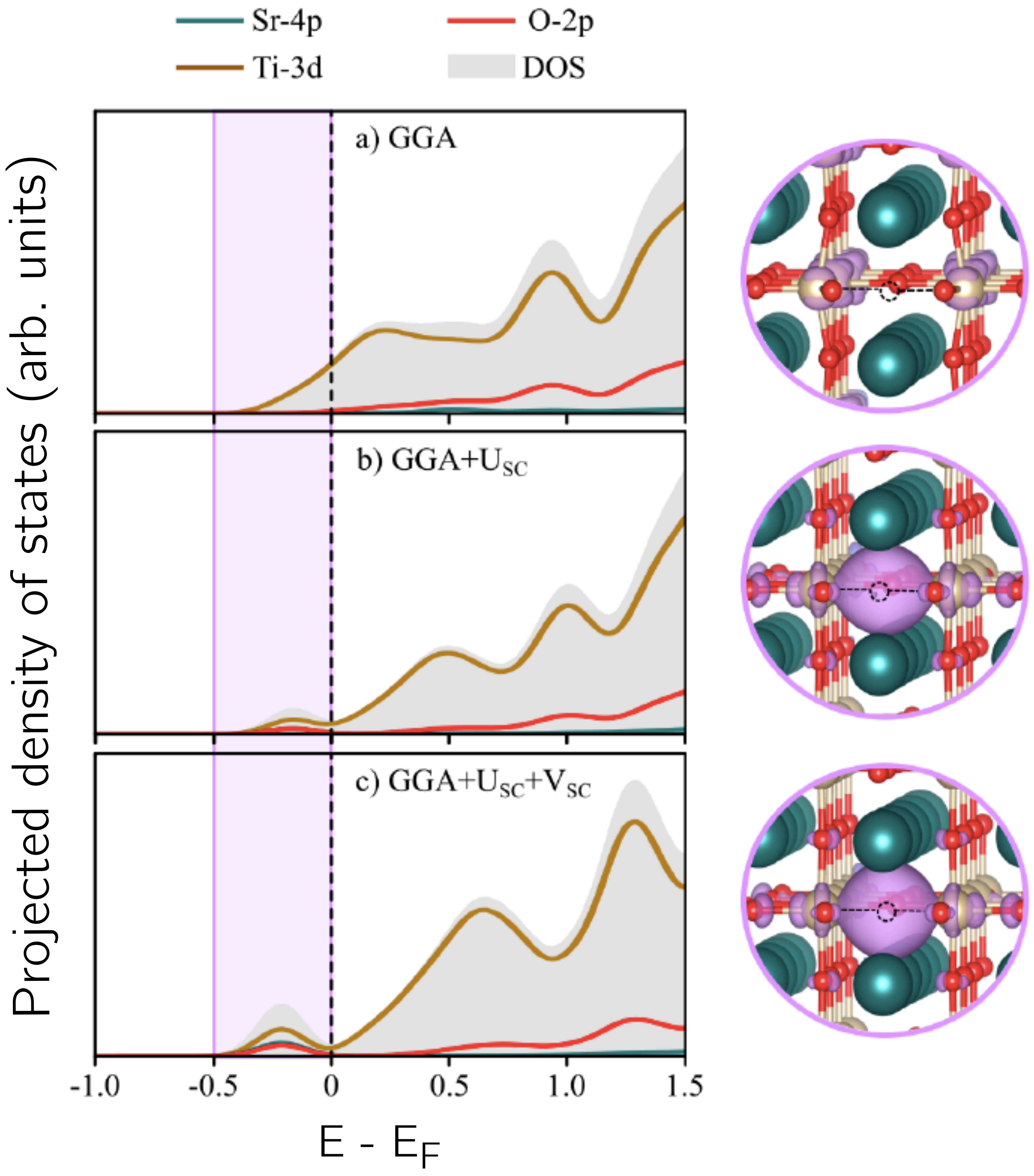

80-atoms supercell

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, in preparation.

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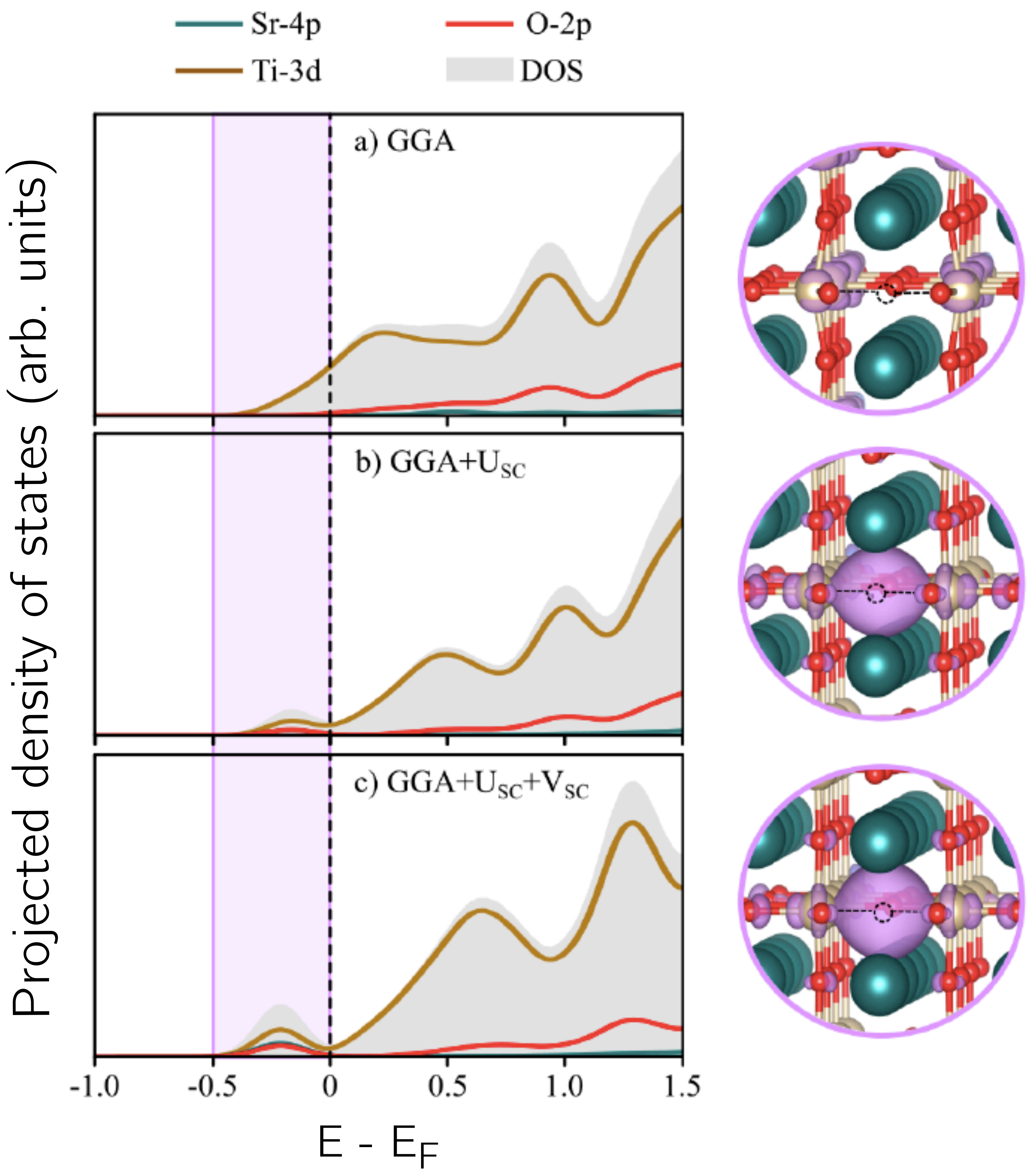
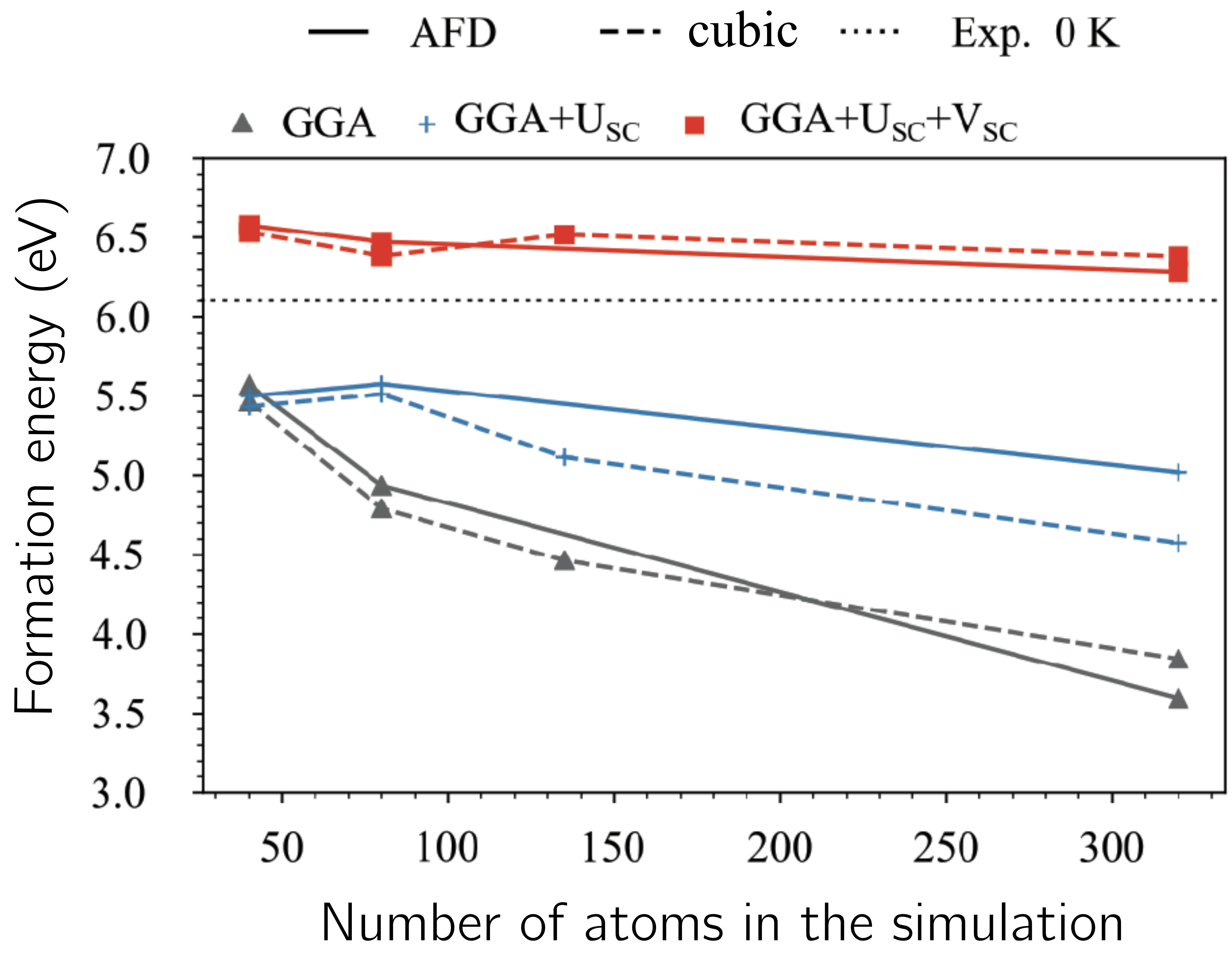




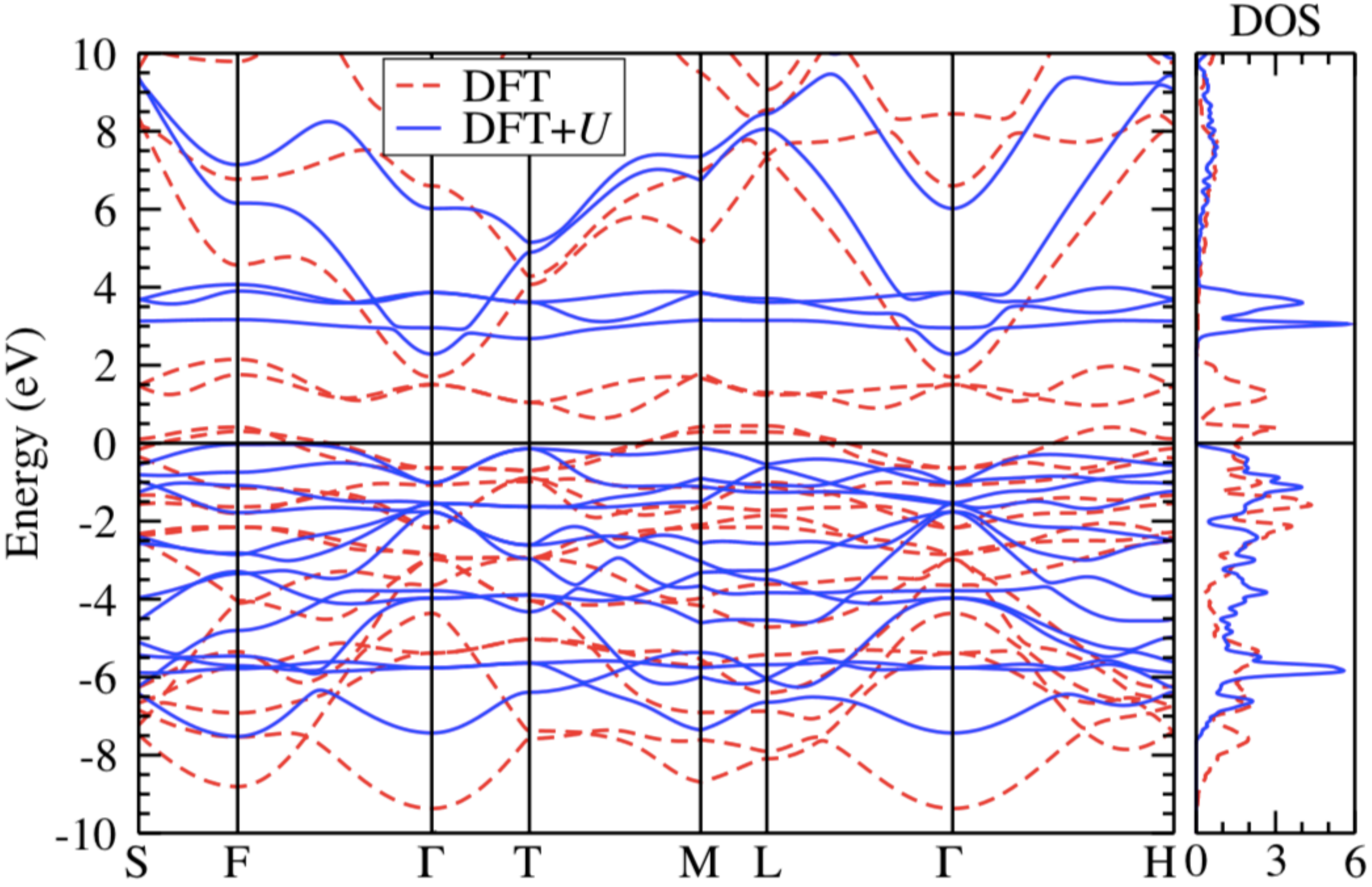
80-atoms supercell

Bigger supercell → Lower concentration of defects

C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, in preparation.

