

FIRESIDE CHATS FOR LOCKDOWN TIMES

The frontiers and the challenges (Part 3)

Nicola Marzari, EPFL



OUTLINE

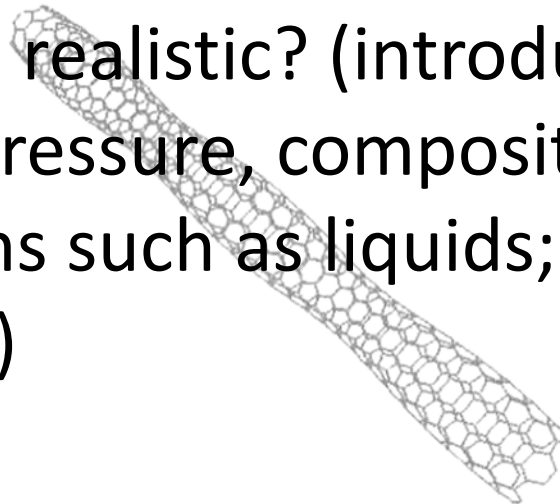
- What is density-functional theory? (Part I)
- What does it take to perform these calculations? (Part II)
- Why is it relevant for science and technology? (Part III)
- What can it do? and cannot do? (Part III)

(to keep in touch, info in the Learn section of the Materials Cloud website, and <https://bit.ly/3eqighg>)

WHAT CAN I DO WITH IT?



- Which properties are “ground state” properties ?
- How accurate are we?
- What is the microscopic origin of the observed behavior ?
- How can we be realistic? (introduce the effects of temperature, pressure, composition; study non-periodic systems such as liquids; go from a few atoms to many)



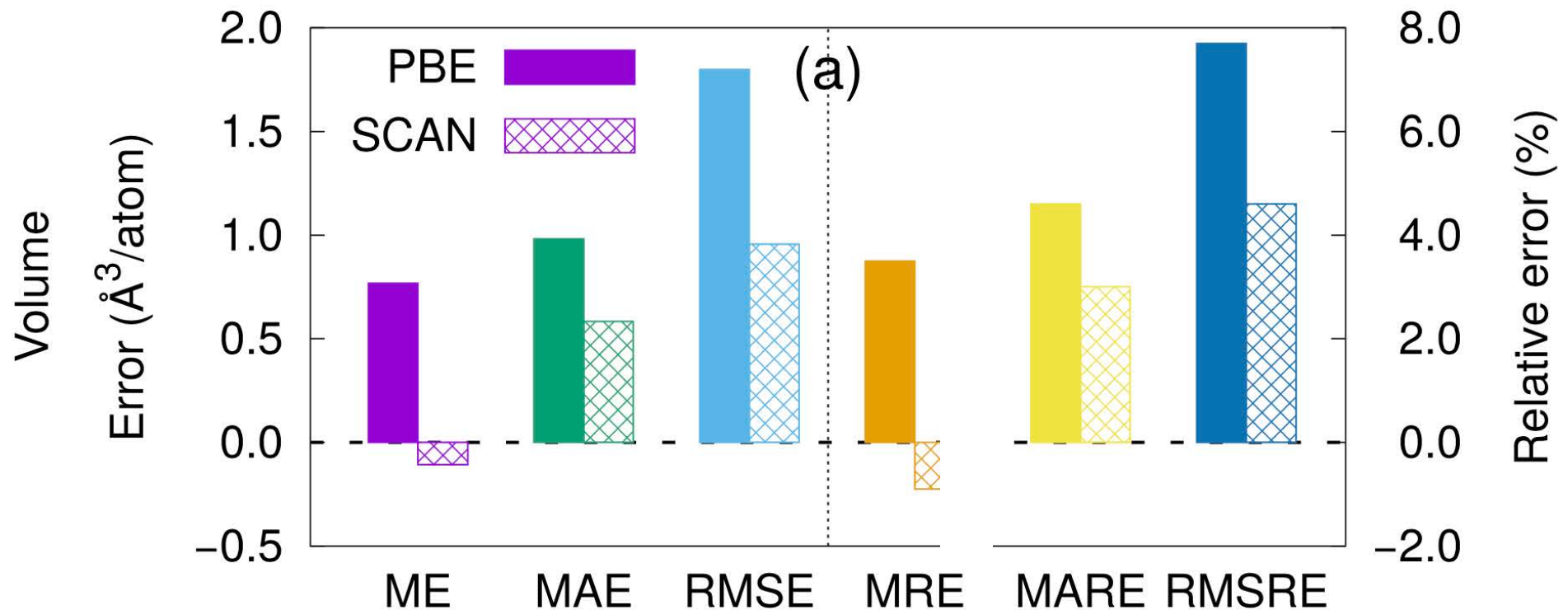
EXAMPLES

- **From total energy to thermodynamics**
 - temperature, pressure, chemical potentials and partial pressures, electrochemical potential, pH
- **From DFT to real electrons**
 - many-body perturbation theory
 - quantum Monte Carlo
 - DMFT, cluster DMFT, DCA

Examples

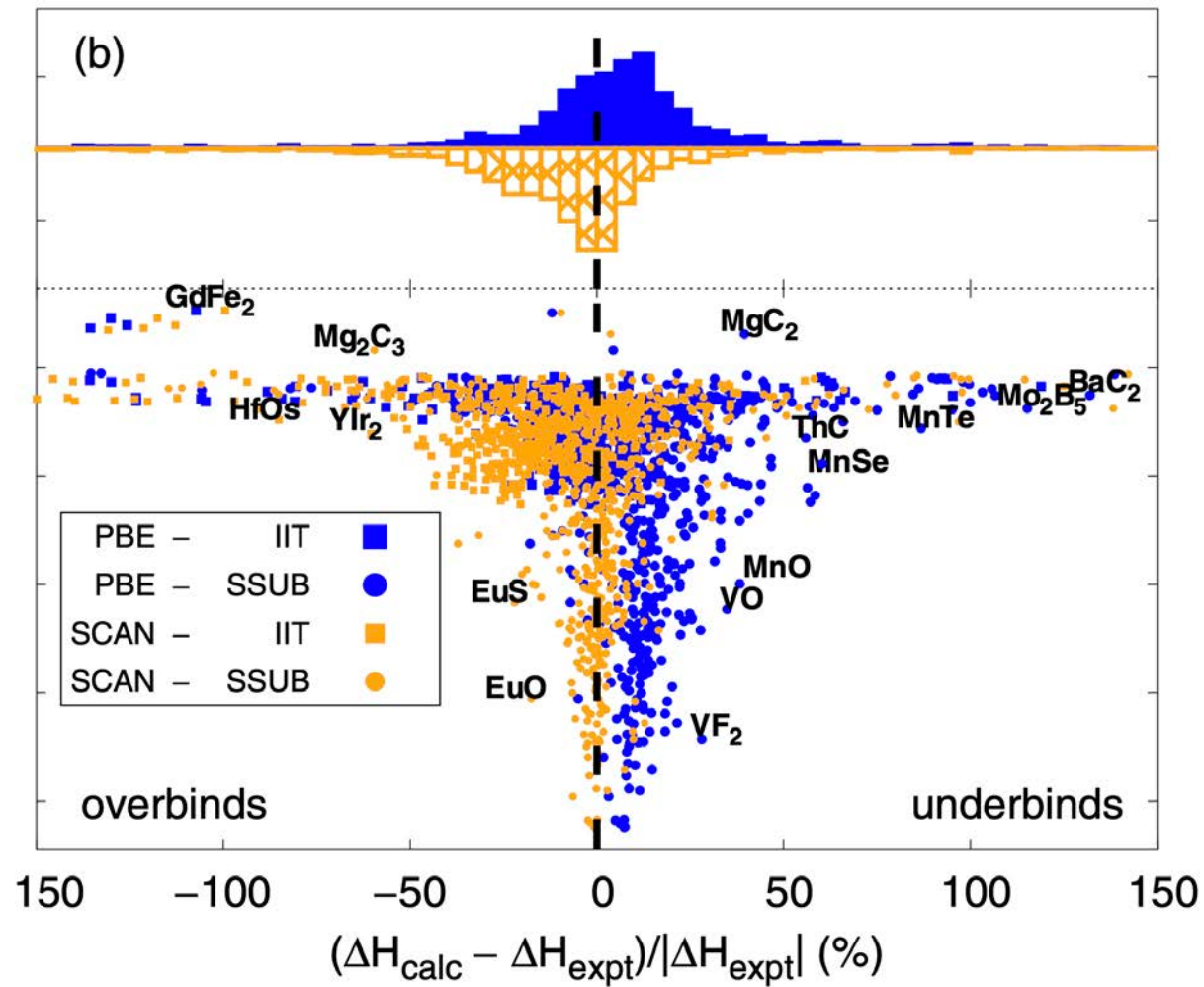
- **Length, time, phase and composition sampling**
 - linear scaling, multiscale,
 - metadynamics, sketch-map
 - minima hopping, random-structure searches
- **Complex properties**
 - phase diagrams
 - spectroscopies and microscopies: IR, Raman, XPS, XANES, NMR, EPR, ARPES, STM, TEM...
 - transport: ballistic, Keldysh, Boltzmann

Easy: equilibrium volume



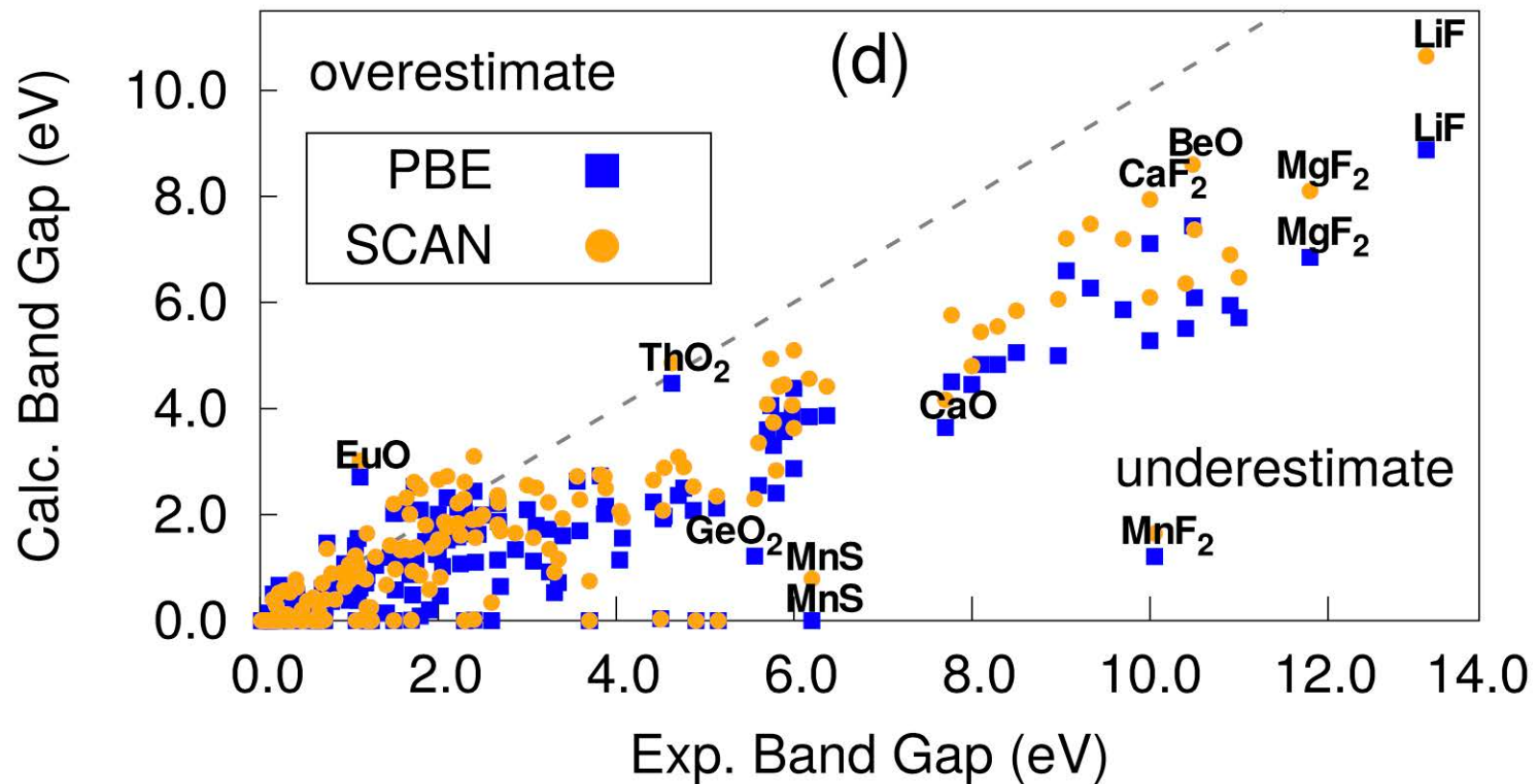
Eric B. Isaacs and Chris Wolverton, *Phys. Rev. Materials* 2, 06380 (2018)

