C’era un A. Volta...
dalla pila alle batterie ricaricabili di domani

Matteo Cococcioni

Past experience…

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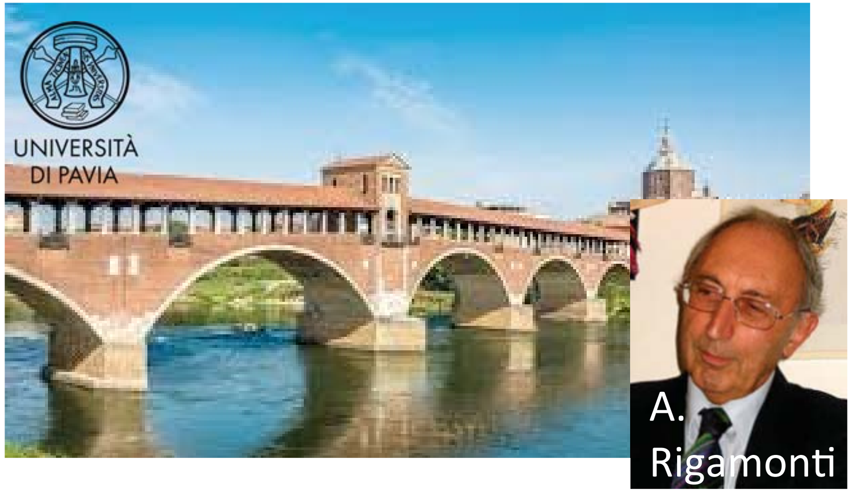

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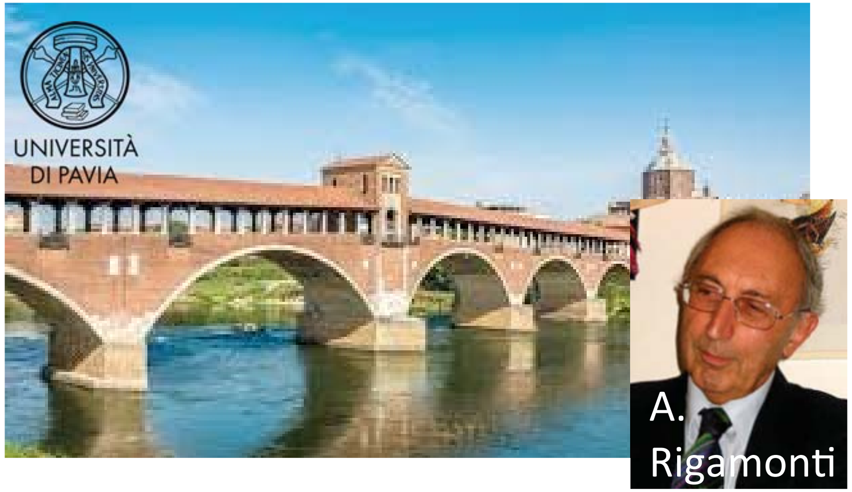

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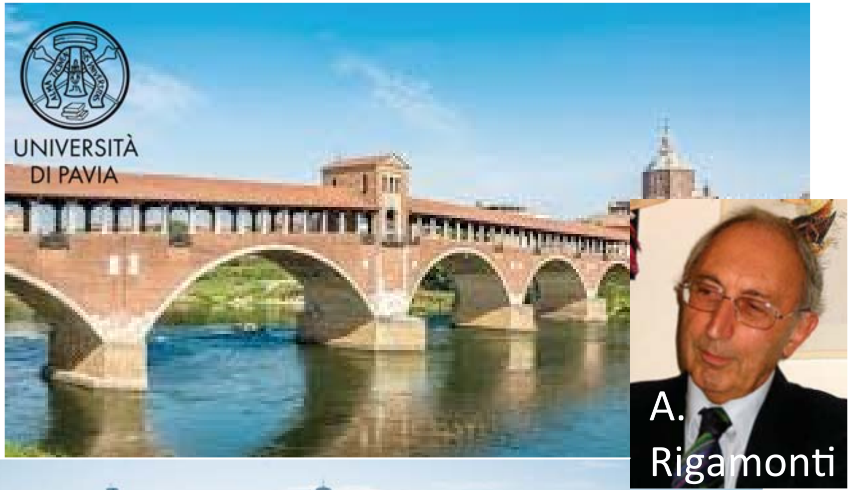

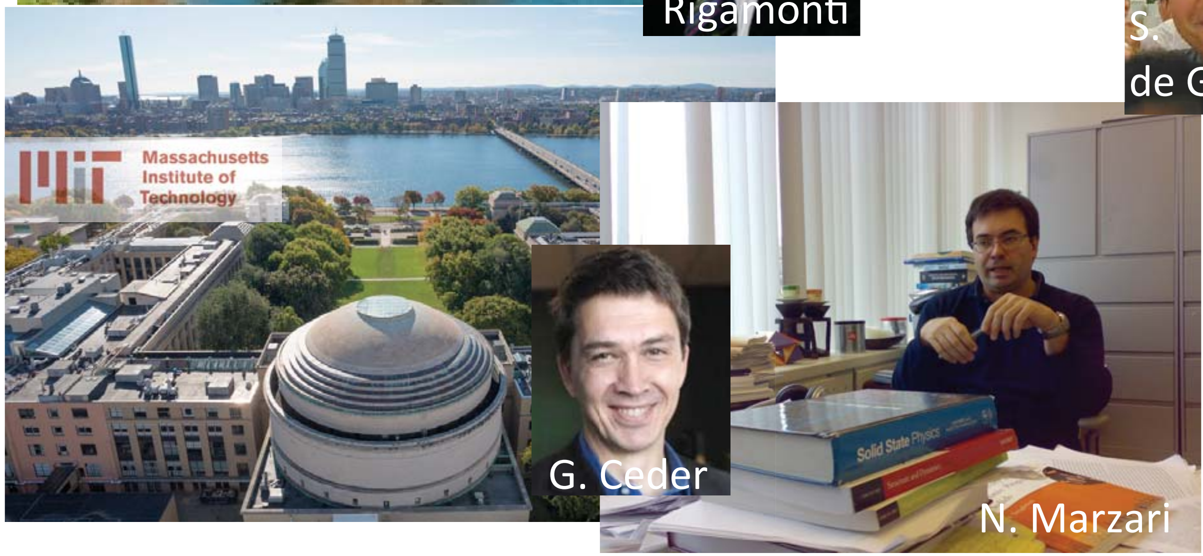

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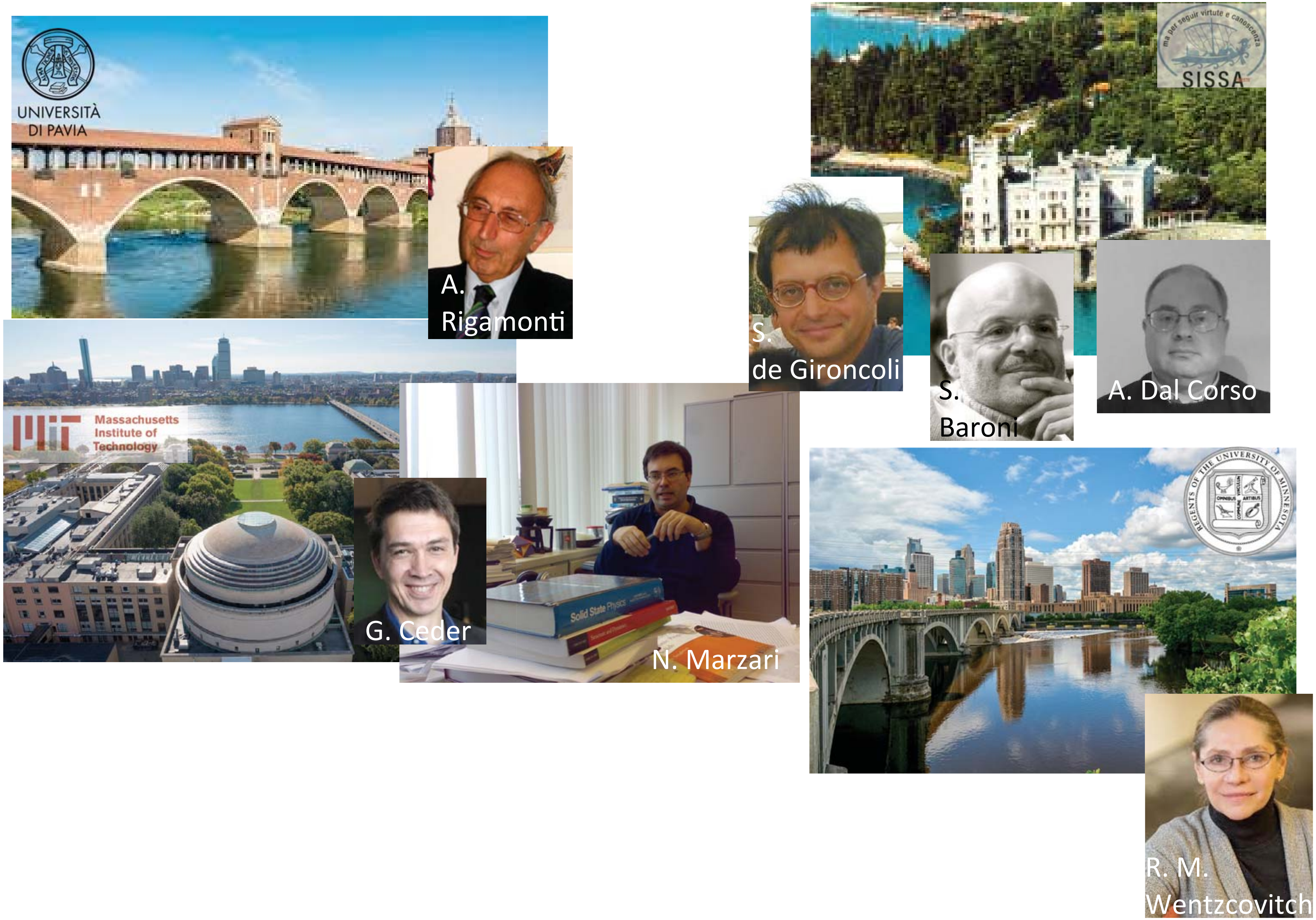
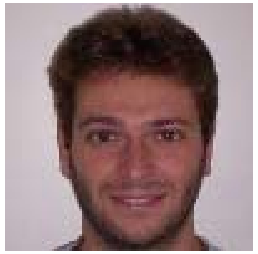


Past experience...

...and present

Part of the condensed matter theory group

L. C. Andreani

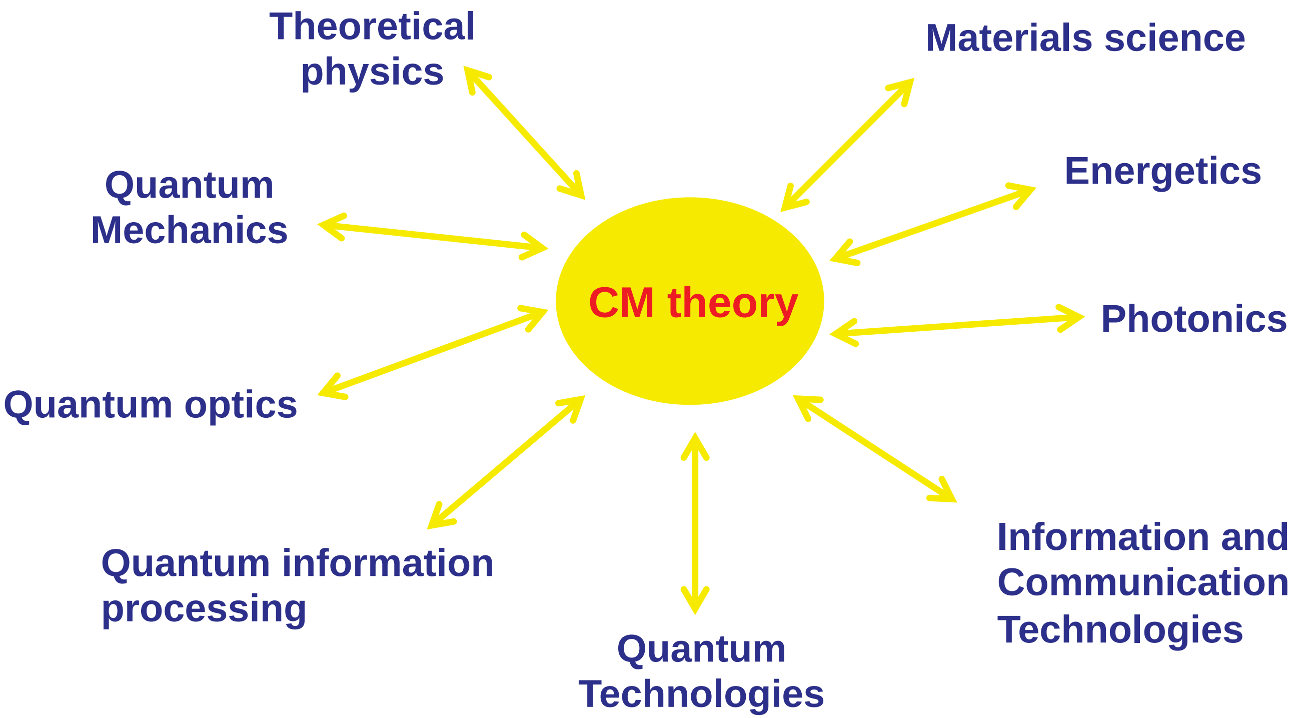


D. Gerace

M. Liscidini

M. Cococcioni

FUNDAMENTAL RESEARCH ⟷ **APPLIED RESEARCH**



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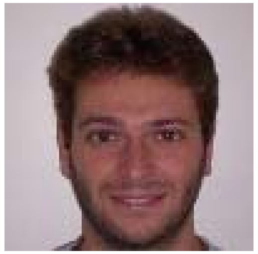
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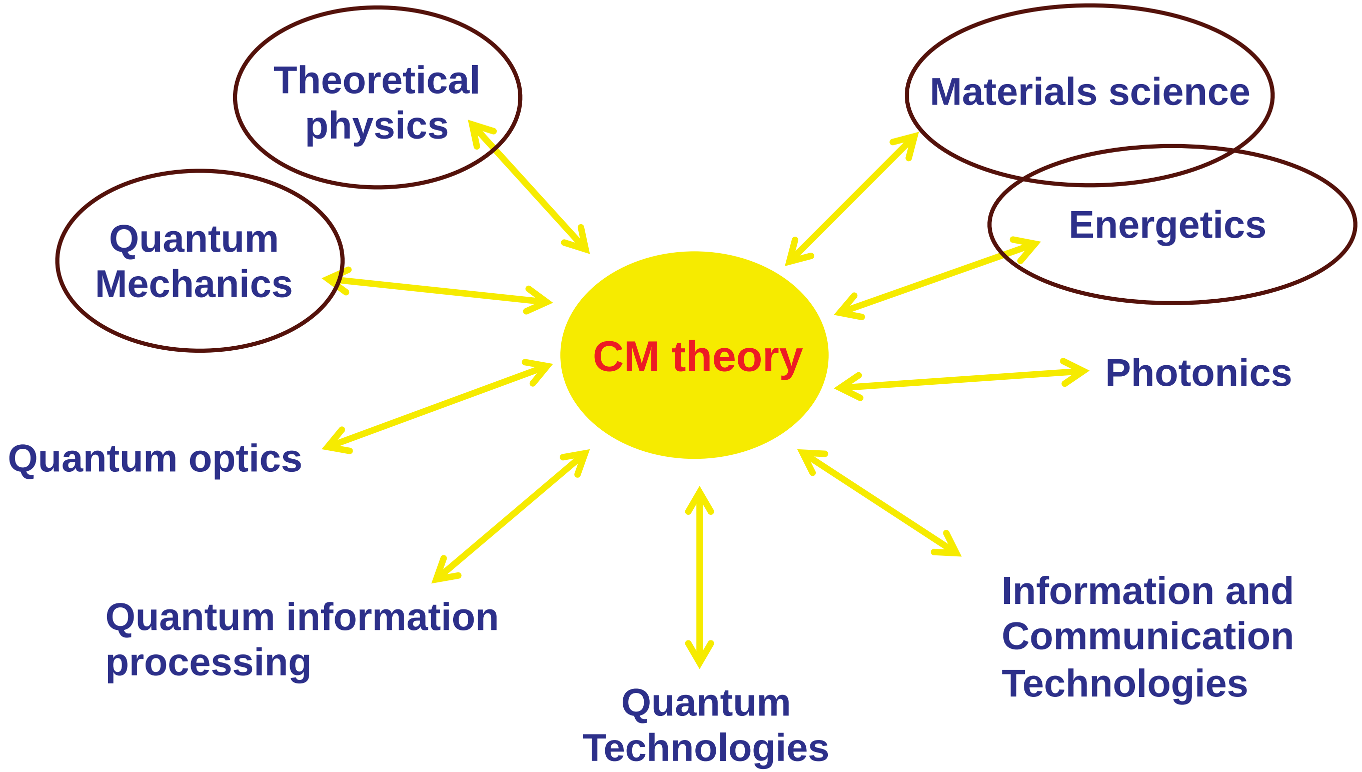

First-principles electronic structure calculations

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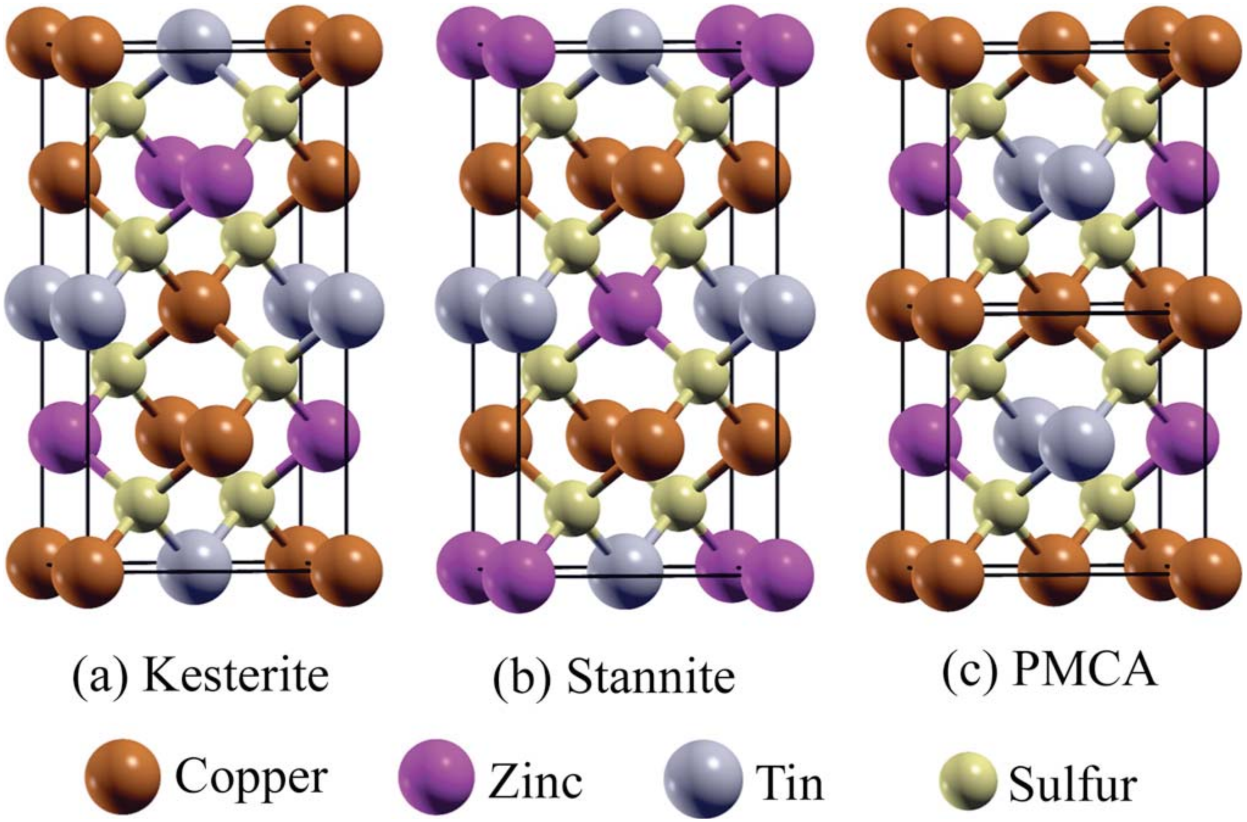

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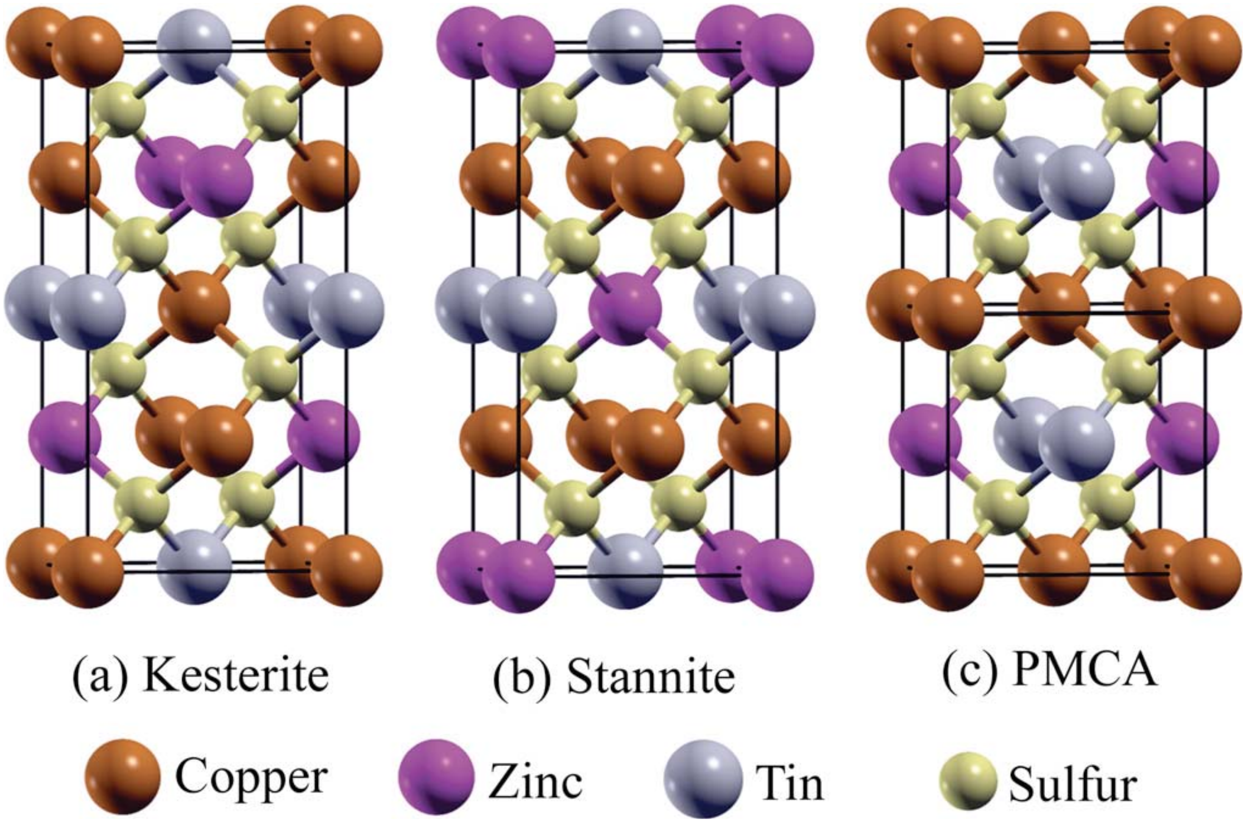

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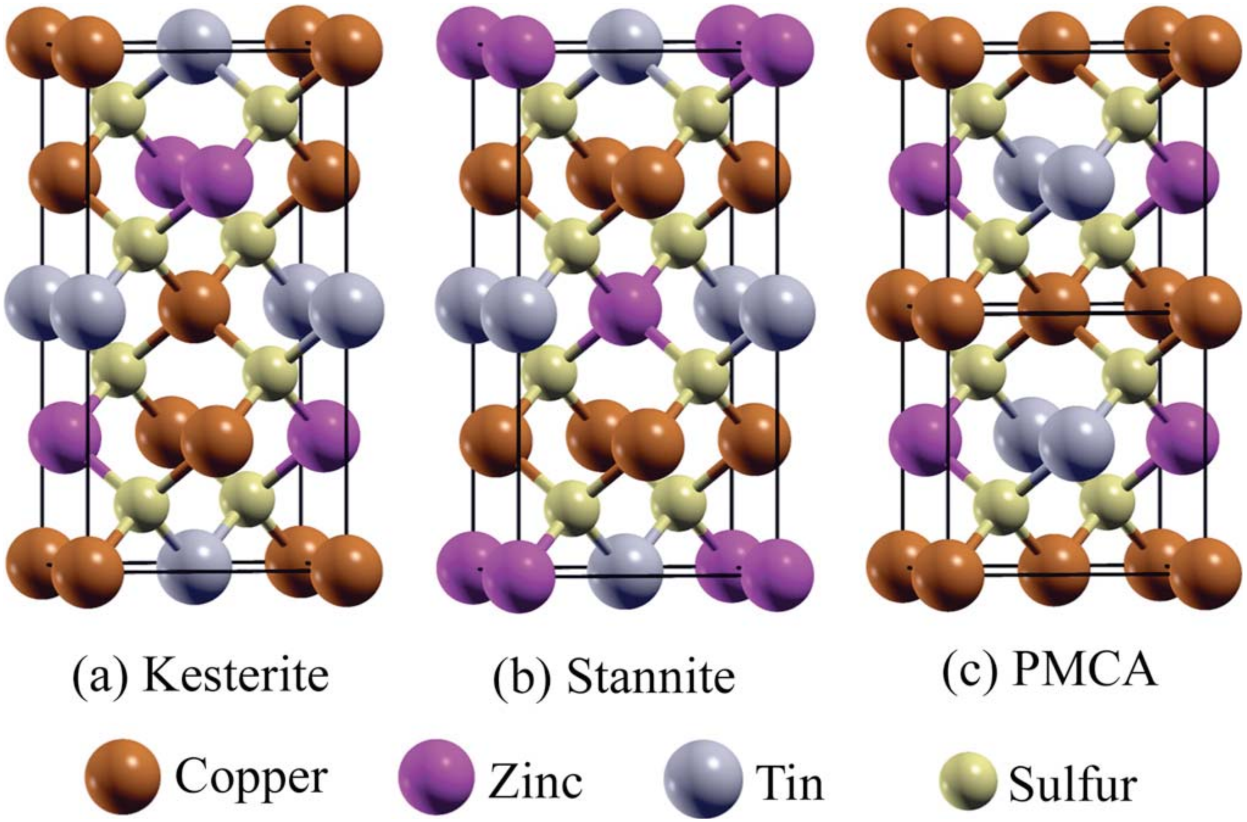