IV. Electronic and vibrational properties of CoO

Electronic band structure



DFT: metallic ground state (wrong)

DFT+U: insulating ground state (correct)

$U_{\mathrm{eff}} = 4.55$ (eV) $E_{\mathrm{GAP}}^{\mathrm{DFT}+U} = 2.3$ (eV) $E_{\mathrm{GAP}}^{expt} = 2.5 - 2.8$ (eV)

A. Floris, I. Timrov, B. Himmetoglu, N. Marzari, S. de Gironcoli, and M. Cococcioni, in preparation.

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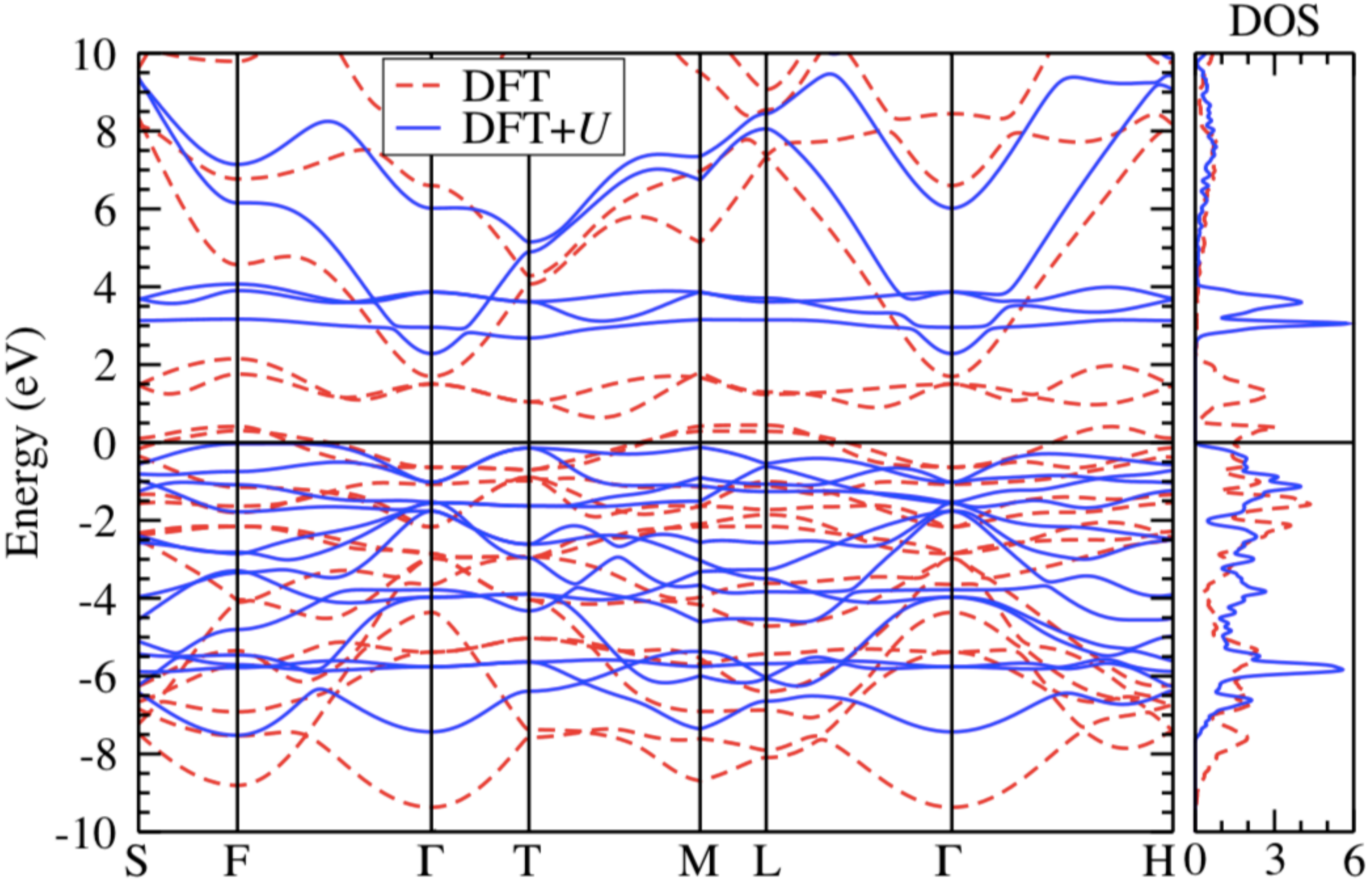
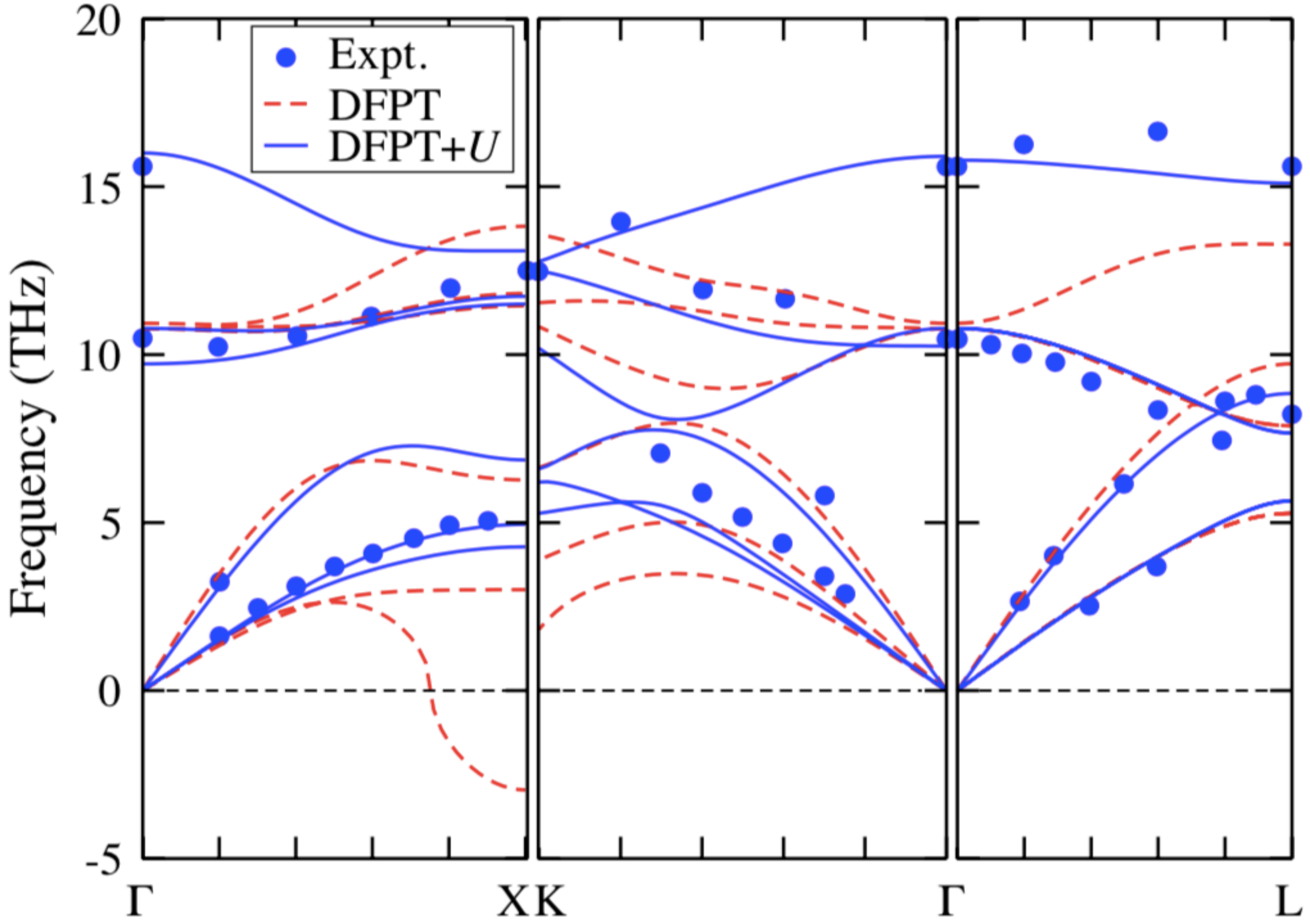


Phonon dispersion



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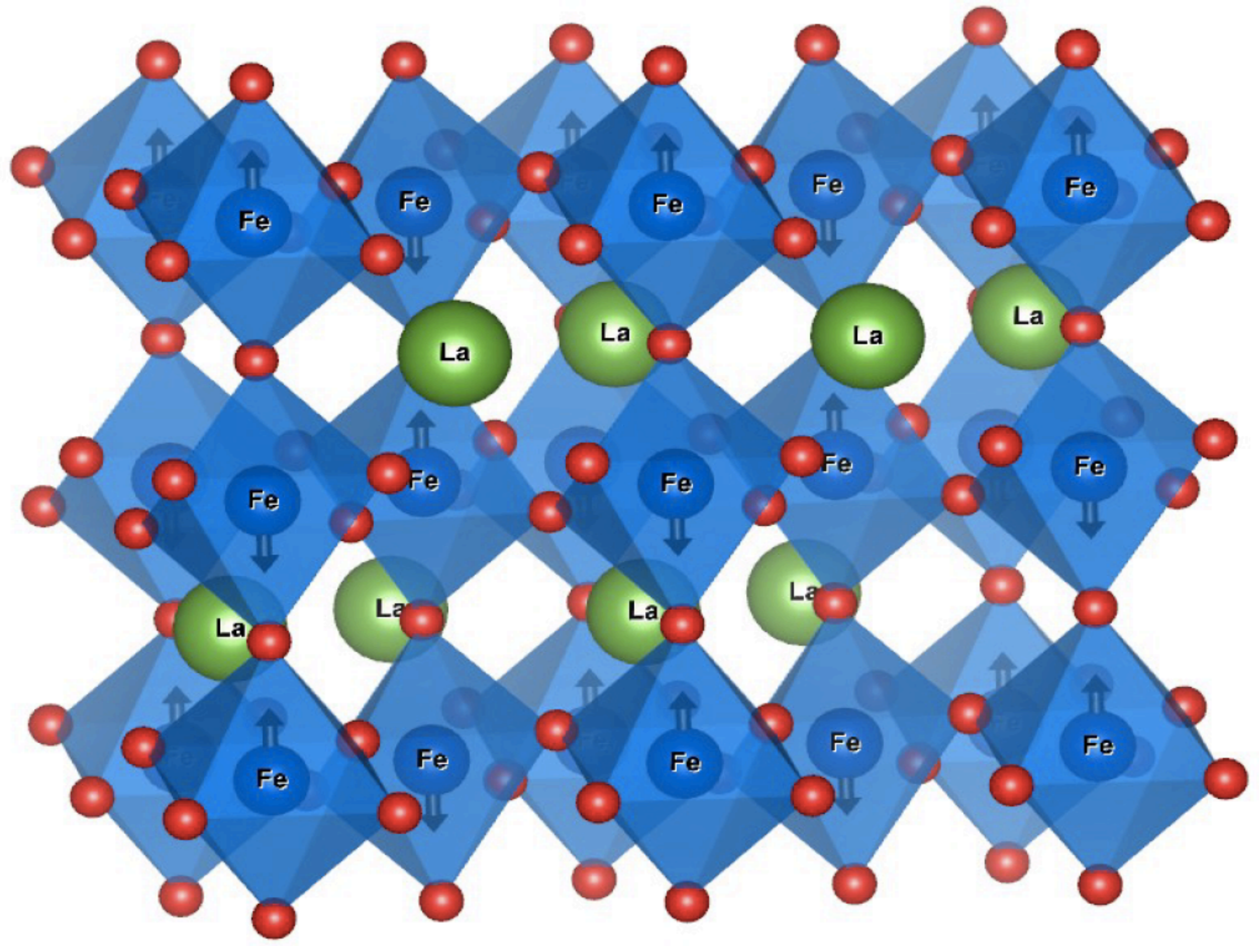
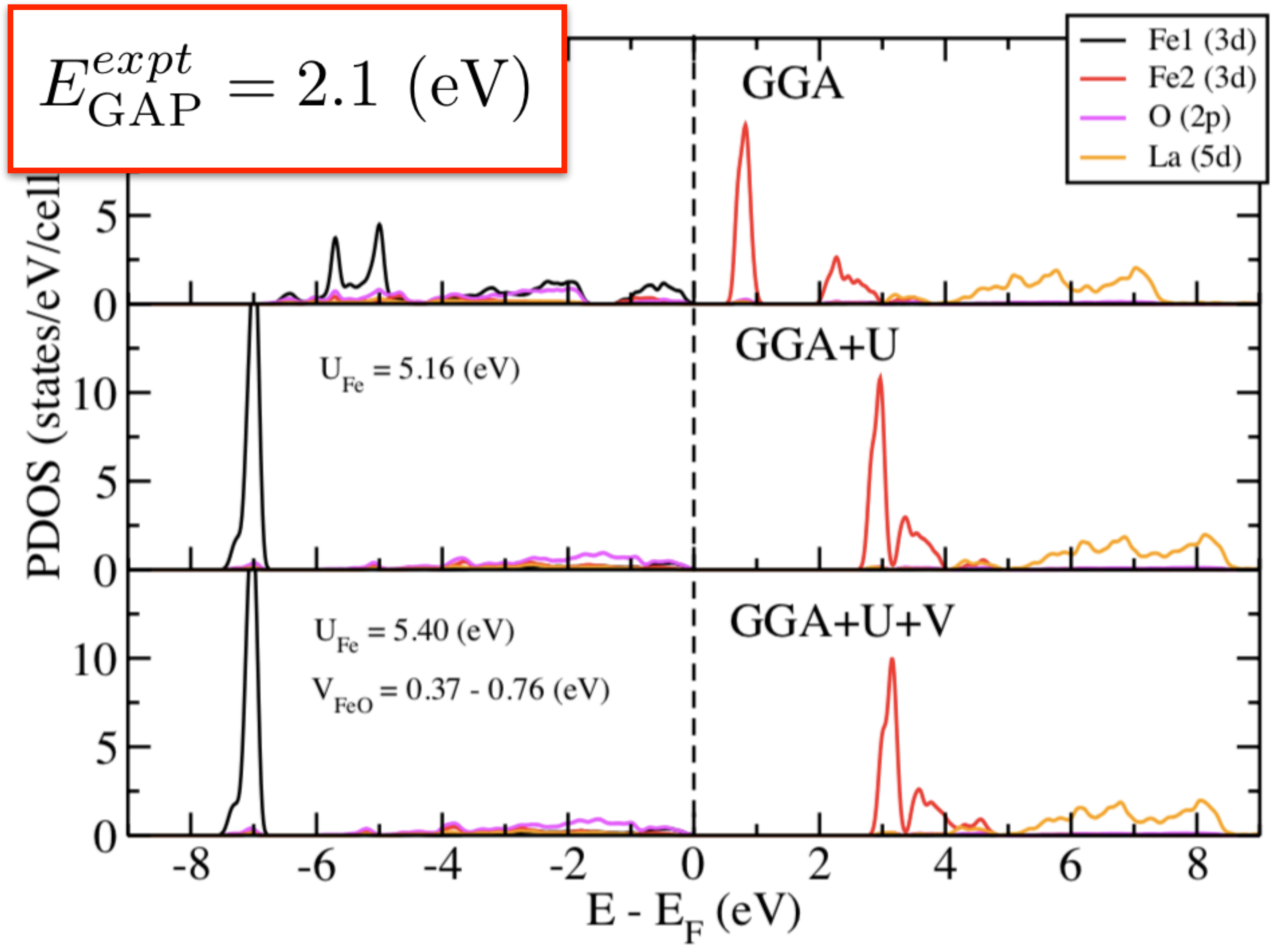
DFPT: the structure is dynamically unstable

DFPT+U: the structure is dynamically stable and the agreement with expt. is very good