Difficult: formation energies



Eric B. Isaacs and Chris Wolverton, *Phys. Rev. Materials* 2, 06380 (2018)

Out-of-bounds: (transport) band gaps



Eric B. Isaacs and Chris Wolverton, *Phys. Rev. Materials* 2, 06380 (2018)

Think beyond the energy



FORCES AND STRESSES IN MOLECULES

$$\frac{dE}{d\lambda} = \int n_{\lambda}(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

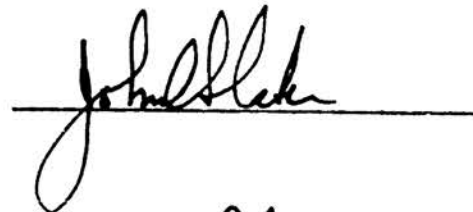
R. P. Feynman

Submitted in Partial Fulfillment of the Requirements for the
Degree of Bachelor of Science in Physics, course VIII,
of the
Massachusetts Institute of Technology

1939

Acceptance:

Instructor in charge of thesis



✓


(Date)

Hellmann-Feynman theorem

$$\frac{dE_\lambda}{d\lambda} = \frac{d}{d\lambda} \langle \Psi | \hat{H}_\lambda | \Psi \rangle = \langle \Psi | d\hat{H}_\lambda / d\lambda | \Psi \rangle$$

Linear-response theory

Perturbation (external potential):

$$V_0 \Rightarrow V_0 + \lambda \Delta V$$

Response (charge density):

$$n_0 \Rightarrow n_\lambda = n_0 + \lambda n_1 + \dots$$

Hellmann-Feynman Theorem:

$$\frac{dE}{d\lambda} = \int n_\lambda(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

Total Energy:

$$E_\lambda = E_0 + \underbrace{\lambda \int n_0(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}}_{1^{\text{st}} \text{ order}} + \underbrace{\frac{\lambda^2}{2} \int n_1(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}}_{2^{\text{nd}} \text{ order}} + \dots$$

S. Baroni *et al.*,
Phys. Rev. Lett.
(’87), Rev. Mod.
Phys (’01)

Linear-response theory

$$\Delta V_{\text{ext}}$$



$$\Delta V_{SCF}(\mathbf{r}) = \Delta V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \Delta n(\mathbf{r}) \mu'_{XC}(n(\mathbf{r}))$$



$$[-\nabla^2 + V_{SCF}(\mathbf{r}) - \epsilon_v] \Delta \psi_v(\mathbf{r}) =$$

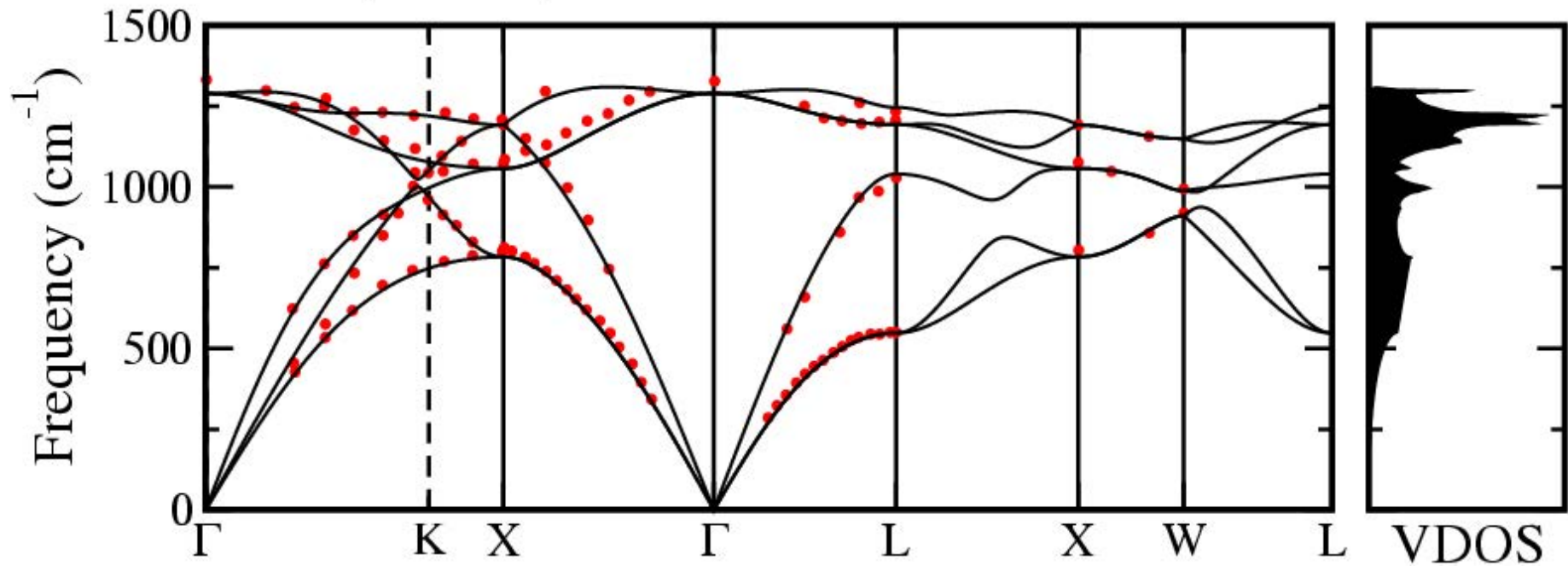
$$[\Delta V_{SCF}(\mathbf{r}) - \langle \psi_v | \Delta V_{SCF} | \psi_v \rangle] \psi_v(\mathbf{r})$$



$$\Delta n(\mathbf{r}) = 2 \sum \psi_v^*(\mathbf{r}) \Delta \psi_v(\mathbf{r}) \theta(\epsilon_F - \epsilon_v)$$

S. Baroni *et al.*,
Phys. Rev. Lett.
(’87), Rev. Mod.
Phys (’01)

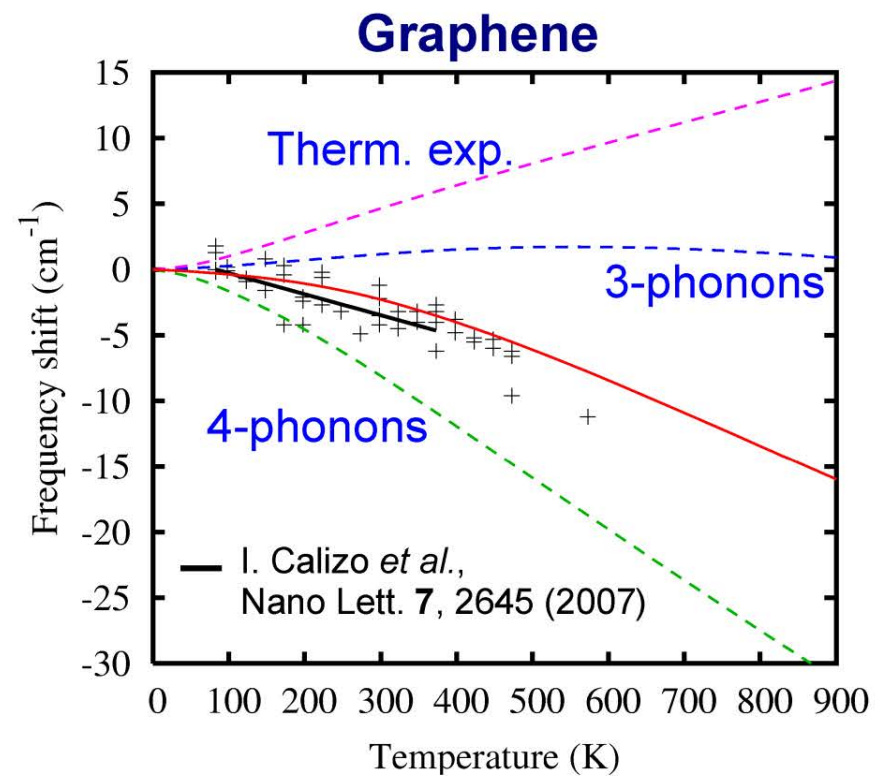
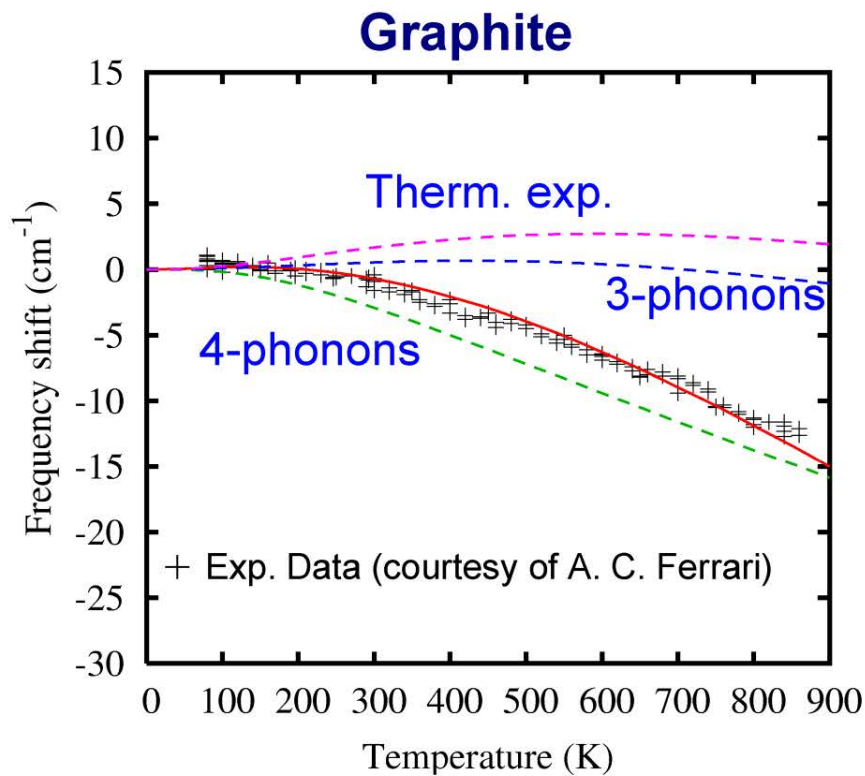
Phonons and temperature



- A harmonic crystal is exactly equivalent to a Bose-Einstein gas of independent, harmonic oscillators.

Vibrational spectroscopies: IR, Raman

Frequency shift of the E_{2g} mode



N. Bonini *et al.*, Phys. Rev. Lett. **99**, 176802 (2007)

Magnetic spectroscopies: NMR Chemical Shifts

TABLE I. ^{11}B NMR chemical shifts δ_{BTE} and ^{13}C NMR chemical shifts δ_{TMS} in the closo-borane molecules. By ortho, meta, and antipodal we indicate the B atoms which are 1st, 2nd, and 3rd nearest neighbors of the C atom, respectively.

Molecule	Atomic site	Experiment	Theory
$(\text{B}_{12}\text{H}_{12})^{2-}$ $(\text{B}_{11}\text{CH}_{12})^{-}$	Ortho Meta Antipodal	B δ_{BTE} -14.9 ^a	B δ_{BTE} (-14.9)
		-16.3 ^b	-16.2
		-13.3 ^b	-11.7
		-6.9 ^b	-5.4
$(\text{B}_{11}\text{CH}_{12})^{-}$		C δ_{TMS} 54.6 ^c	C δ_{TMS} (54.6)

^aIn CD_3CN solvent, Ref. [18].

^bIn hexadeuterioacetone, Ref. [19].

^cRef. [20].

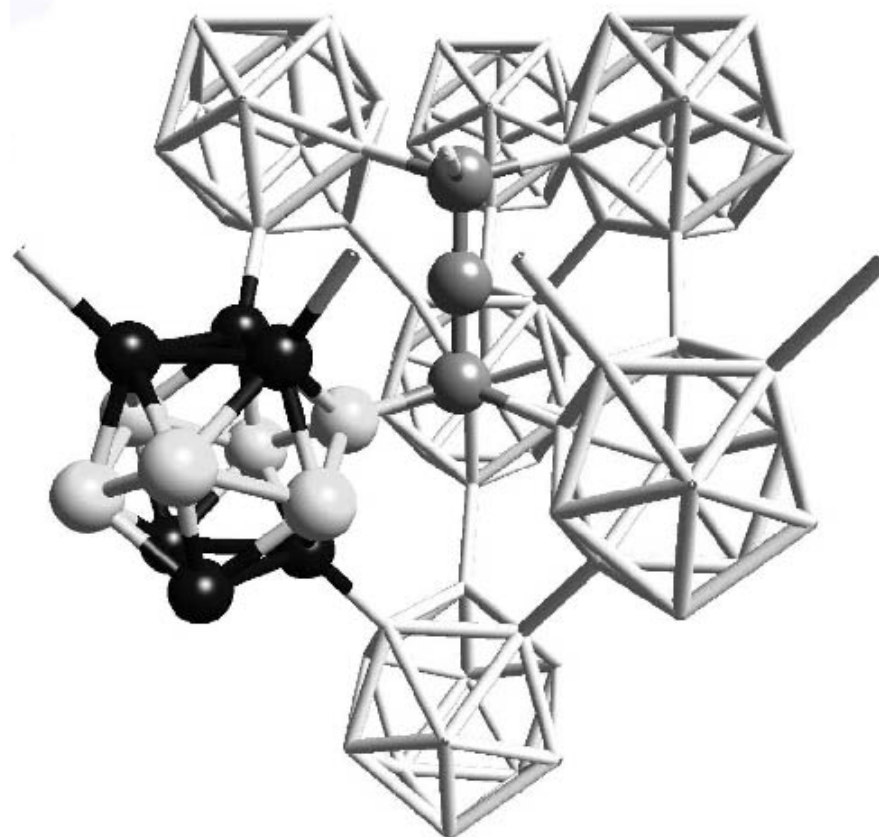


FIG. 1. Atomic structure of B_4C . The black atoms are on the so-called polar sites, bonded to neighboring icosahedra. The white atoms form a puckered hexagon and are in equatorial sites. The grey atoms form the chain, to which the equatorial atoms are bonded.