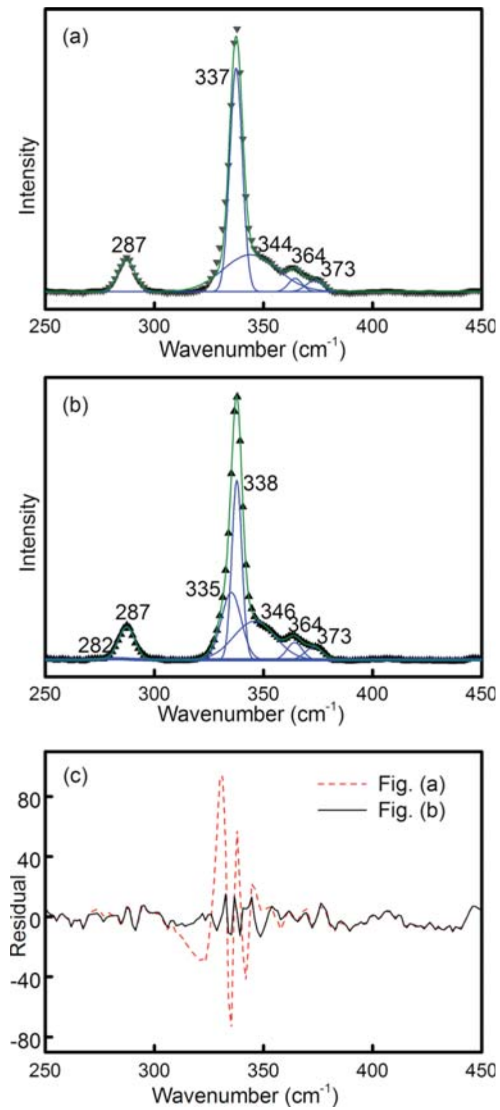

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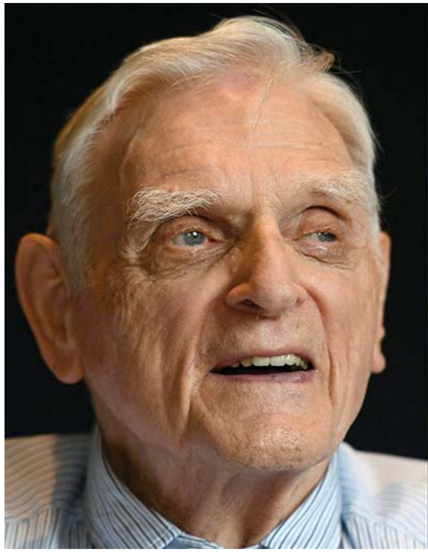
A. Khare *et al.,* J. Appl. Phys. **111,** 083707 (2012); J. Appl. Phys. **111,** 123704 (2012)

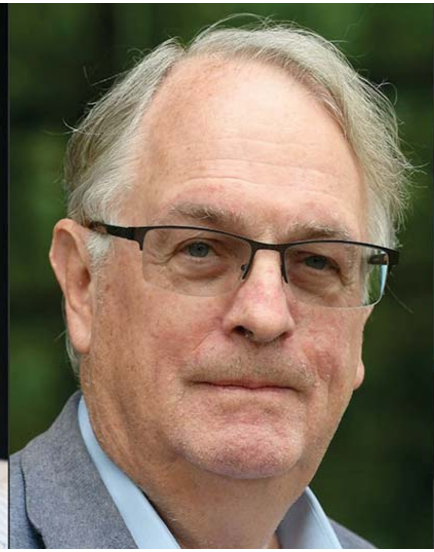
Alessandro Volta

The 2019 Nobel Prize in Chemistry

Alessandro Volta



John B. Goodenough
The University of Texas at Austin, USA



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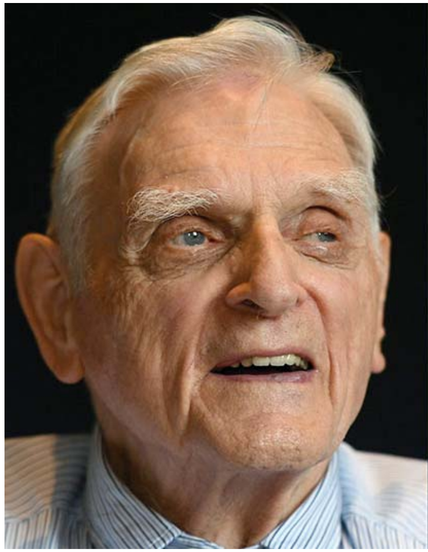

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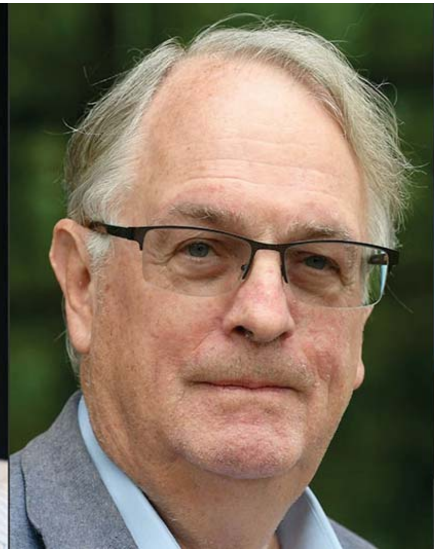

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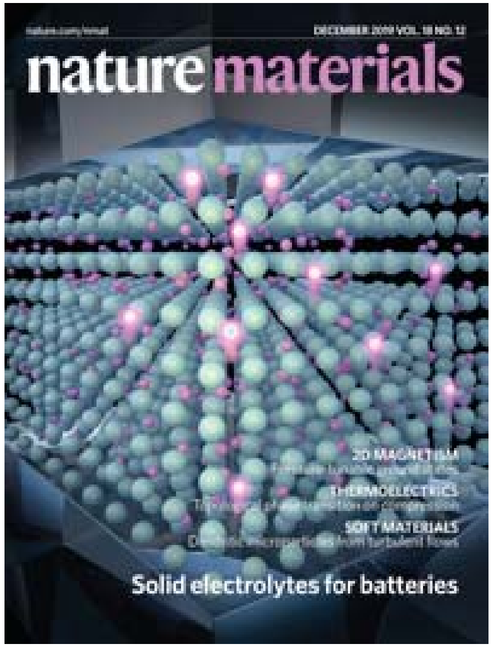

A long-expected party

Nature Materials **18,** 1265 (2019)

editorial

Battery revolution to evolution

The revolutionary work of John Goodenough, M. Stanley Whittingham and Akira Yoshino has finally been awarded the Nobel Prize in Chemistry. Scientific discovery and engineering brilliance continue to shape battery technology.

Nature Energy **4,** 893 (2019)

A rechargeable world

"for the development of lithium-ion batteries"

They created a rechargeable world

The Nobel Prize in Chemistry 2019 rewards the development of the lithium-ion battery. This light-weight, rechargeable and powerful battery is now used in everything from mobile phones to laptops and electric vehicles. It can also store significant amounts of energy from solar and wind power, making possible a fossil fuel-free society.

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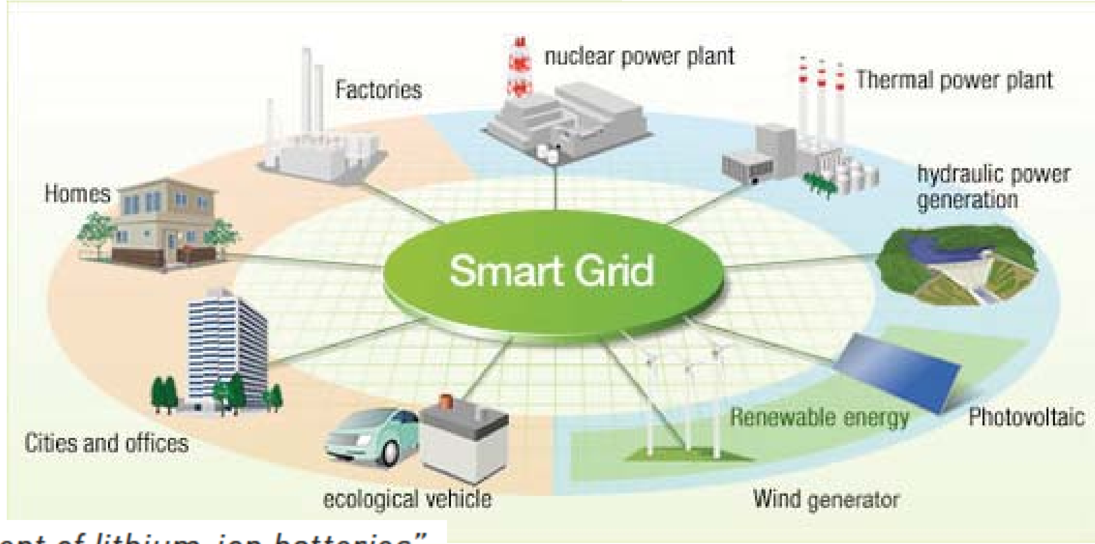

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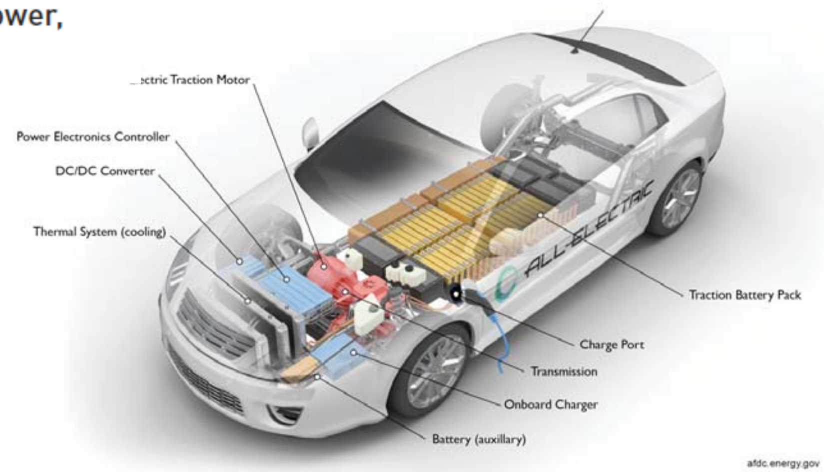

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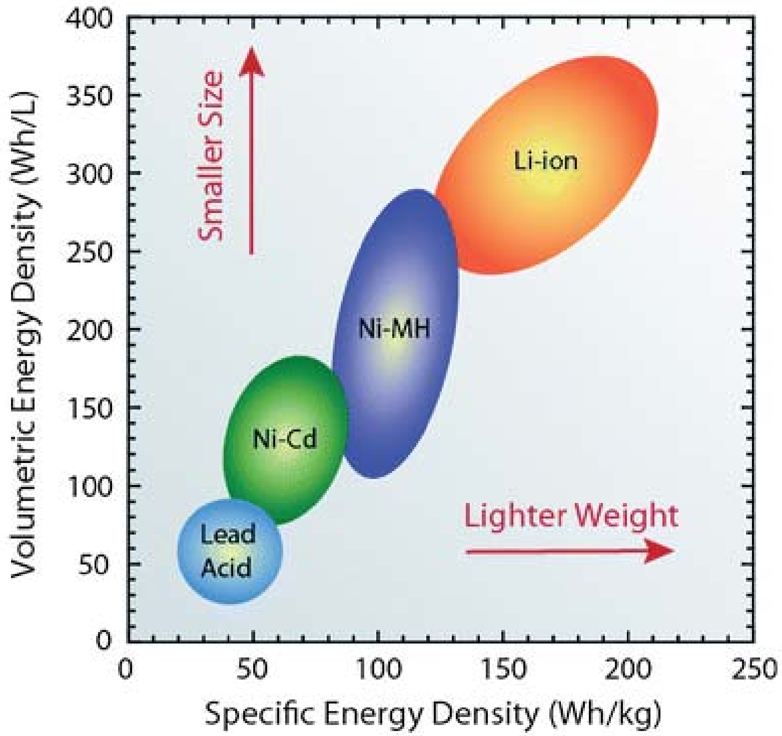

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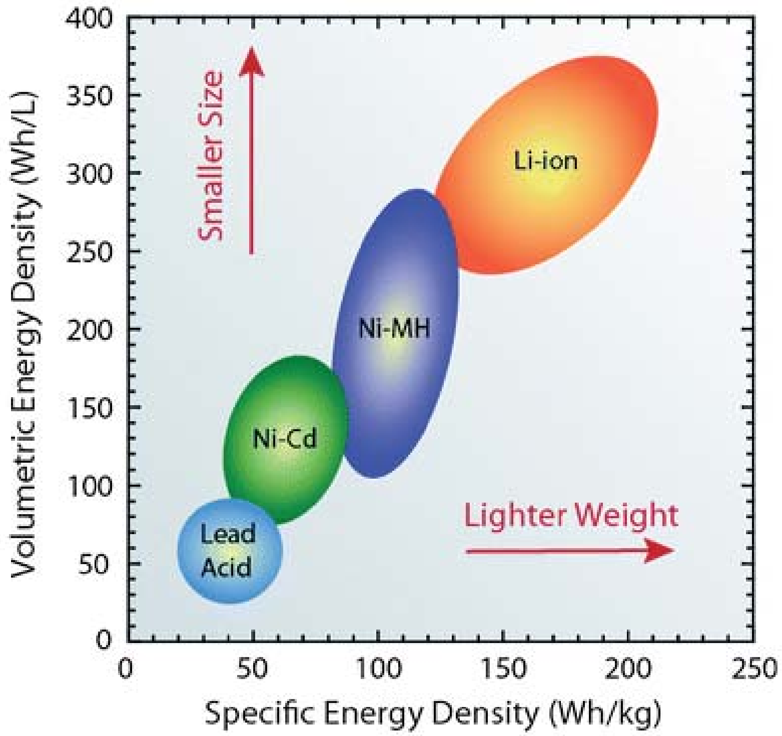

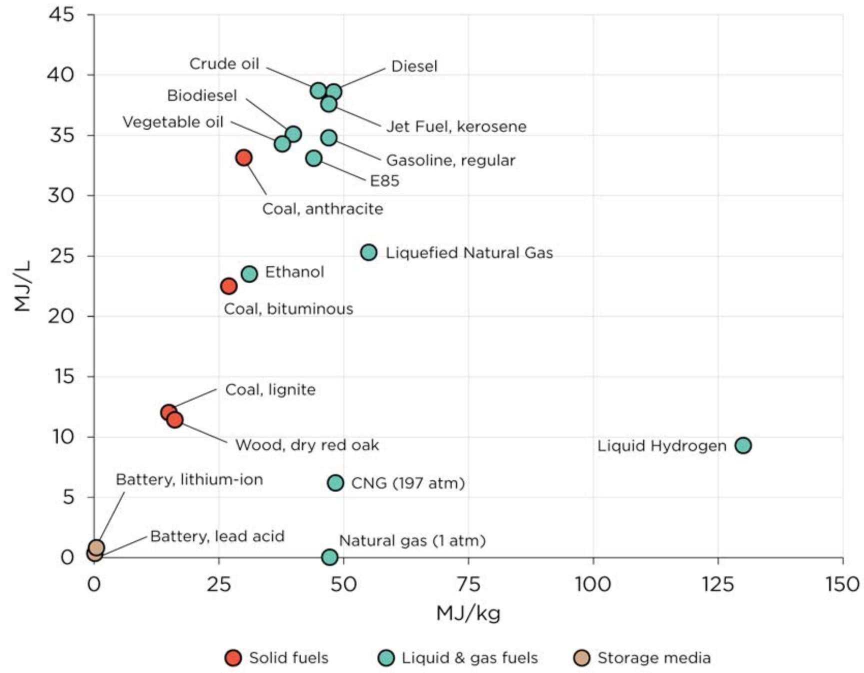

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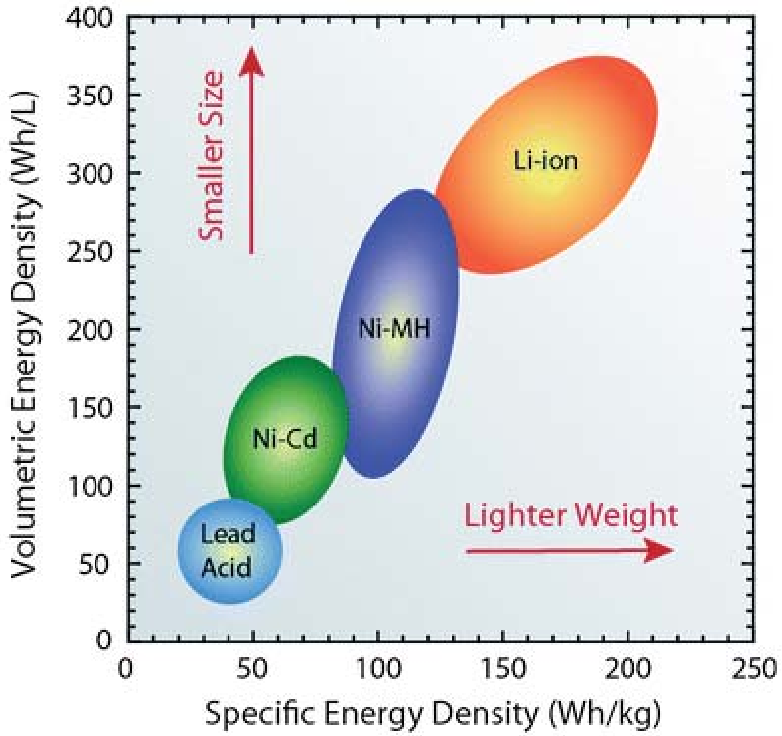

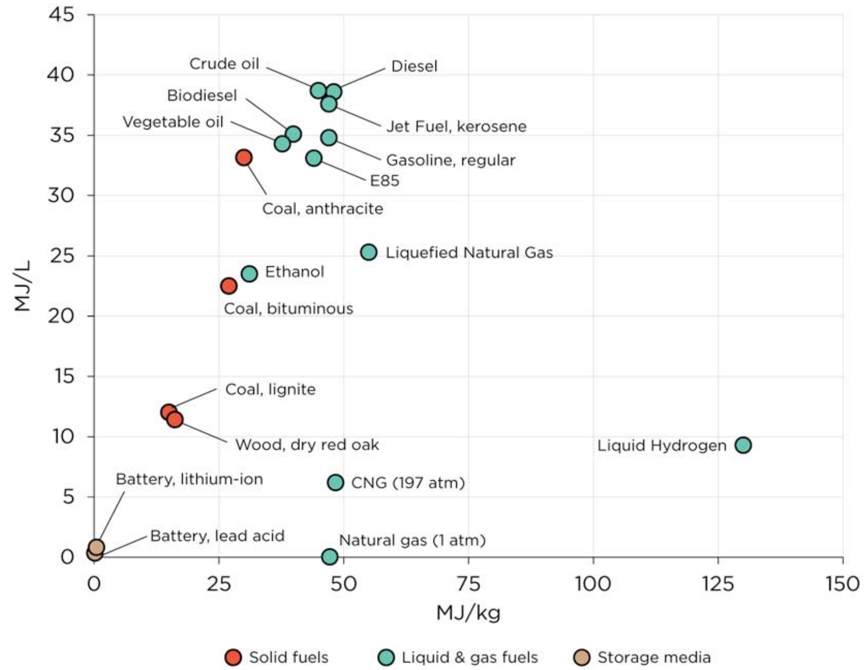

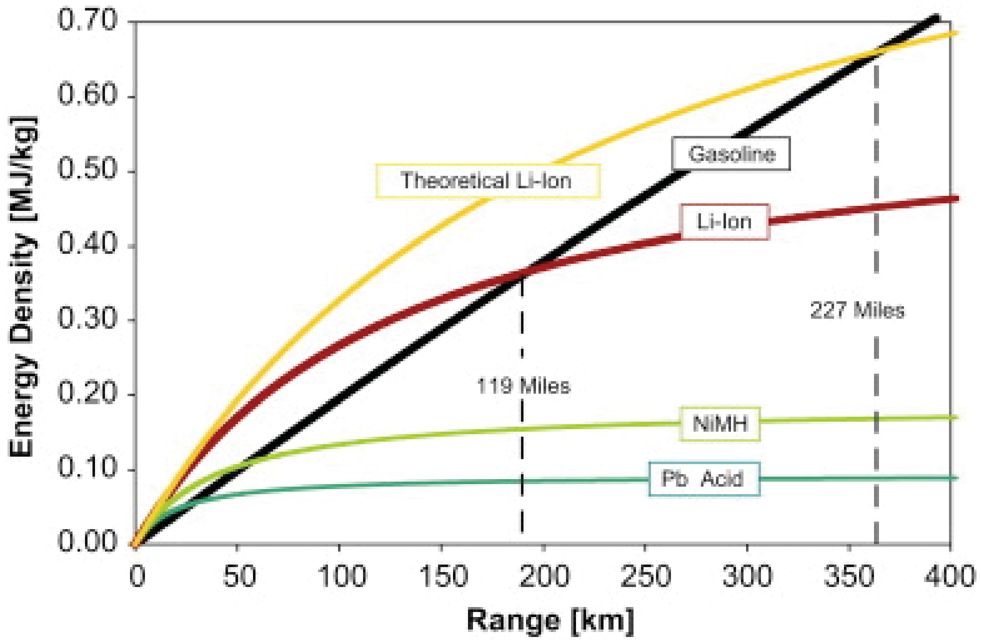

M. Fischer et al., Energy Policy 37, 2639 (2009)

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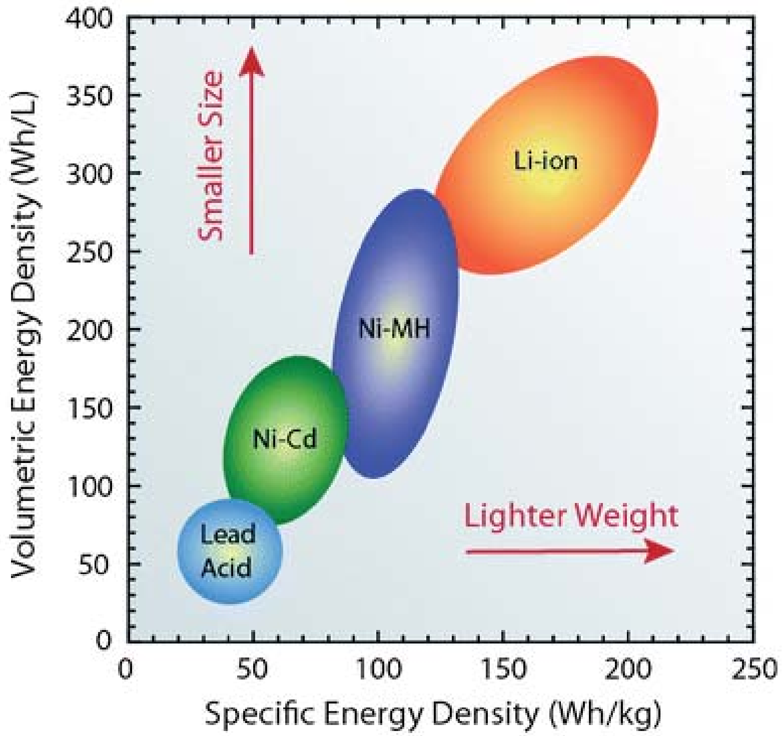

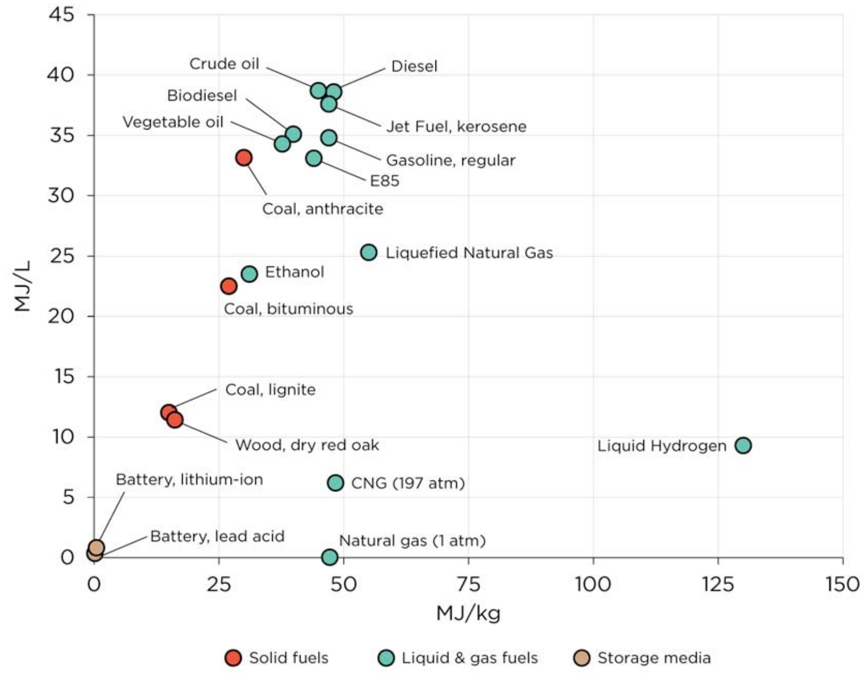

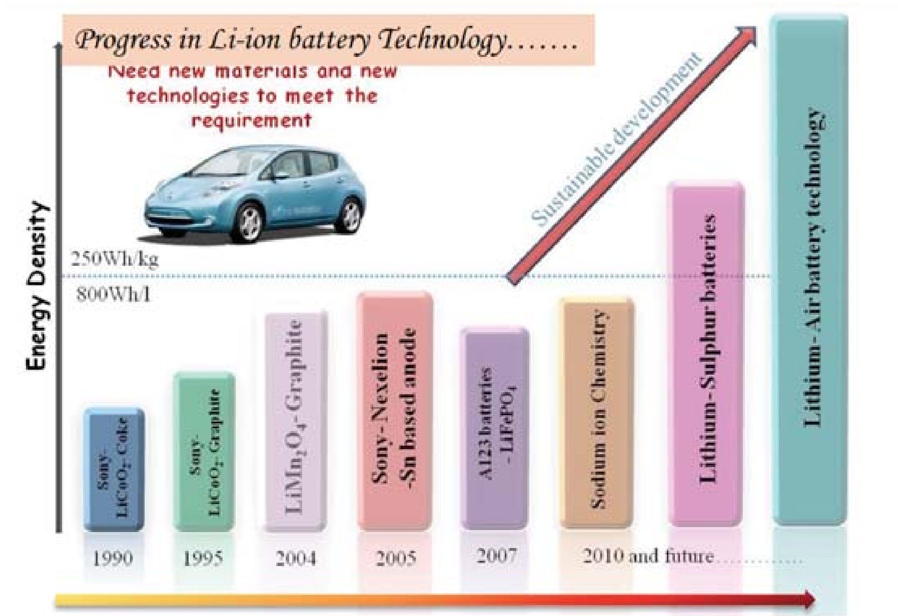

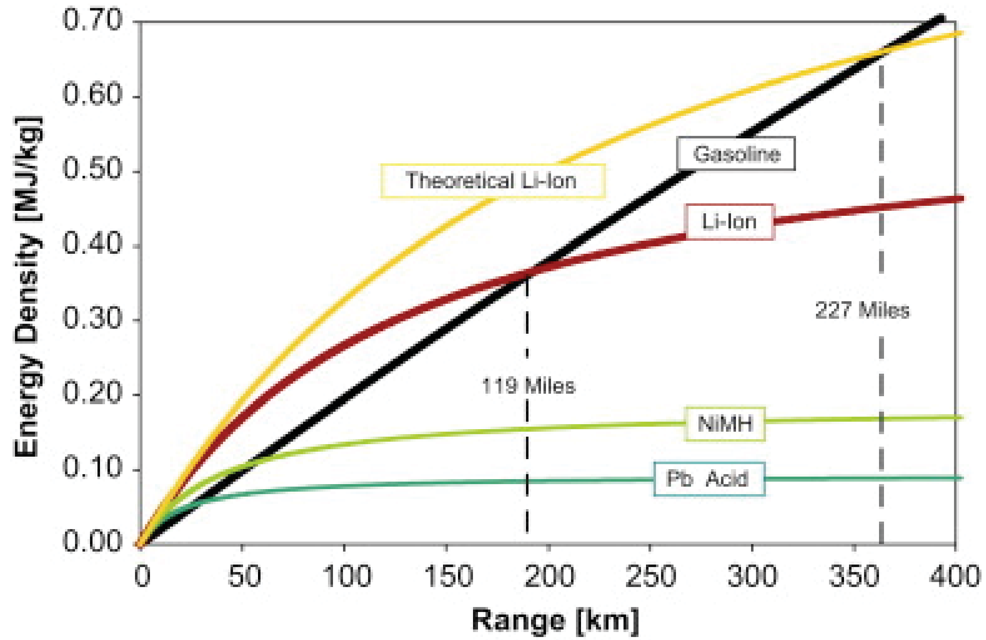

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Problems and challenges

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Safety

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Energy and power density

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Environmental/health friendliness