A. Floris, I. Timrov, B. Himmetoglu, N. Marzari, S. de Gironcoli, and M. Cococcioni, in preparation.

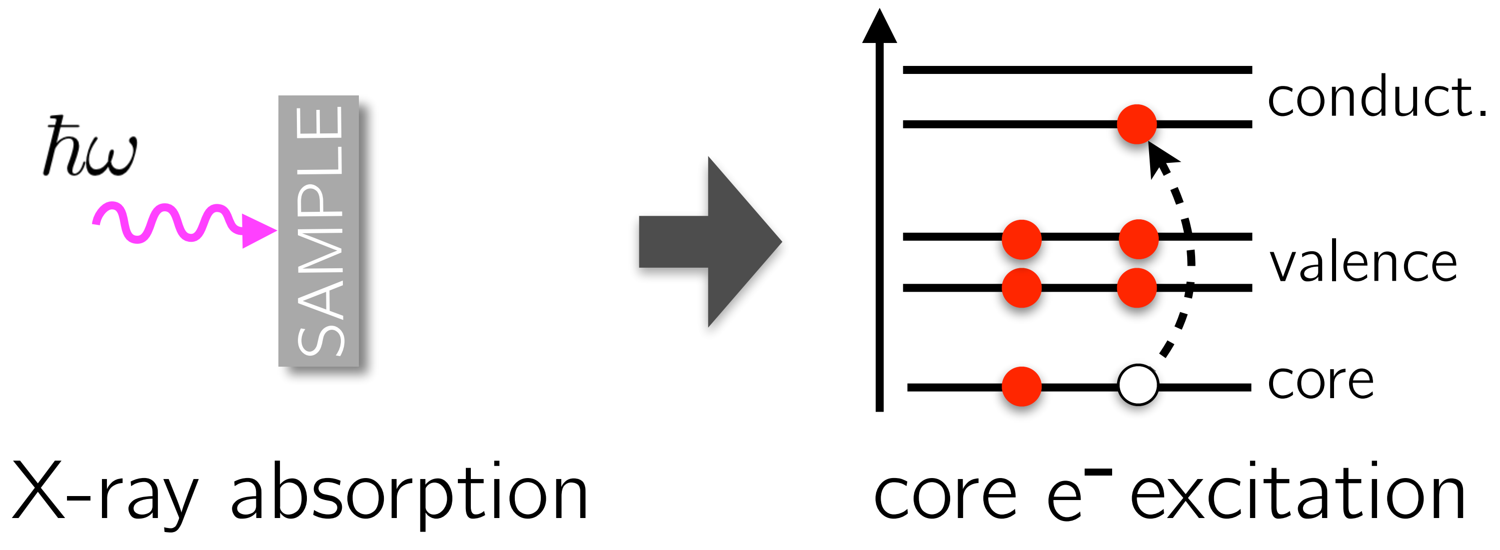
V. X-ray absorption near-edge structure of $LaFeO_3$





$$E^{expt}_{\mathrm{GAP}} = 2.1 \ (\mathrm{eV})$$

Experiment:



X-ray absorption

core e⁻ excitation

I. Timrov, P. Agrawal, Z. Zhang, S. Erat, R. Liu, A. Braun, M. Cococcioni, M. Calandra, N. Marzari, and D. Passerone, in preparation.

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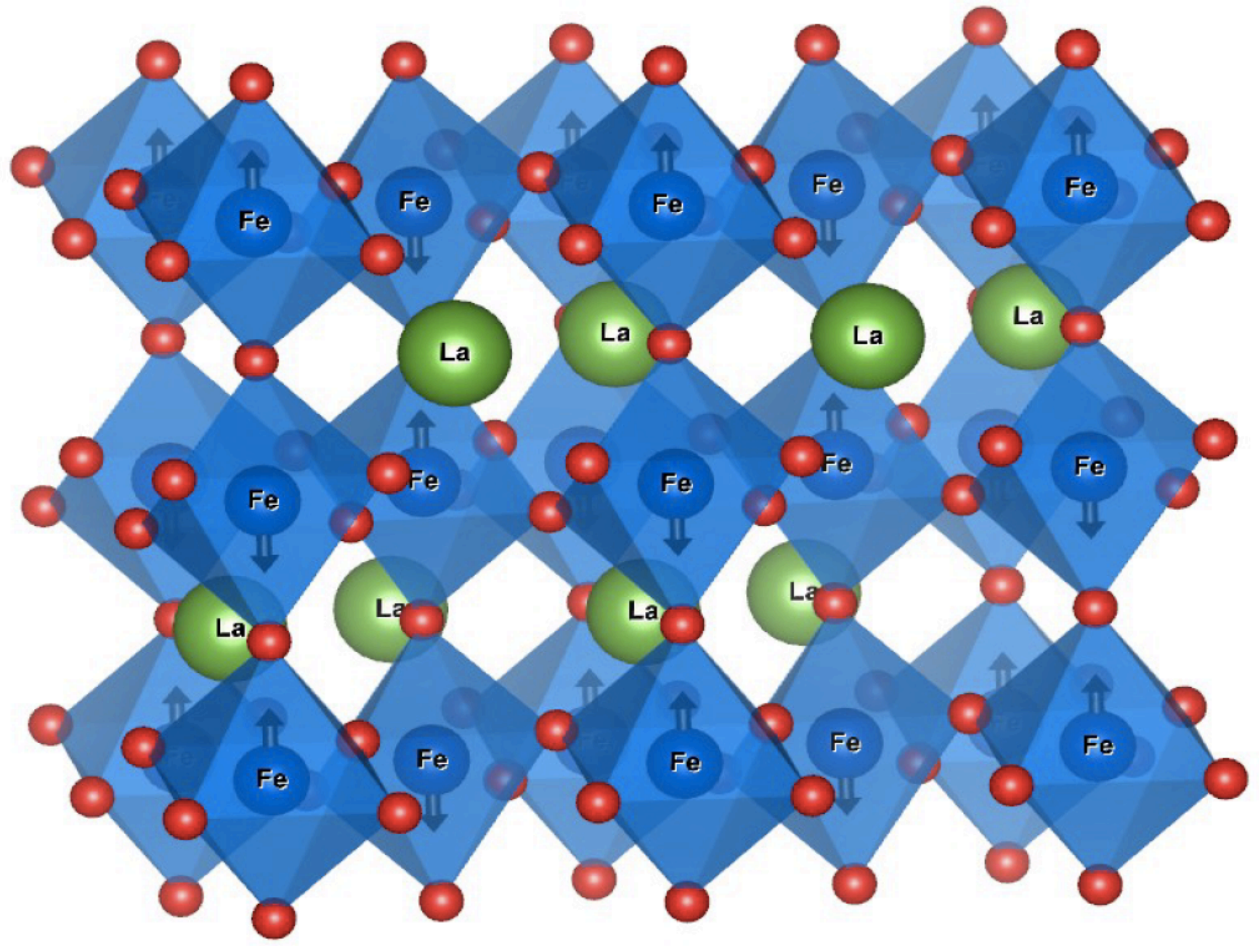
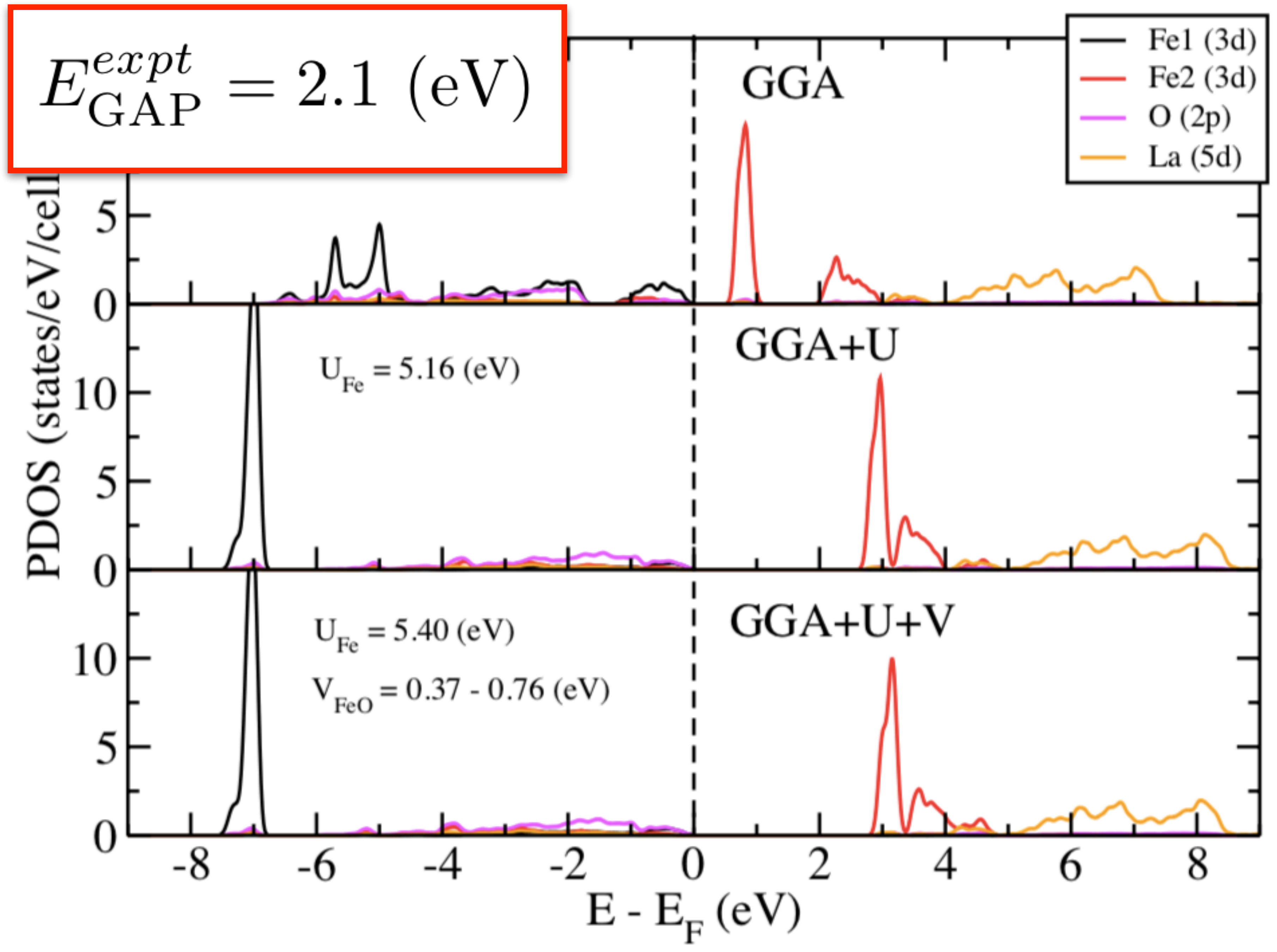
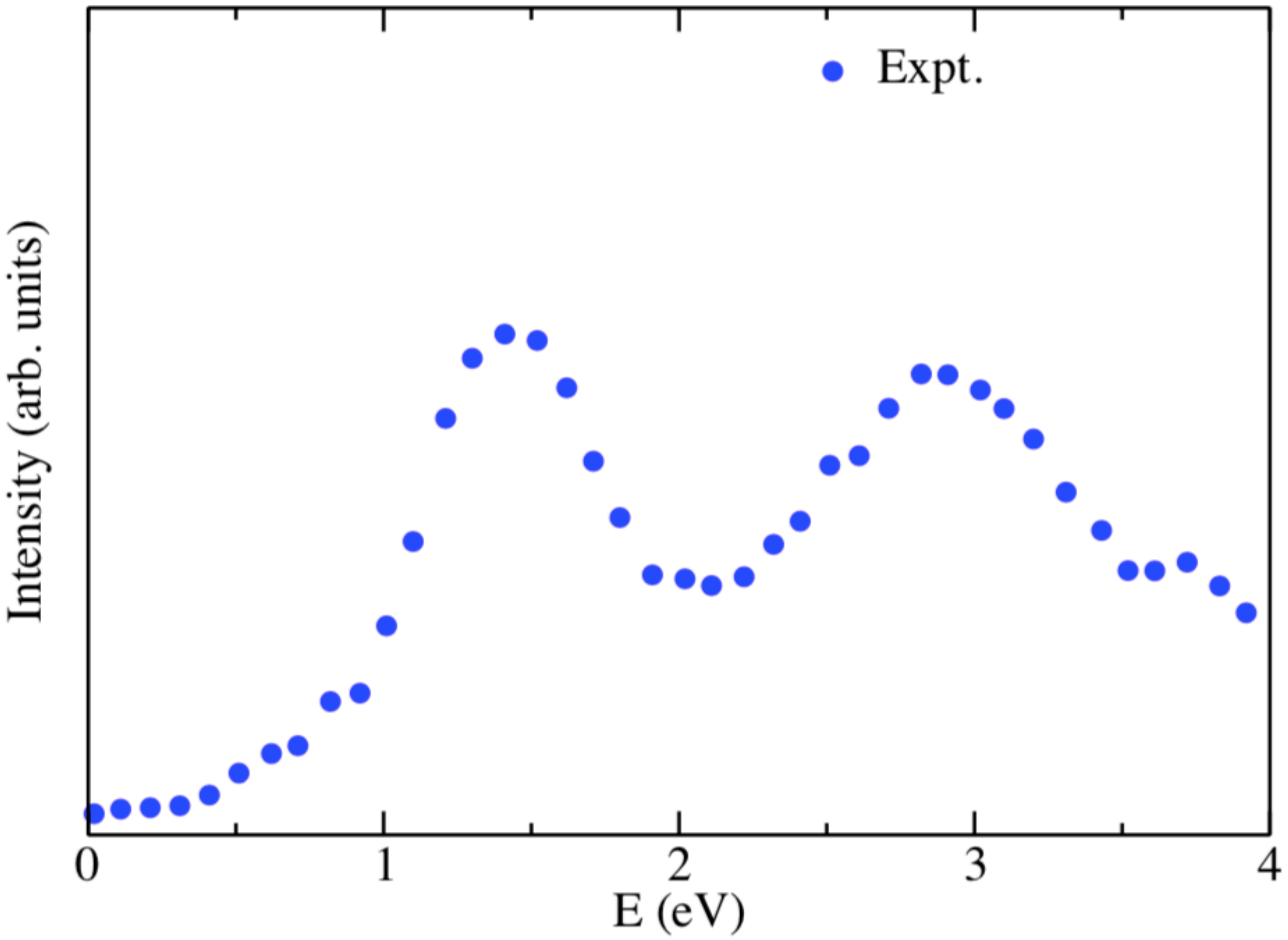