Sampling excitations

Electronic

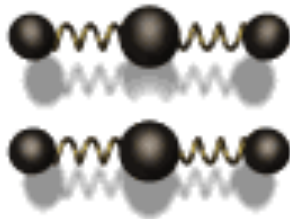
Occupation

Magnetic (electron spin)

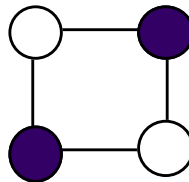
$$\Psi \longrightarrow \Phi$$

$$\uparrow \longrightarrow \downarrow$$

Vibrational



Configurational



In polymers and bio-molecules, vibrational and configurational can not always be distinguished

Conformational

Statistical mechanics on relevant degrees of freedom

Ensemble Collection of microscopic states consistent with thermodynamic boundary conditions

$$P_i = \frac{\exp[-\beta E_i]}{Q} \longrightarrow \text{Probability to be in a given state } i$$

$$Q = \sum_i \exp[-\beta E_i] \longrightarrow \text{Partition Function}$$

$$F = -\beta \ln[Q] \longrightarrow \text{Free energy (Helmholtz)}$$

$$S = -k_B \sum_i P_i \ln(P_i) \longrightarrow \text{Entropy}$$

For the vibrational free energy, analytically!

Quantization of phonons' energy:

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})(n + \frac{1}{2})$$

Partition function of one phonon (microcanonical ensemble - T & V constant):

$$Z_{\mathbf{q},j} = \sum_n \exp(-\frac{\hbar\omega_j(\mathbf{q})}{k_B T}(n + \frac{1}{2})) = \frac{1}{2 \sinh \frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

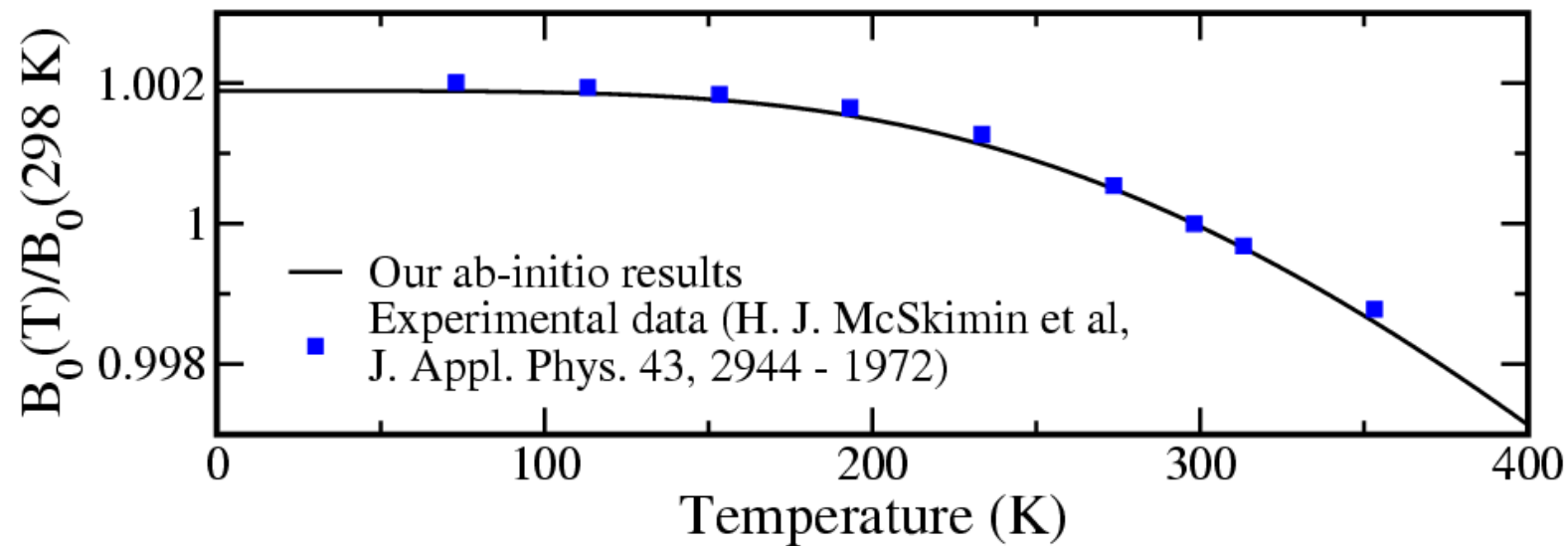
Total partition function:

$$Z_{total} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j} = \frac{1}{\prod_{\mathbf{q},j} 2 \sinh \frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

Free energy: ($\{a_i\}$ = lattice parameters)

$$\begin{aligned} F(\{a_i\}, T) &= E(\{a_i\}) + F_{vib} \\ &= E(\{a_i\}) - k_B T \ln Z_{total} \\ &= E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_{\mathbf{q},j}}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar\omega_{\mathbf{q},j}}{k_B T})) \end{aligned}$$

Thermomechanics (bulk modulus of diamond)

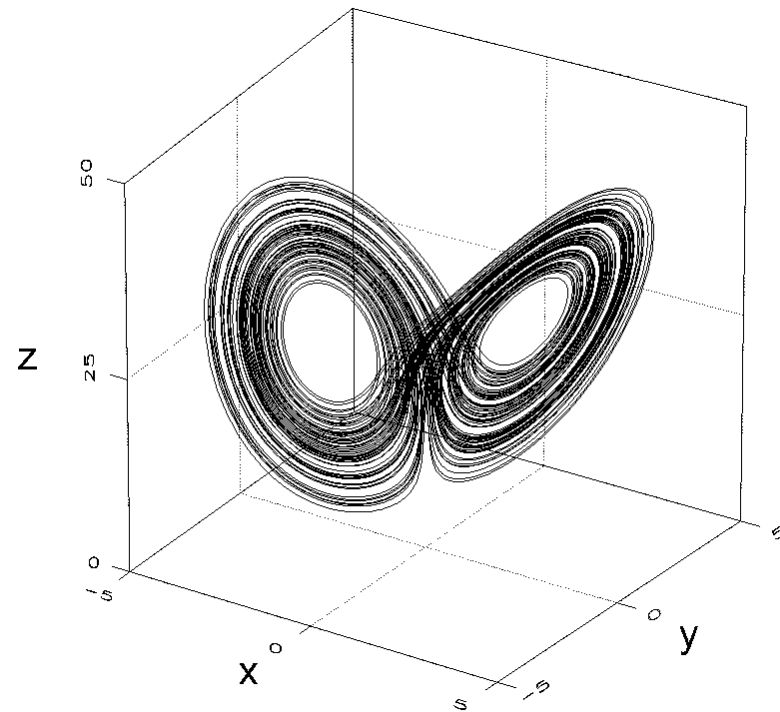


Otherwise, thermodynamical averages

Under hypothesis of ergodicity, we can assume that the temporal average along a trajectory is equal to the ensemble-average over the phase space

$$\langle A \rangle = \frac{\int A \exp(-\beta E) d\vec{r} d\vec{p}}{\int \exp(-\beta E) d\vec{r} d\vec{p}}$$

$$\overline{A} = \frac{1}{T} \int_0^T A(t) dt$$



Molecular dynamics

$$m \frac{d^2 \vec{r}}{dt^2} = \vec{F}(\vec{r}) = -\vec{\nabla} V(\vec{r}) \quad \longrightarrow \quad \begin{array}{l} \vec{r}(t) \\ \vec{v}(t) \end{array}$$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 + (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 - (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \mathbf{a}(t)\Delta t^2 + O(\Delta t^4)$$



A drop to drink

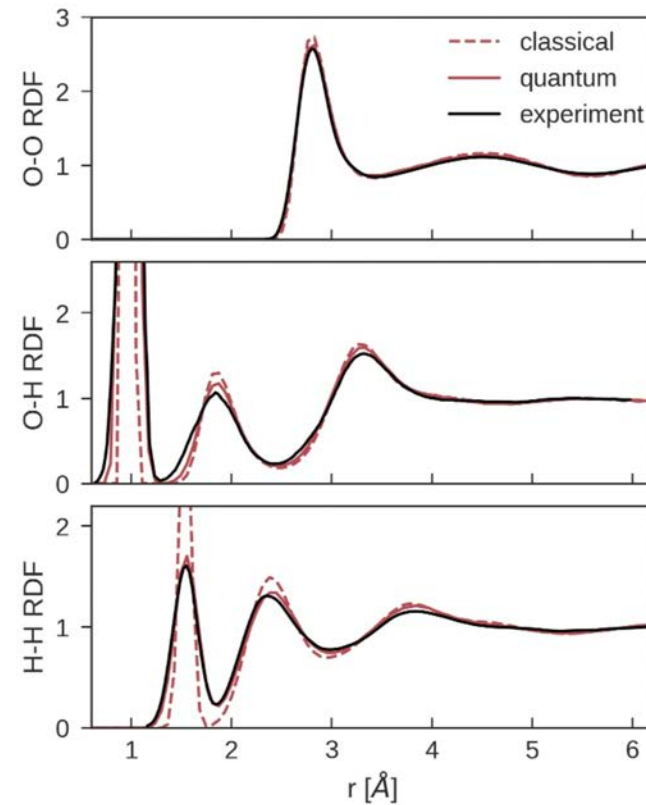
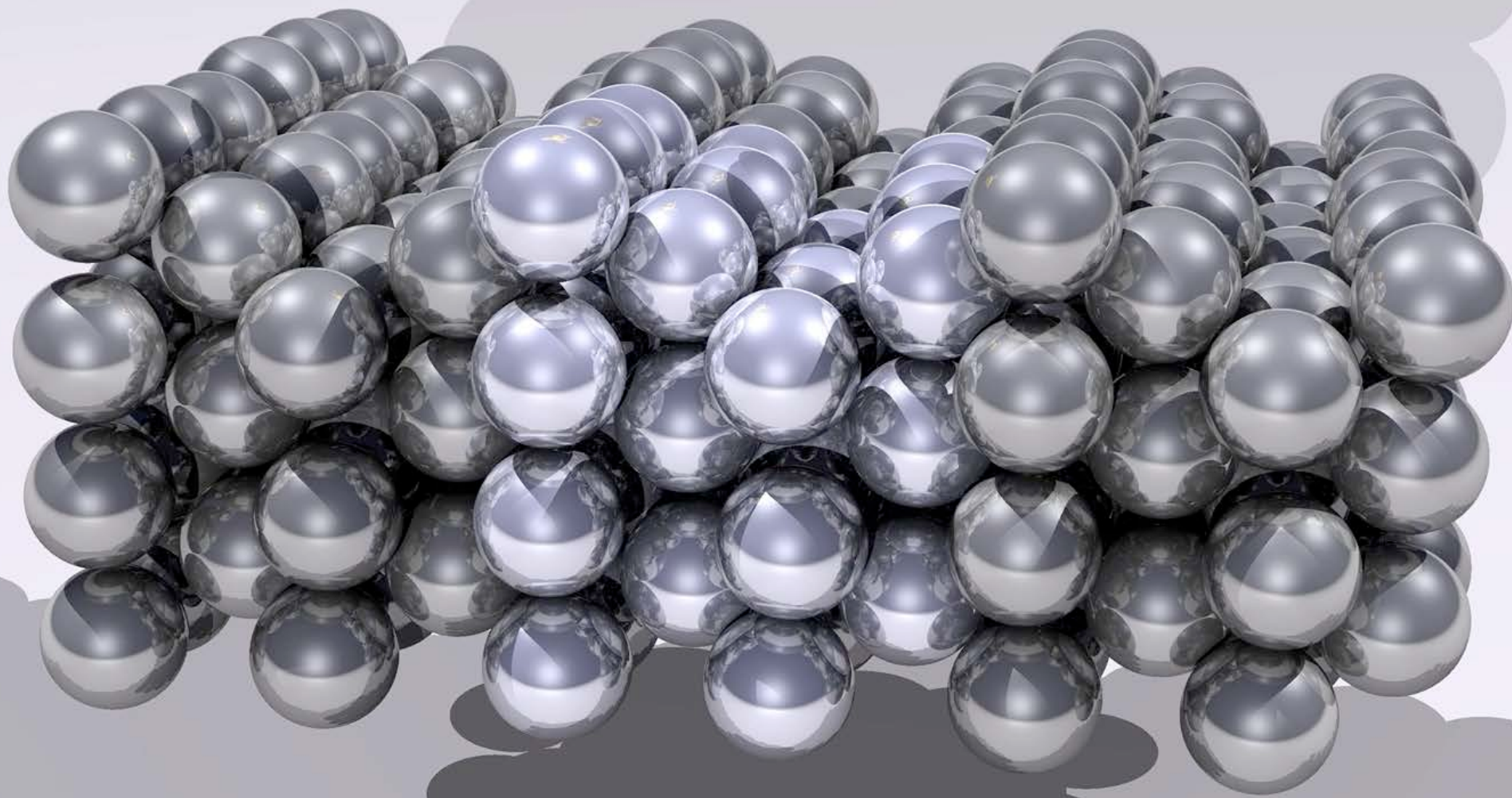


Fig. 2. Oxygen–oxygen, oxygen–hydrogen, and hydrogen–hydrogen RDFs at 300 K and experimental density computed via (PI)MD simulations in the constant number of particles, volume, and temperature (NVT) ensemble using the NN potential. The experimental O–O RDF was obtained from ref. 37, and the experimental O–H and H–H RDFs were taken from refs. 38 and 39.