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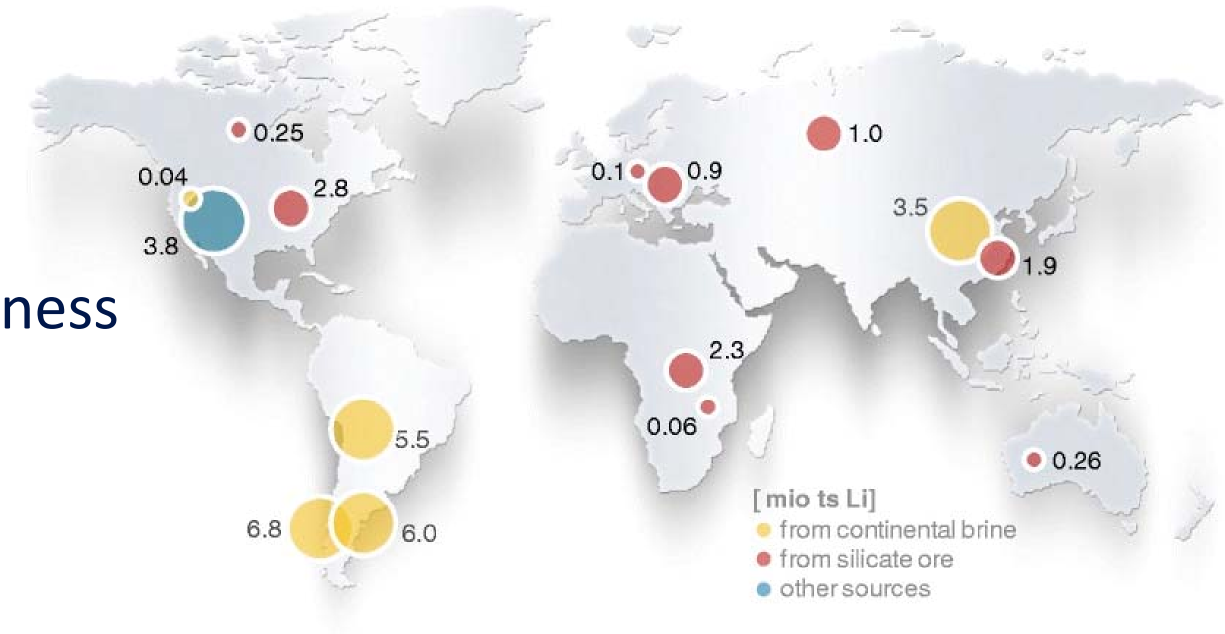
Low costs



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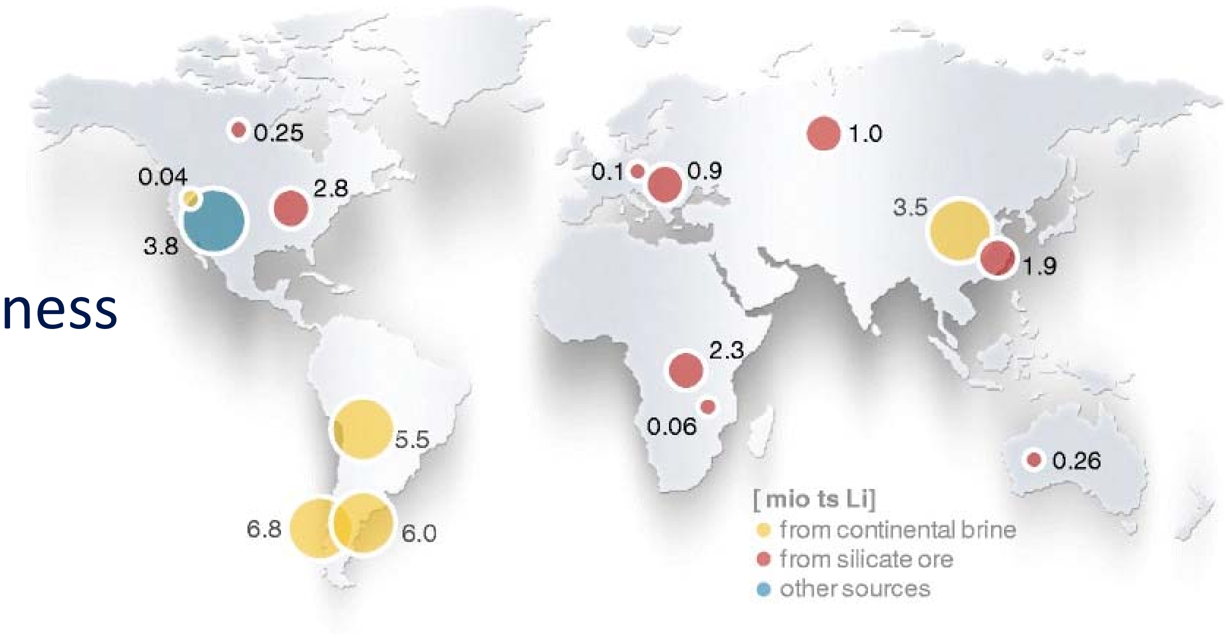

How do Li-ion batteries work?

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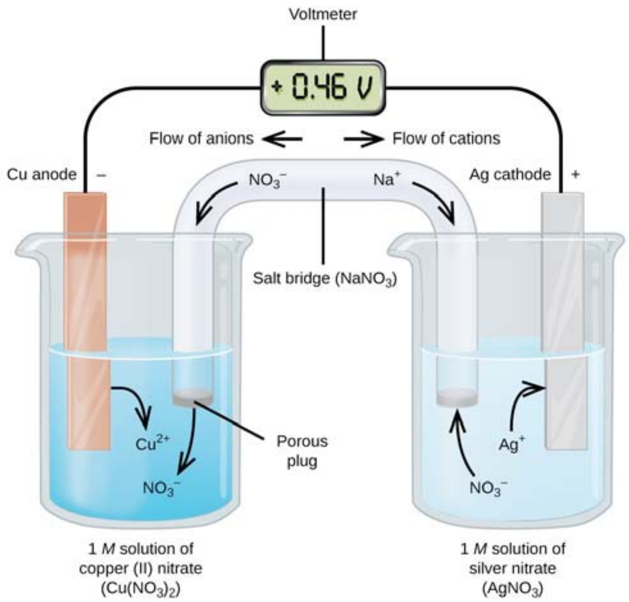

Galvanic/Voltaic cell: the driving force is the difference between the electrode potentials (~ the two metals work functions).

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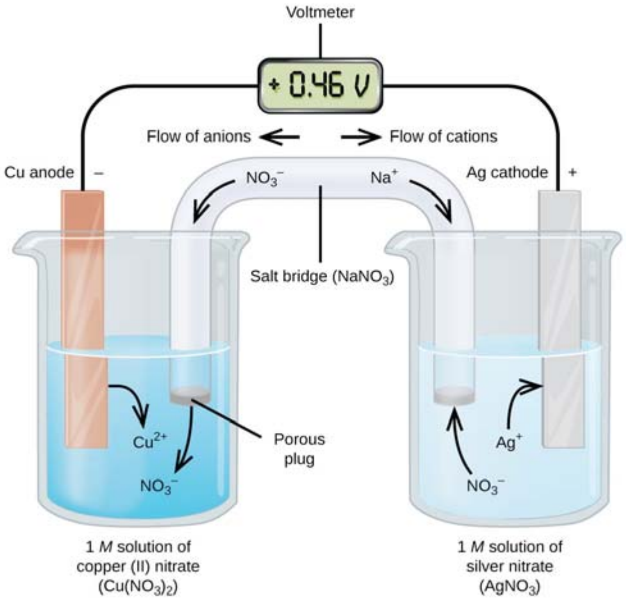
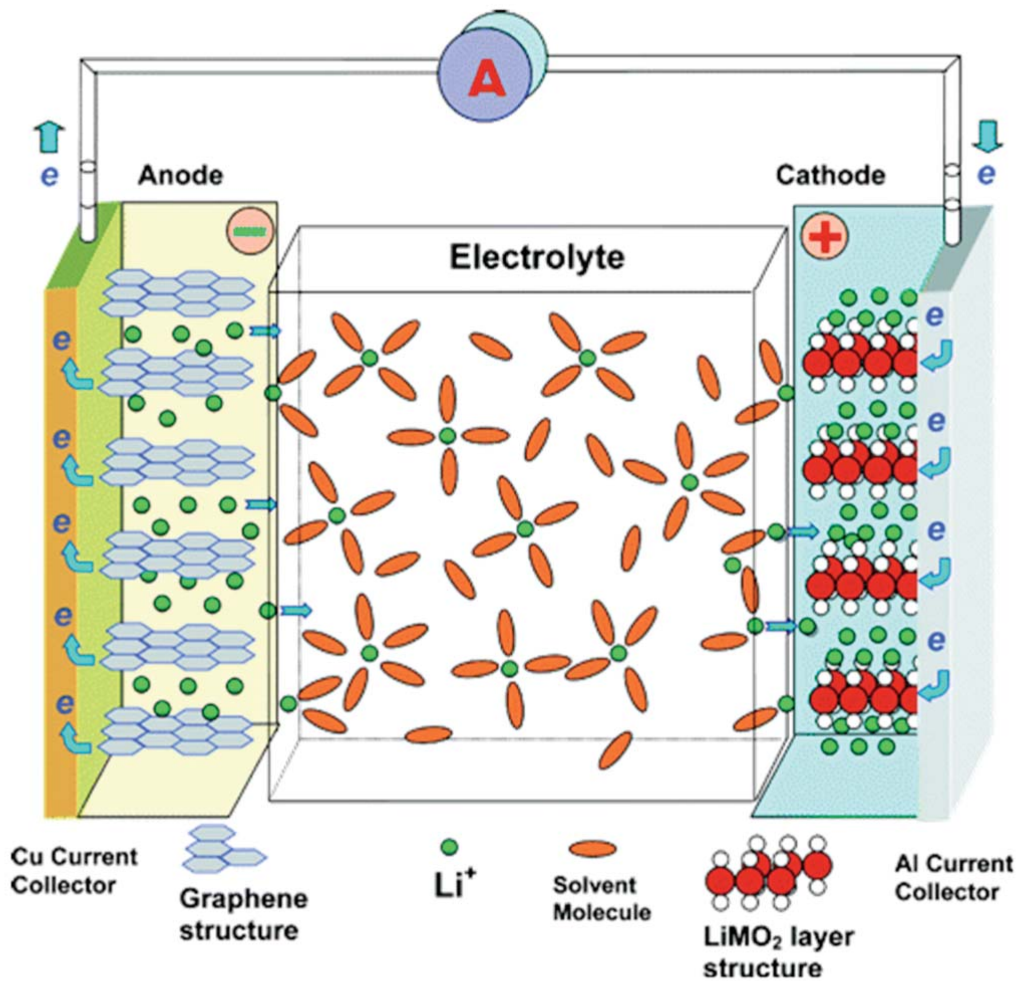


Galvanic/Voltaic cell: the driving force is the difference between the electrode potentials (~ the two metals work functions).

Rechargeable Li-ion battery: the driving force is the **chemical potential difference** for Li between electrodes. Li ions shuttle between anode and cathodes.



Good cathodes should be able to reversibly absorb and release Li ions for many cycles

Where does energy come from?

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$$\langle V \rangle = -\frac{\mu_{Li}^{cathode} - \mu_{Li}^{anode}}{e}$$

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In practice, given a system *X* able to intercalate various amounts of Li (X --> LiX) from a pure Li reference anode, one has:

$$\langle V \rangle = -\frac{E(LiX) - E(X) - E(Li_{met})}{e}$$

Where does energy come from?

Example: Li_xCoO_2

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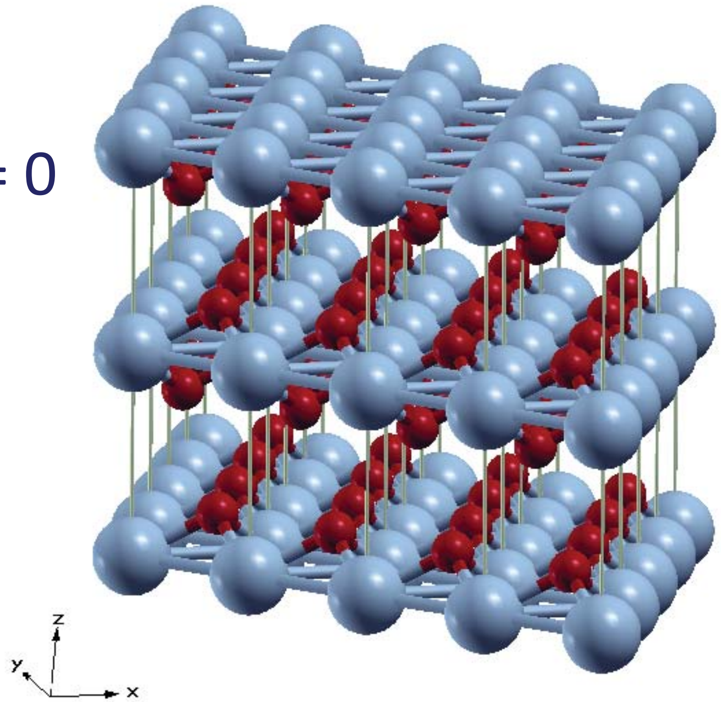
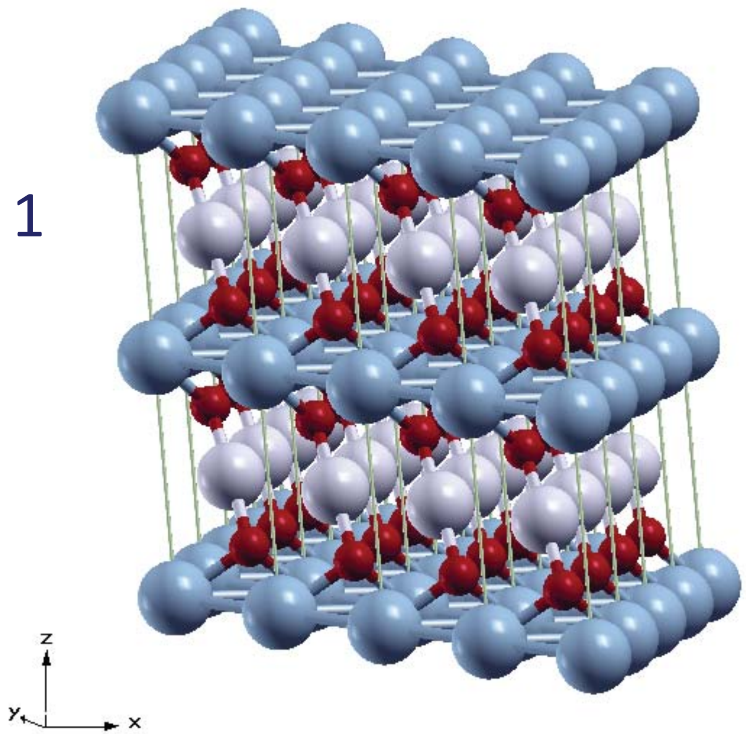
Example: Li_xCoO_2

x = 0



x = 1



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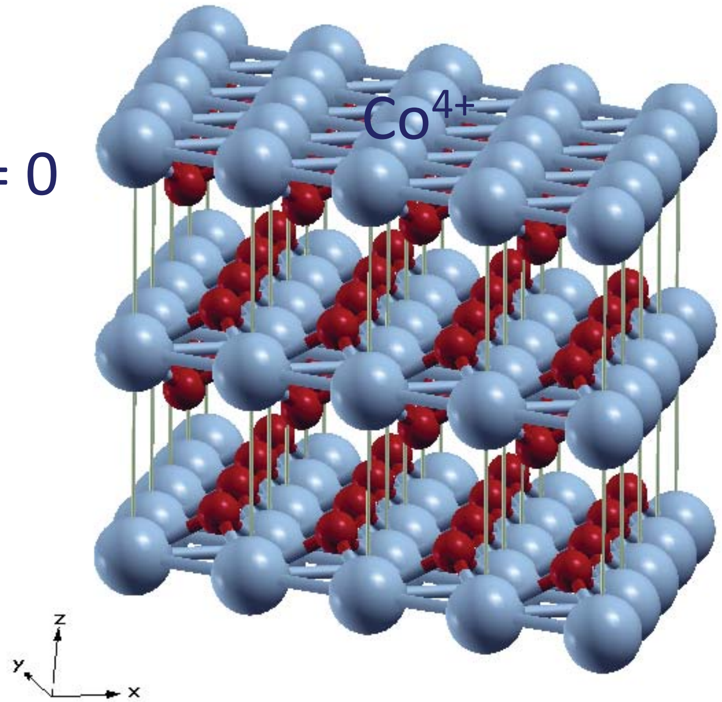

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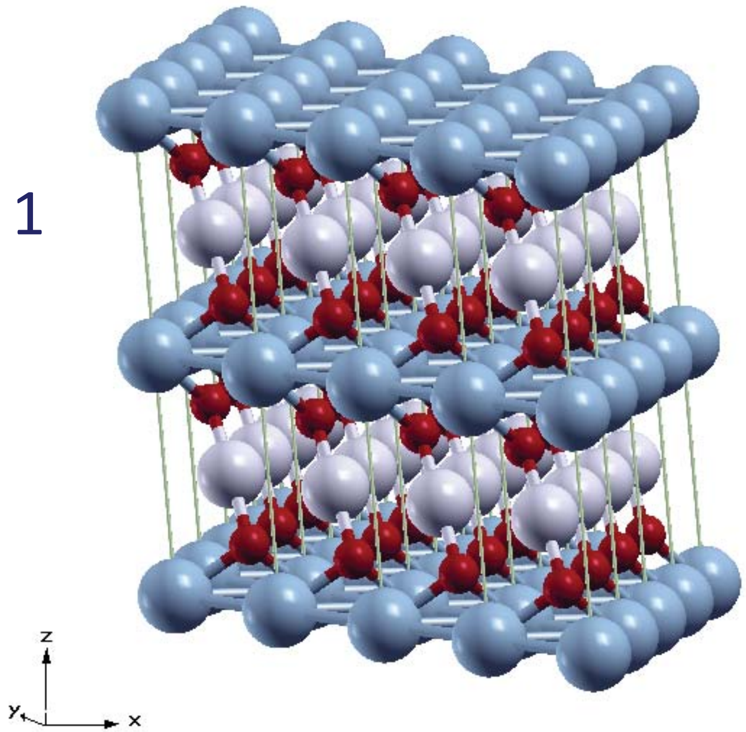

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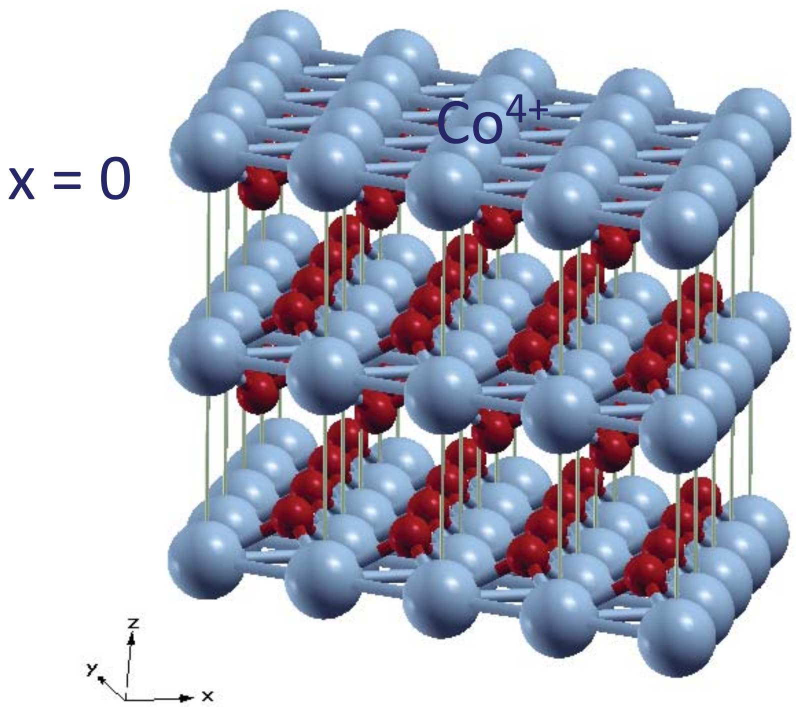

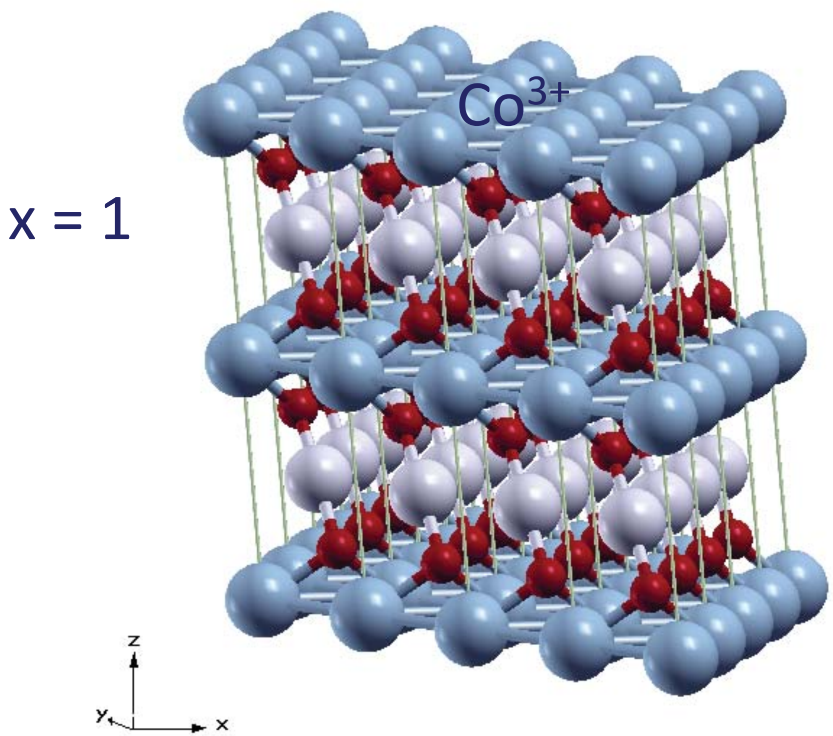

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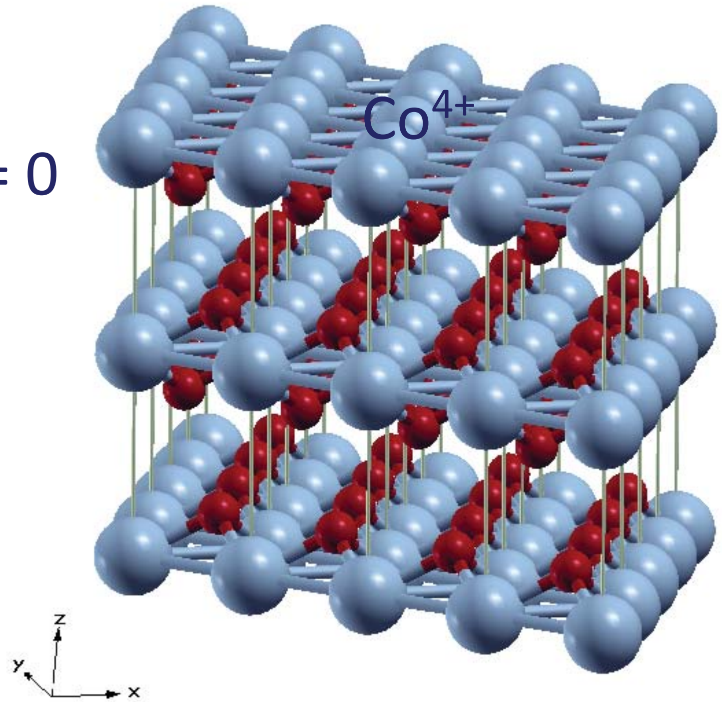

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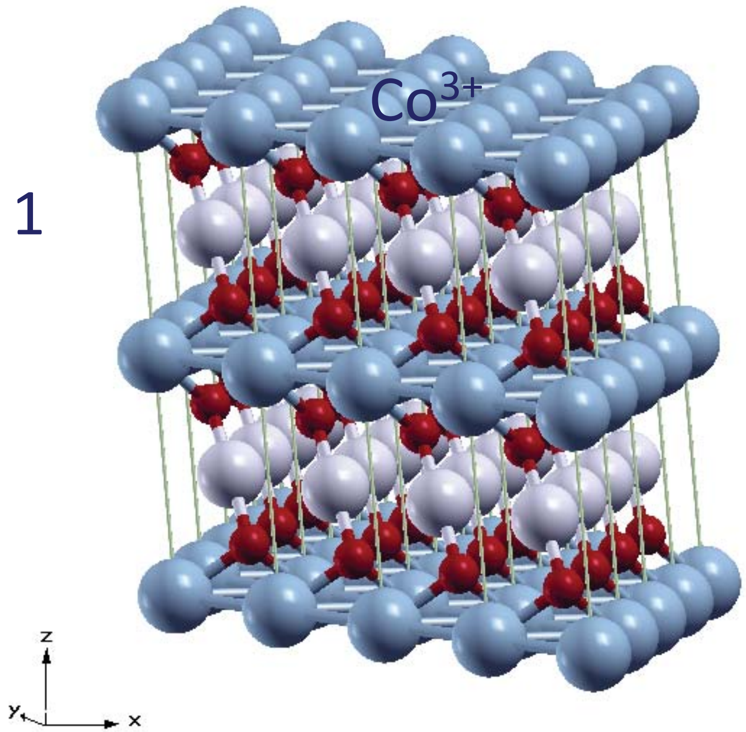
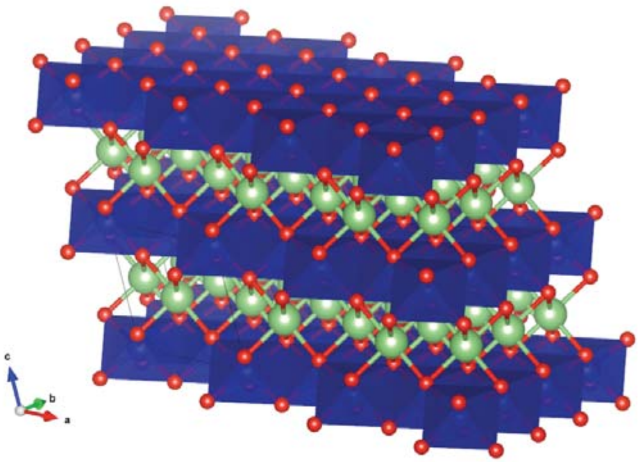
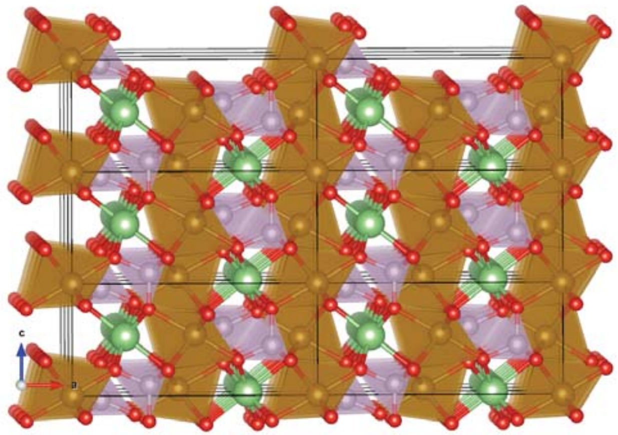