$$E^{expt}_{\mathrm{GAP}} = 2.1\ (\mathrm{eV})$$



Oxygen *K* pre-edge spectrum



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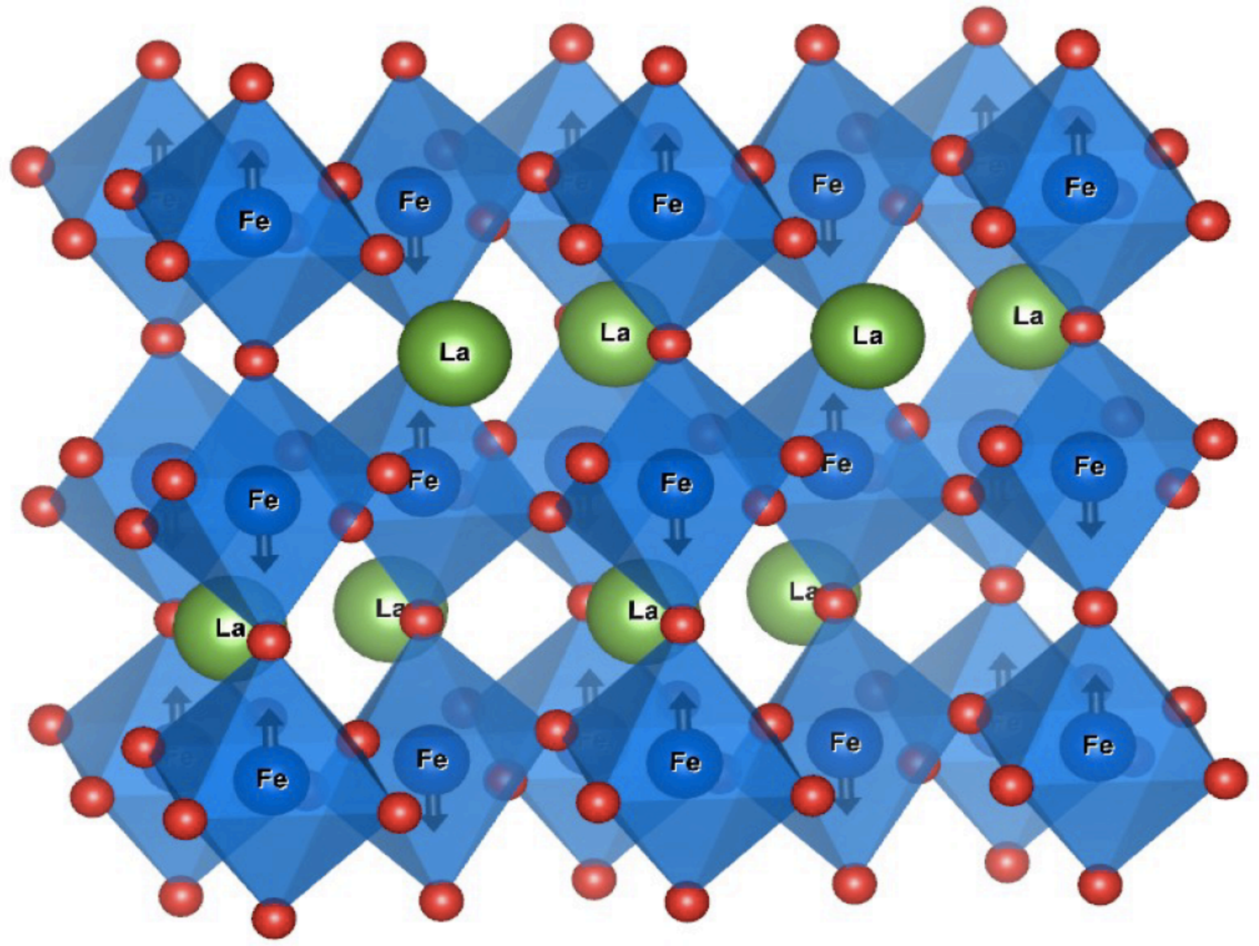
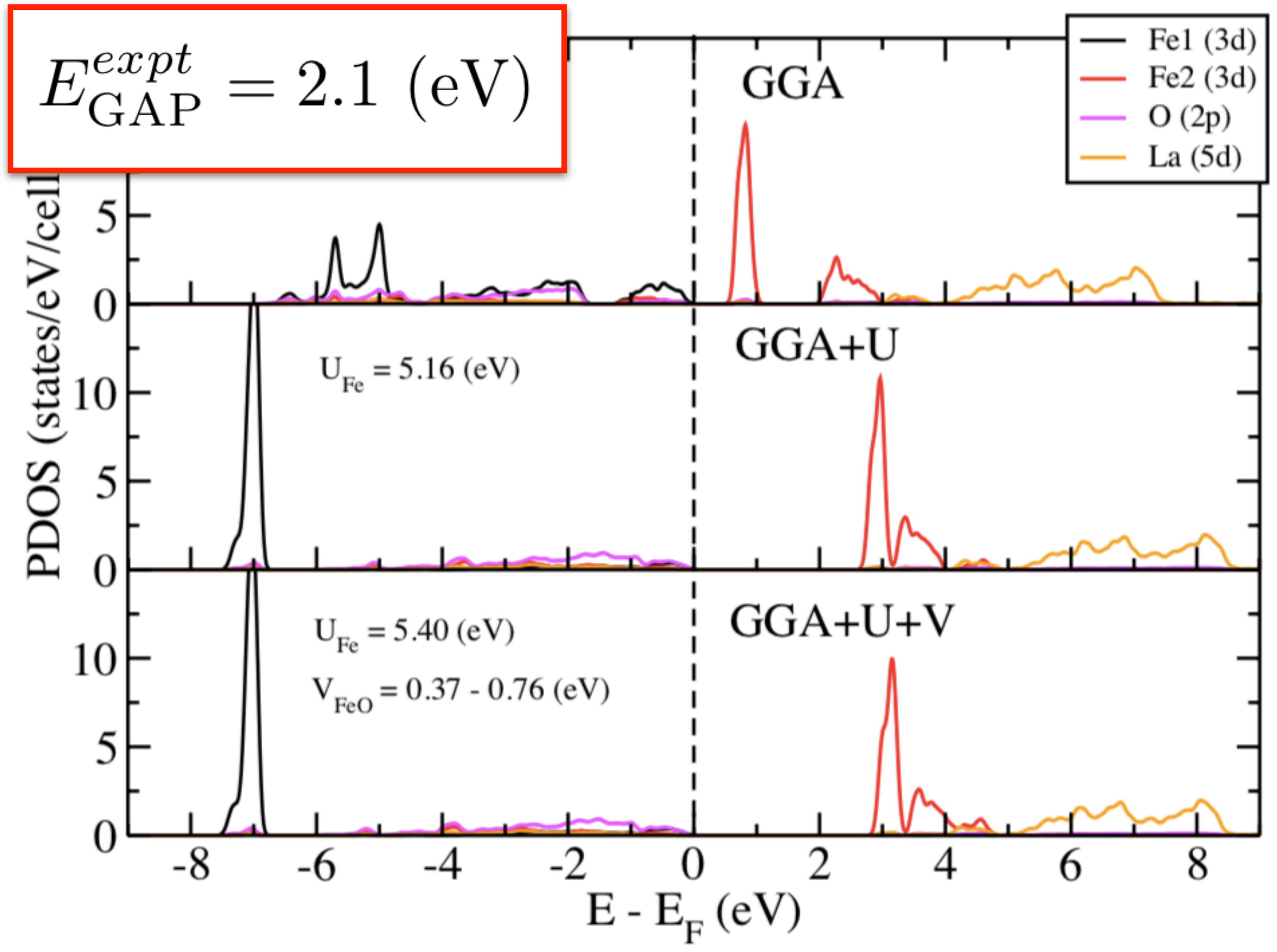


$$E_{\mathrm{GAP}}^{expt} = 2.1\ (\mathrm{eV})$$



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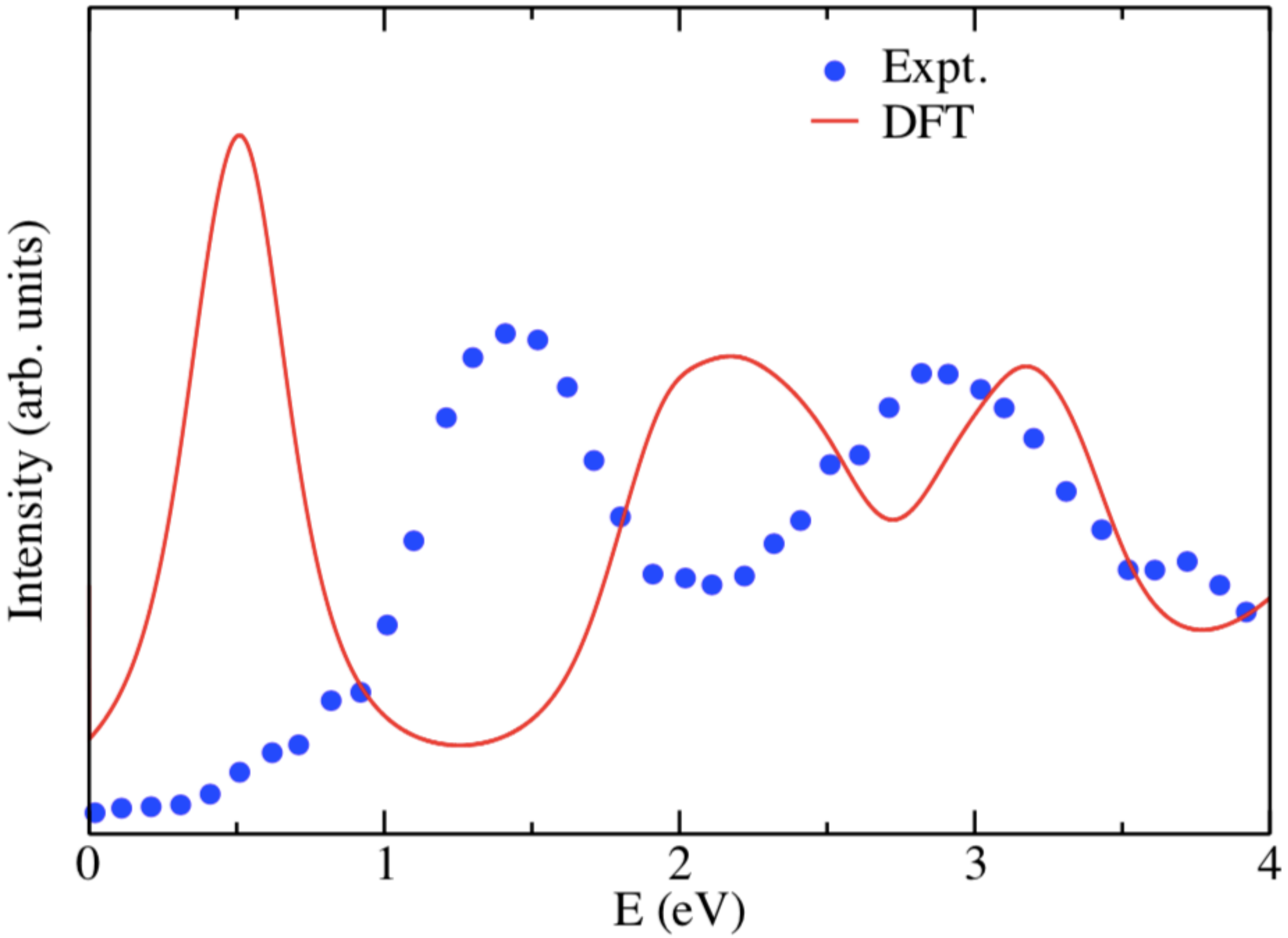

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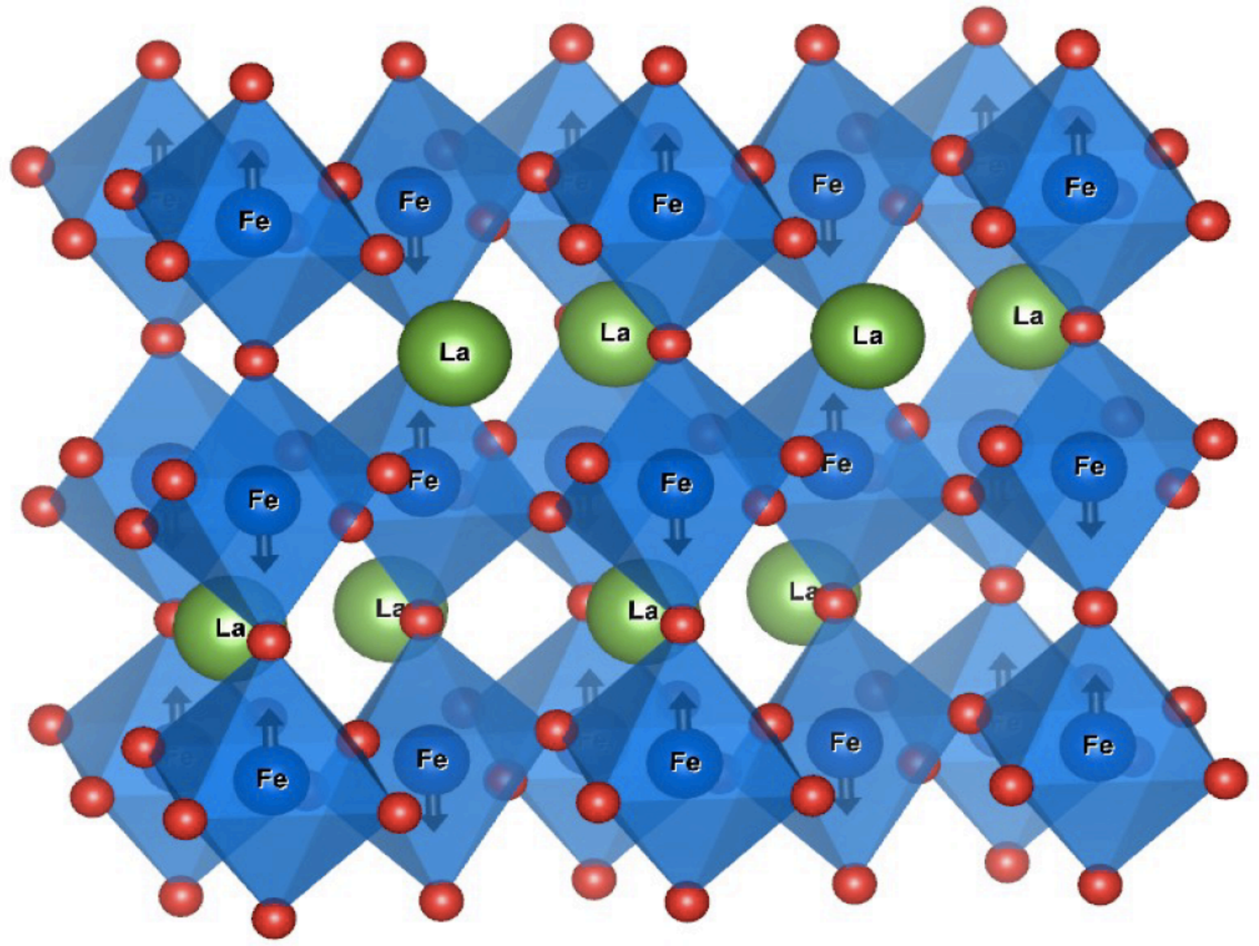