Bingqing Cheng, Edgar A. Engel, Jörg Behler, Christoph Dellago, Michele Ceriotti, PNAS 116 1110 (2019)



We'll always have Monte Carlo

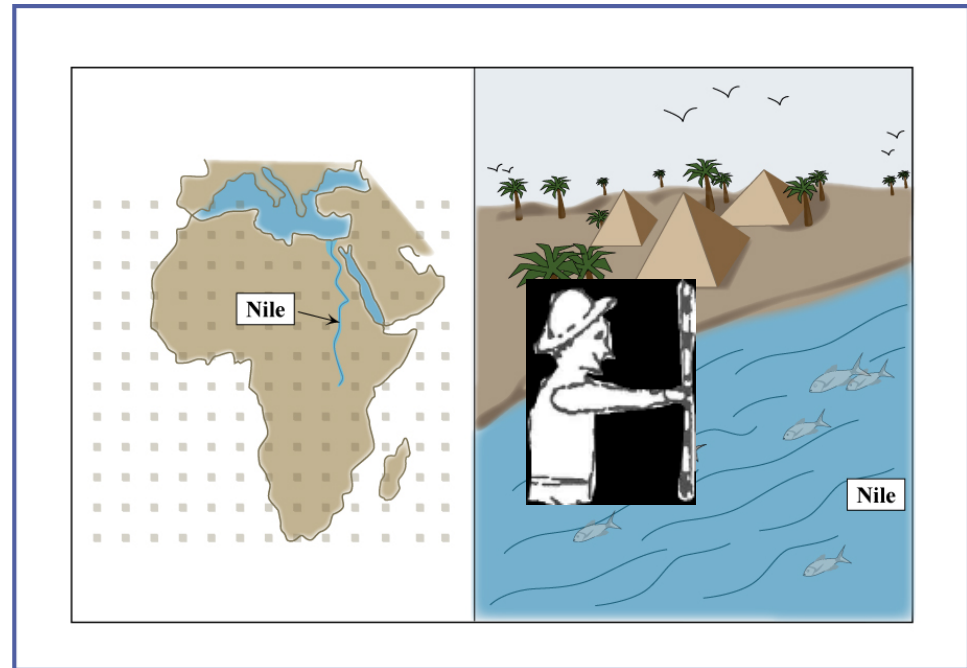
$$\langle A \rangle = \frac{\int A \exp(-\beta E) d\vec{r} d\vec{p}}{\int \exp(-\beta E) d\vec{r} d\vec{p}}$$

Metropolis algorithm
(by Arianna and Marshall Rosenbluth)

$$P_{i \rightarrow j} = 1 \quad \text{when } E_j < E_i$$

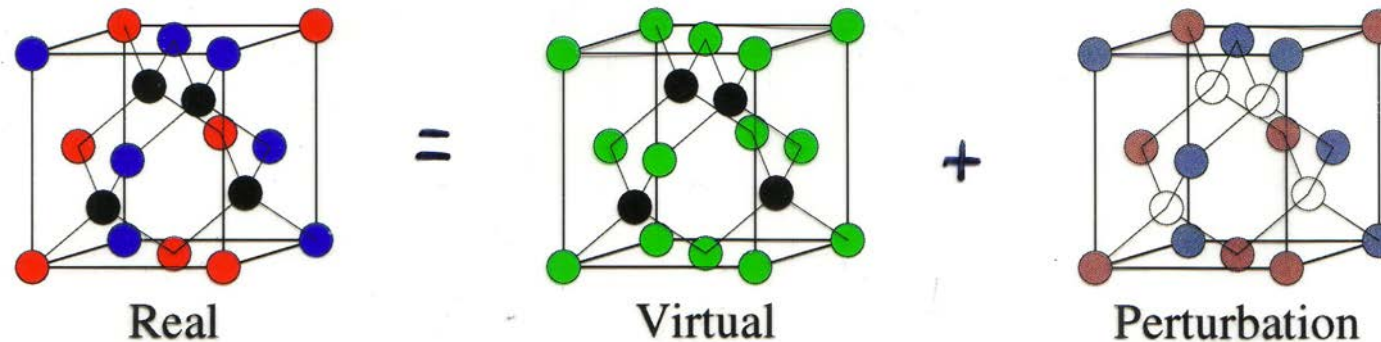
$$P_{i \rightarrow j} = \exp(-\beta(E_j - E_i)) \quad \text{when } E_j > E_i$$

Downhill moves always accepted, uphill
moves with some “thermal-like”
probability



redrawn from the book by D. Frenkel and B. Smith,
Understanding Molecular Simulation Academic Press

Thermodynamics of substitutional alloys



Perturbation (external potential):

$$V_0 \Rightarrow V_0(\mathbf{r}) + \sum \sigma_{\mathbf{R}} \Delta v(\mathbf{r} - \mathbf{R})$$

Total energy:

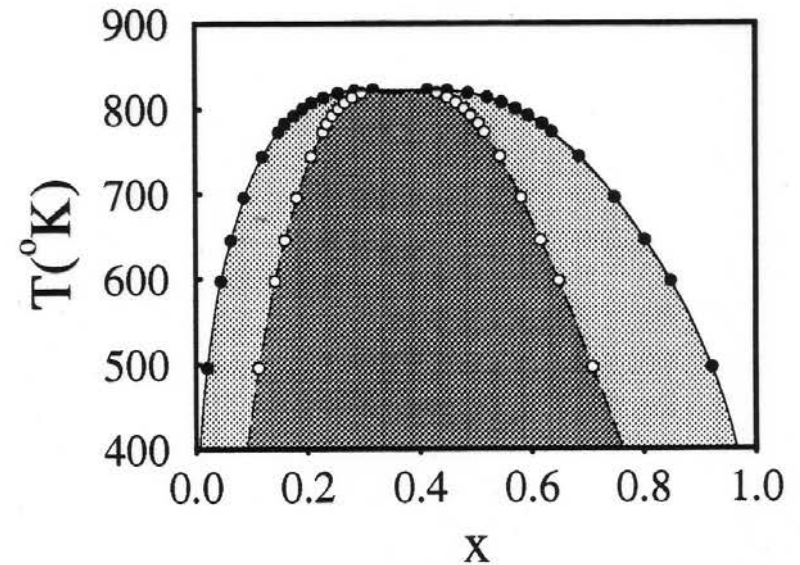
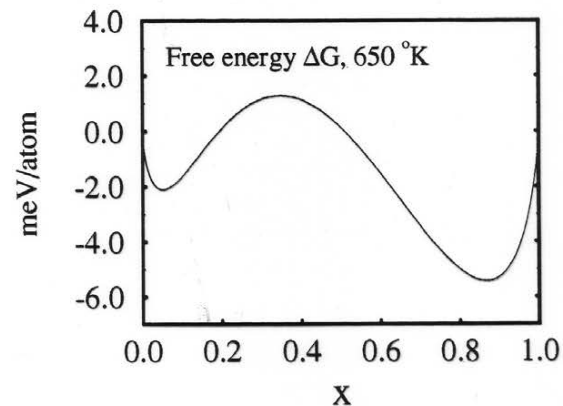
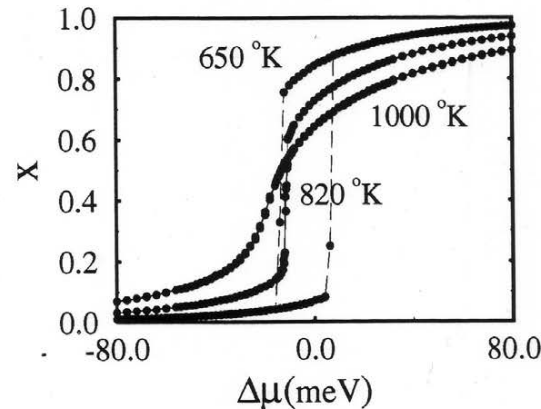
$$E(\{\sigma_{\mathbf{R}}\}) = E_0 + K \sum_{\mathbf{R}} \sigma_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \sigma_{\mathbf{R}} J(\mathbf{R} - \mathbf{R}') \sigma_{\mathbf{R}'}$$

Free energy from thermodynamic integration of the dependence of the chemical potential

Monte Carlo simulations :
 $\langle x \rangle = \langle x \rangle(\Delta\mu)$



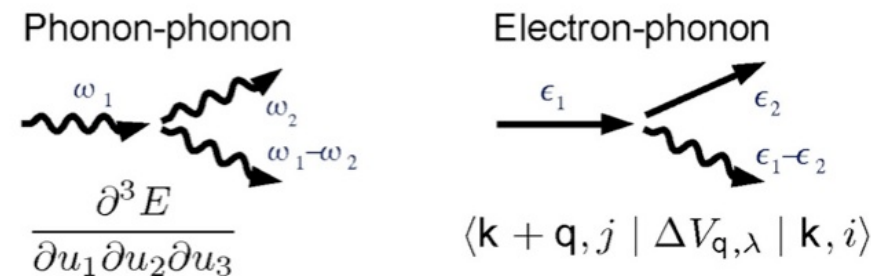
$G(x) = \int \Delta\mu(\xi) d\xi$:
 common tangent



Nicola Marzari, Stefano de Gironcoli, and
 Stefano Baroni, Phys. Rev. Lett. 72, 4001

Multi-scale, multi physics: semiclassical transport

1. Vibrational properties from density-functional theory, electrons from many-body perturbation theory
2. Carriers' scattering rates from density-functional perturbation theory

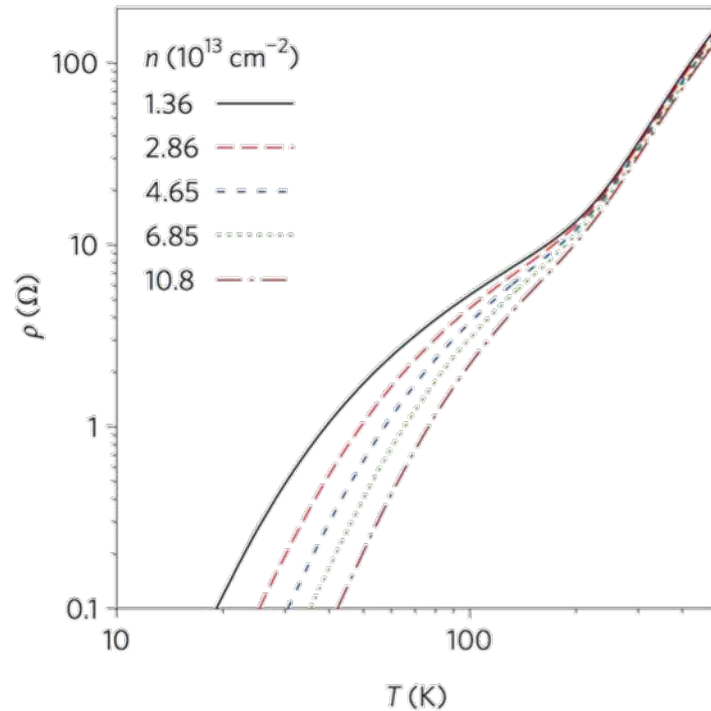


3. Wannier interpolations for electrons
4. Transport properties from Boltzmann's equation

$$\left\{ \begin{array}{ll} \frac{\partial n_\lambda}{\partial t} \Big|_{scatt} = \frac{\partial \omega_\lambda}{\partial \mathbf{q}} \cdot \nabla T \left(\frac{\partial n_\lambda}{\partial T} \right) & \text{(phonons)} \\ \frac{\partial f_\mu}{\partial t} \Big|_{scatt} = \frac{1}{\hbar} \frac{\partial \epsilon_\mu}{\partial \mathbf{k}} \cdot \nabla T \left(\frac{\partial f_\mu}{\partial T} \right) + \frac{e}{\hbar} \mathbf{E} \cdot \frac{\partial f_\mu}{\partial \mathbf{k}} & \text{(electrons)} \end{array} \right.$$