Voltage: broadly associated with **red-ox potential of TM ions**

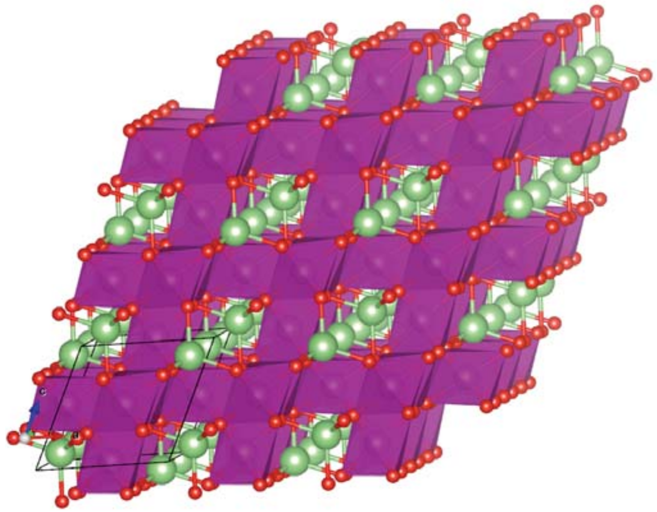
Some typical cathode materials



$LiMO_2$ layered oxide



$LiMPO_4$ olivine phosphate



LiM_2O_4 spinel

(M = metal)

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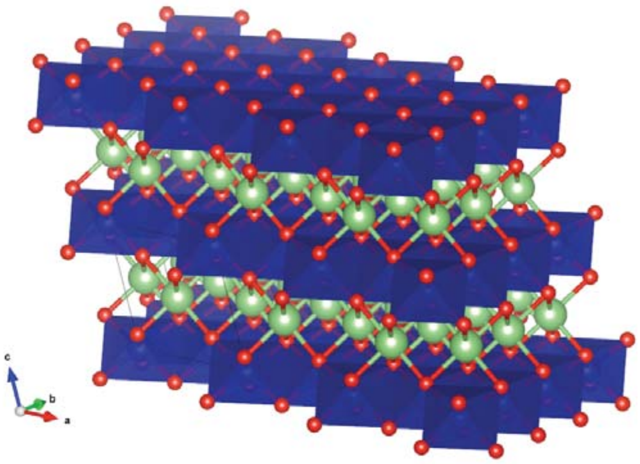

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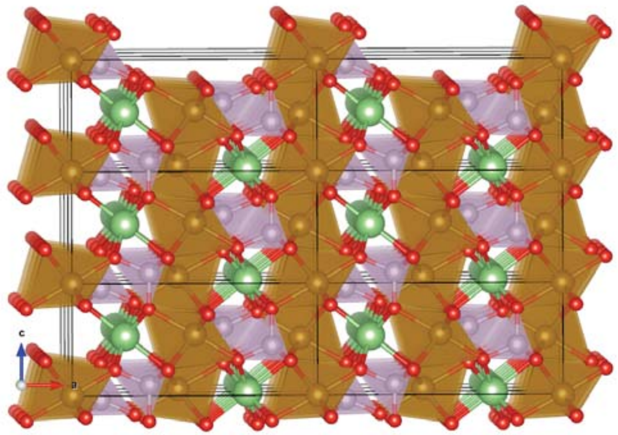

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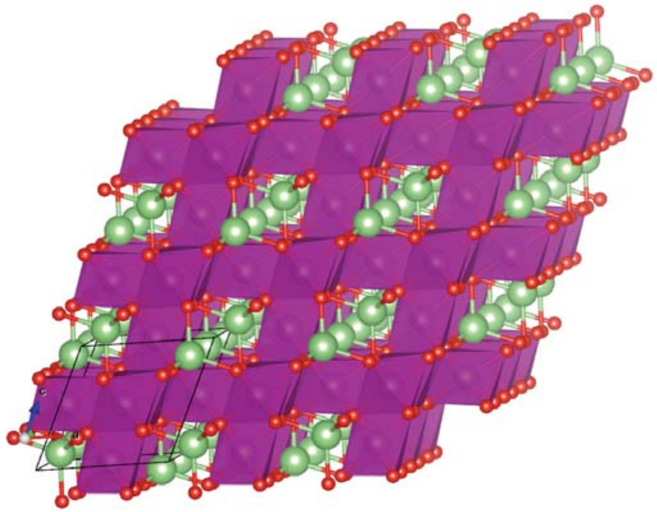

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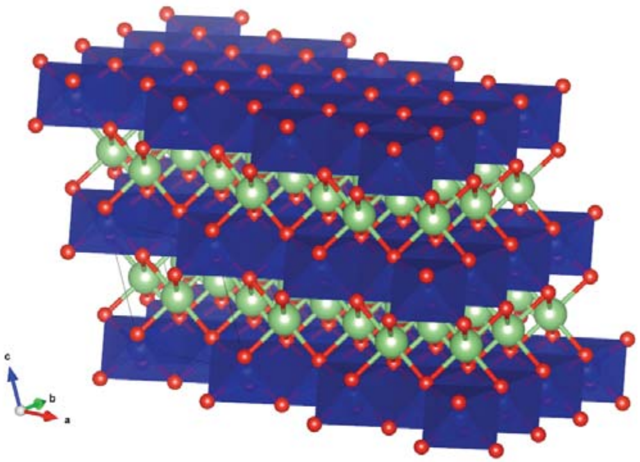

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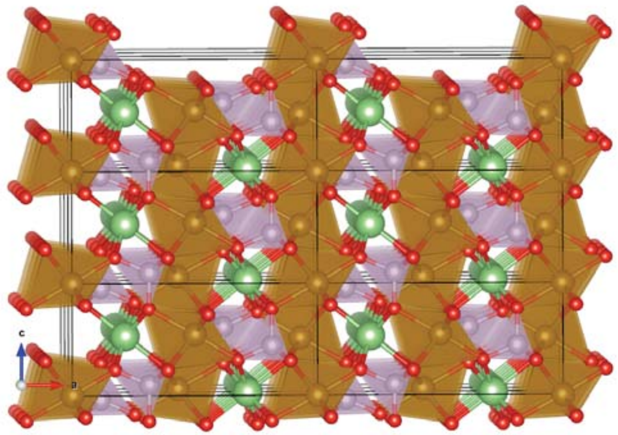

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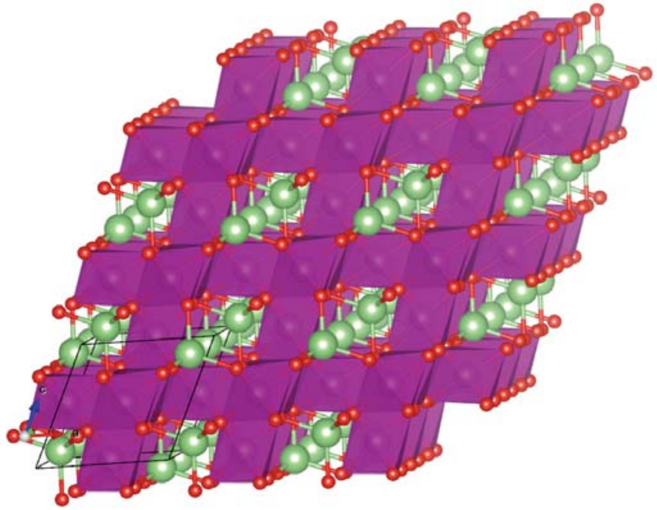

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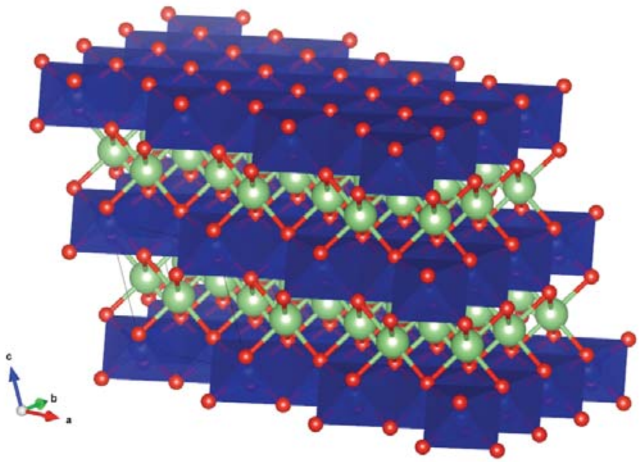

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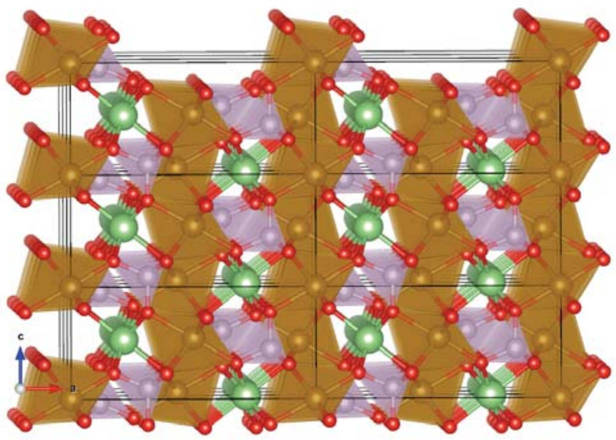

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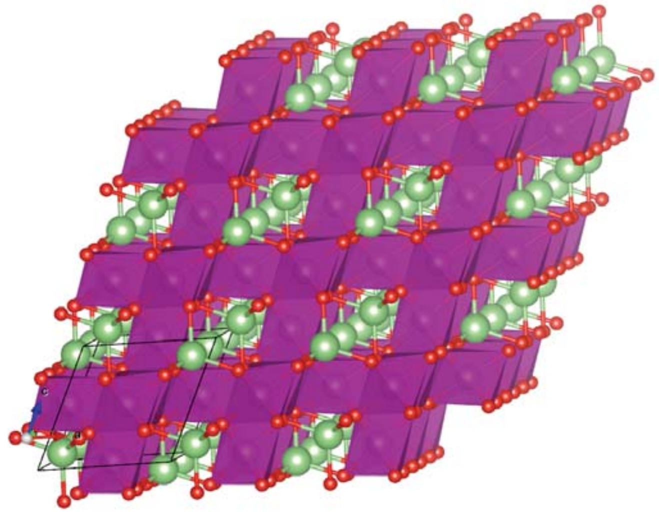

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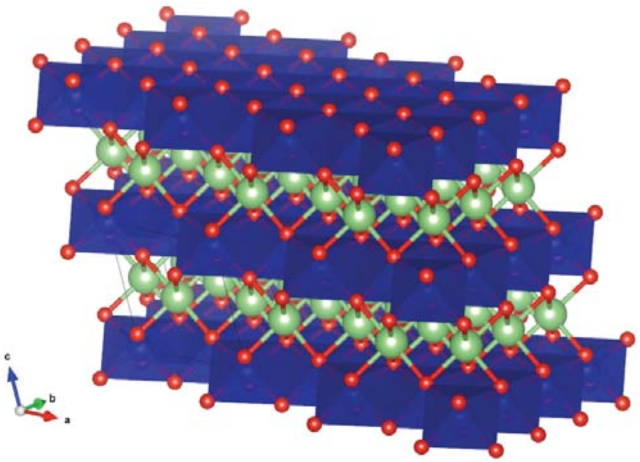

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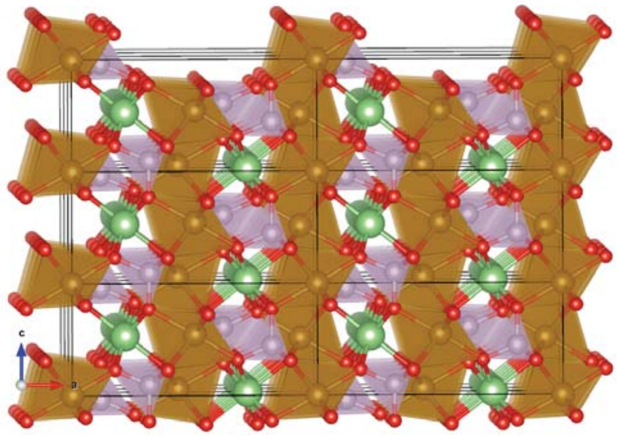

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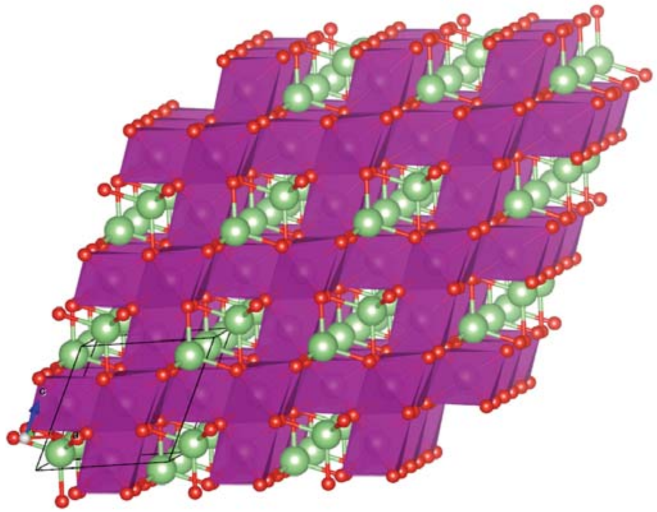

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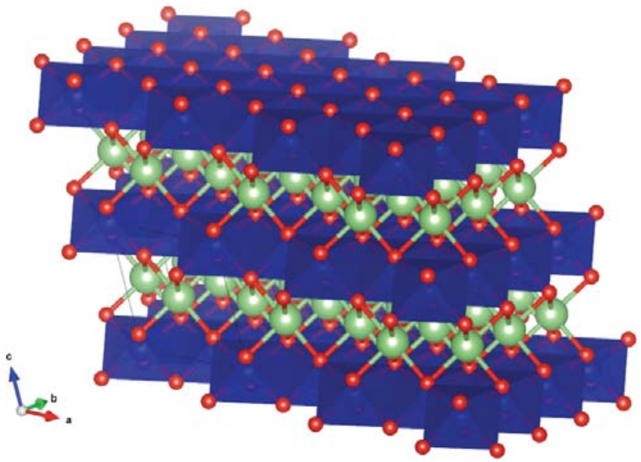

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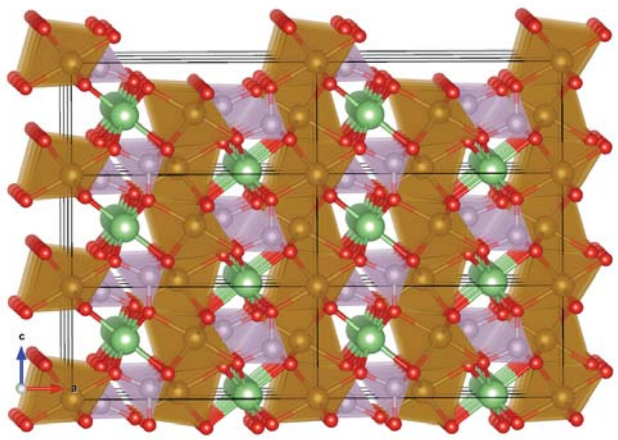
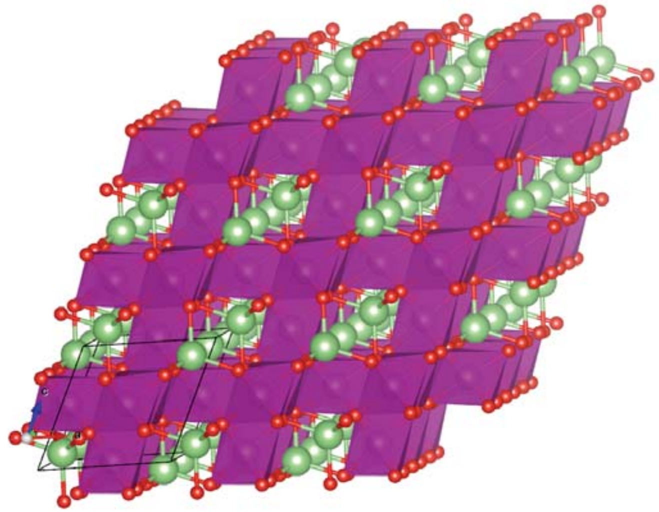


$LiMPO_4$ olivine phosphate



LiM_2O_4 spinel

(M = metal)

General requirements:

Intercalate large amounts of Li (energy density/capacity)

High Li+ and e- mobility (power density)

Retain structure with low damage rate and low volume change (cyclability)

High binding energy for Li+ and electron (high voltage)

Avoid parasitic reactions, decompositions and oxygen release (safety)

Importance of calculations

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Structural analysis (e.g. interface strain, etc)

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Charge localization, conduction properties and magnetism

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Relative stability of various phases and Li concentrations (phase diagram)

$$F.E. = E(Li_xSys) - xE(LiSys) - (1-x)E(Sys)$$

Performance of the battery

Average voltage

$$\langle V \rangle_{x_1,x_2} = -\frac{E(Li_{x_2}Sys) - E(Li_{x_1}Sys) - (x_2 - x_1)E(Li_{bulk})}{(x_2 - x_1)e}$$

Density-functional theory

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The father: **W. Kohn**
1998 Nobel Laureate in Chemistry for developing DFT (mid 1960's)

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Main advantage of DFT:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N)$$

N-electrons wavefunction

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$$\rho(\mathbf{r})$$

electronic charge density

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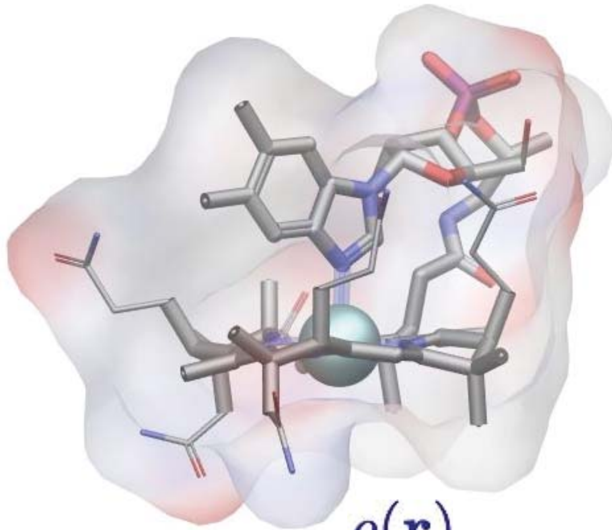

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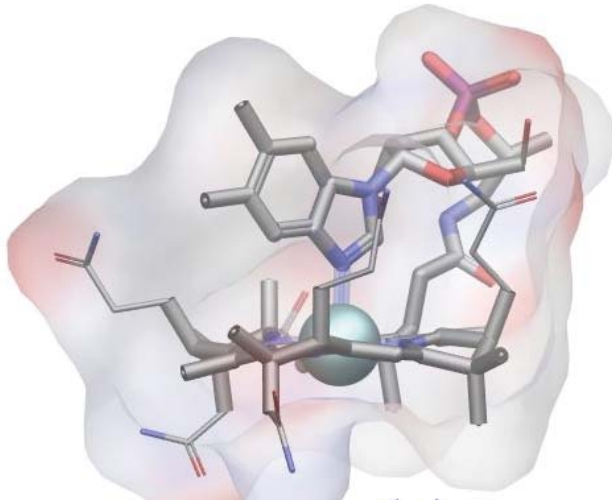

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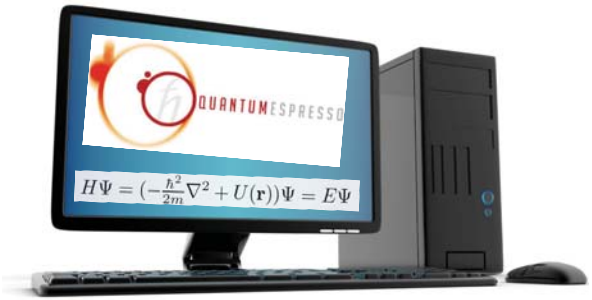

Energy minimization:

Ground state total energy and density

Total energy derivatives (forces, stresses, etc)

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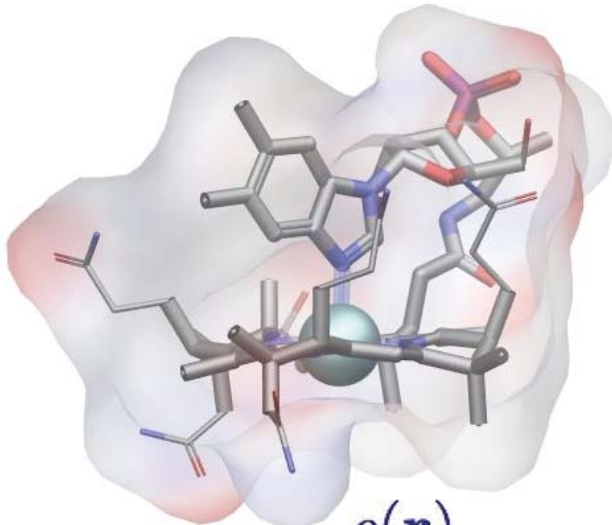

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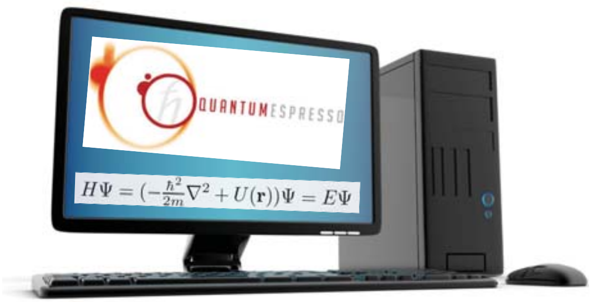

Energy minimization:

Ground state total energy and density

Total energy derivatives (forces, stresses, etc)

DFT is **formally exact** but approximations are used in all current implementations

Understand, predict, design

Understand, predict, and design complex materials with first-principles electronic-structure simulations

- **Bulk (skutterudites) and nanostructured thermoelectrics (Bosch)**
- **Ageing of niobium-tin superconductors (ARO)**
- **Organic photovoltaics (ENI)**
- **Solar fuels (via first-principles EPR) (DOE)**
- **Lead-free piezoelectrics (Bosch)**
- **Electrochemical reactions in PEM fuel cells/batteries (NSF)**
- **Nanoparticles' catalytic activity, stability (NSF)**
- **Carbon nanomaterials (Darpa)**
- **Ionic transport in solid state electrolytes (NIMS)**
- **Viscosity and conductivity of ionic liquids (DuPont)**
- **Methane catalysis (including biomimetic) (DOE)**
- **Hydrogen storage materials (DOE)**
- **Novel dielectrics (Intel)**
- **Decoding the structure of concrete via NMR (Portland Association)**

DFT: aims and capabilities

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DFT is a **ground state** theory and is excellent to evaluate

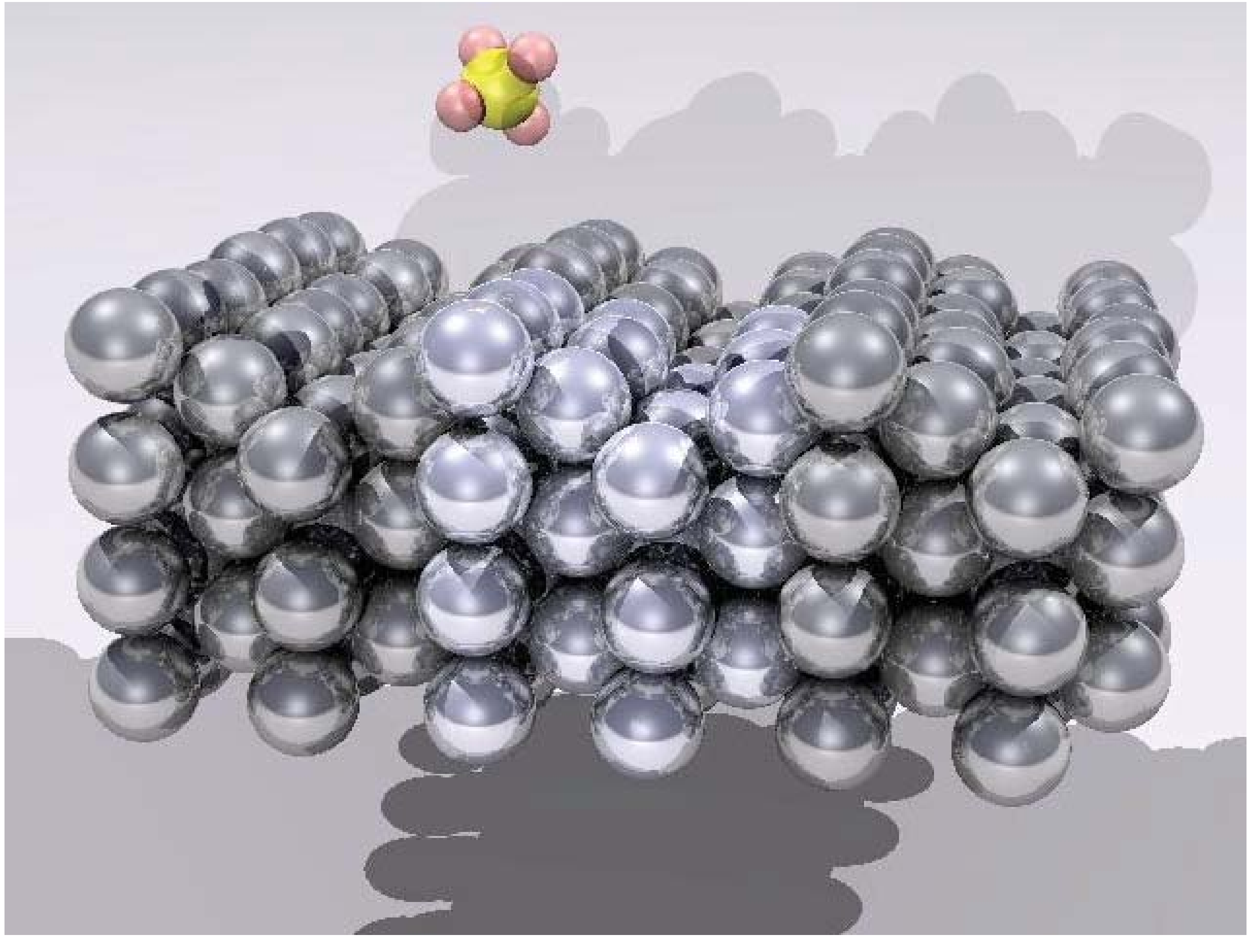
total energies and energy differences

- magnetic, electronic, structural properties and phase stability (ambient to extreme conditions)
- phase transitions
- vibrational properties (harmonic and anharmonic), Raman and IR spectra, P-T free energies
- finite-temperature elastic constants
- electrical and thermal conductivity
- molecular dynamics and metadynamics
- orbital and magnetic ordering; magneto-structural couplings
- quasi-particle and optical excitations

Car-Parrinello molecular dynamics

Catalysis (video courtesy of N. Marzari)