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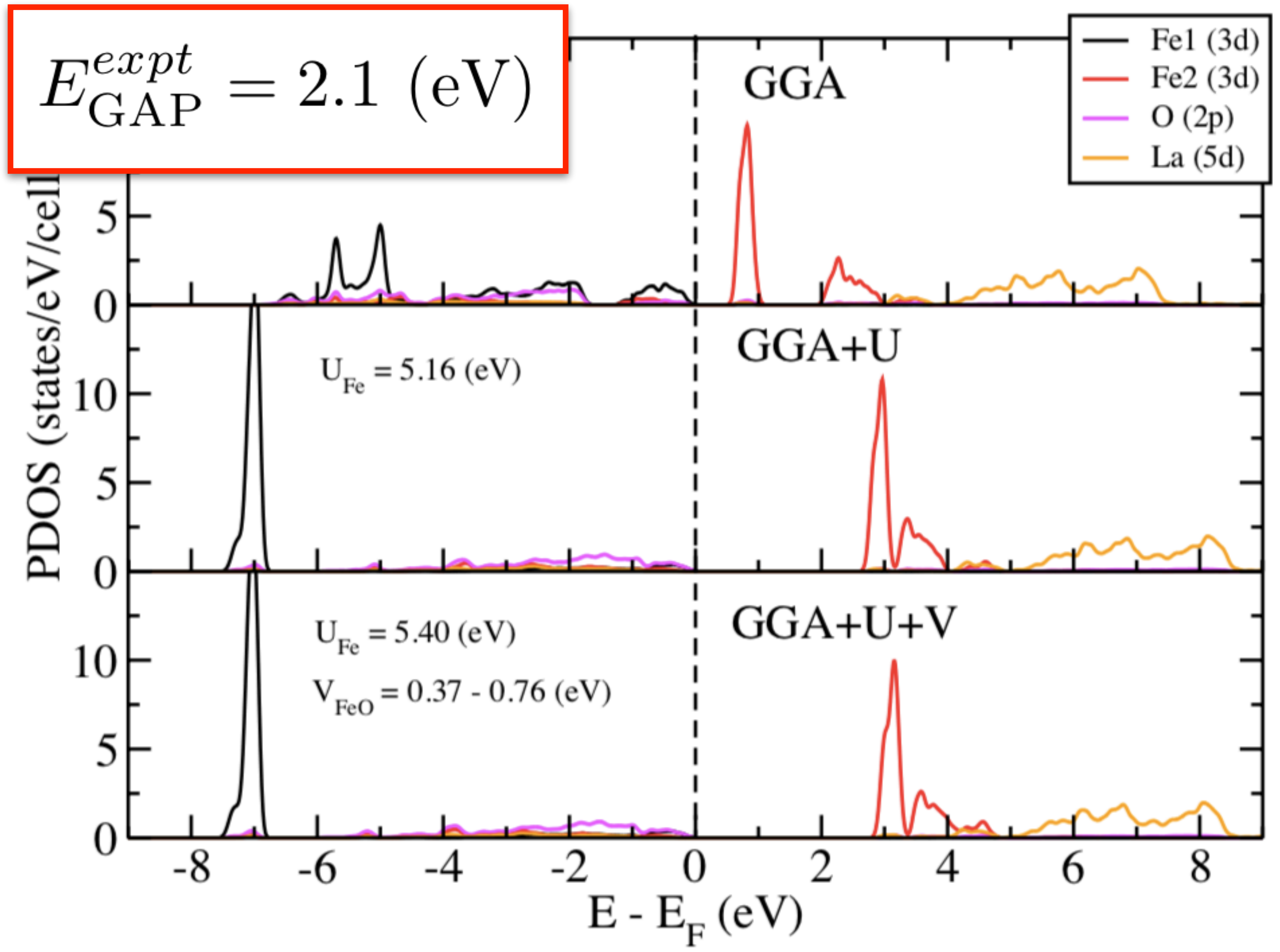

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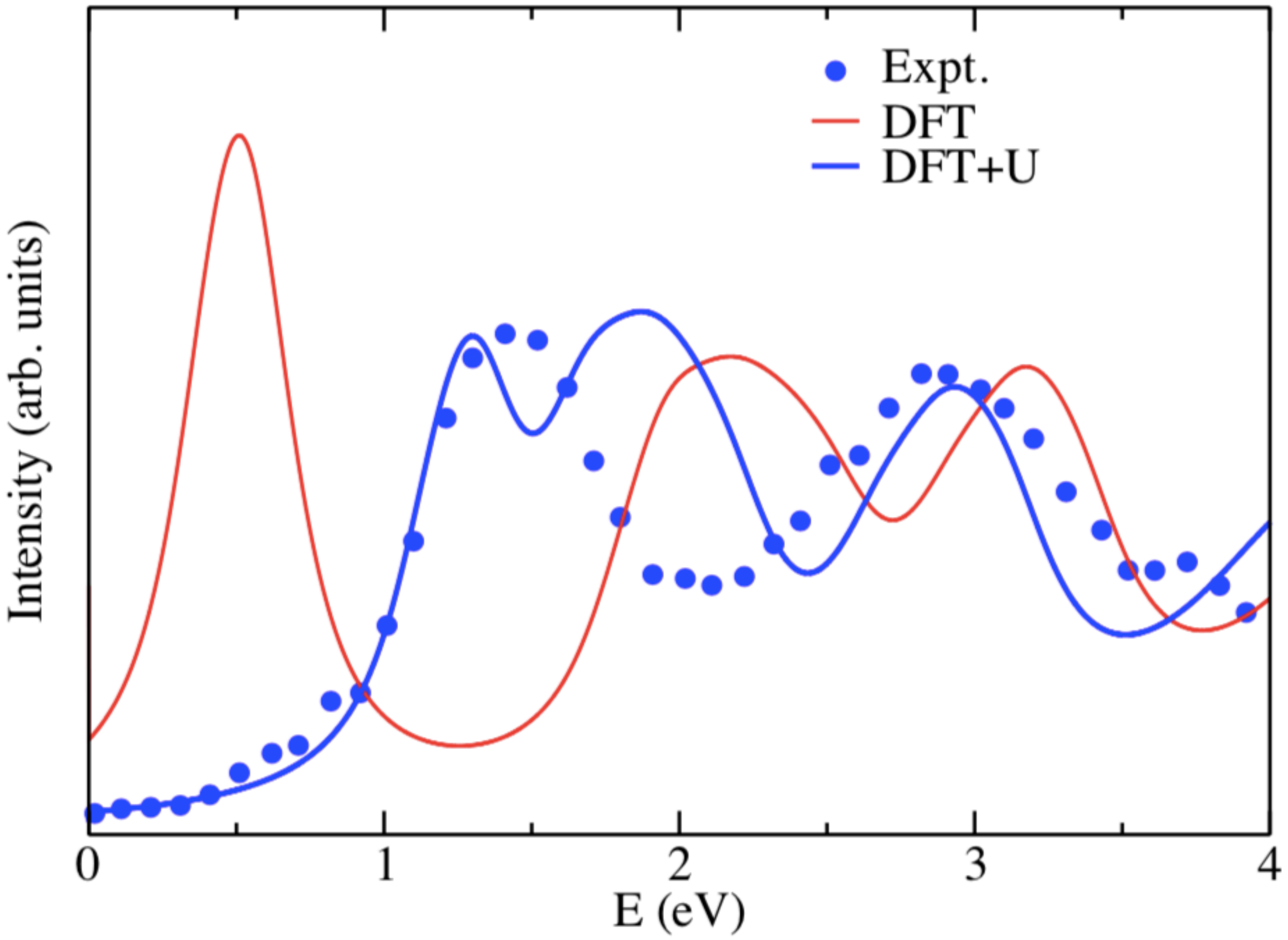

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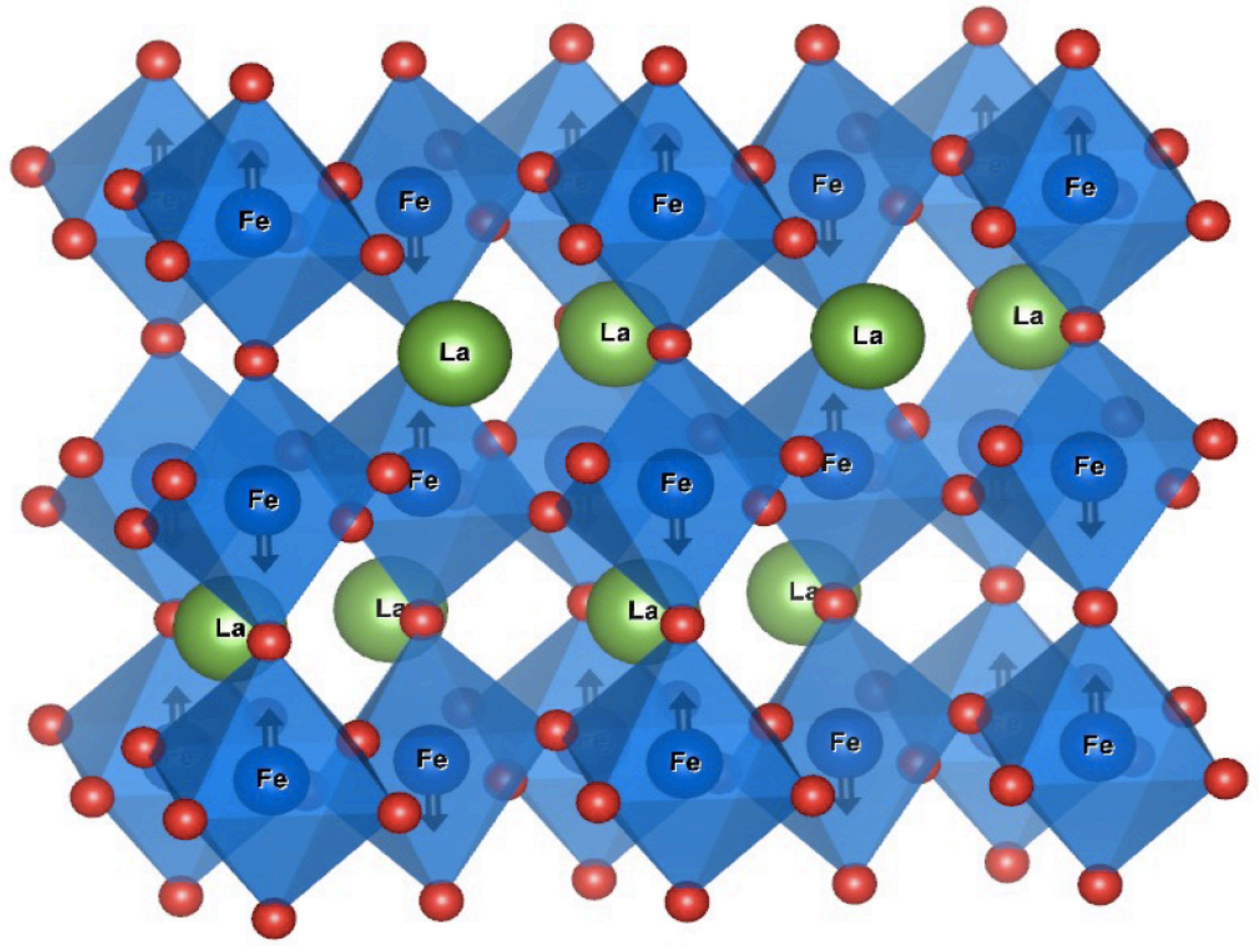
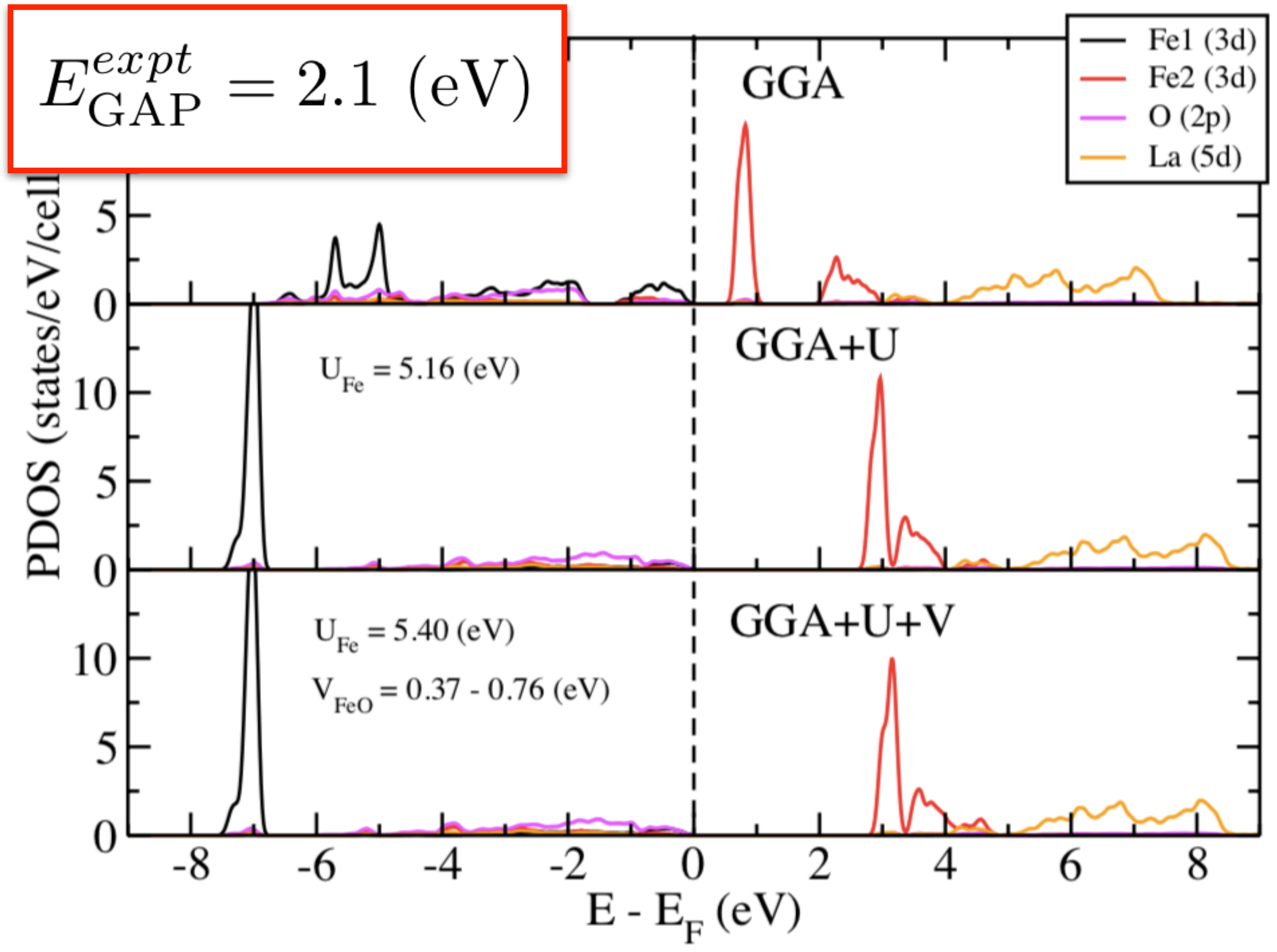
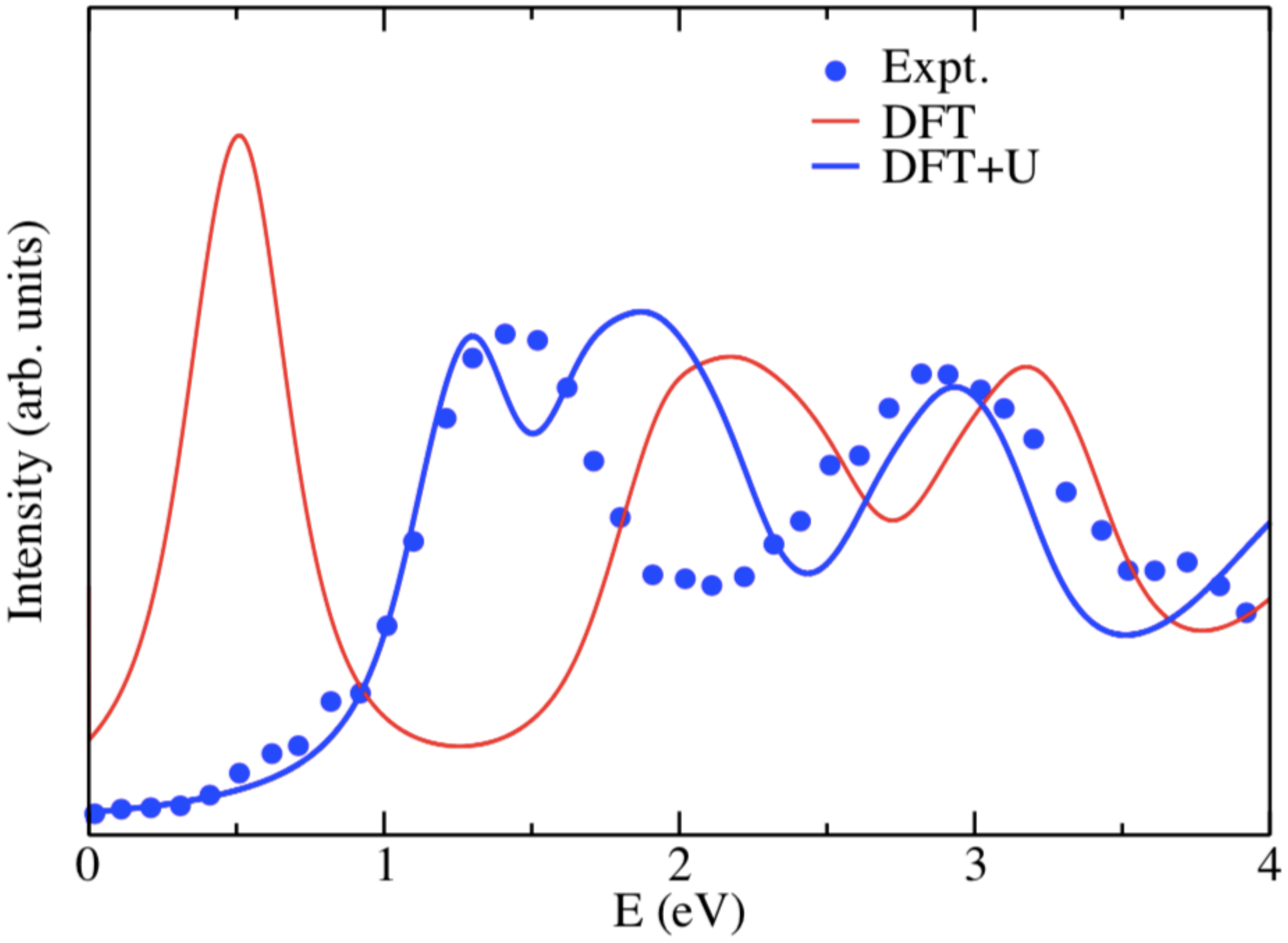