Resistivity in doped graphene

FIRST-PRINCIPLES



EXPTS (Efetov and Kim)

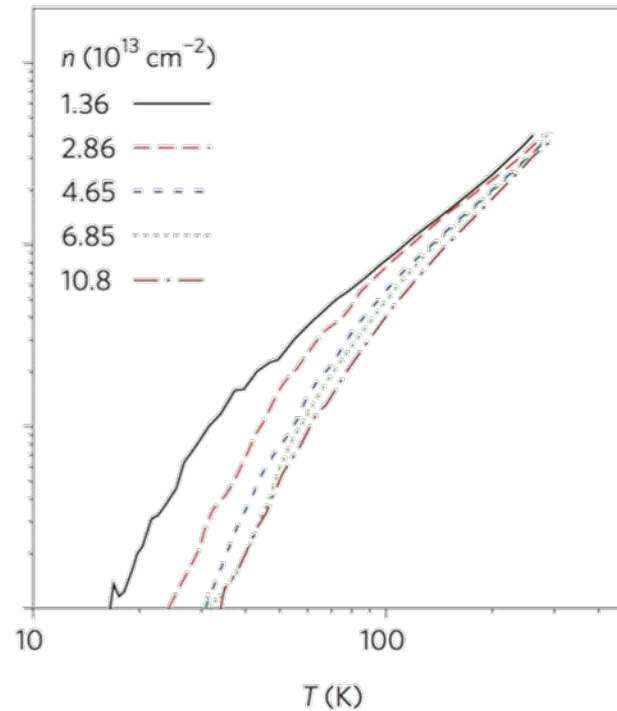


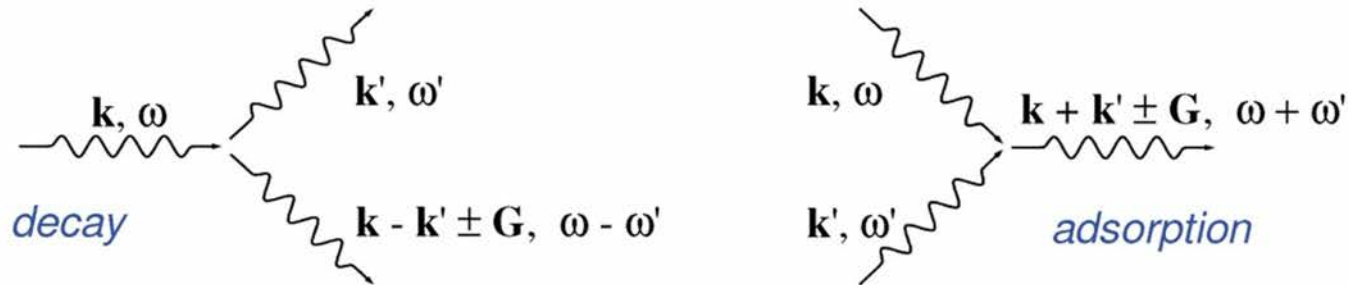
Figure 1 | Electrical resistivity of graphene as a function of temperature and doping (ρ , electrical resistivity; T , temperature; n , carrier density). Left panel: first-principles results obtained using a combination of density-functional perturbation theory, many-body perturbation theory and Wannier interpolations to solve the Boltzmann transport equation. Right panel: experimental data. Adapted from ref. 4, American Chemical Society.

C.-H. Park *et al.*, *Nano Letters* (2014)

T. Y. Kim, C.-H. Park, and N. Marzari, *Nano Letters* (2016)

Anharmonicity = finite lifetimes

Third-order anharmonic interactions



The anharmonic linewidth of a zone center phonon is given by

$$\Gamma_{0\nu} = \frac{\pi \hbar}{8 N_q \omega_\nu(\mathbf{0})} \sum_{\mathbf{q}, \mu, \eta} \left| \frac{\partial^3 E}{\partial u_\nu(\mathbf{0}) \partial u_\mu(\mathbf{q}) \partial u_\eta(-\mathbf{q})} \right|^2 \frac{I^D_{\mathbf{q}\nu\mu\eta} + I^A_{\mathbf{q}\nu\mu\eta}}{\omega_\mu(\mathbf{q}) \omega_\eta(-\mathbf{q})},$$

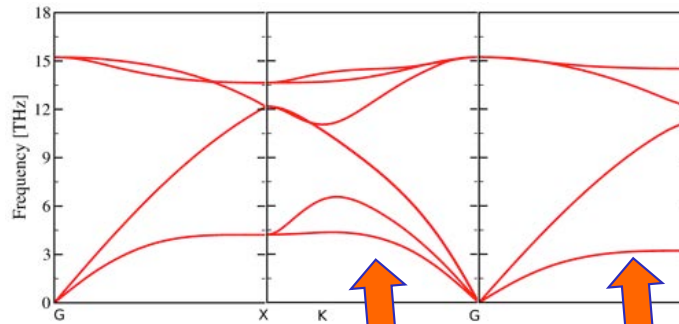
$$I^D_{\mathbf{q}\nu\mu\eta} = [n_\mu(\mathbf{q}) + n_\eta(-\mathbf{q}) + 1] \delta(\omega_\nu(\mathbf{0}) - \omega_\mu(\mathbf{q}) - \omega_\eta(-\mathbf{q})) \quad (\text{decay})$$

$$I^A_{\mathbf{q}\nu\mu\eta} = 2[n_\mu(\mathbf{q}) - n_\eta(-\mathbf{q})] \delta(\omega_\nu(\mathbf{0}) - \omega_\mu(\mathbf{q}) + \omega_\eta(-\mathbf{q})) \quad (\text{adsorption})$$

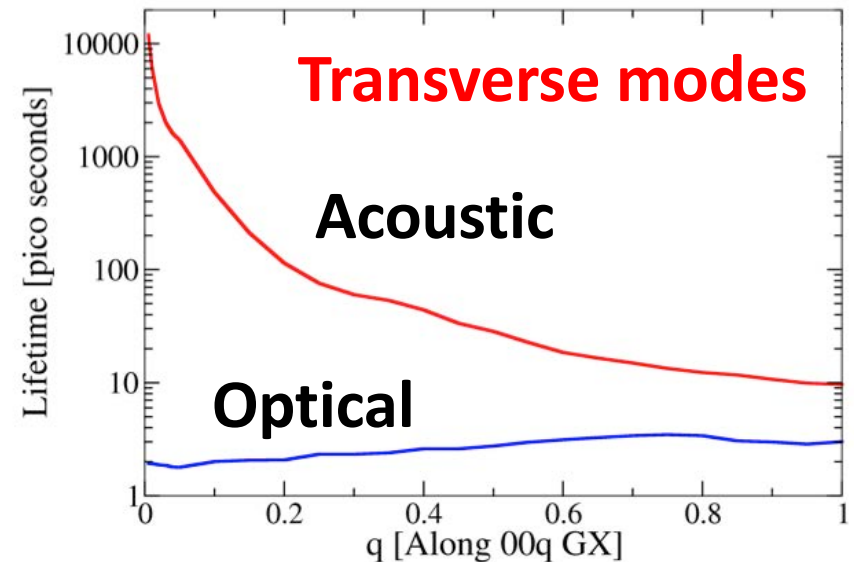
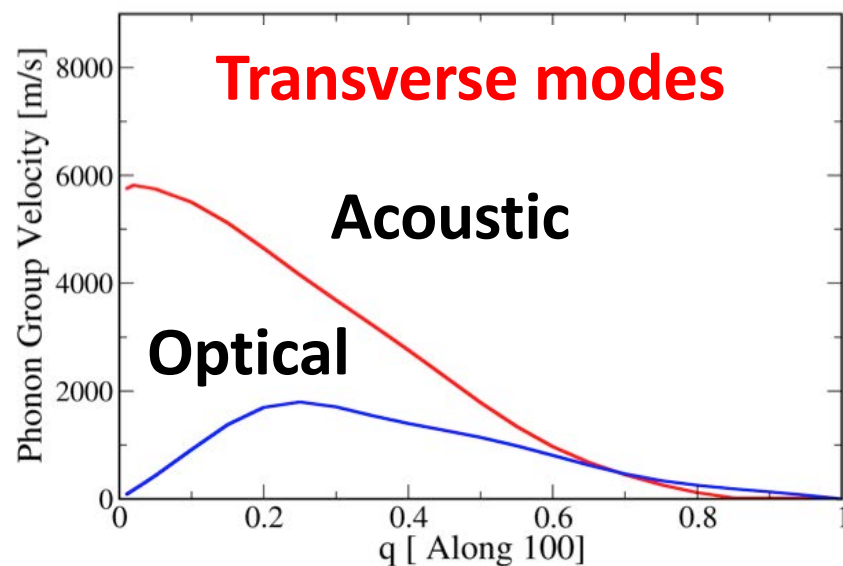
$$\frac{\partial^3 E}{\partial u_\nu(\mathbf{0}) \partial u_\mu(\mathbf{q}) \partial u_\eta(-\mathbf{q})}$$

calculated using DFPT and the $2n+1$ theorem

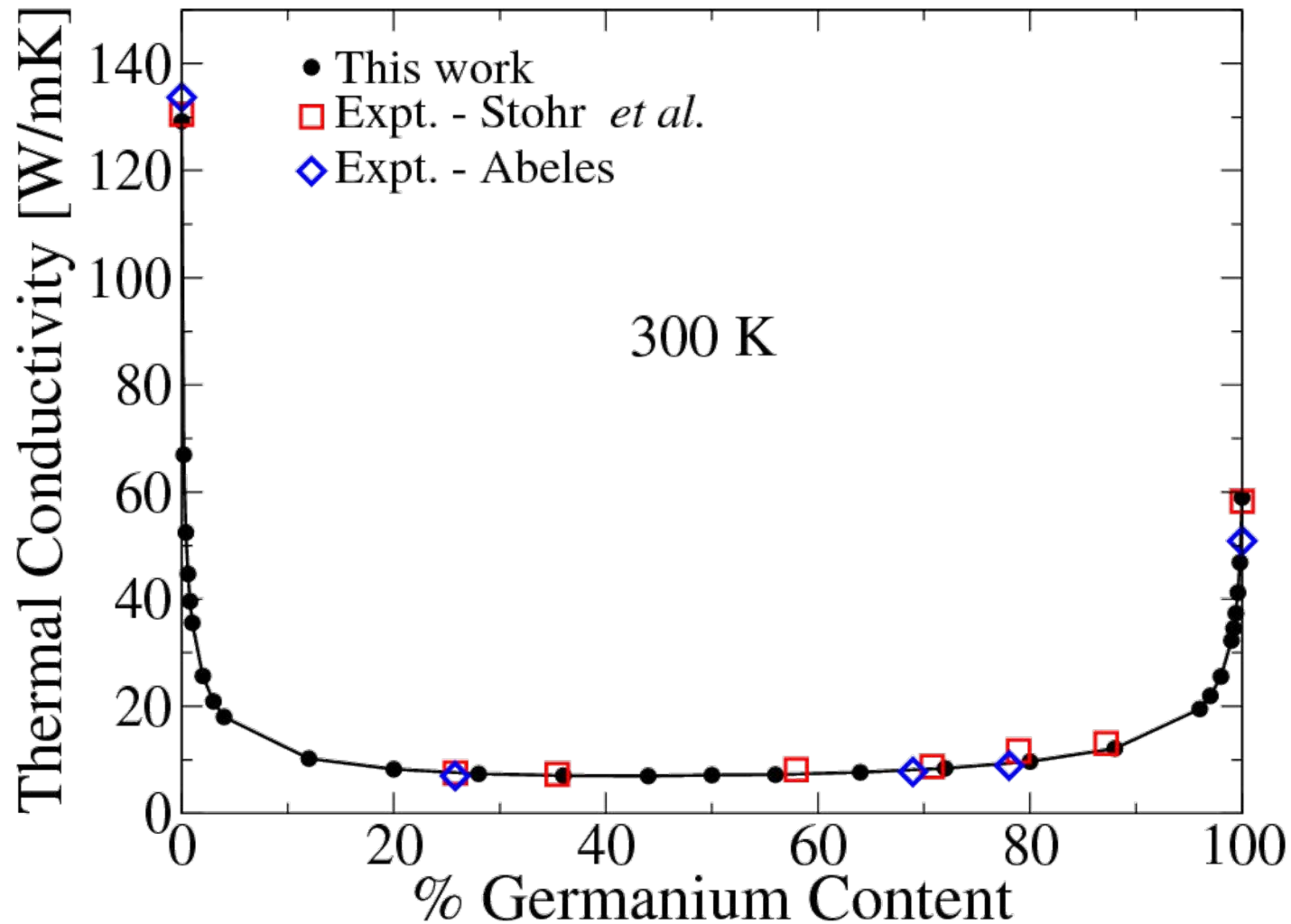
Thermal conductivity (SMRTA)



$$K = \frac{\hbar^2}{3N_0 \Omega k_B T^2} \sum_{qs} c_s^2(q) \omega^2(qs) \bar{n}_{qs} (\bar{n}_{qs} + 1) \tau_{qs}$$