Car-Parrinello molecular dynamics



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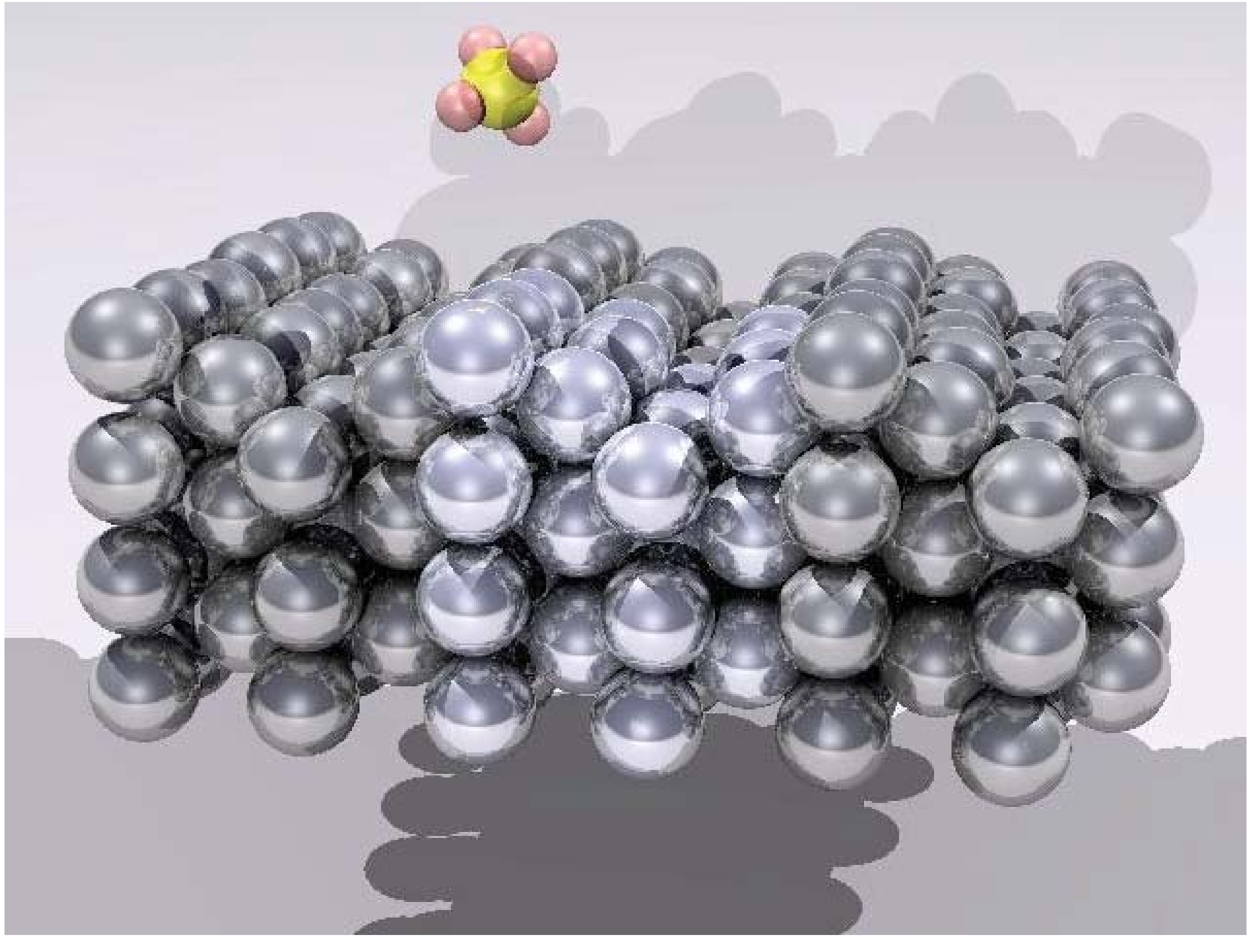

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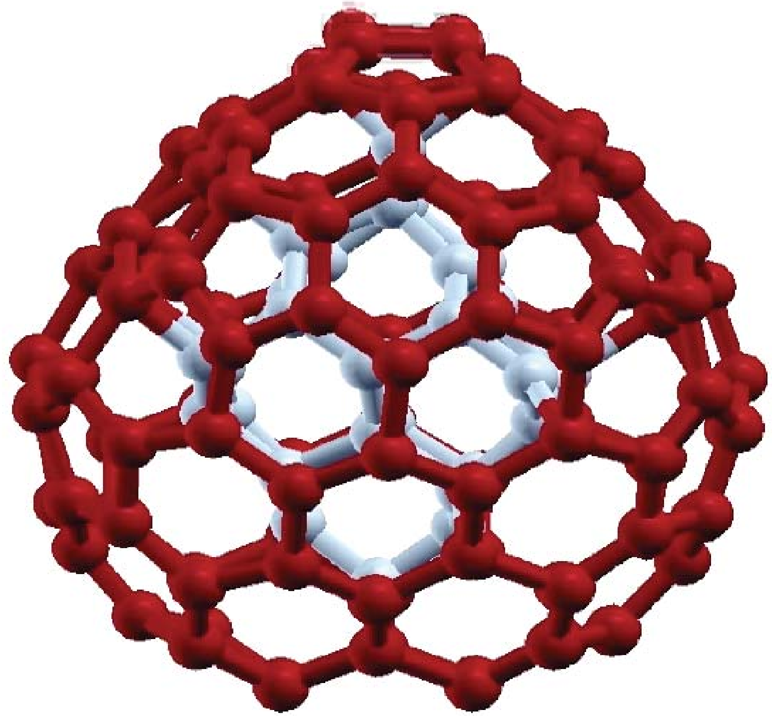

Squeezing bucky-diamonds (looking for stress-induced plastic deformations)

Water and (the color of) wine

From time-dependent DFT (TDDFT)

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dyes of the family of cyanines are responsible for the purple color (and the antioxidant properties)

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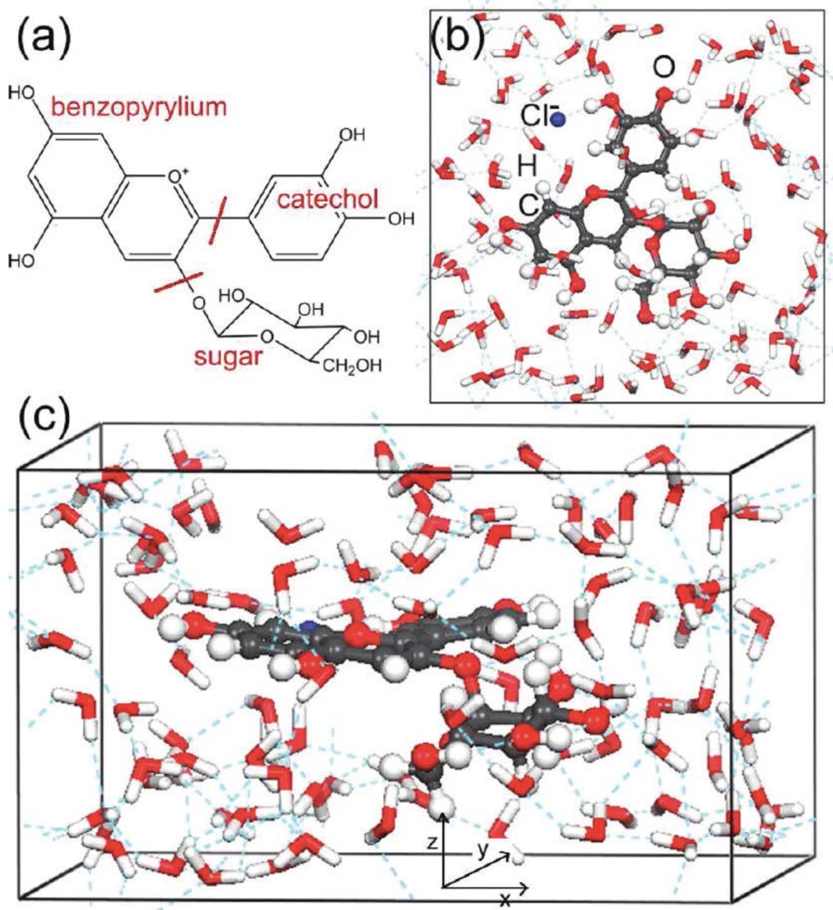
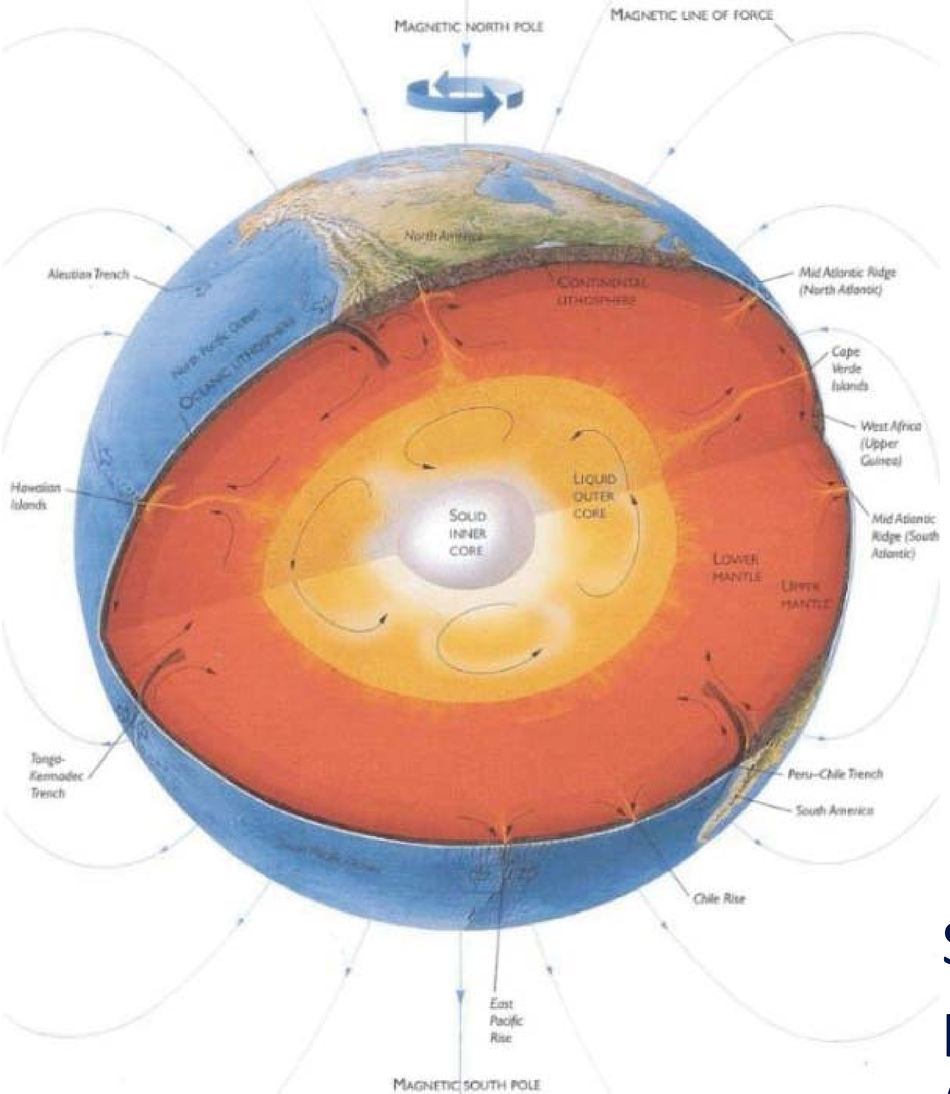


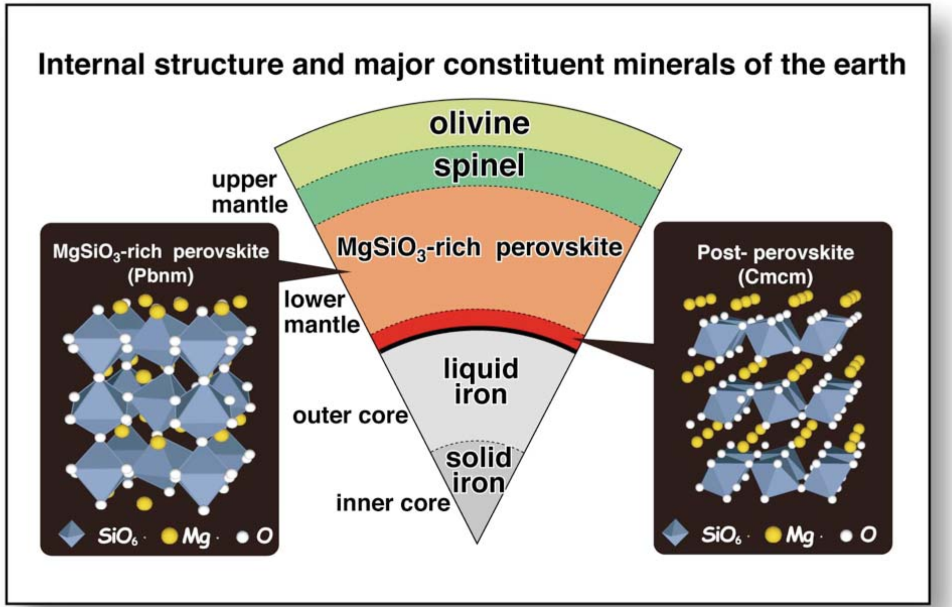
O. B. Malcioglu et al. JACS 133, 15425 (2011)

dyes of the family of cyanines are responsible for the purple color (and the antioxidant properties)

The solvent (water) is fundamental to determine the thermal fluctuations that (on average) give cyanine dyes their color

Deep inside our Earth





Structural, magnetic and electronic properties of minerals at high P and T (sometimes extreme)

Approximate DFT: difficulties

Unfortunately the exact energy functional is not known and approximations are needed

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Notable failures: <u>molecular dissociations</u> (e.g. H_2):

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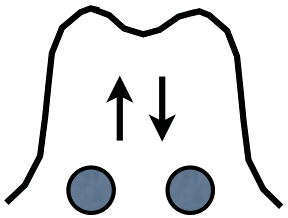
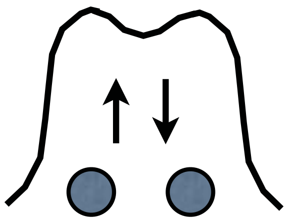


DFT:



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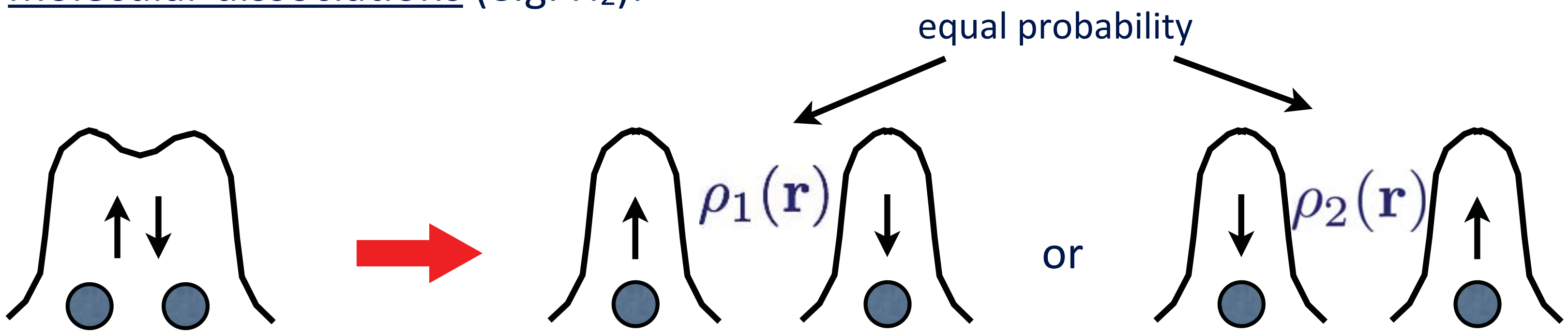

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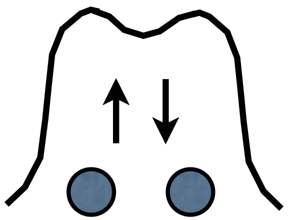

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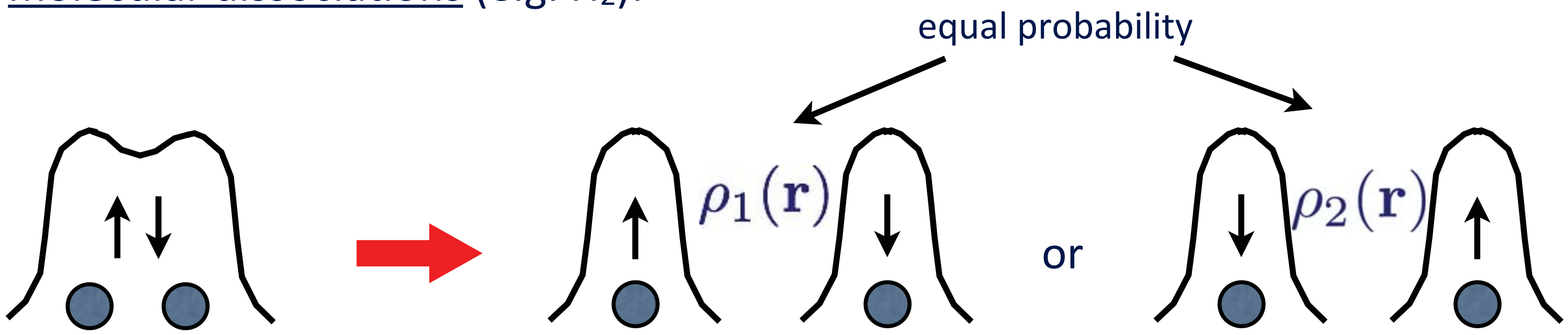

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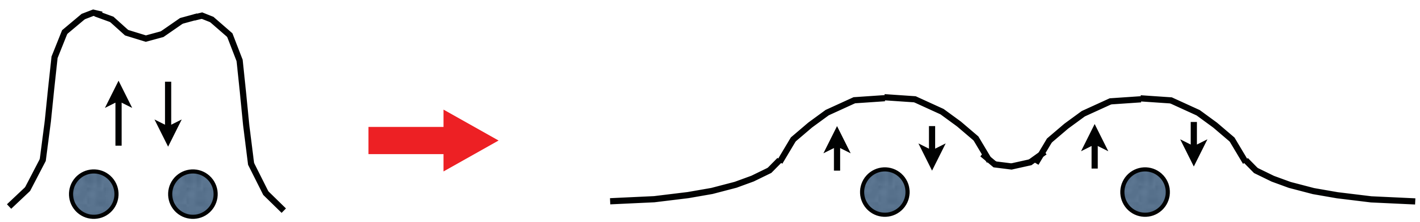

$$\rho(\mathbf{r}) = \tfrac{1}{2}\rho_1(\mathbf{r}) + \tfrac{1}{2}\rho_2(\mathbf{r})$$

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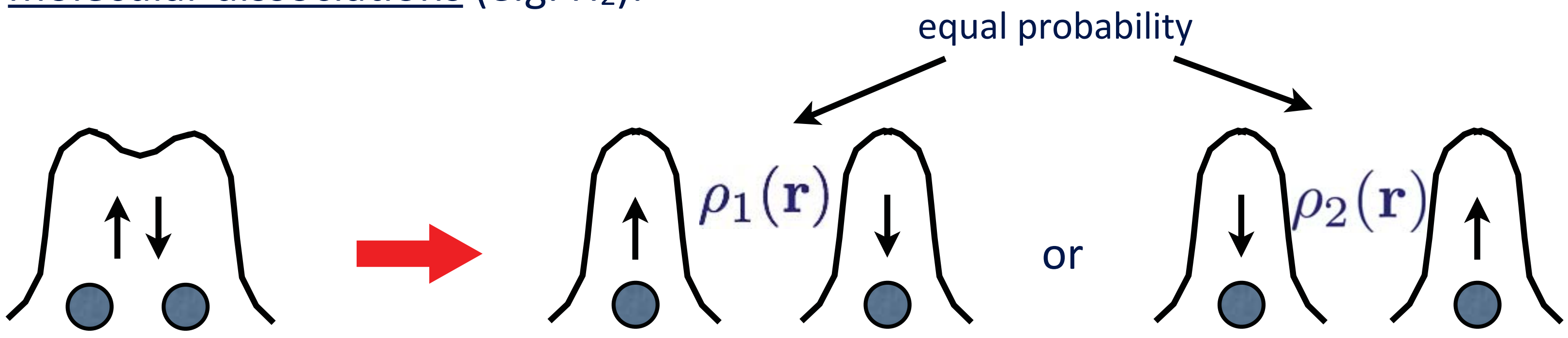
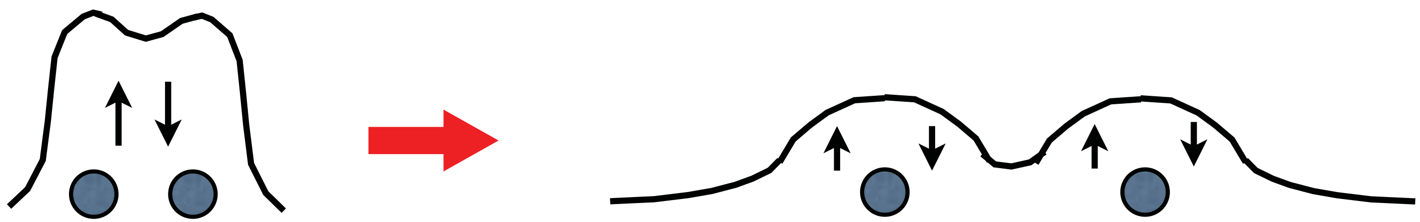


$$E = \frac{1}{2}E_1 + \frac{1}{2}E_2$$

DFT:



$$\rho(\mathbf{r}) = \tfrac{1}{2}\rho_1(\mathbf{r}) + \tfrac{1}{2}\rho_2(\mathbf{r}) \qquad E[\rho(\mathbf{r})] \neq \tfrac{1}{2}\mathbf{E}[\rho_1(\mathbf{r})] + \tfrac{1}{2}\mathbf{E}[\rho_2(\mathbf{r})]$$

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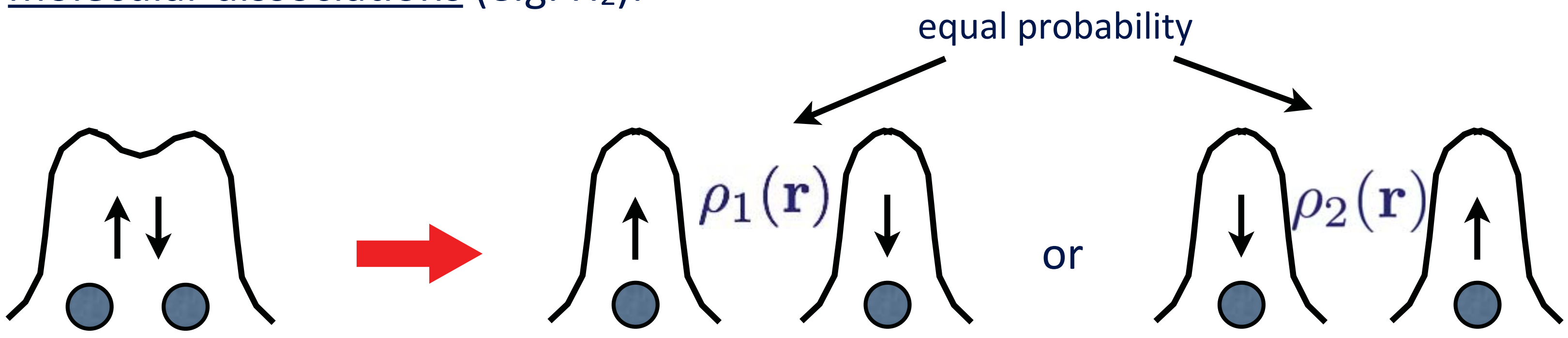

The curvature of the energy is exaggerated

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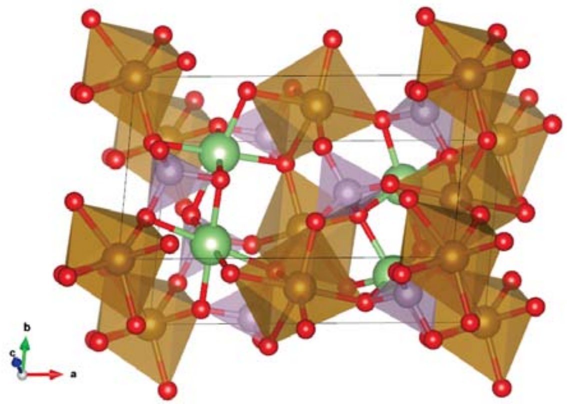
$LiCoPO_4$: e^- localization and energetics



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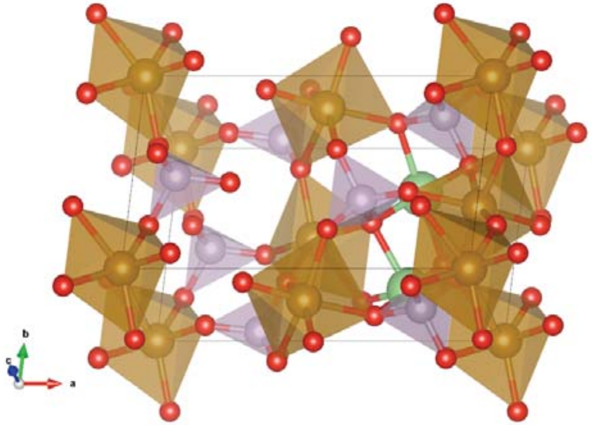
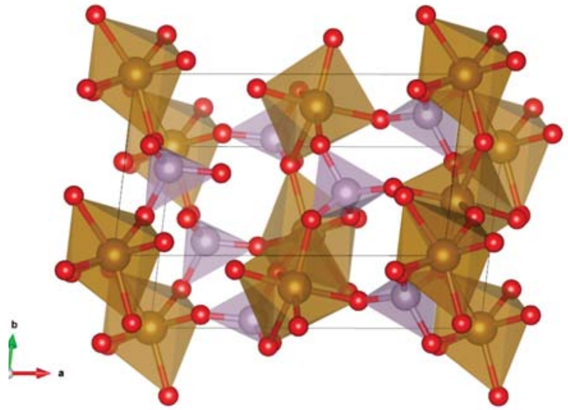


$Li_{0.5}CoPO_4$



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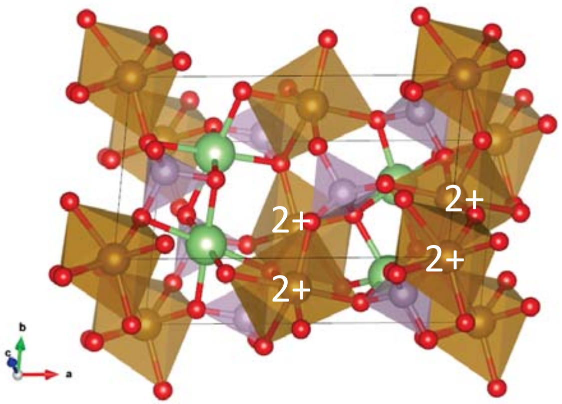

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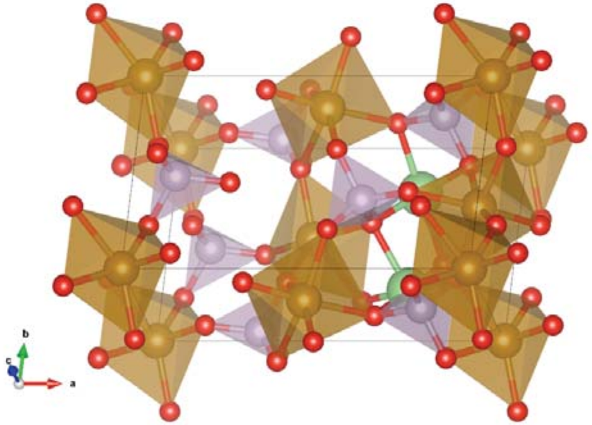

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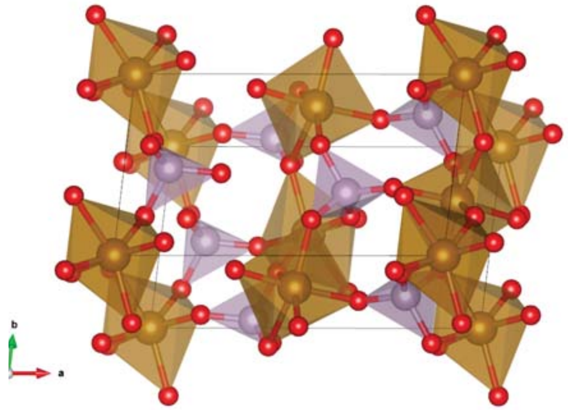