$E^{expt}_{\mathrm{GAP}} = 2.1$ (eV)

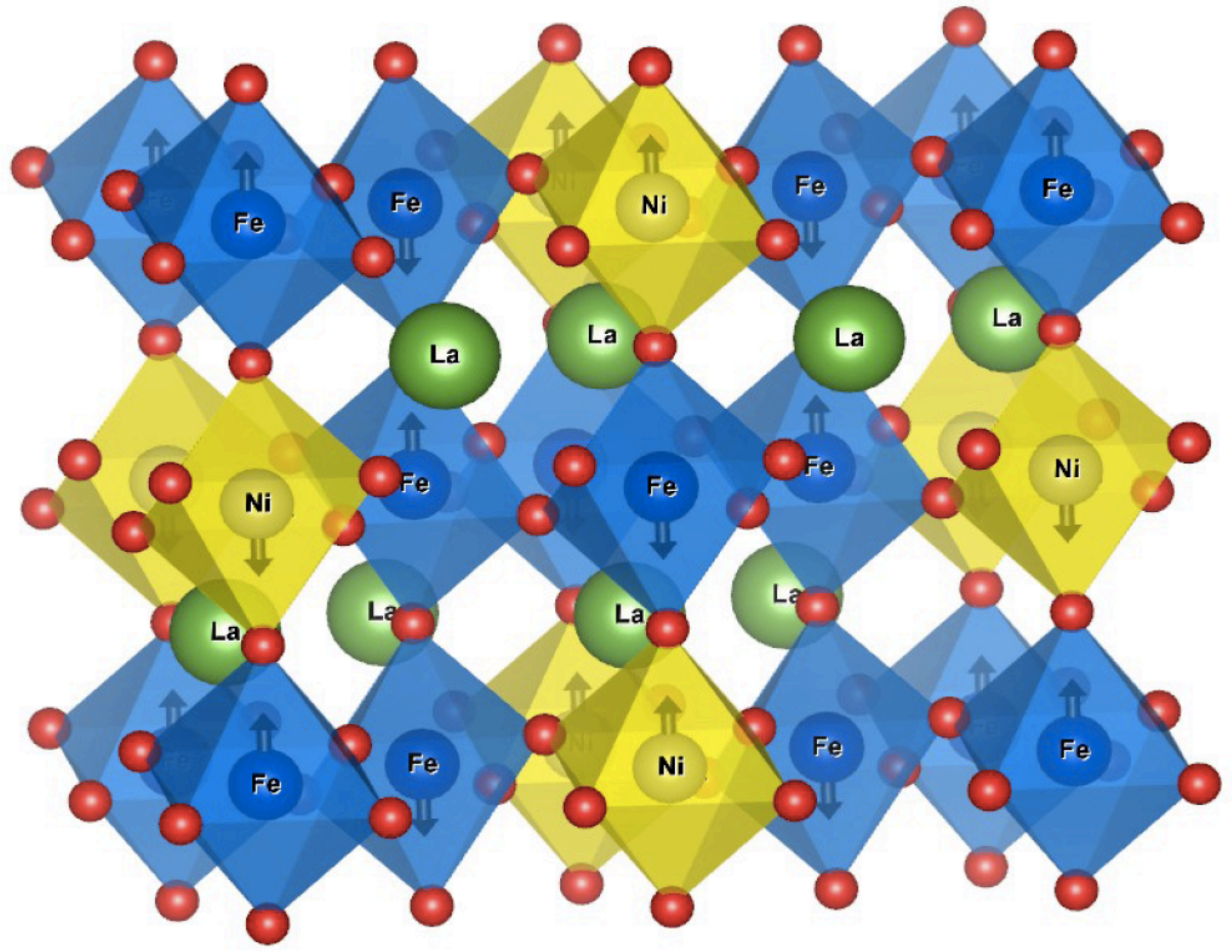
Oxygen *K* pre-edge spectrum

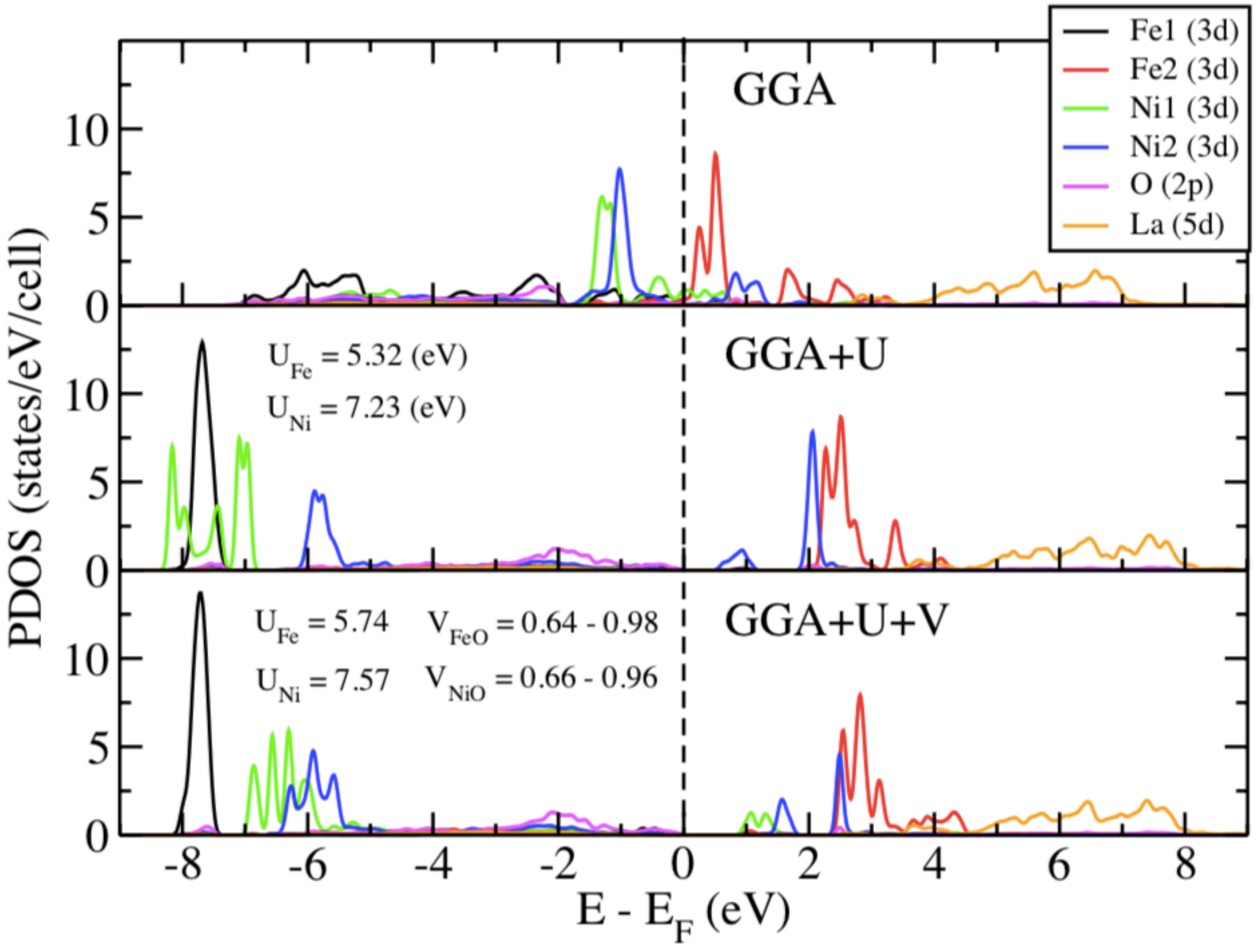


Inclusion of the inter-site Hubbard V and of the core-hole effect is needed

I. Timrov, P. Agrawal, Z. Zhang, S. Erat, R. Liu, A. Braun, M. Cococcioni, M. Calandra, N. Marzari, and D. Passerone, in preparation.

VI. X-ray absorption near-edge structure of $LaFe_{0.75}Ni_{0.25}O_3$





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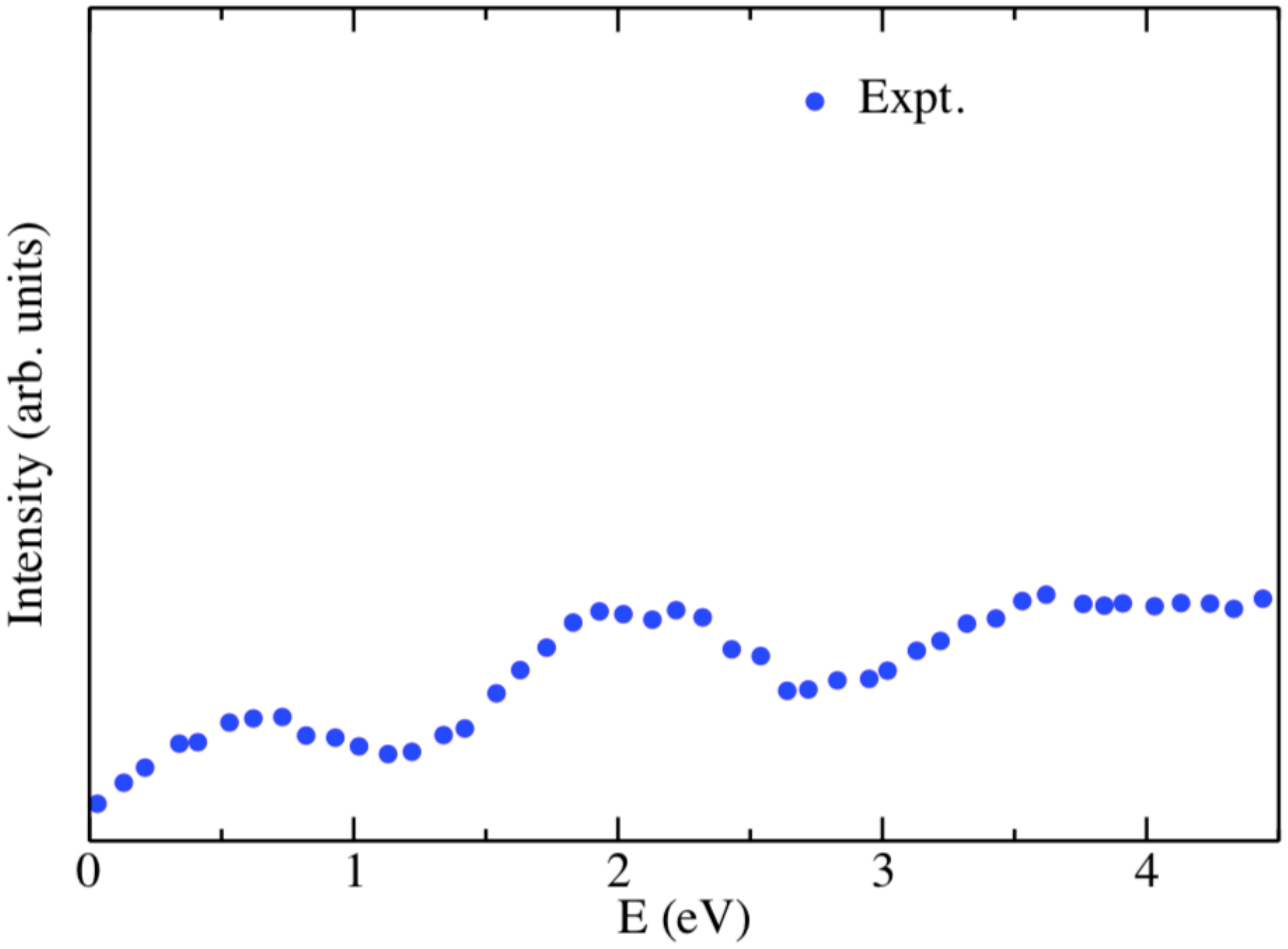