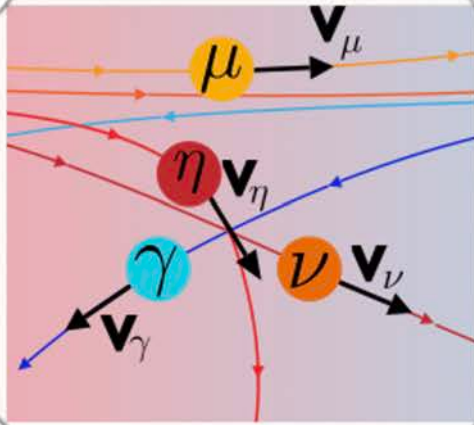


Composition dependence in SiGe alloys



J. Garg, N. Bonini, B. Kozinsky and N. Marzari, *Phys. Rev. Lett.* (2011)

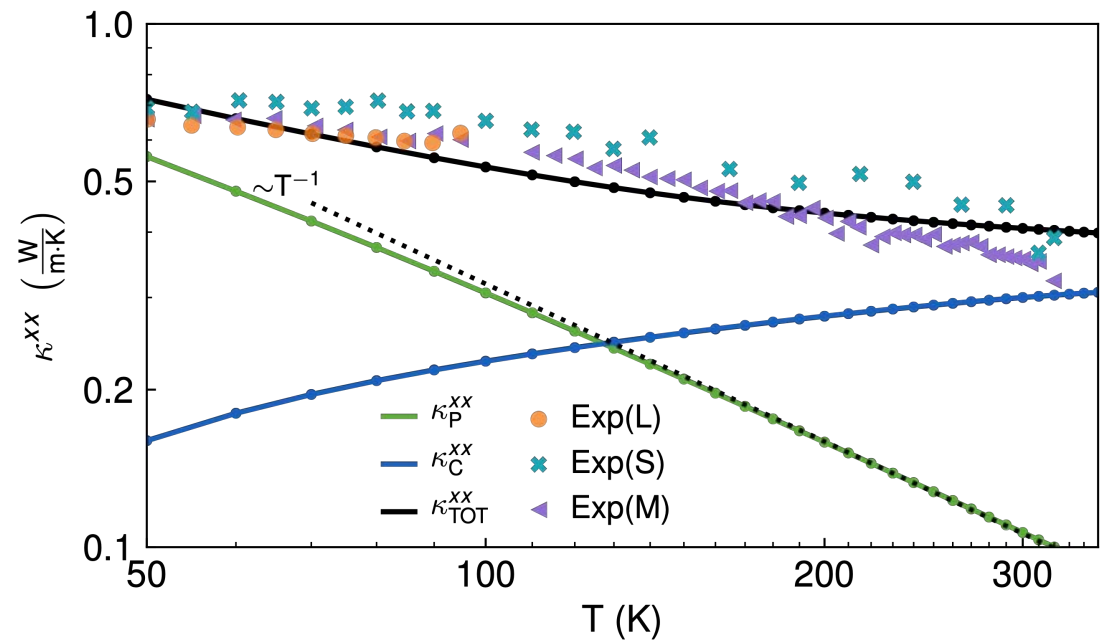
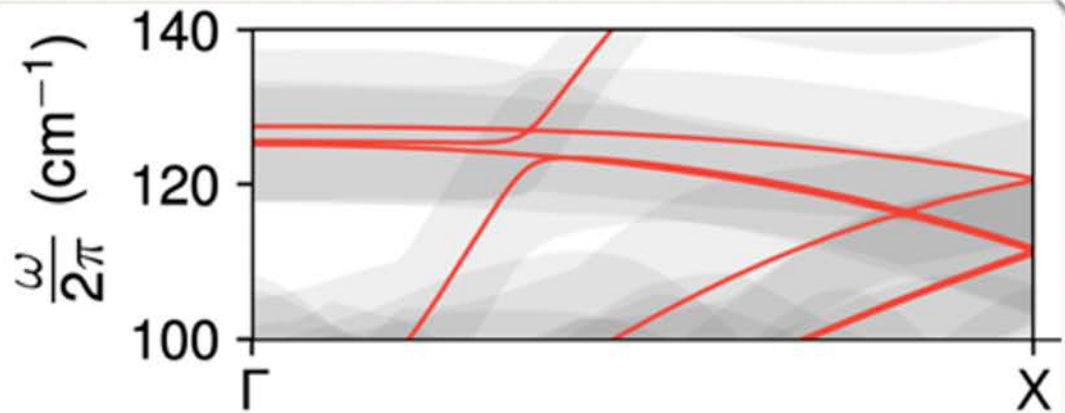
Generalized Wigner Boltzmann



Simoncelli, Marzari, Mauri,
Nature Physics (2019)

$$\kappa^{\alpha\beta} = \kappa_P^{\alpha\beta} + \kappa_C^{\alpha\beta}$$

Total K = **Peierls** + **coherences**



Article

Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride

<https://doi.org/10.1038/s41586-020-1955-z>

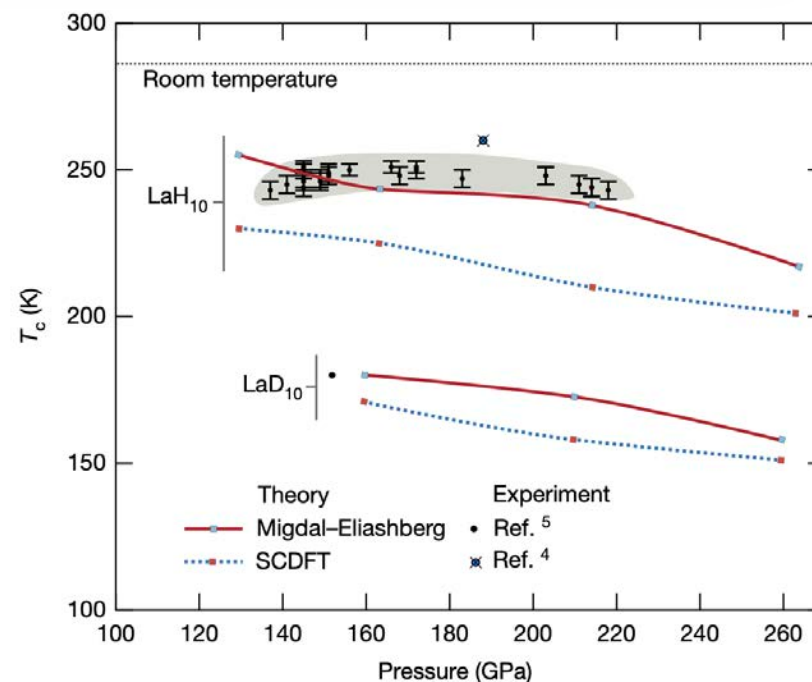
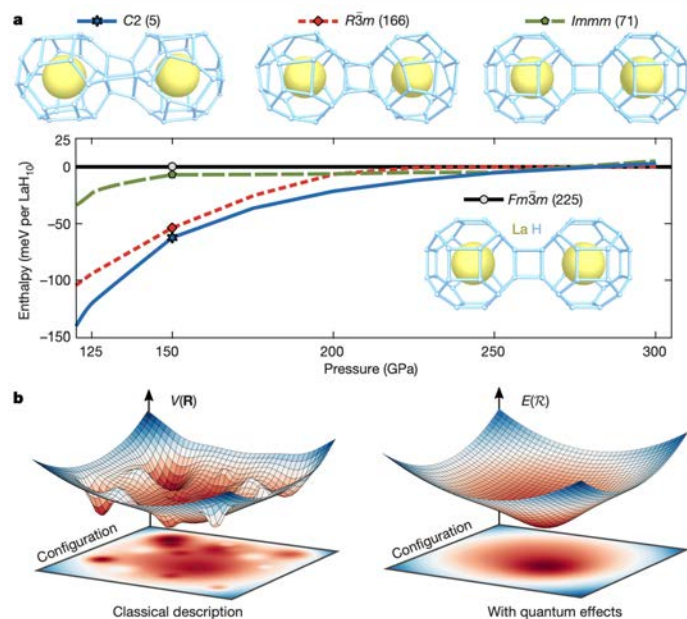
Received: 24 July 2019

Accepted: 14 November 2019

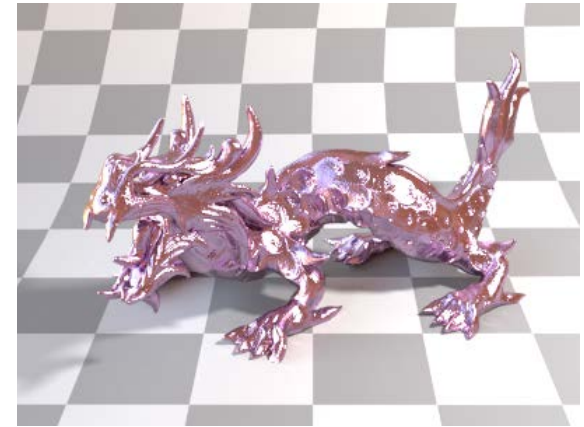
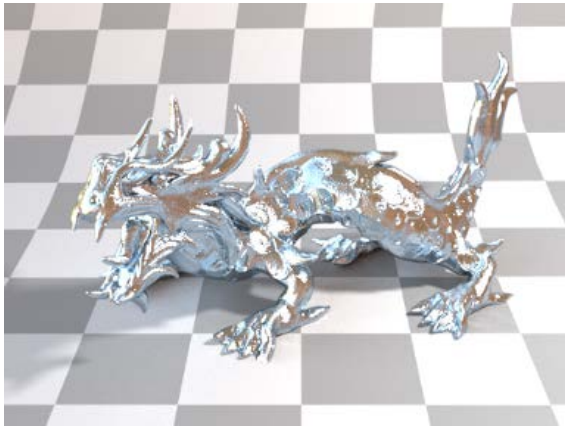
Published online: 5 February 2020

Ion Errea^{1,2,3}, Francesco Belli^{1,2}, Lorenzo Monacelli⁴, Antonio Sanna⁵, Takashi Koretsune⁶, Terumasa Tadano⁷, Raffaello Bianco², Matteo Calandra⁸, Ryotaro Arita^{9,10}, Francesco Mauri^{4,11} & José A. Flores-Livas^{4*}

The discovery of superconductivity at 200 kelvin in the hydrogen sulfide system at