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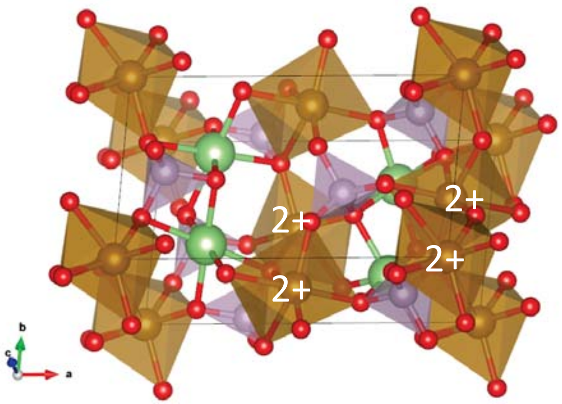

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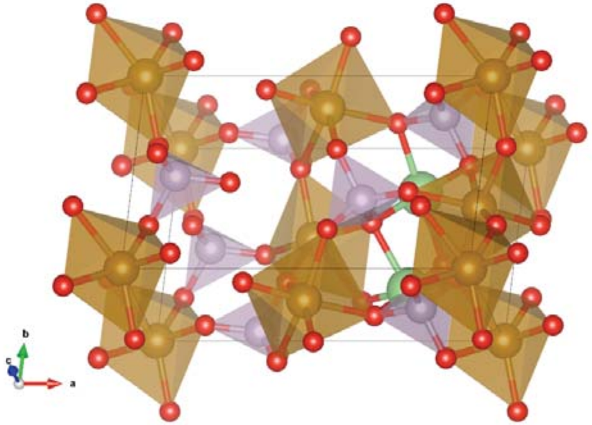

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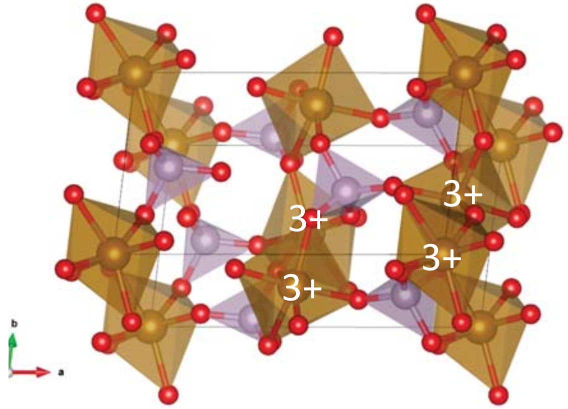

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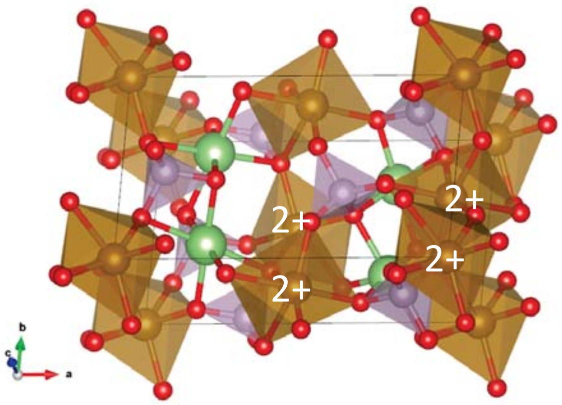

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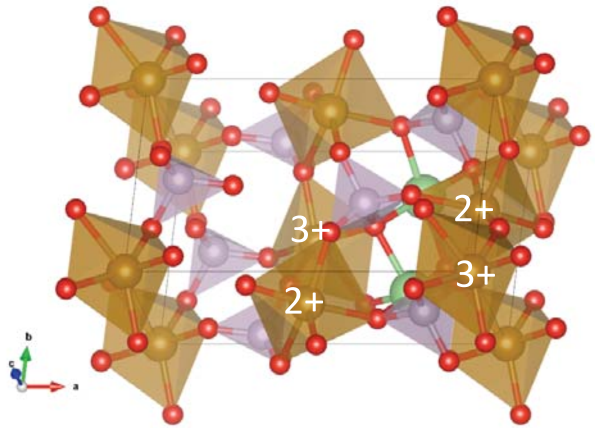

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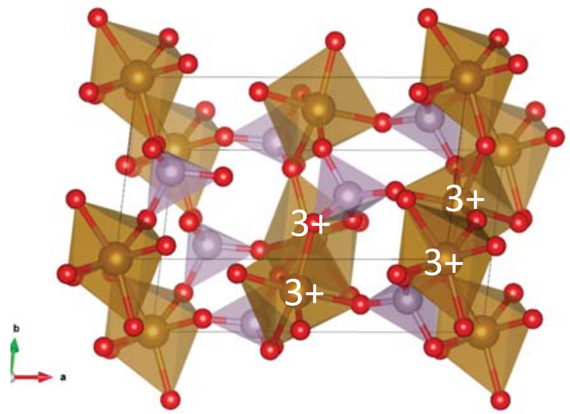

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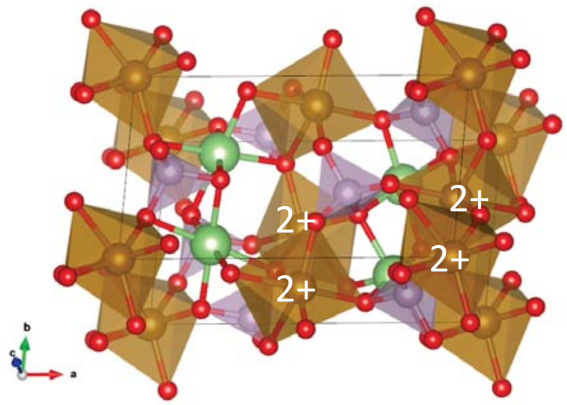

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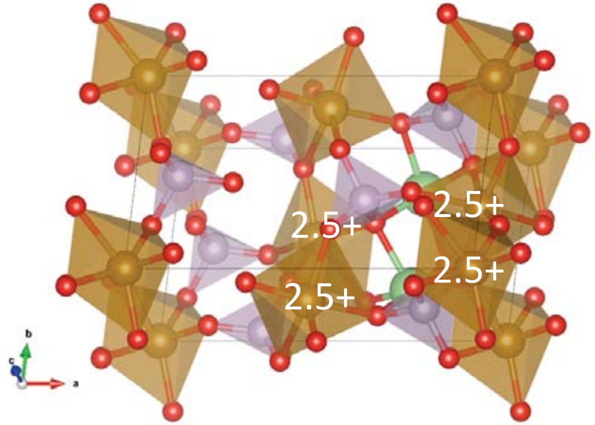

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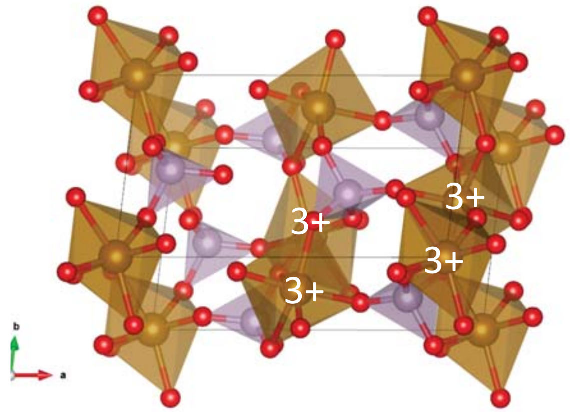

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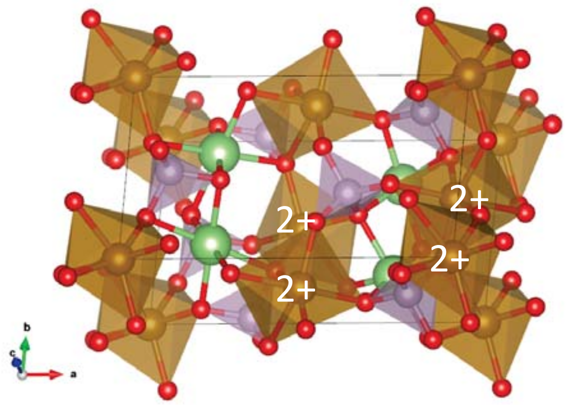

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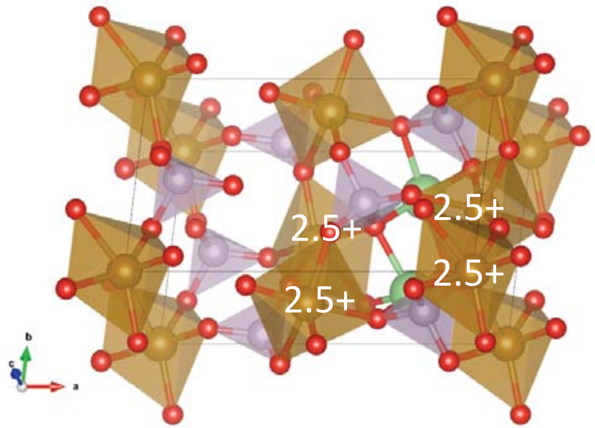

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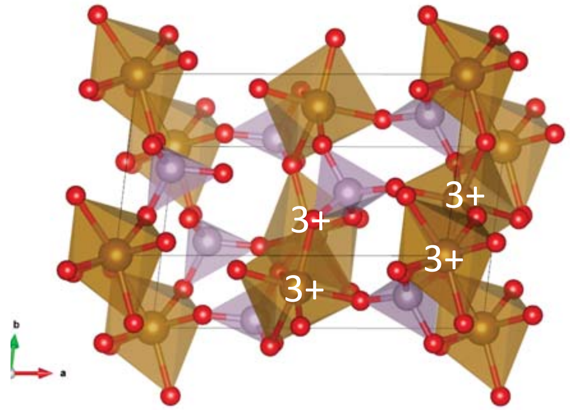

$CoPO_4$

	$LiCoPO_4$	$Li_{0.5}CoPO_4$		$CoPO_4$	F. E.	Voltage
	Co 2+	Co 2+	Co 3+	Co 3+	meV/FU	V
Exp					> 0	~4.8
DFT	7.35			7.06		

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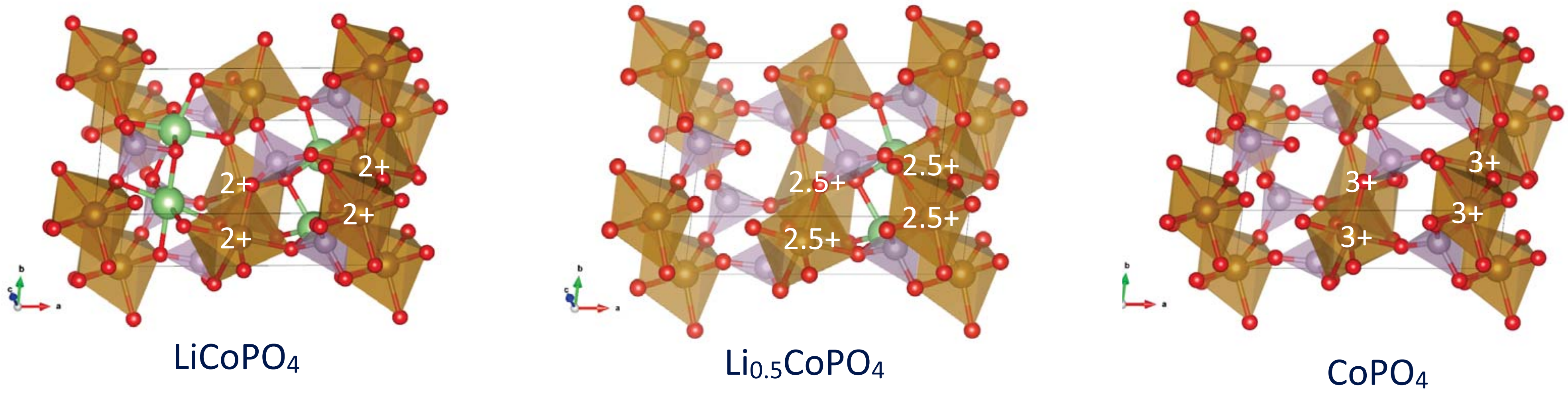

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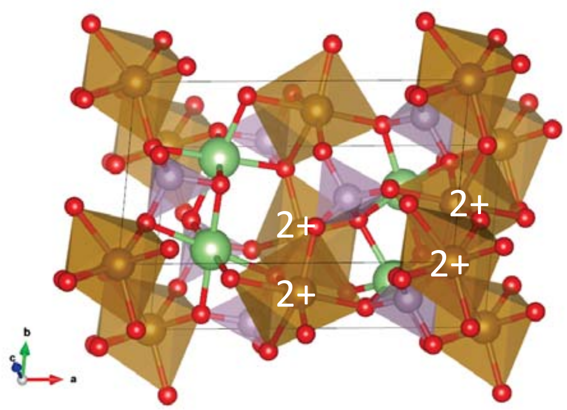

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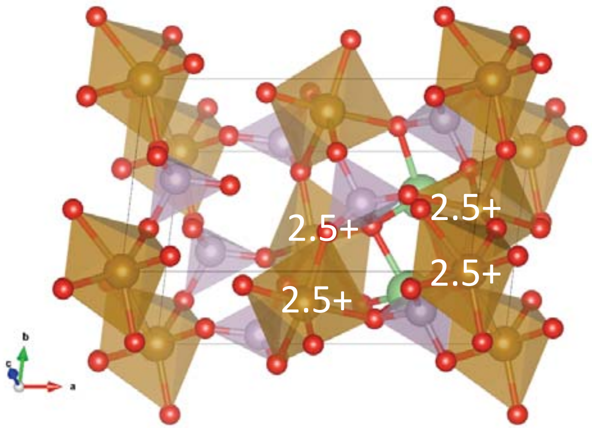

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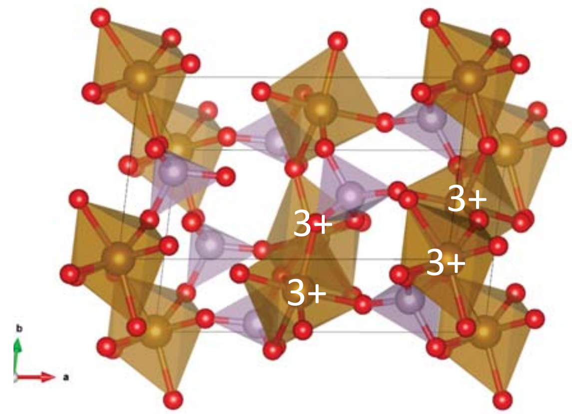

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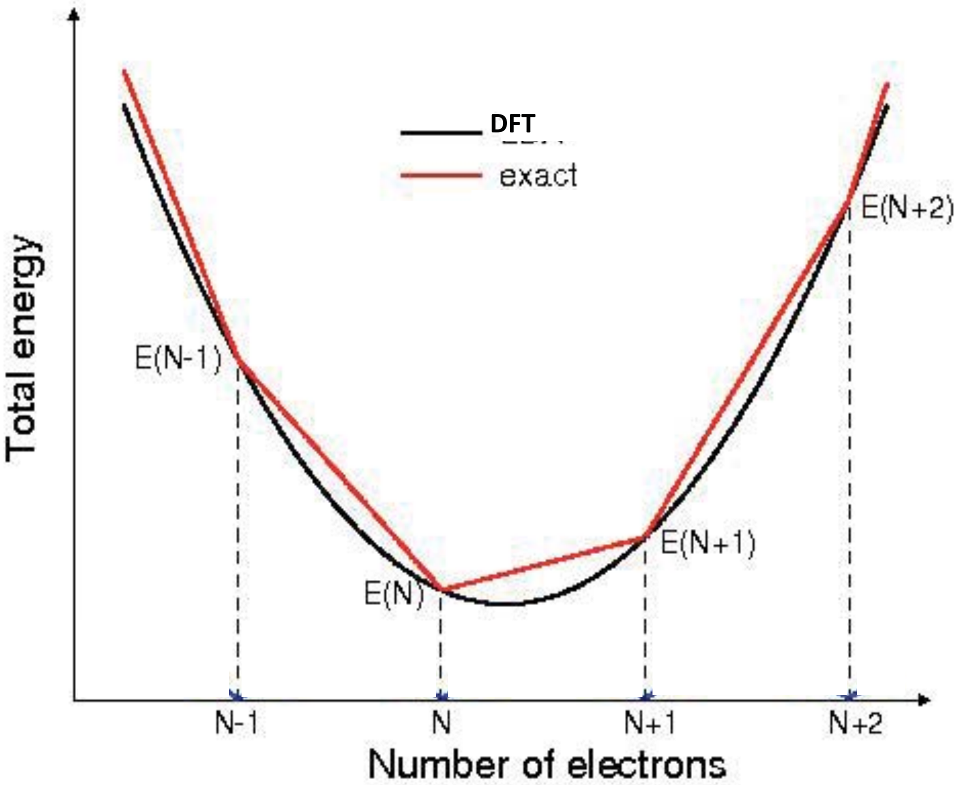
Getting rid of curvature

$$E_{exact} \neq E_{DFT}$$



<u>The (approximate) DFT energy</u> has an *unphysical curvature*

<u>The exact solution</u> *is piecewise linear*

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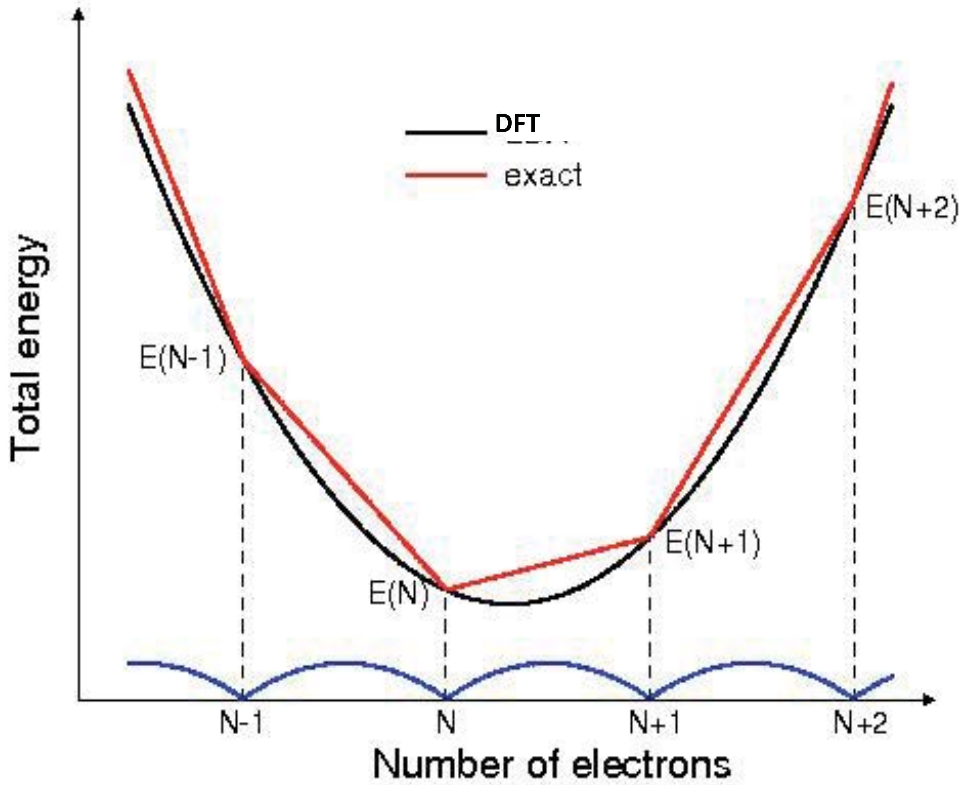

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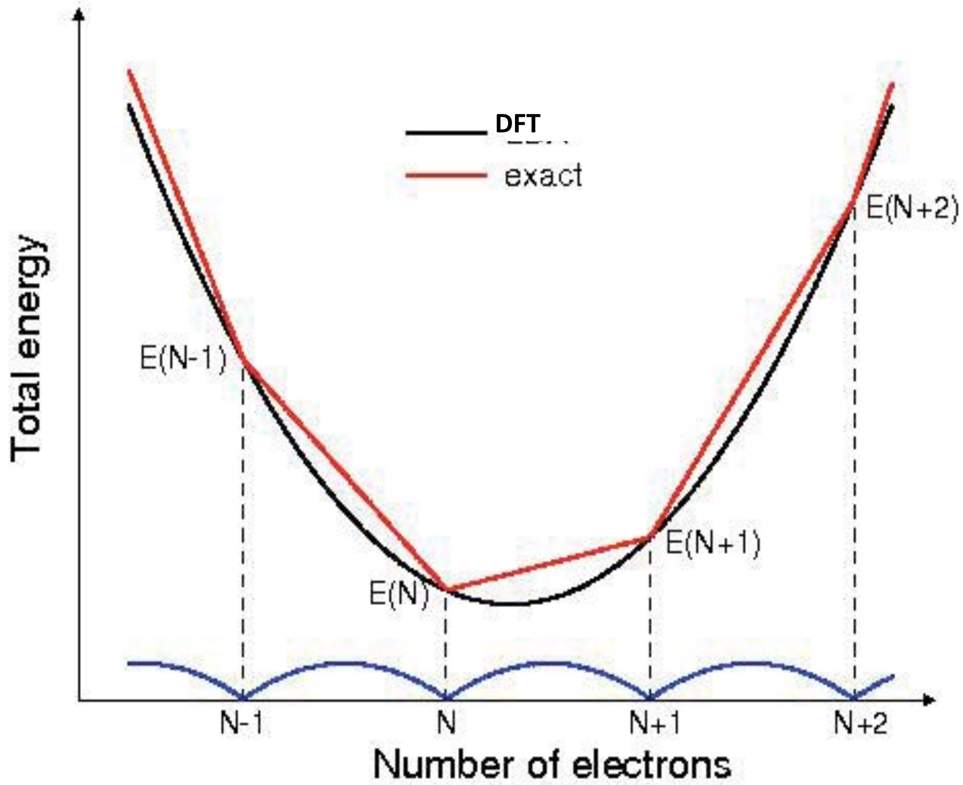
The exact solution *is piecewise linear*

+U correction reproduces the exact solution

Getting rid of curvature

$$E_{exact} \approx E_{DFT} + \sum_I \frac{U^I}{2} \sum_{mm'\sigma} \left[n^{I\sigma}_{mm'} \left(\delta_{mm'} - n^{I\sigma}_{mm'} \right) \right] = E_{DFT+U}$$



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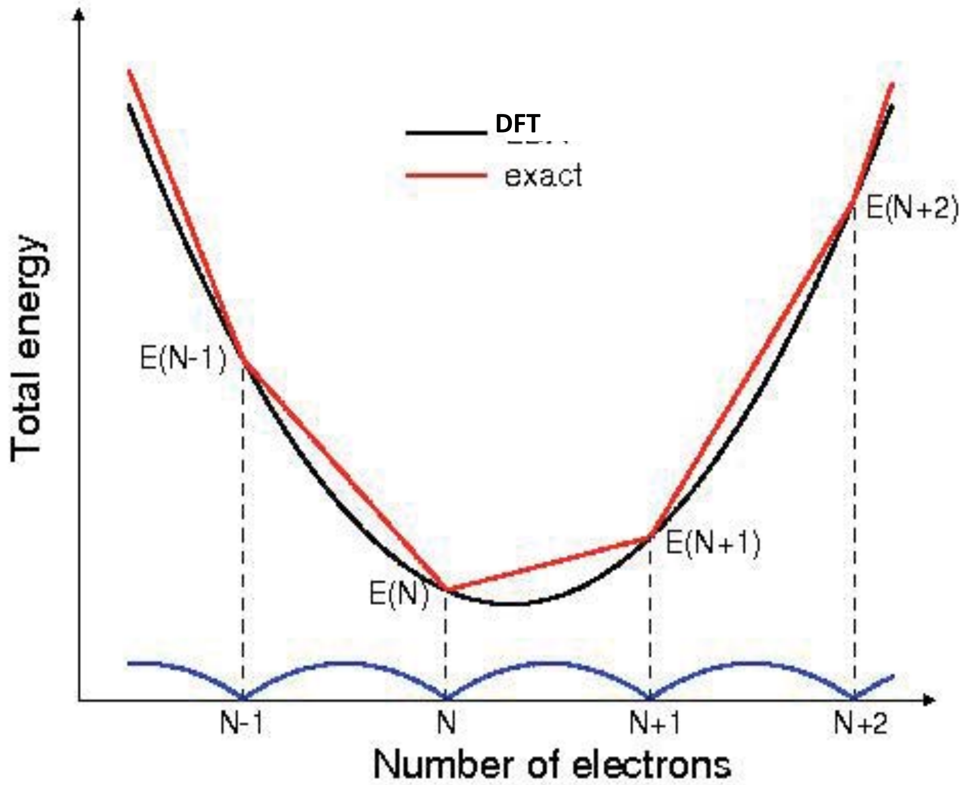

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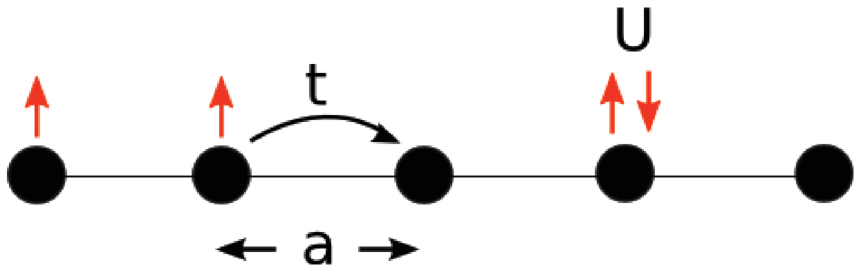
+U correction reproduces the exact solution

$$U = \frac{d^2 E_{DFT}}{dn^2}$$

DFT+U: correcting DFT with the Hubbard model



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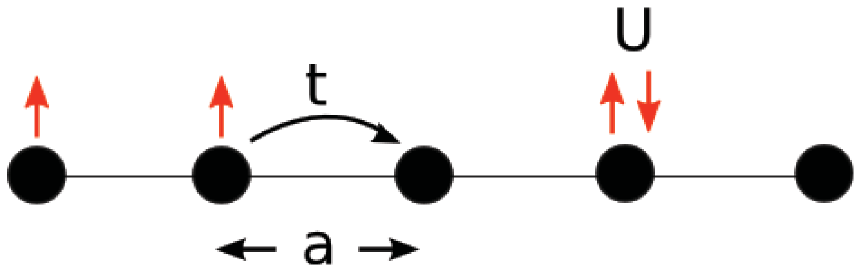

Interface this model with DFT energy:

$$E_{DFT}\left[\rho(\mathbf{r})\right] + \sum_{I,\sigma} \frac{U^I}{2} Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1} - \mathbf{n}^{I\sigma}\right)\right]$$

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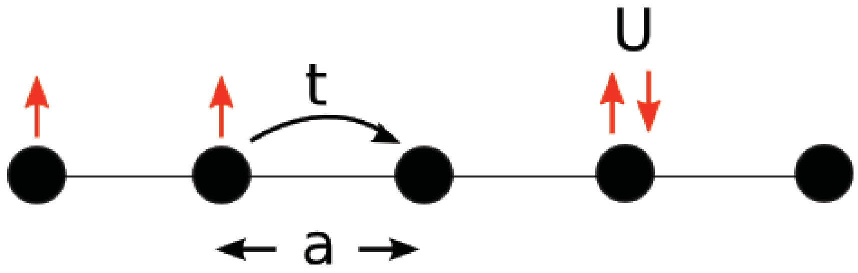