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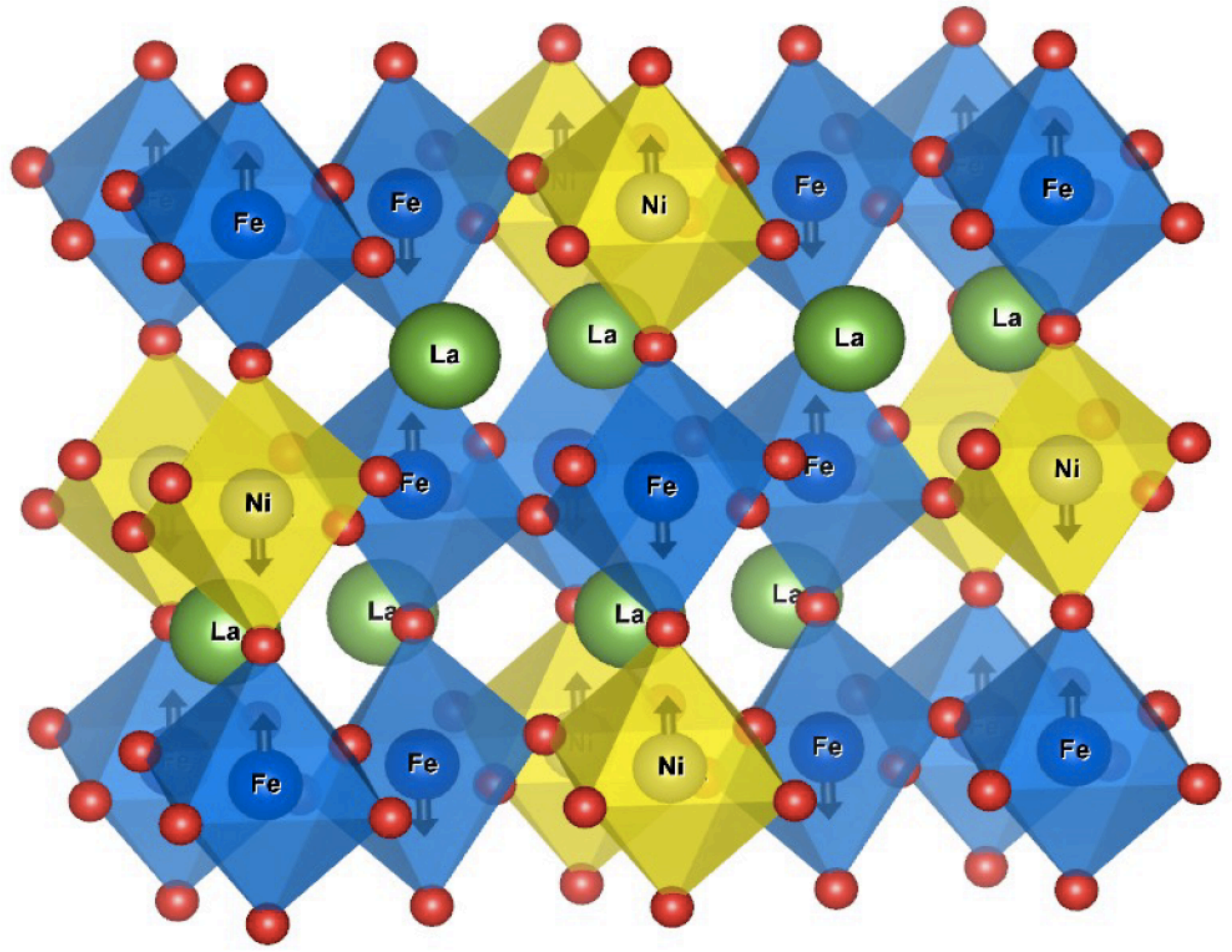
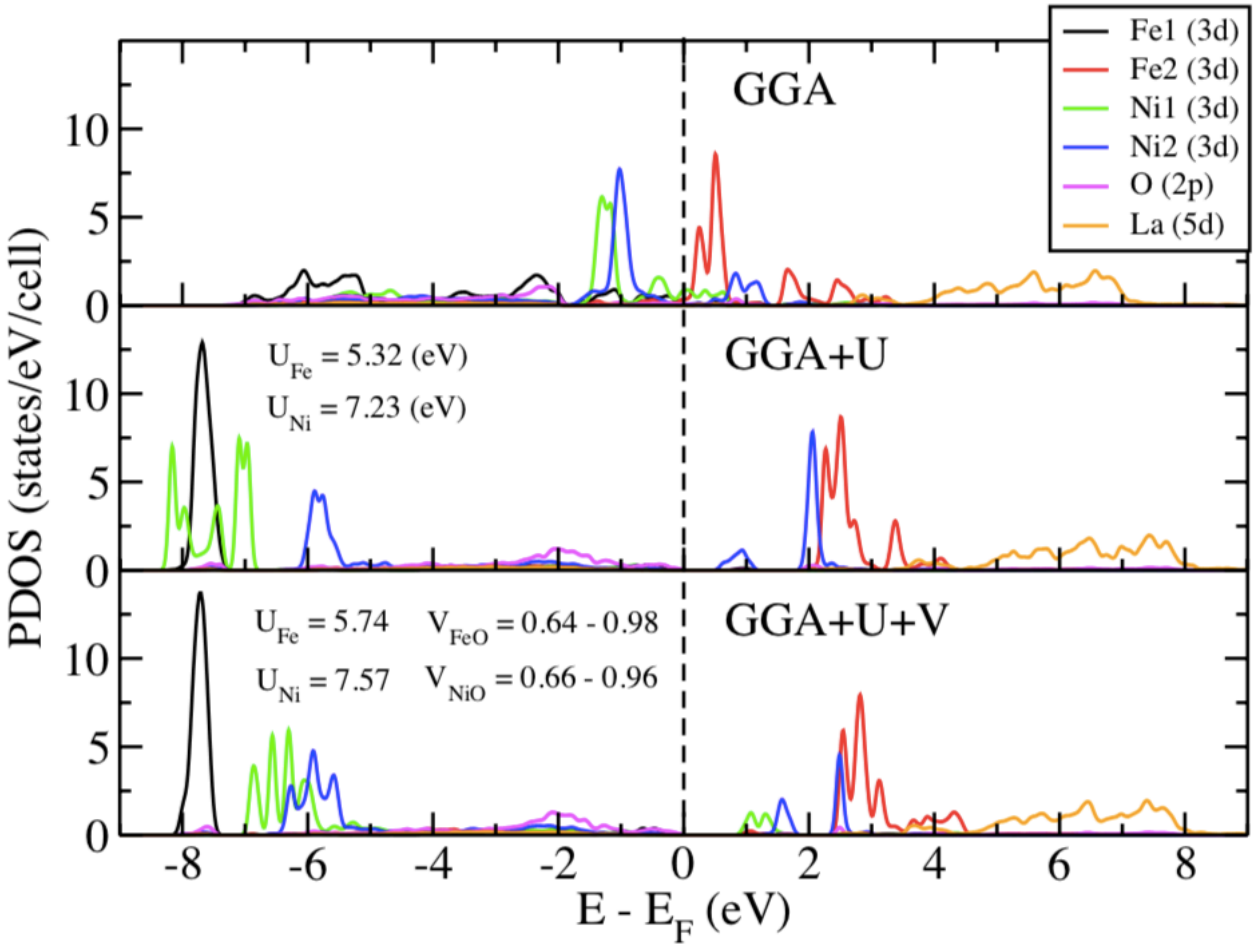
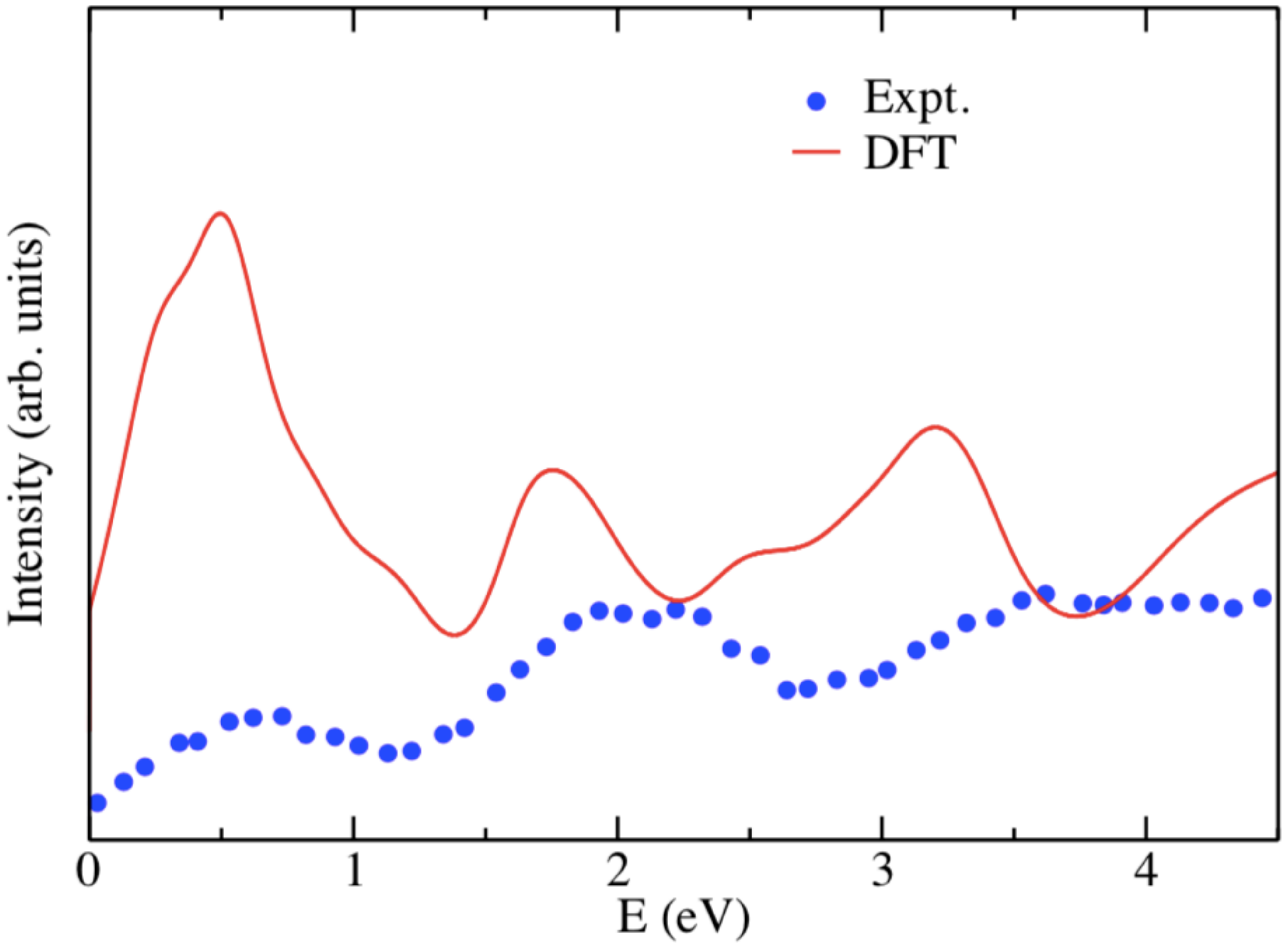




Oxygen *K* pre-edge spectrum



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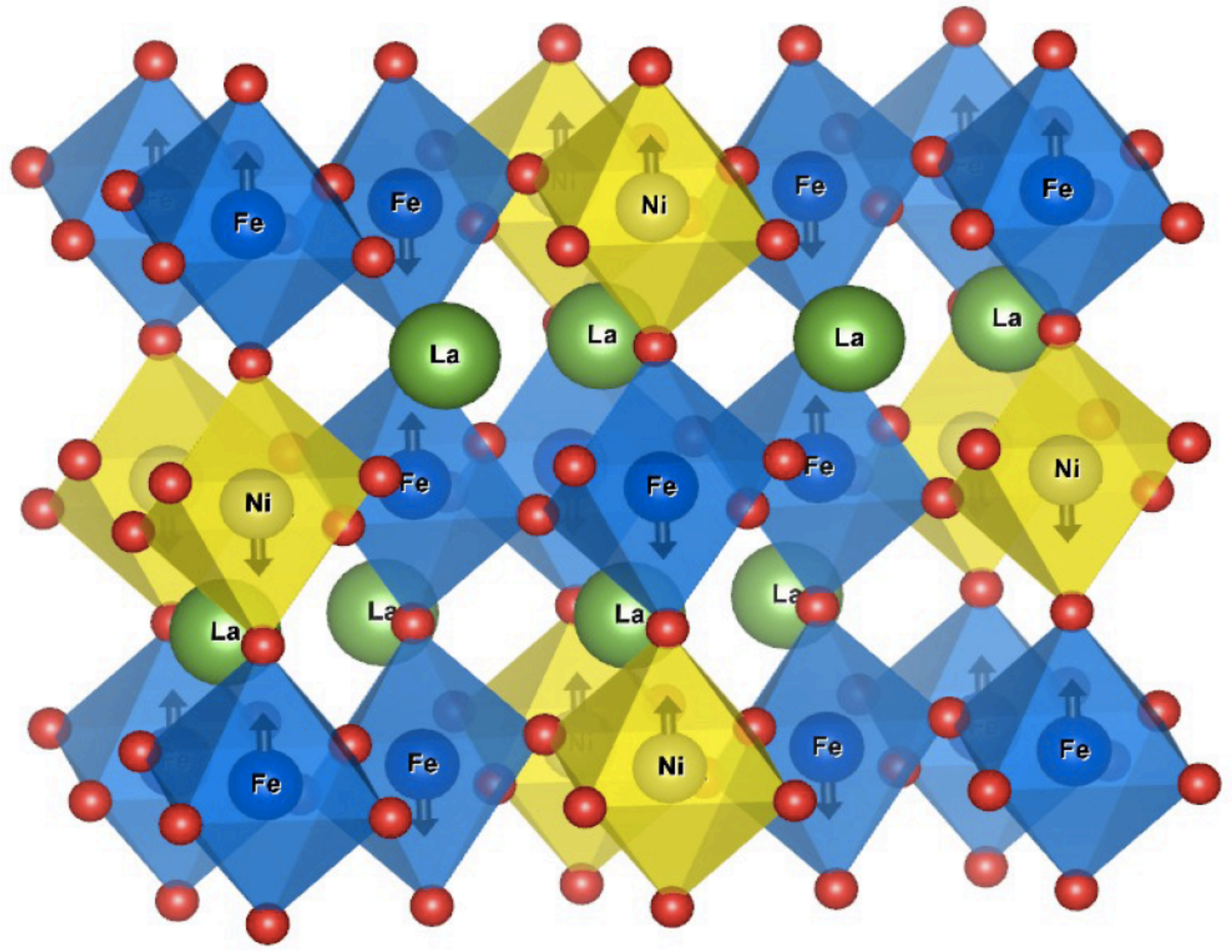
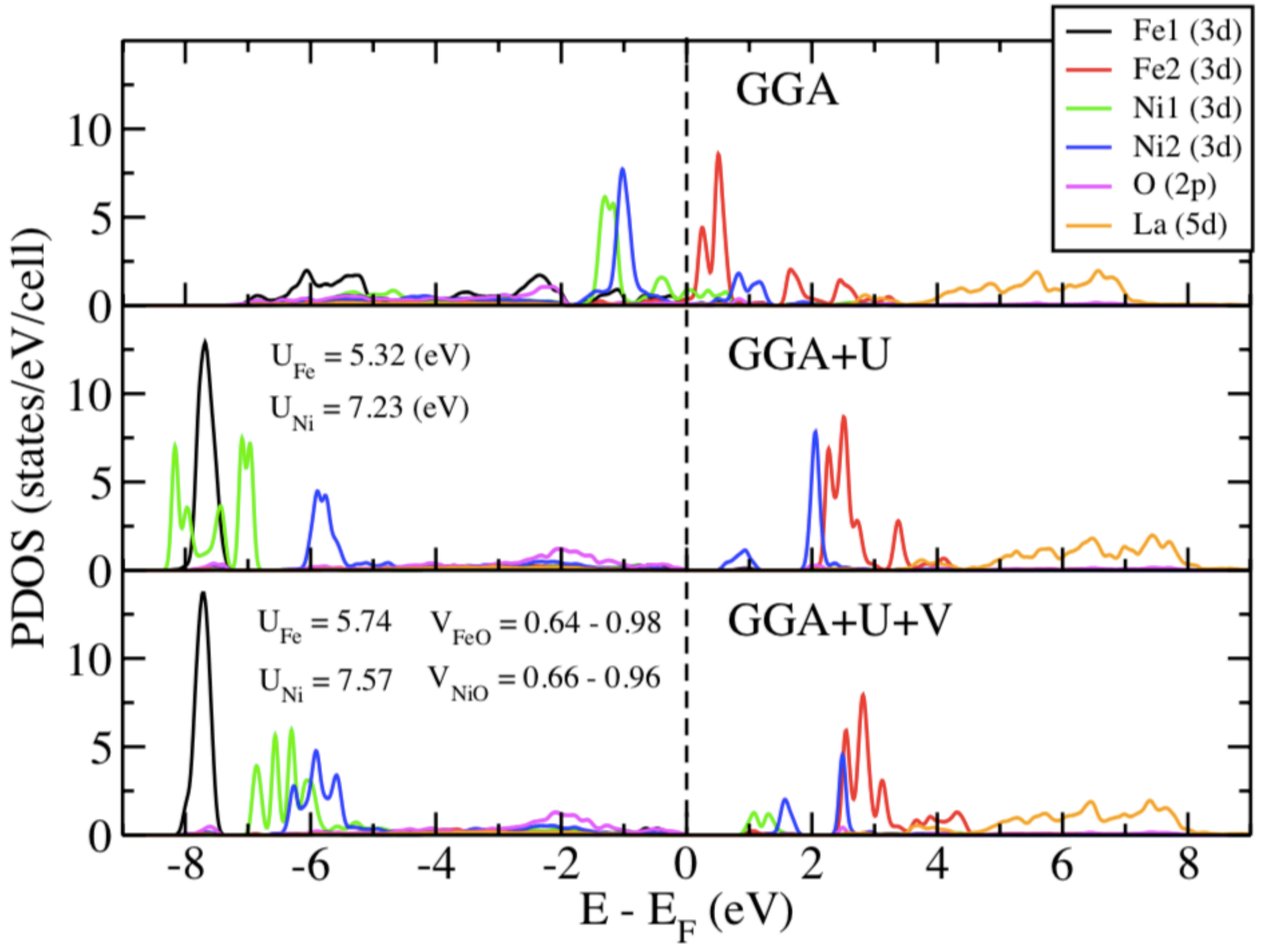
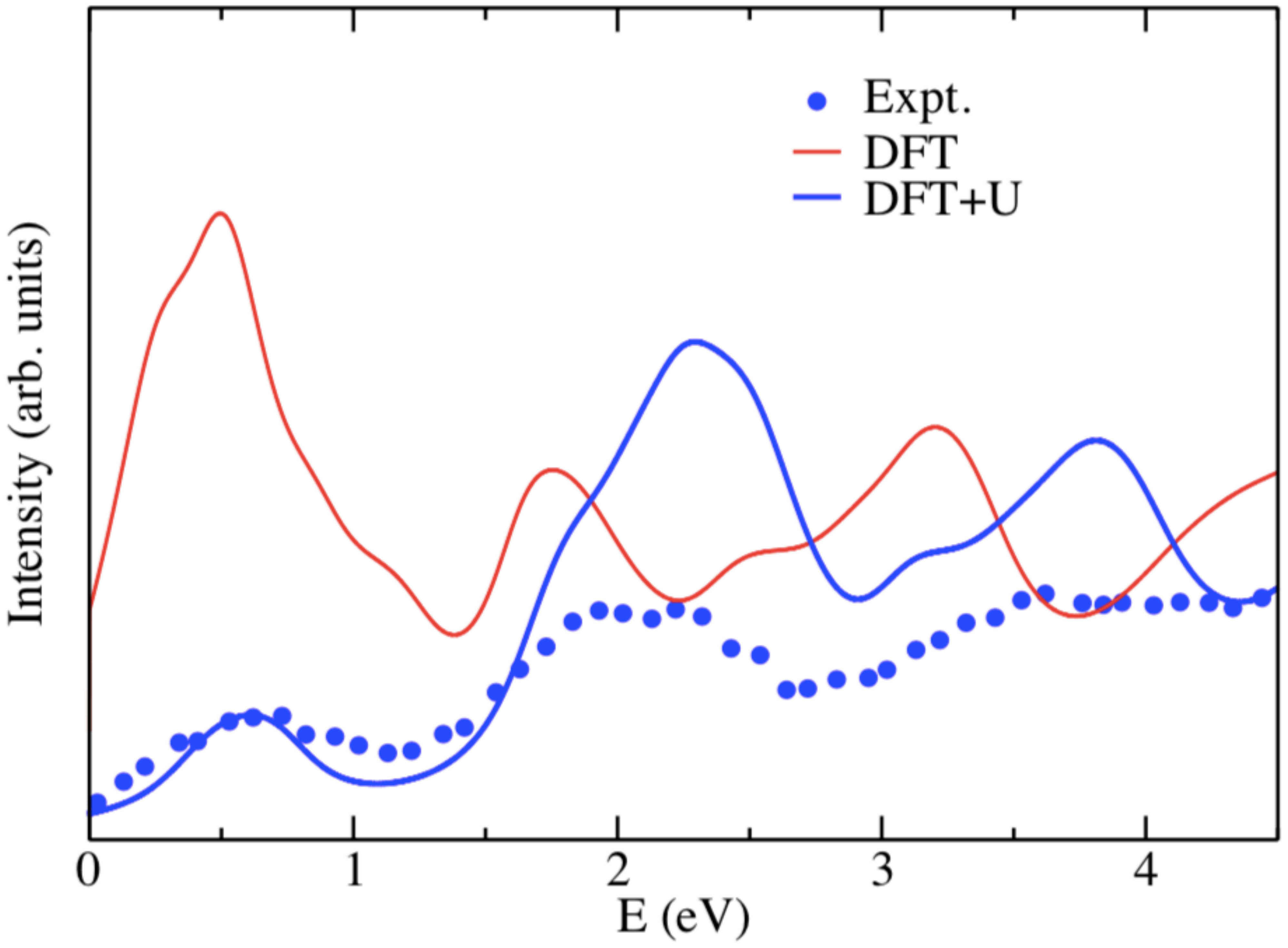