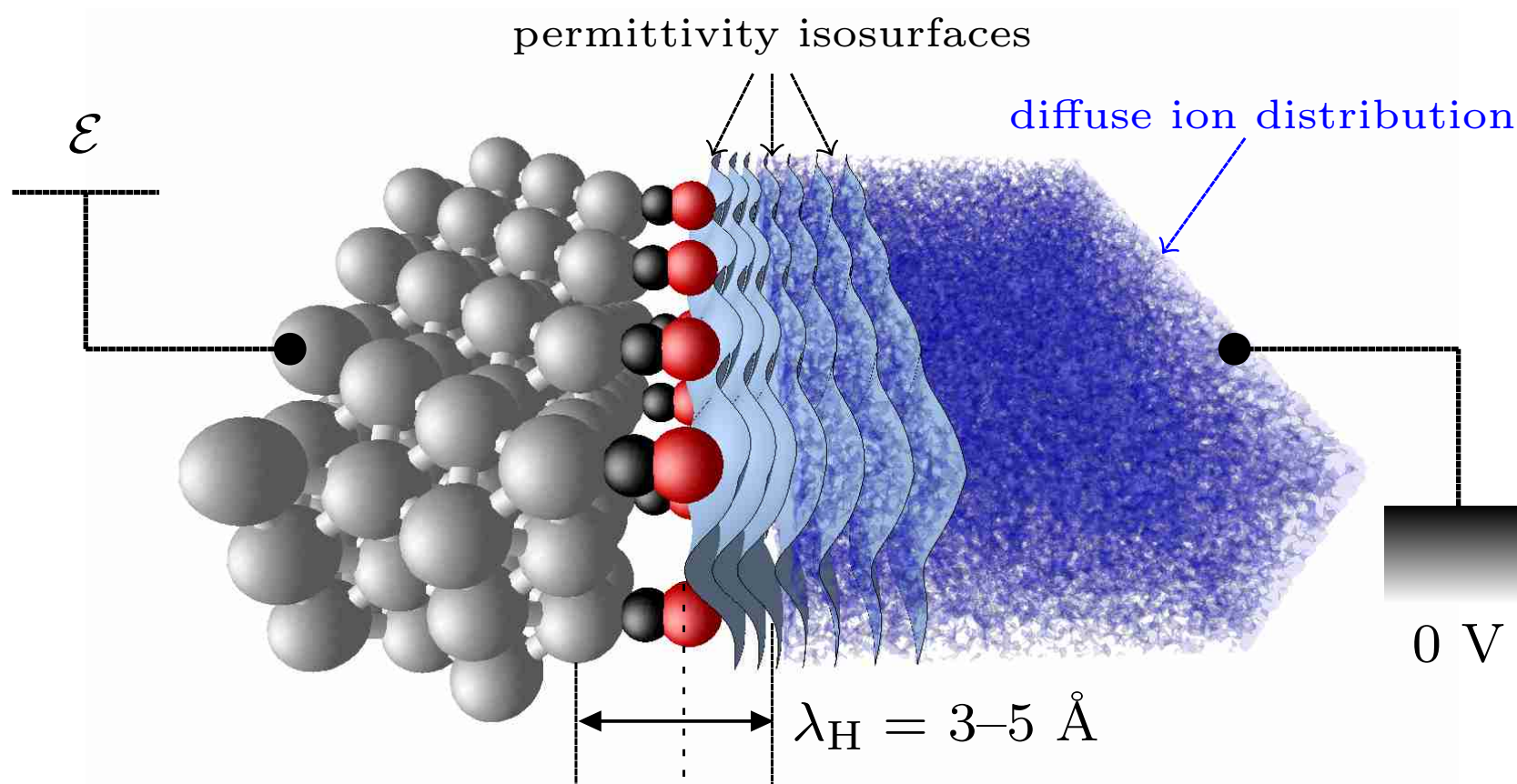


A FUN EXAMPLE



G. Prandini, G.M. Rignanese, and N. Marzari,
npj Computational Materials 5, 129 (2019)

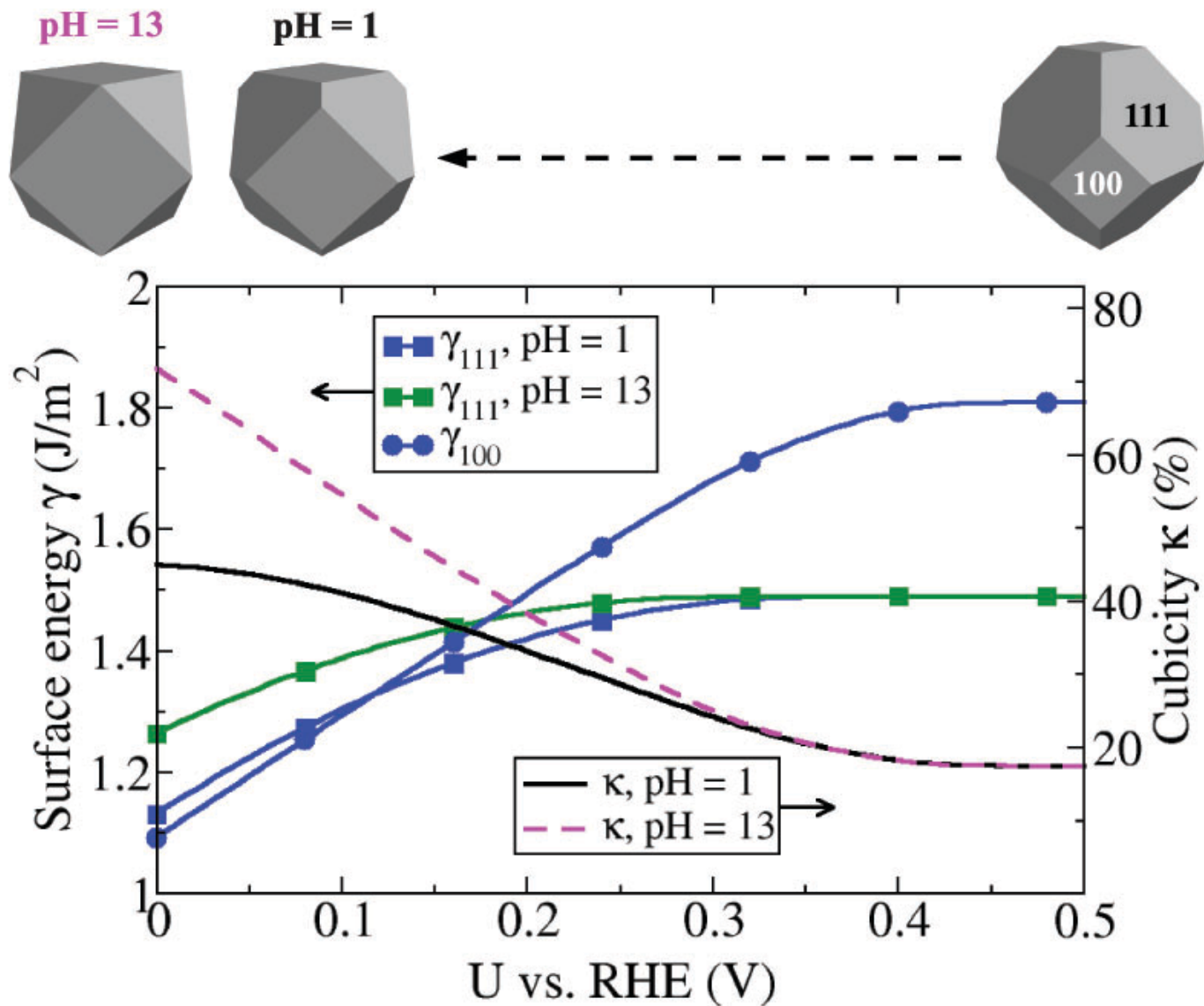
Multi-scale/physics: electrochemistry



Dabo, Bonnet, Li and Marzari, "*Ab-initio Electrochemical Properties of Electrode Surfaces*", in *Fuel Cell Science: Theory, Fundamentals and Bio-Catalysis*, A. Wiecowski and J. Nørskov (2011).

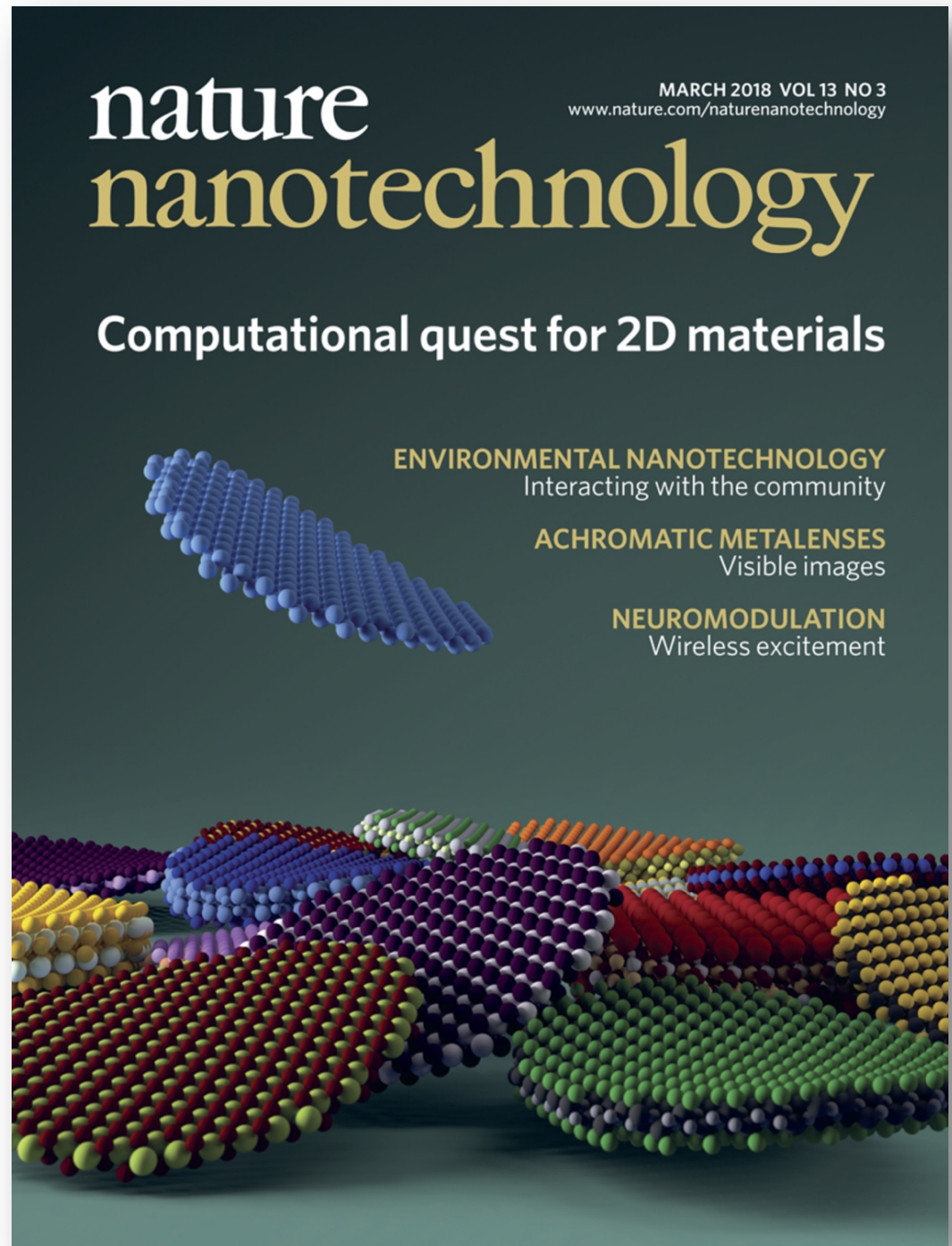
O. Andreussi, I. Dabo and N. Marzari, "Revised self-consistent continuum solvation in electronic structure calculations", *J. Chem. Phys.* 136, 064102 (2012). www.quantum-environment.org