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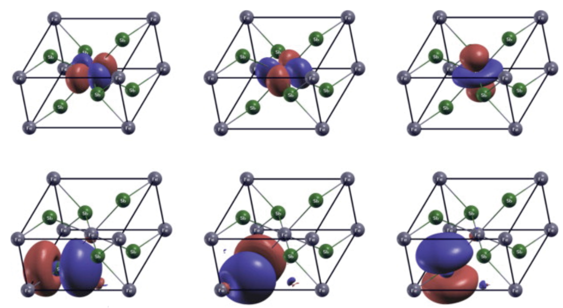
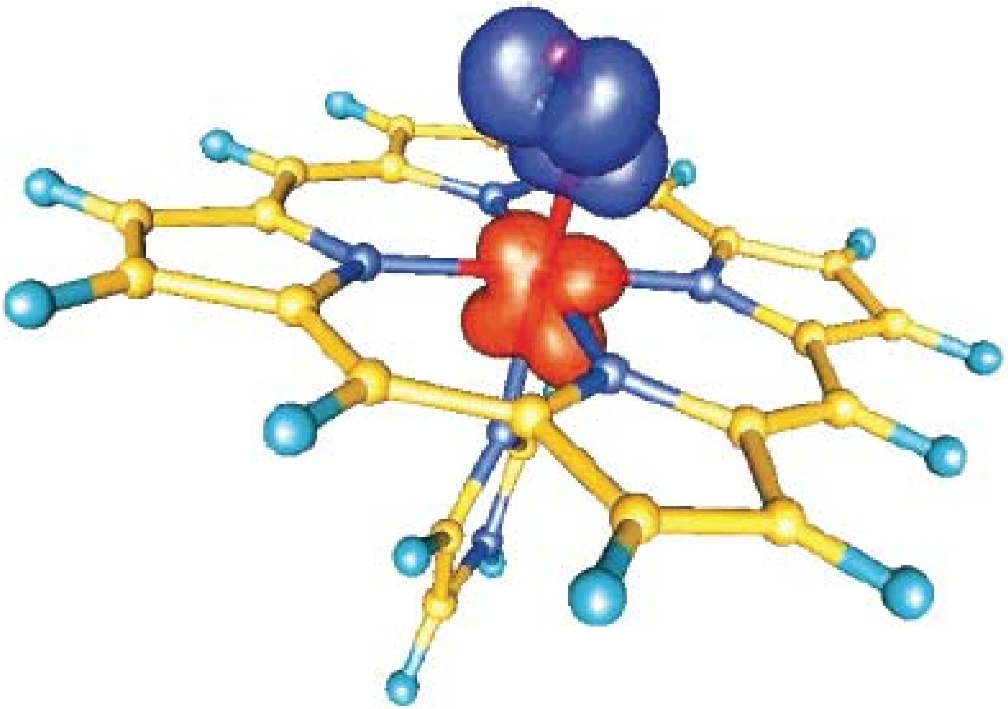
The Hubbard correction acts selectively on localized states

$$n^{I\sigma}_{mm'} = \sum_i f_i \langle \psi_i^\sigma | \phi^I_{m'} \rangle \langle \phi^I_m | \psi_i^\sigma \rangle$$

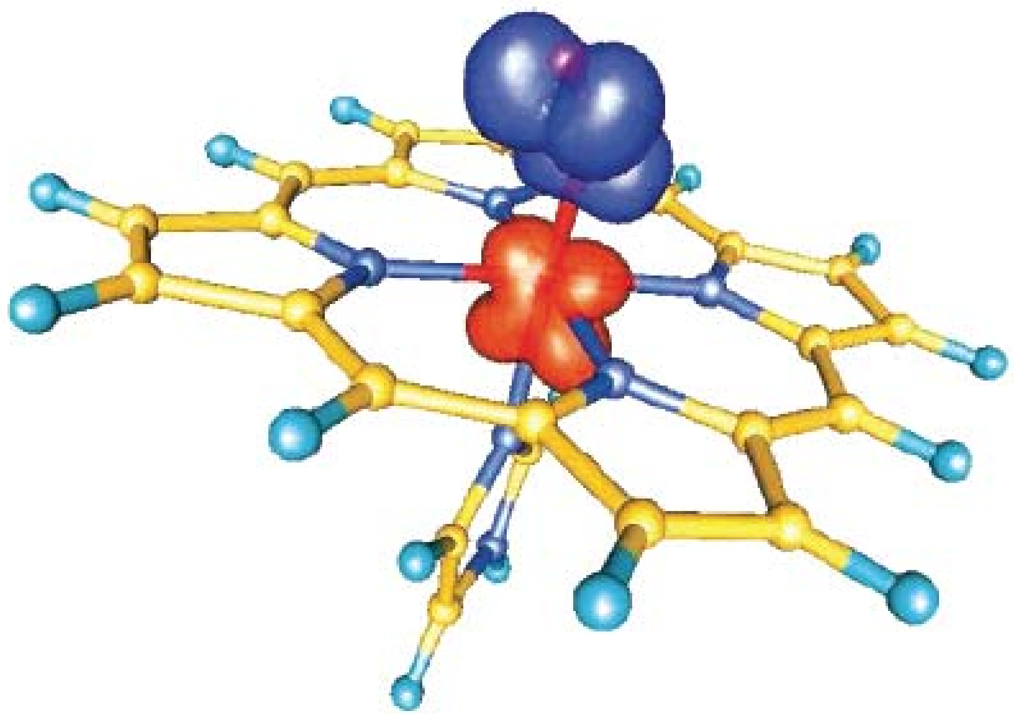


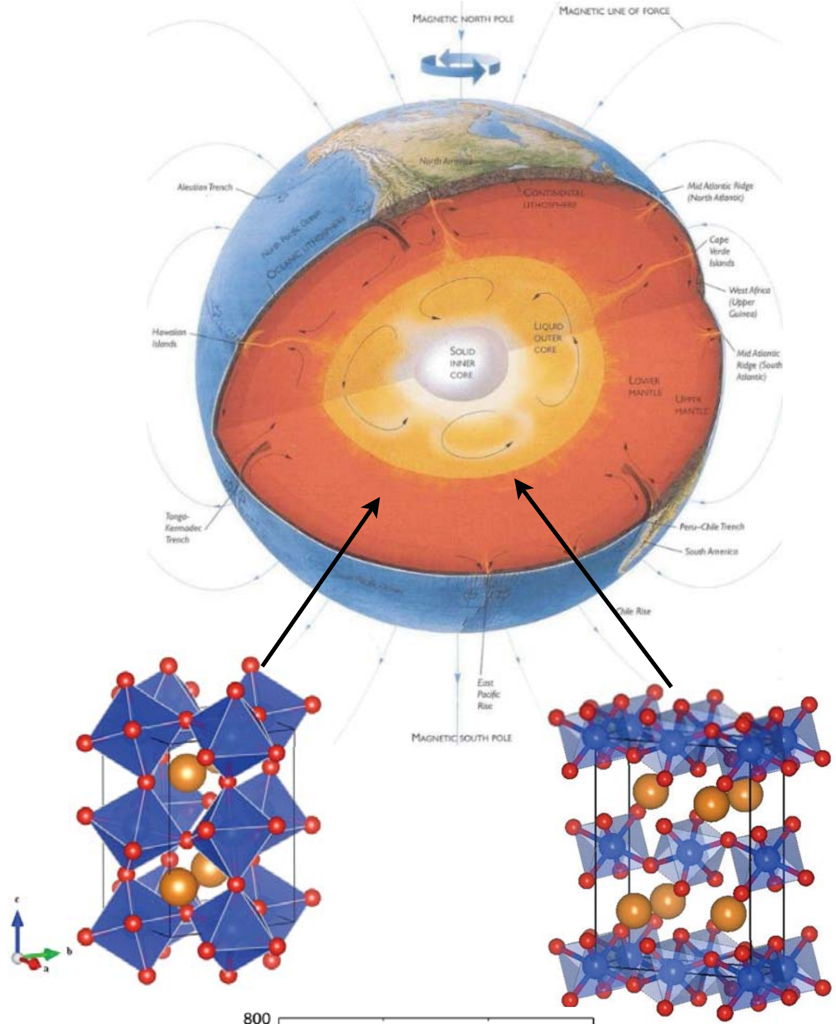
Electron localization and magnetism

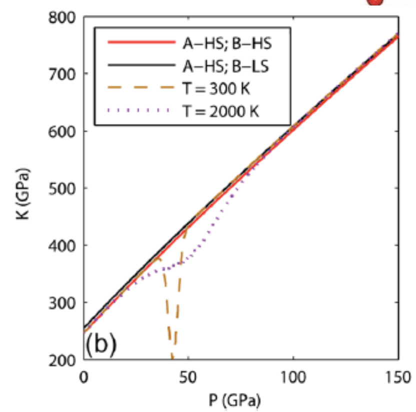
Electron localization and magnetism



Electron localization and magnetism







$LiCoPO_4$: e^- localization and energetics

Occupations of Co ions from projecting the occupied manifold on atomic orbitals (Löwdin charges)

	$LiCoPO_4$	$Li_{0.5}CoPO_4$		$CoPO_4$	F. E.	Voltage
	Co 2+	Co 2+	Co 3+	Co 3+	meV/FU	V
DFT	7.35	7.17	7.16	7.06	-137	3.47

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	Co 2+	Co 2+	Co 3+	Co 3+	meV/FU	V
DFT	7.35	7.17	7.16	7.06	-137	3.47
DFT+U	7.18	7.17	6.82	6.81	54	4.82
Exp					> 0	4.8

$LiMnPO_4$: e^- localization and energetics

Occupations of Mn ions from atomic orbital projections

	$LiMnPO_4$	$Li_{0.5}MnPO_4$		$MnPO_4$
	Mn 2+	Mn 2+	Mn 3+	Mn 3+
DFT	5.30			5.11

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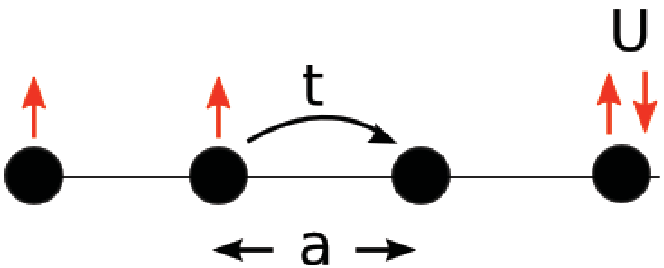
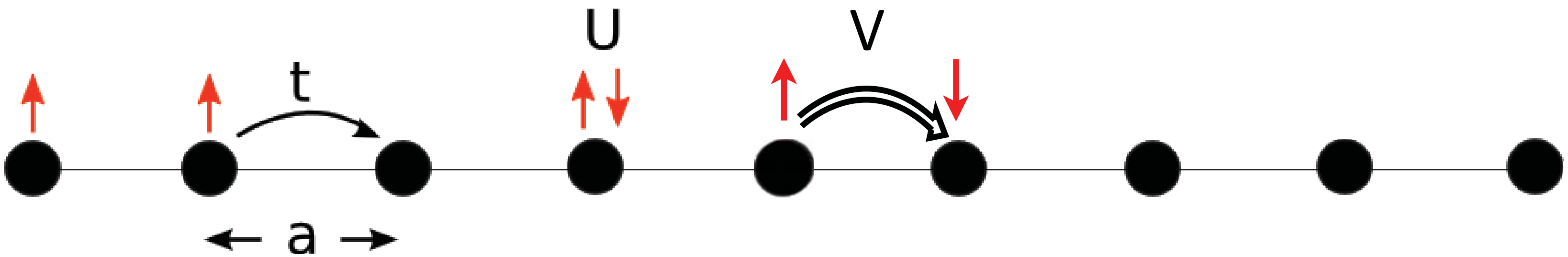
	Mn^{2+}	Mn^{2+}	Mn^{3+}	Mn^{3+}
DFT	5.30	5.19	5.17	5.11
DFT+U	5.19	5.11	5.05	4.96

	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 4.1
DFT	63	2.82
DFT+U	212	4.31

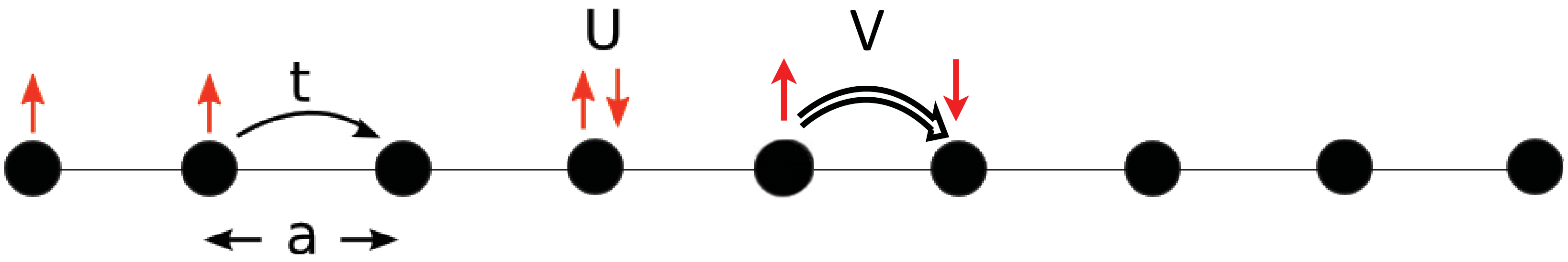
Localization and covalency: DFT+U+V



Localization and covalency: DFT+U+V



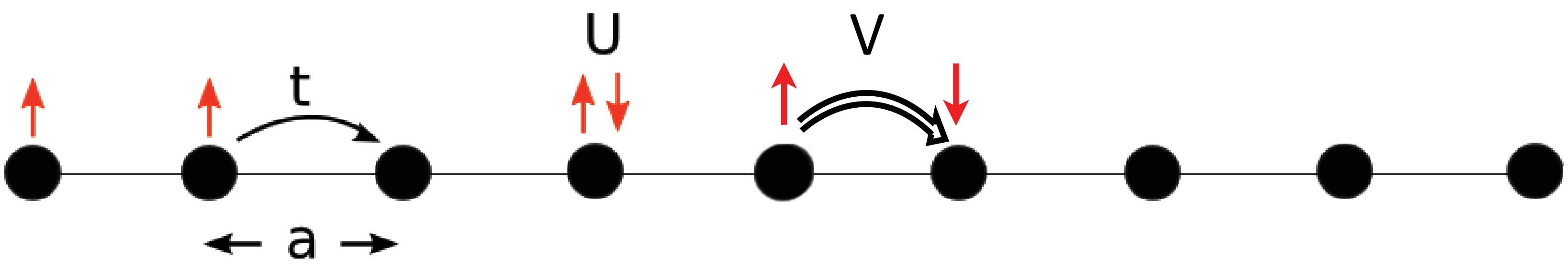
Localization and covalency: DFT+U+V



The same interface procedure with DFT now originates the DFT+U+V functional

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

Localization and covalency: DFT+U+V



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DFT+U+V captures electronic localization even in presence of **hybridization**

V. L. Campo Jr and M. Cococcioni, J. Phys.: Condens Matter 22, 055602 (2010)

$LiMnPO_4$: e^- localization and energetics

Occupations of Mn ions from atomic orbital projections

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	$LiMnPO_4$	$Li_{0.5}MnPO_4$		$MnPO_4$
	Mn^{2+}	Mn^{2+}	Mn^{3+}	Mn^{3+}
DFT	5.30	5.19	5.17	5.11
DFT+U	5.19	5.11	5.05	4.96
DFT+U+V	5.23	5.22	4.99	4.99

$LiMnPO_4$: e⁻ localization and energetics

Occupations of Mn ions from atomic orbital projections

	$LiMnPO_4$	$Li_{0.5}MnPO_4$		$MnPO_4$
	Mn^{2+}	Mn^{2+}	Mn^{3+}	Mn^{3+}
DFT	5.30	5.19	5.17	5.11
DFT+U	5.19	5.11	5.05	4.96
DFT+U+V	5.23	5.22	4.99	4.99

	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 4.1
DFT	63	2.82
DFT+U	212	4.31
DFT+U+V	206	4.15

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

$LiFePO_4$: e^- localization and energetics

Occupations of Fe ions from atomic orbital projections

	$LiFePO_4$	$Li_{0.5}FePO_4$		$FePO_4$
	Fe 2+	Fe 2+	Fe 3+	Fe 3+
DFT	6.22	6.11	6.08	5.93
DFT+U	6.19	6.19	5.68	5.65
DFT+U+V	6.22	6.22	5.77	5.76

$LiFePO_4$: e⁻ localization and energetics

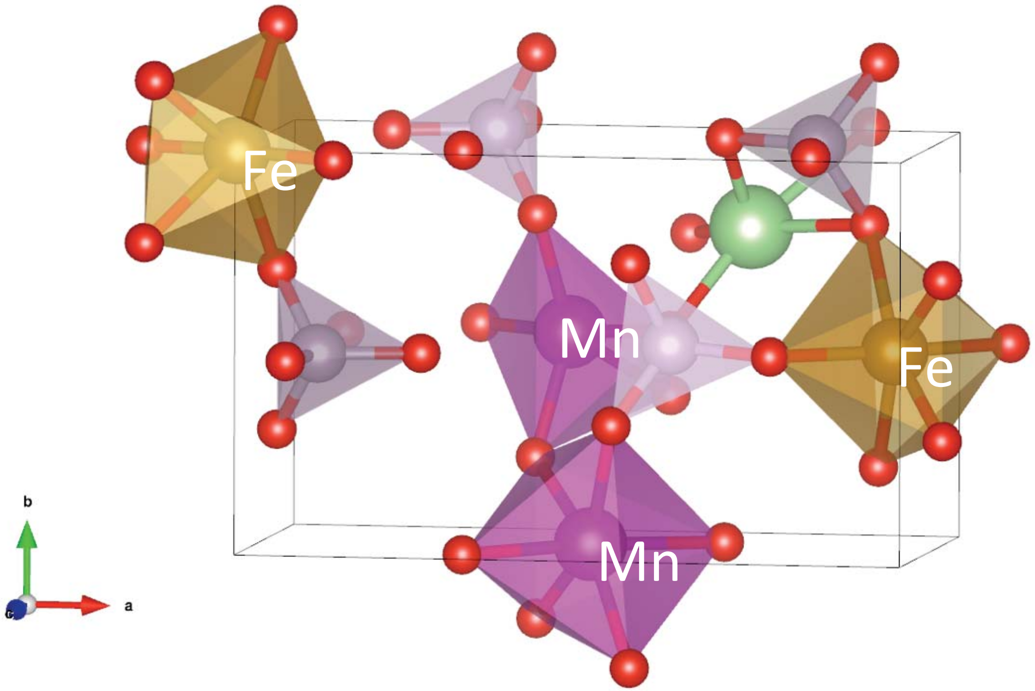
Occupations of Fe ions from atomic orbital projections

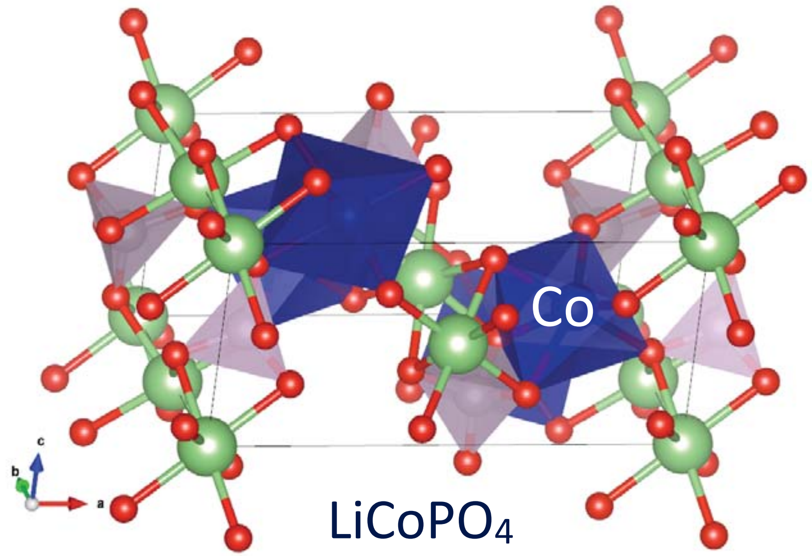
	$LiFePO_4$	$Li_{0.5}FePO_4$		$FePO_4$
	Fe 2+	Fe 2+	Fe 3+	Fe 3+
DFT	6.22	6.11	6.08	5.93
DFT+U	6.19	6.19	5.68	5.65
DFT+U+V	6.22	6.22	5.77	5.76

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 3.5
DFT	-126	2.73
DFT+U	159	4.06
DFT+U+V	128	3.48

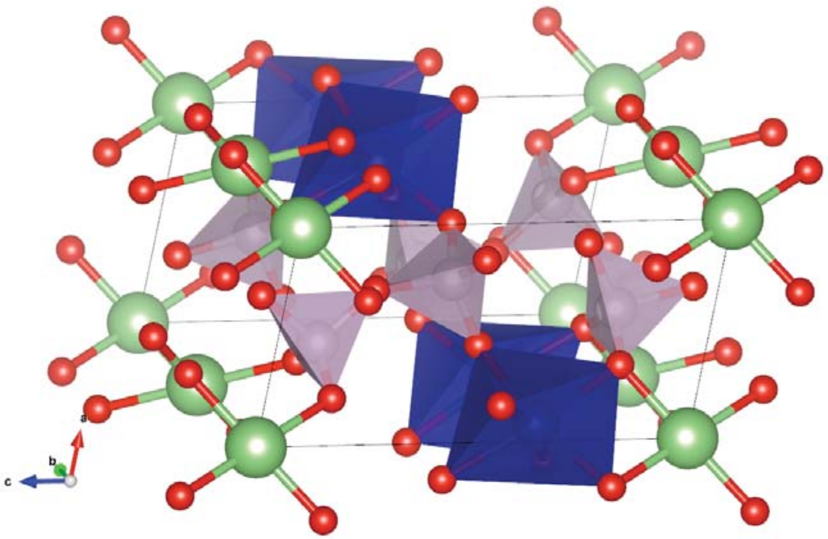
M. Cococcioni and N. Marzari, Phys. Rev. Mater. 3, 033801 (2019)

Other systems under study

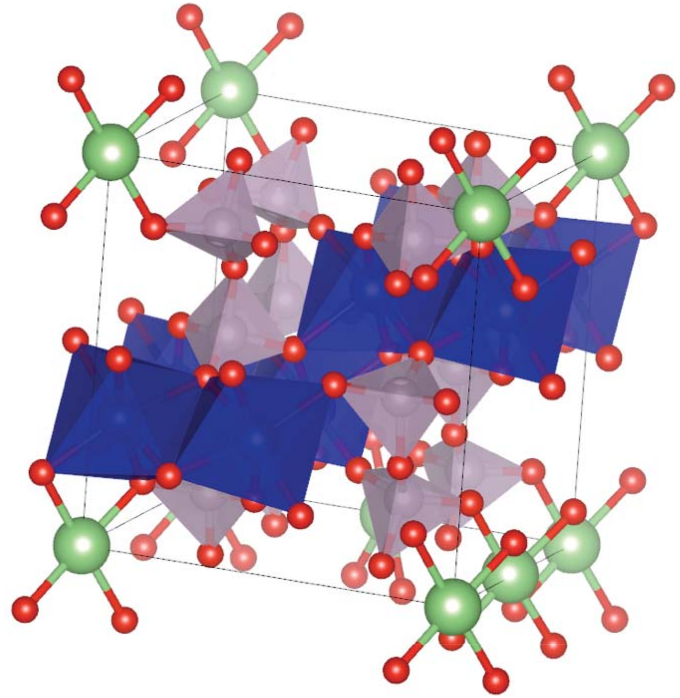




$LiCoPO_4$



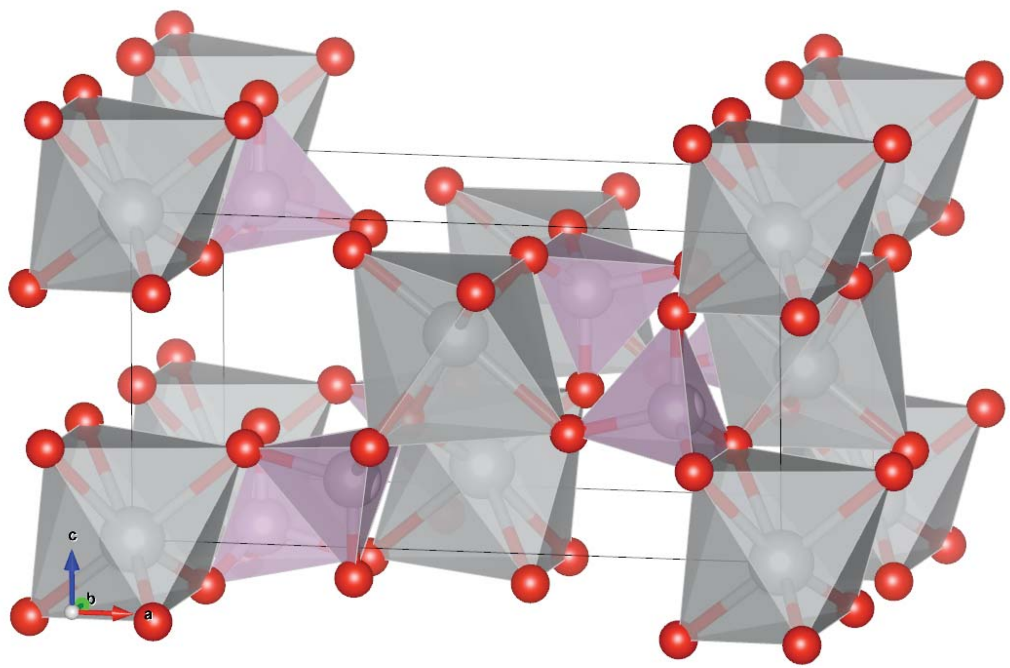
$LiCo_2P_3O_{10}$



$Li_{0.75}Co_2P_3O_{10}$

$LiNiPO_4$: electron localization and voltage

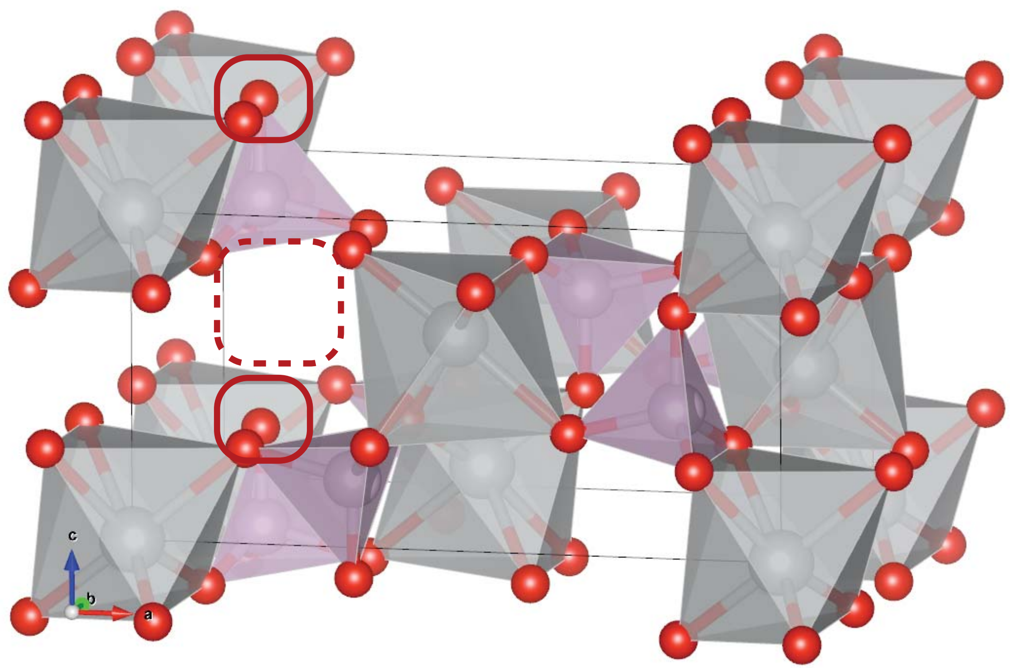
	$LiNiPO_4$			$NiPO_4$			Voltage
	O1	O2	O3	O1	O2	O3	V
Exp							5.1
DFT	4.92	4.92	4.86	4.85	4.87	4.79	3.85
DFT+U+V	4.94	4.95	4.91	4.84	4.81	4.85	5.33
DFT+U*+V	4.94	4.94	4.91	4.97	4.48	4.92	4.81



$LiNiPO_4$: electron localization and voltage

	$LiNiPO_4$			$NiPO_4$			Voltage
	O1	O2	O3	O1	O2	O3	V
Exp							5.1
DFT	4.92	4.92	4.86	4.85	4.87	4.79	3.85
DFT+U+V	4.94	4.95	4.91	4.84	4.81	4.85	5.33
DFT+U*+V	4.94	4.94	4.91	4.97	4.48	4.92	4.81

Li vacancies leave holes in the p states of the O ions closest to the vacant site.
These O also develop a finite magnetization



Higher voltage/capacity materials?