Oxygen *K* pre-edge spectrum



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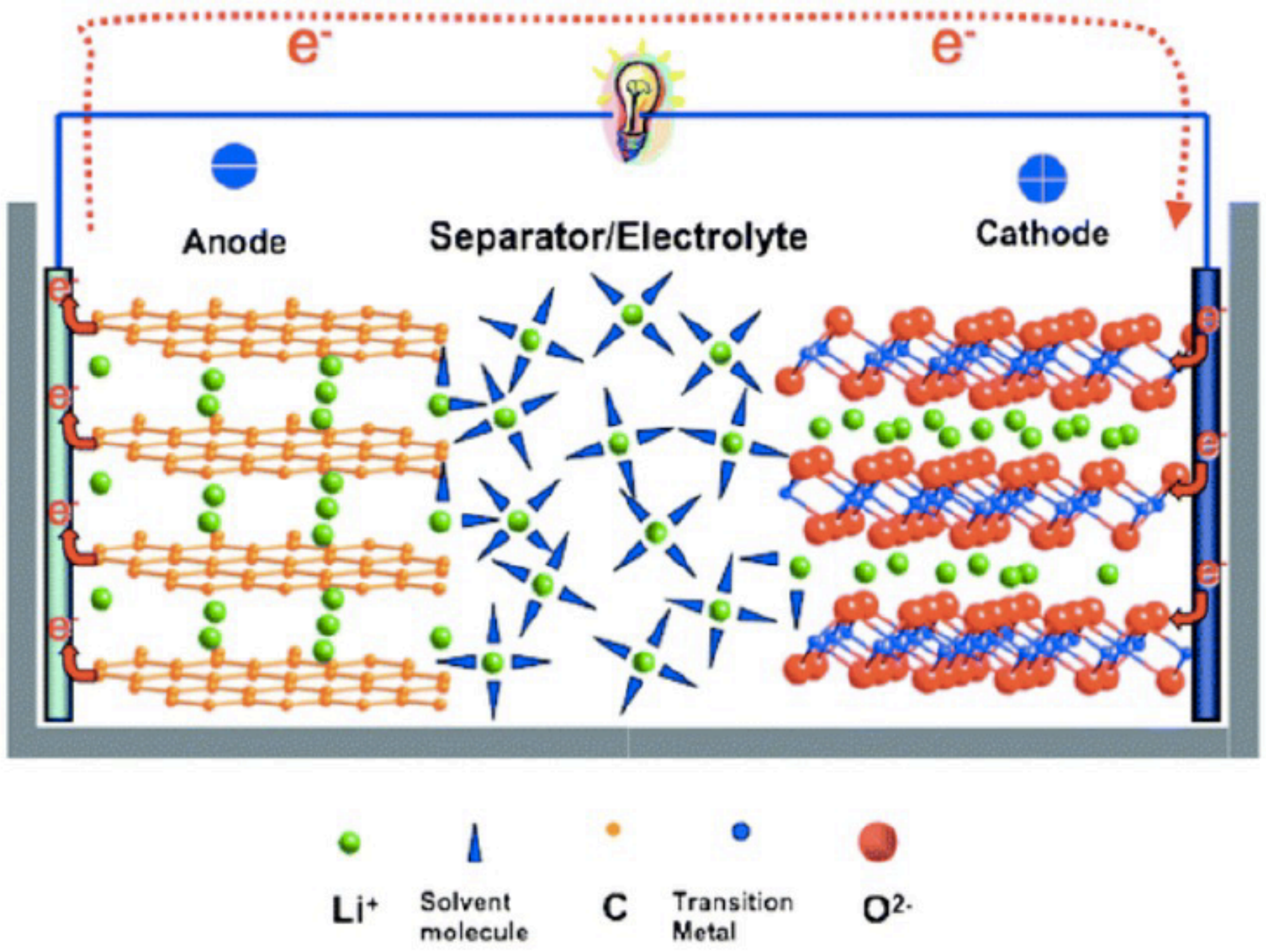
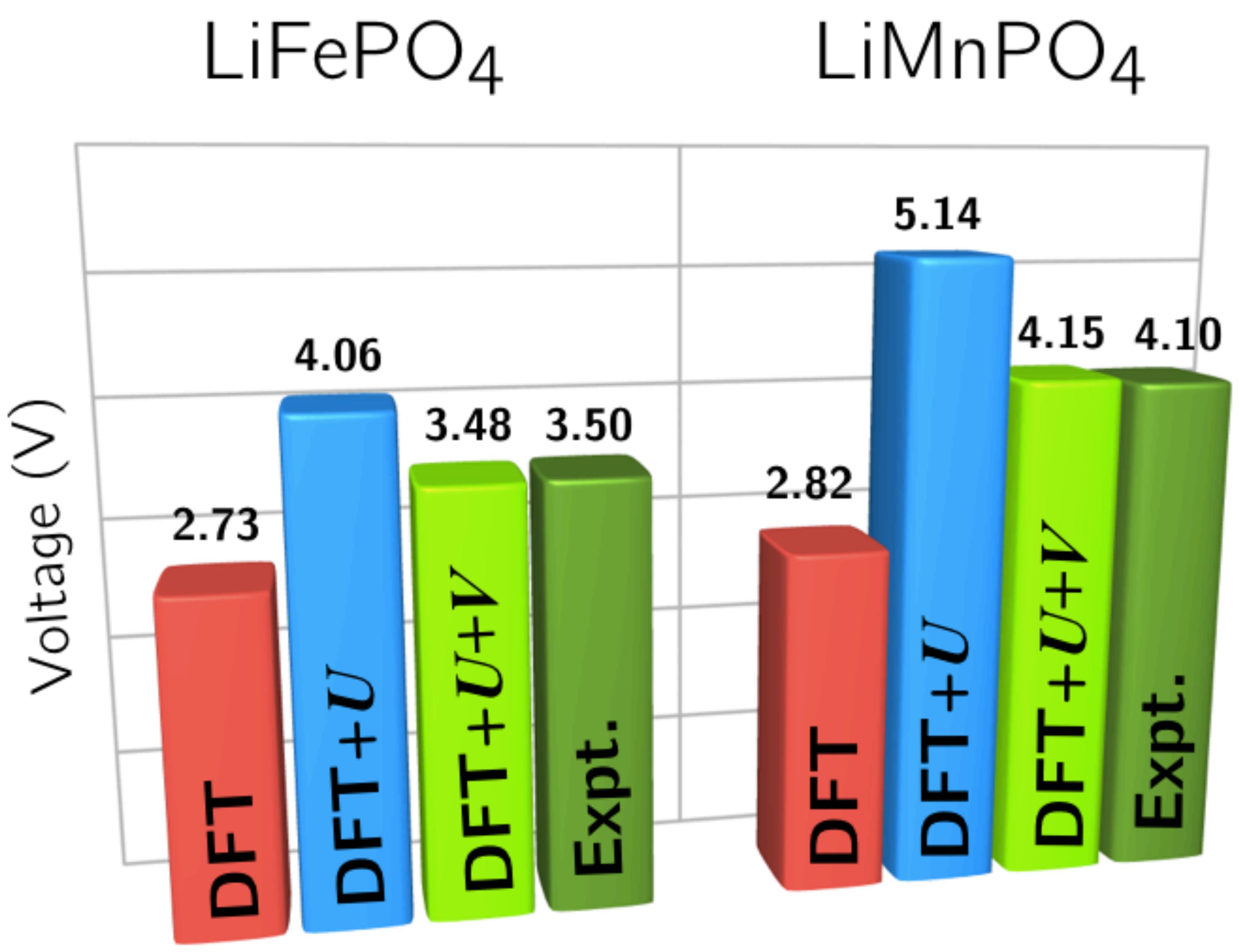
VII. Voltages of Li-ion batteries: $LiFePO_4$ & $LiMnPO_4$





Average voltage:

$$\langle V \rangle = -\frac{E(Li_{x_2}MPO_4) - E(Li_{x_1}MPO_4) - (x_2 - x_1)E(Li_{bulk})}{e(x_2 - x_1)}$$

DFT: underestimate voltages

DFT+*U*: overestimate voltages

DFT+*U*+*V*: excellent agreement with experiments

M. Cococcioni and N. Marzari, Phys. Rev. Materials 3, 033801 (2019).

Take-home messages

- Hubbard parameters can be computed from first-principles using density-functional perturbation theory (fast, accurate, efficient approach);
- On-site Hubbard U greatly improves the description of structural, electronic, magnetic, and vibrational properties;
- However, inter-site Hubbard V is crucial for accurate energetics of complex oxides with covalent interactions;
- Extended Hubbard functionals with U & V should be used for a complete and accurate modelling of correlated materials.

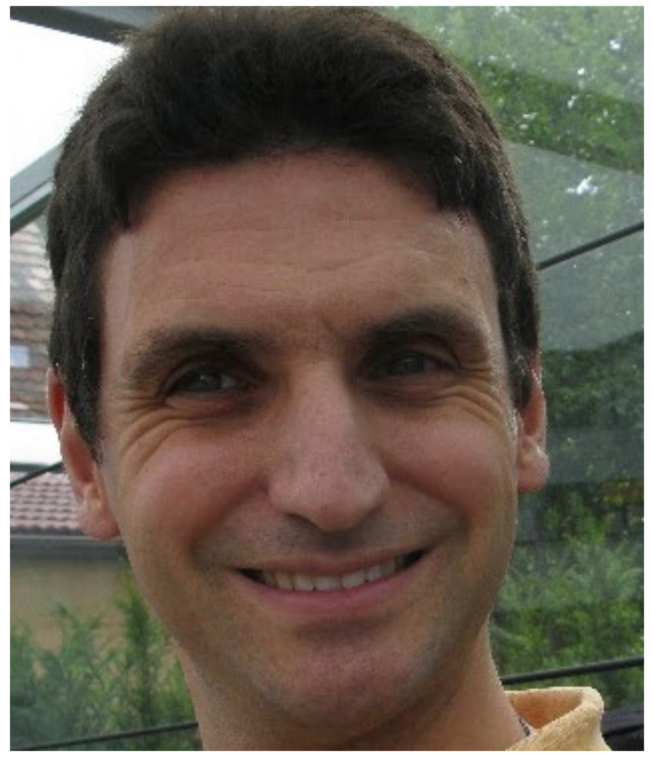
Acknowledgments

N. Marzari (EPFL)

M. Cococcioni (U. Pavia)

C. Ricca (U. Bern)

U. Aschauer (U. Bern)



D. Passerone (Empa)

A. Floris (U. Lincoln)

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The National Centres of Competence in Research are a research instrument of the Swiss National Science Foundation

Thank you for your attention!