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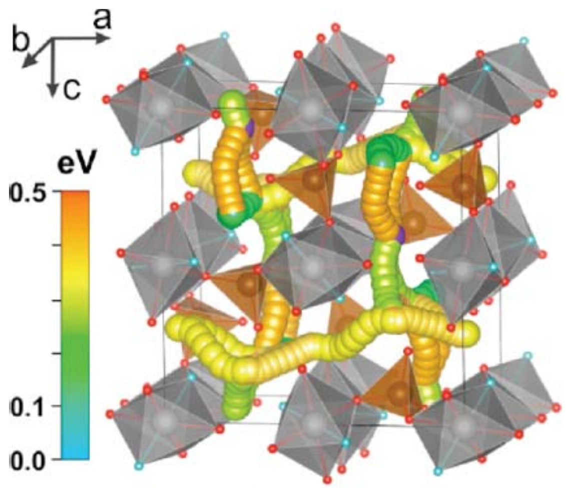
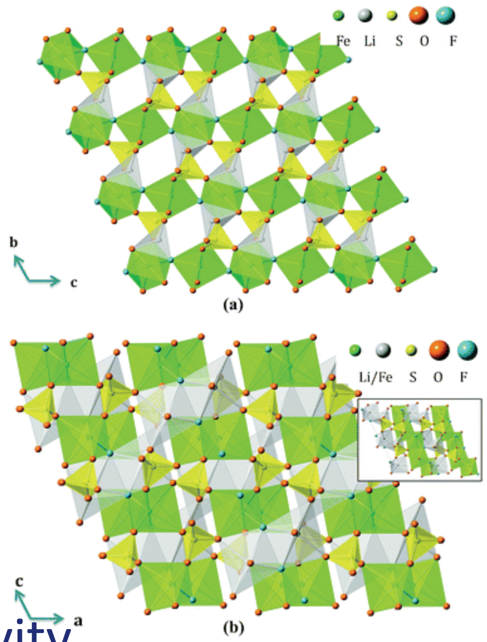


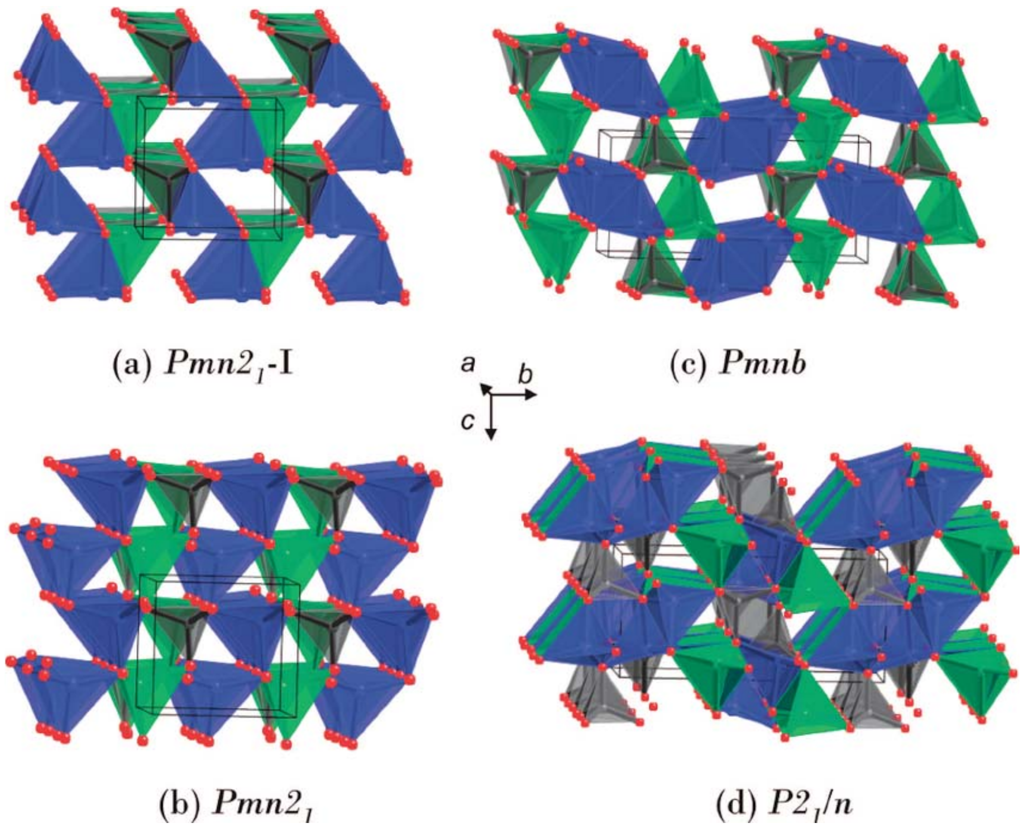
Li_2CoPO_4F



Fluoro-sulphates
or phosphates
Higher voltage
from F electronegativity

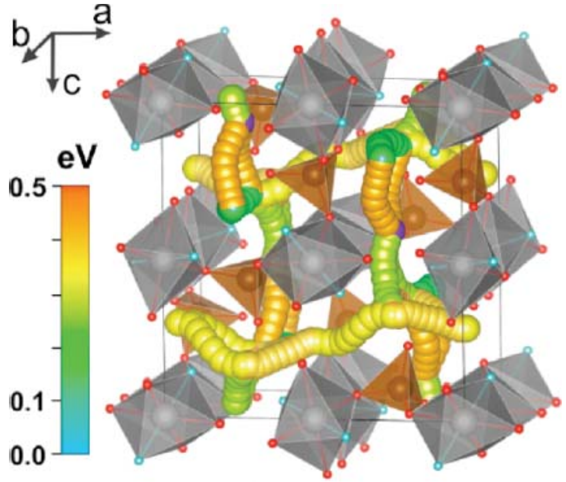
$LiFeSO_4F$

Higher voltage/capacity materials?



Ortho-silicates: Li_2MSiO_4

Higher voltage: M^{2+} to M^{4+}



Li_2CoPO_4F

Fluoro-sulphates
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Higher voltage
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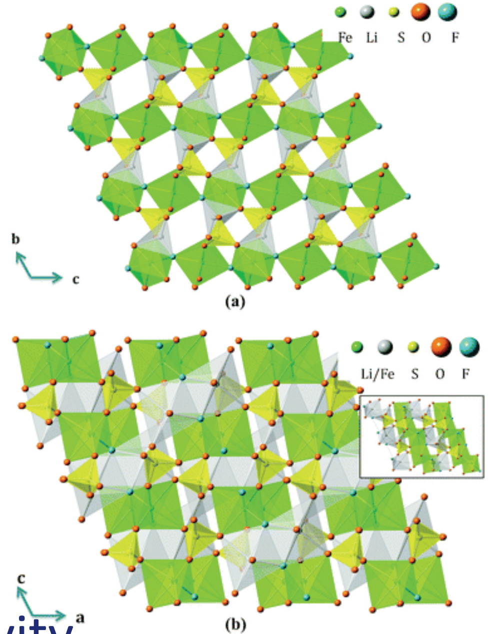
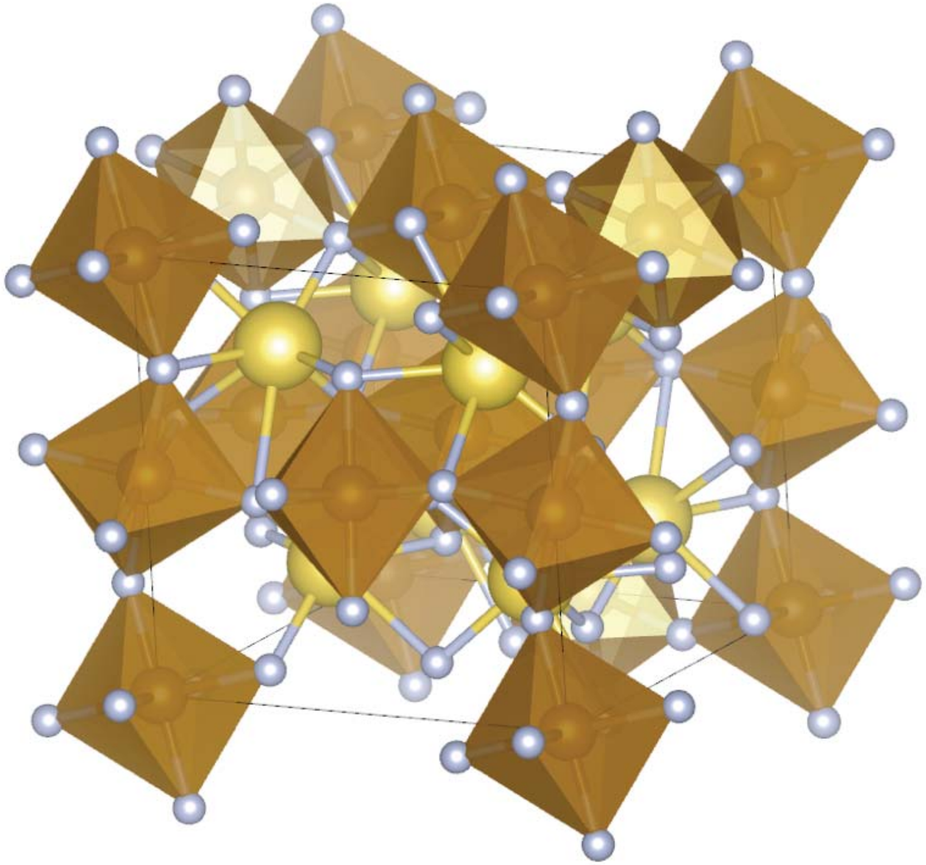


$LiFeSO_4F$

Under development

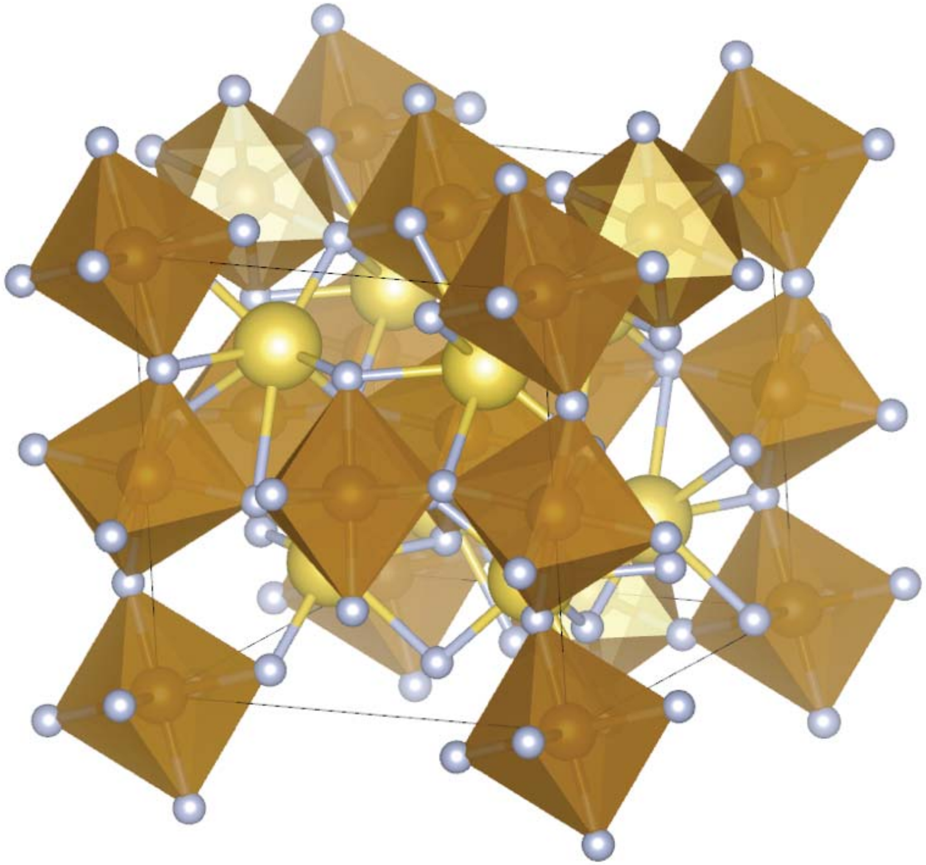
Under development



$NaFeF_3$ for Na-ion batteries

(with C. Tealdi, E. Quartarone,
@ Chemistry)

Under development



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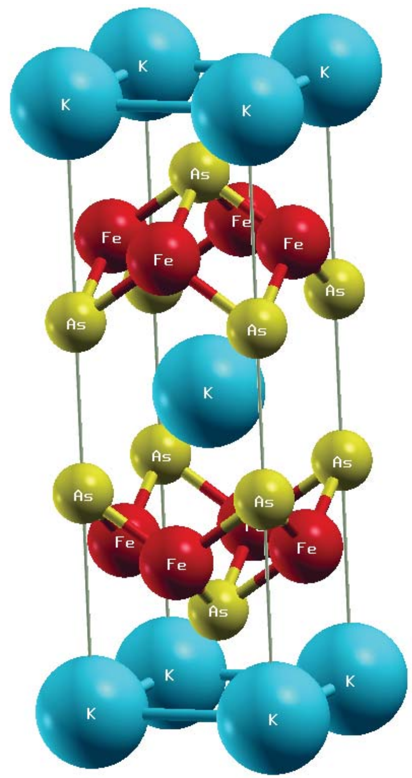
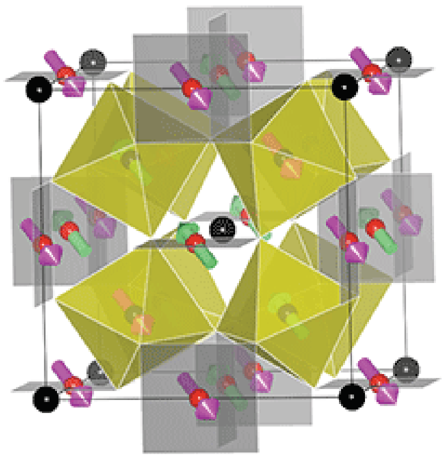


Fe-based superconductors, orbital-dependent physics (P. Carretta, G. Prando)

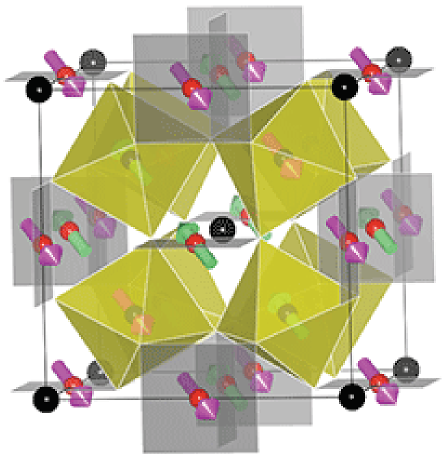
Other systems of interest

Other systems of interest



Perovskites and other complex oxides
coupled electronic, magnetic, structural transitions,
multiferroics, spintronics, photonics, functional materials
E.g. nickelates, manganites

Other systems of interest



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layered perovskites for solar cells

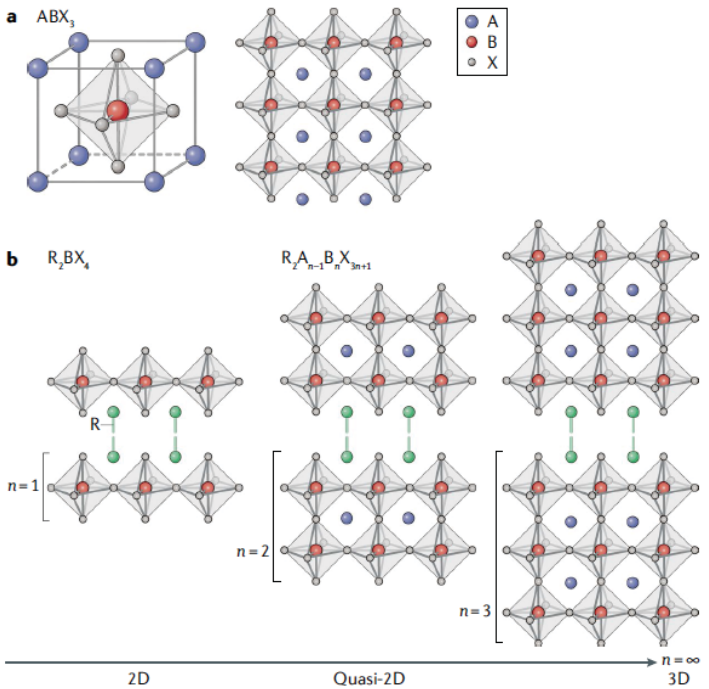
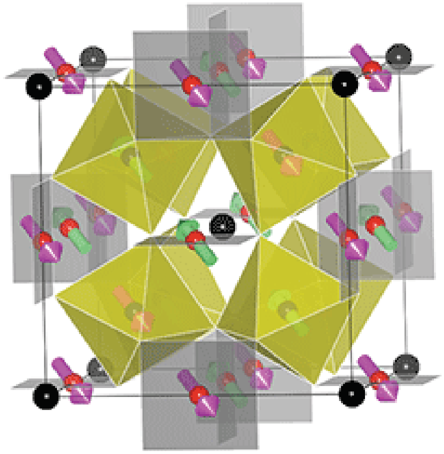


Fig. 1 Crystal structure of 3D (a) and hybrid (2D - 3D) perovskites (b) with various thicknesses of the inorganic layers. Adapted from G. Grancini and M. K. Nazeeruddin, Nat. Rev. Mater. 4, 4 (2019)

Other systems of interest



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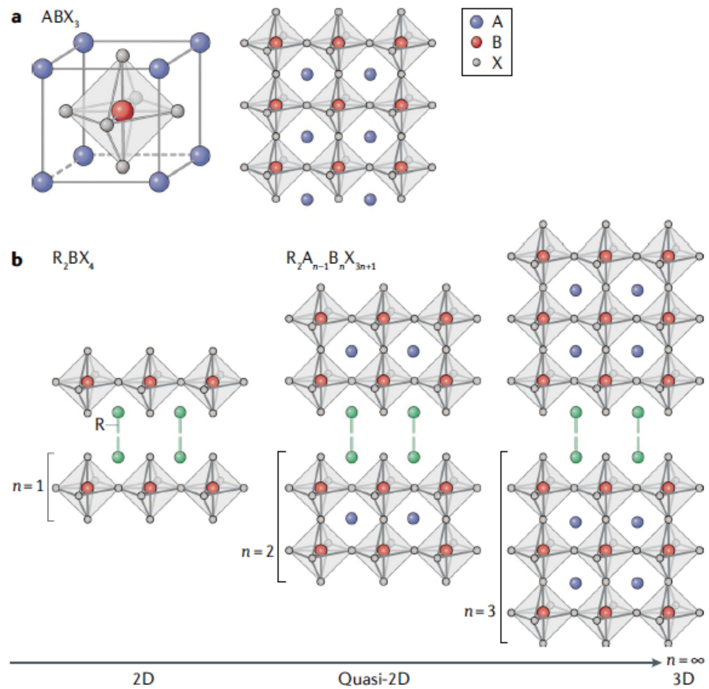

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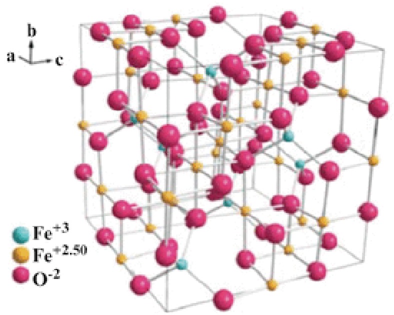
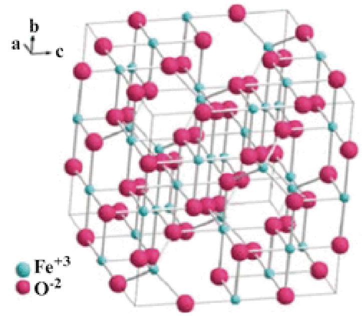
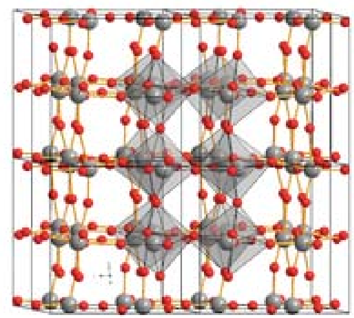
Fe_3O_4



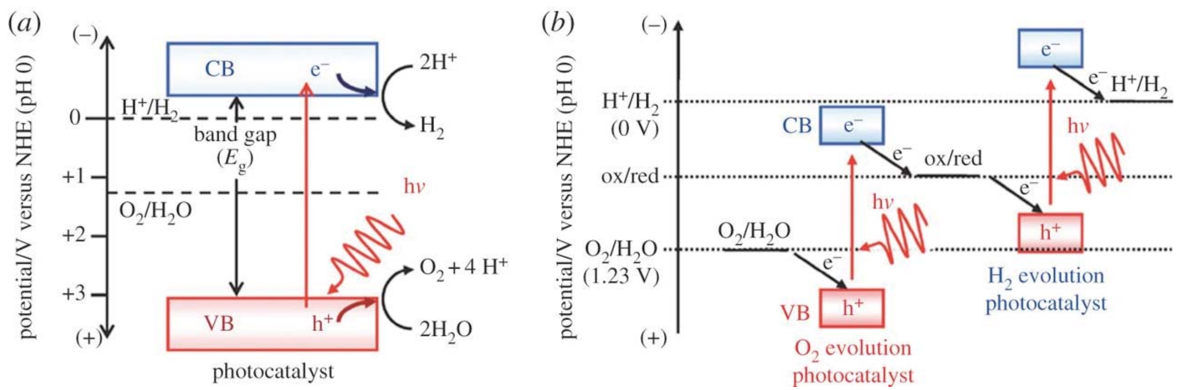
γ-Fe_2O_3



WO_3

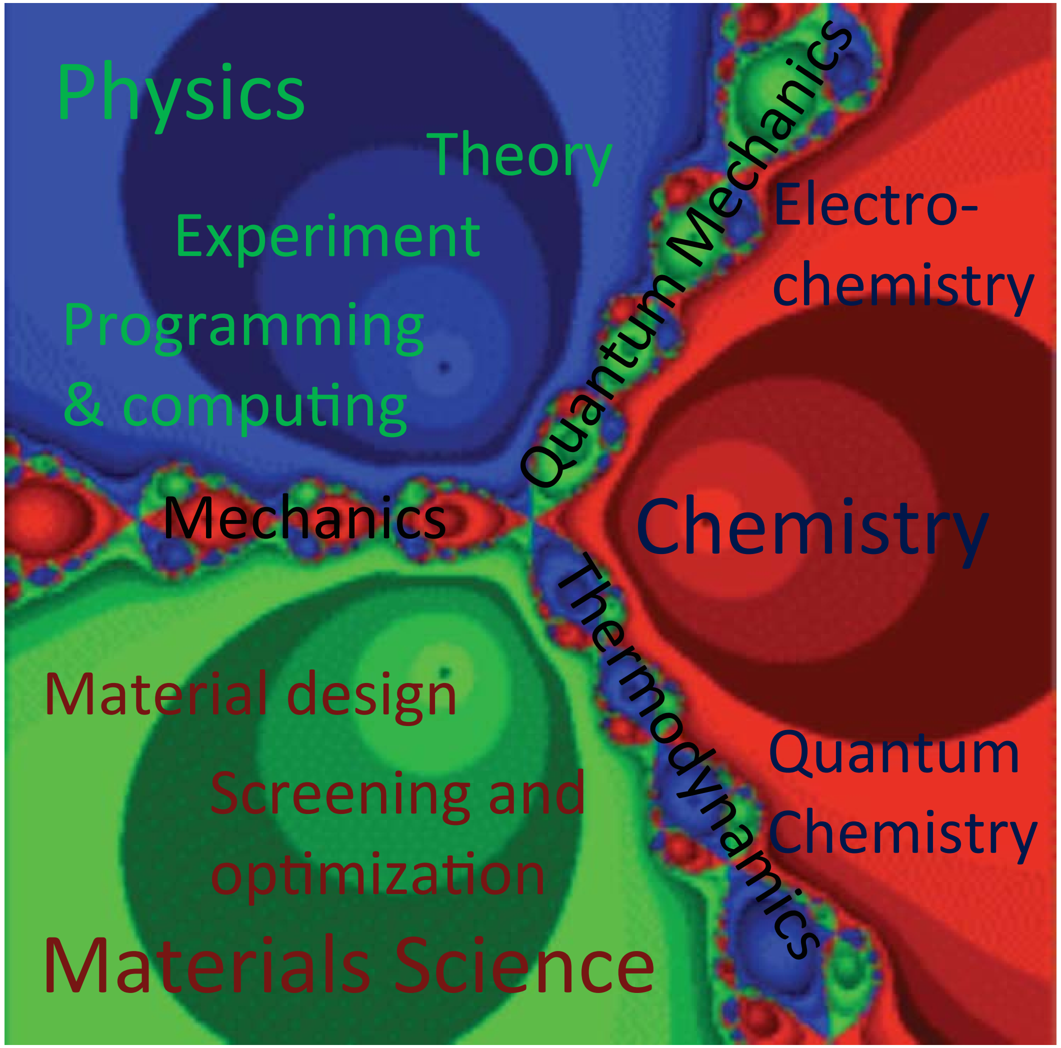


catalysts for water photolysis



Other projects and collaborations

Theory: developing better functionals and interface with existing algorithms (e.g., for transport properties, Raman, XAS, el-ph, excitations)	N. Marzari @ EPFL, Switzerland D. Ceresoli @ CNR, Milan M. Calandra @ Sorbonne, Paris A. Floris @ Lincoln, UK
Other materials for Li- and Na-ion batteries	N. Marzari @ EPFL, Switzerland T. Vegge @ DTU, C. Frayret @ U Picardie C. Tealdi, E. Quartarone @ Chemistry P. C. Mustarelli, R. Ruffo @ UniMib
Layered perovskites for photovoltaics	G. Grancini, L. Malavasi @ Chemistry L. Andreani, D. Gerace
Minerals of inner Earth and their thermoelastic properties	R. M. Wentzcovitch @ Columbia NYC, USA
Complex oxides (e.g., multiferroics, photocatalysts)	I. Dabo @ Penn State, USA S. Piccinin @ CNR, Trieste D. Passerone @ EMPA, Switzerland C. Weber @ King's, London U. Aschauer @ U Bern P. Galinetto
High Tc superconductors	P. Carretta and G. Prando


Physics
Theory
Experiment
Programming
& computing
Quantum Mechanics
Electro-
chemistry
Mechanics
Chemistry
Thermodynamics
Material design
Screening and
optimization
Quantum
Chemistry
Materials Science