Wulff construction, nanoparticle shape

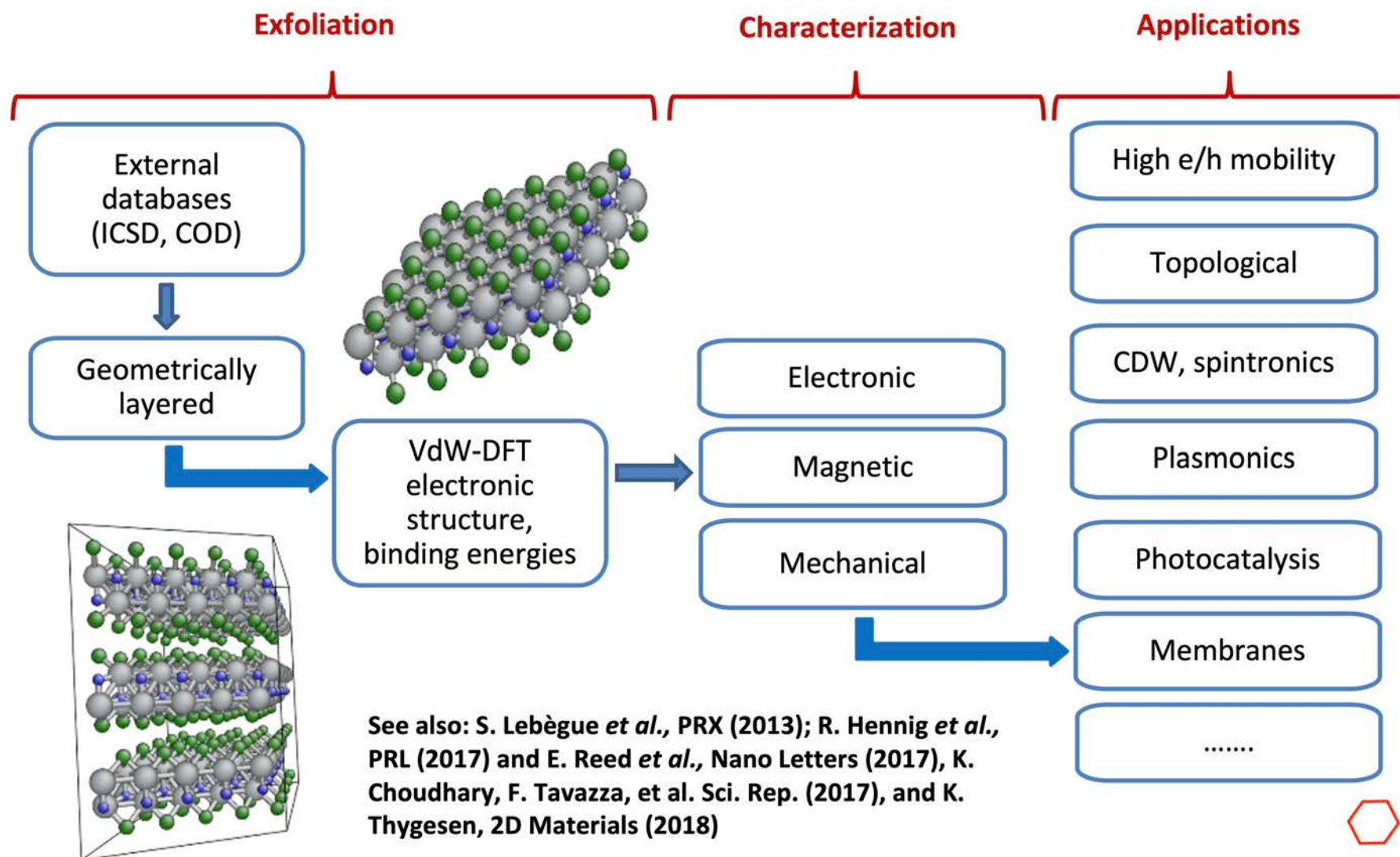


N. Bonnet and N. Marzari, Phys. Rev. Lett. 110, 086104 (2013)

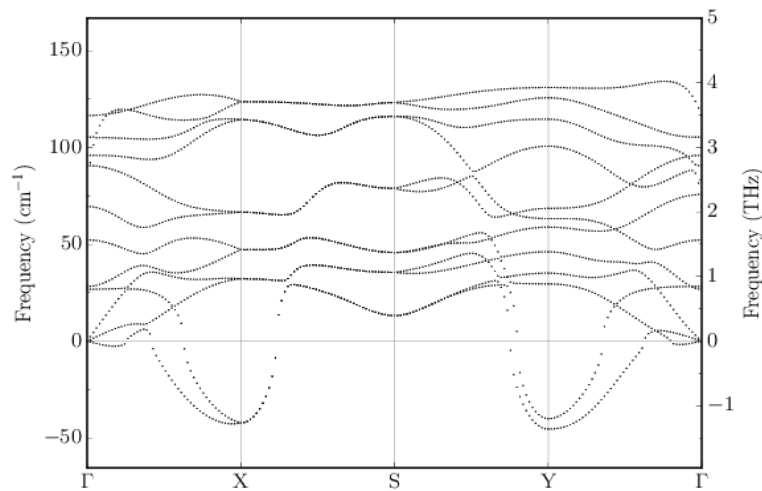
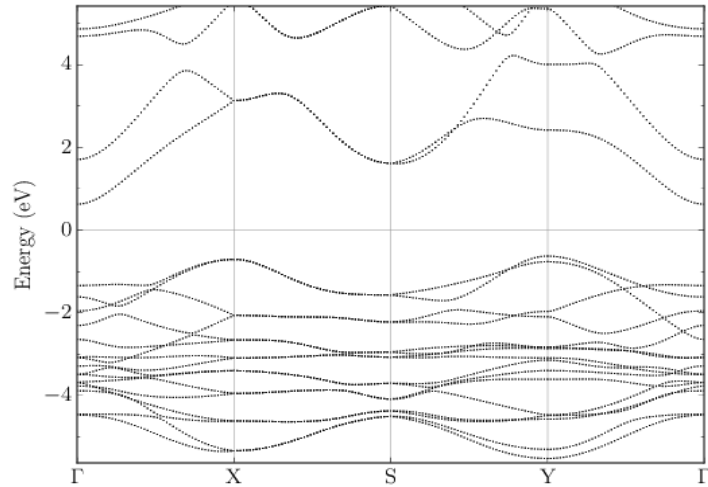
COMPUTATIONAL
EXFOLIATION OF
ALL KNOWN
INORGANIC
MATERIALS



HIGH-THROUGHPUT COMPUTATIONAL EXFOLIATION

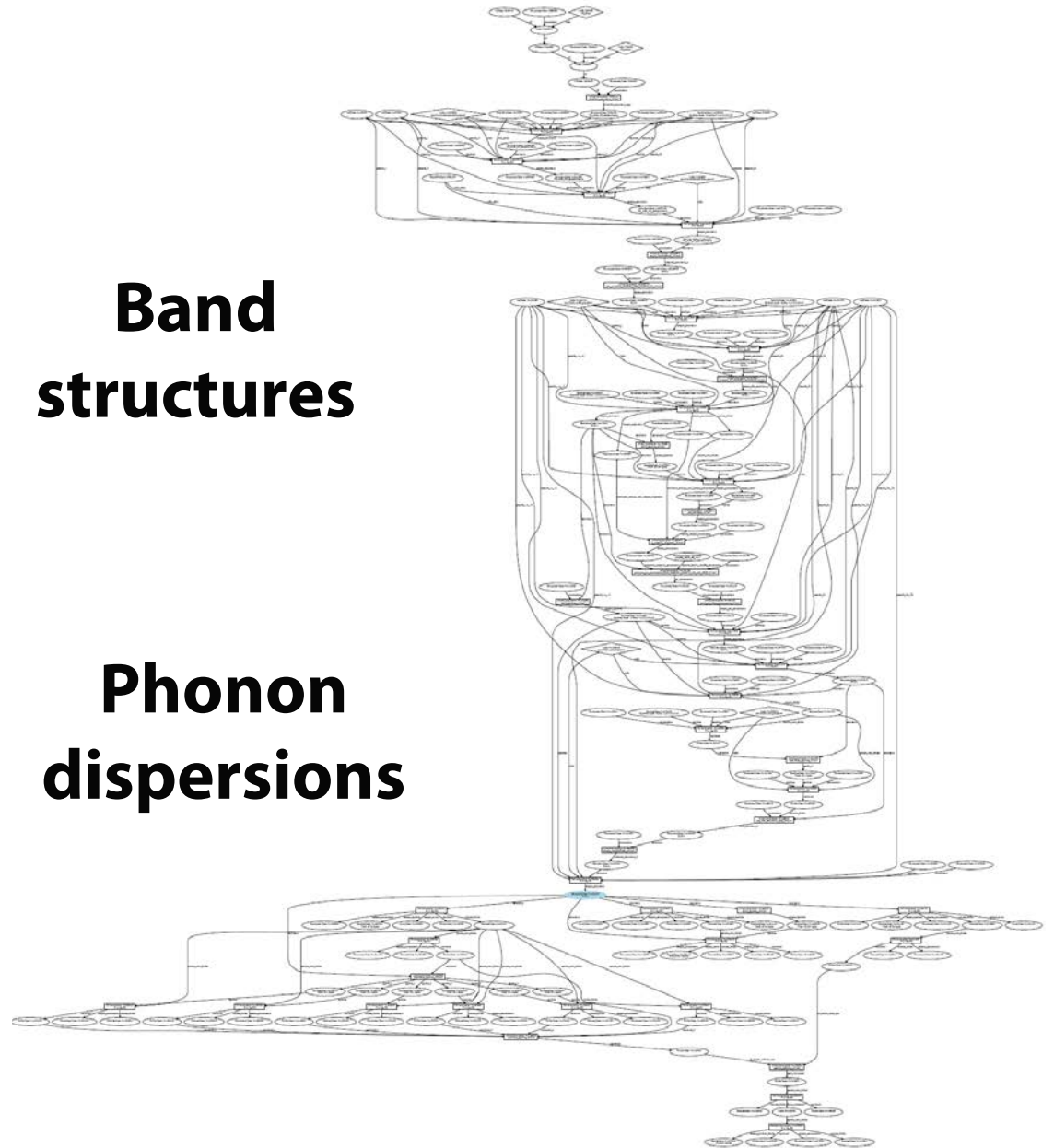


ALL AUTOMATED WITH AiiDA (<http://aiida.net>)

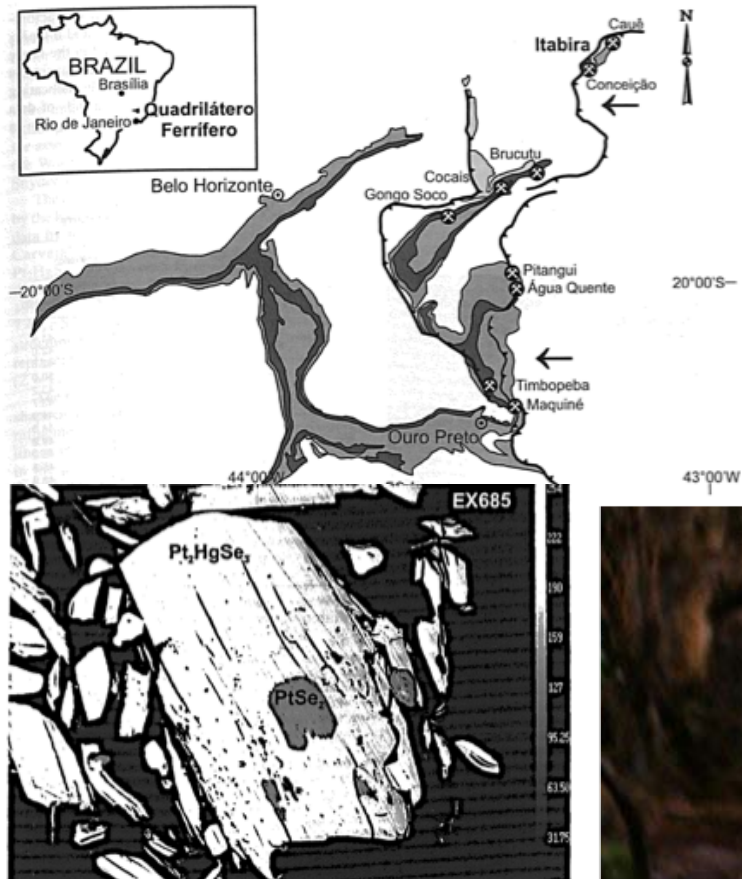


**Band
structures**

**Phonon
dispersions**

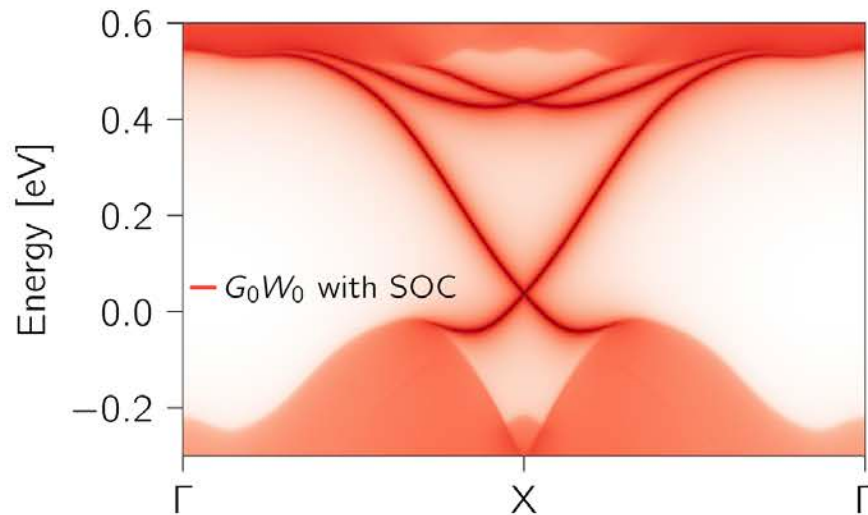


THE DISCOVERY OF JACUTINGAITE



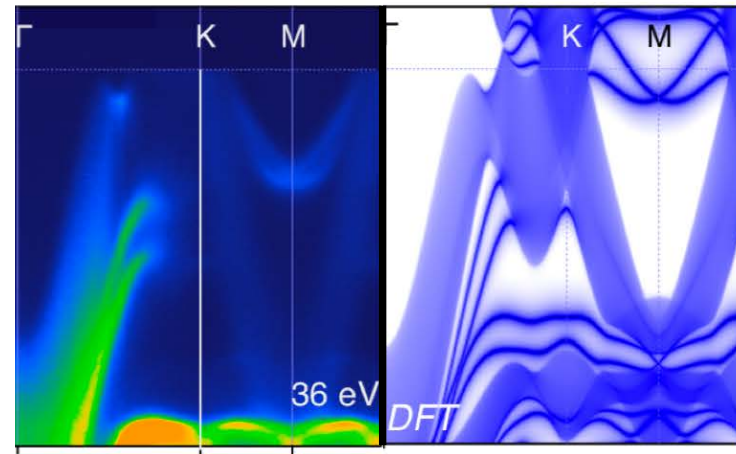
THE DISCOVERY OF JACUTINGAITE

Monolayer: room-temperature Kane-Mele quantum spin Hall insulator – G_0W_0 with S.O.C.



A. Marrazzo et al., Phys. Rev. Lett. 120, 117701 (2018)

Bulk: topologically-protected 001-surface states, exp vs DFT



C. Cucchi et al., Phys. Rev. Lett. 124, 106402 (2020)

A. Marrazzo et al., Phys. Rev. Research 2, 012063(R) (2020)

$$H = \underbrace{t \sum_{\langle ij \rangle \alpha} c_{i\alpha}^\dagger c_{j\alpha}}_{1^{st} NN} + \underbrace{it_2 \sum_{\langle\langle ij \rangle\rangle \alpha\beta} v_{ij} s_{\alpha\beta}^z c_{i\alpha}^\dagger c_{j\beta}}_{KM \text{ SOC}}$$

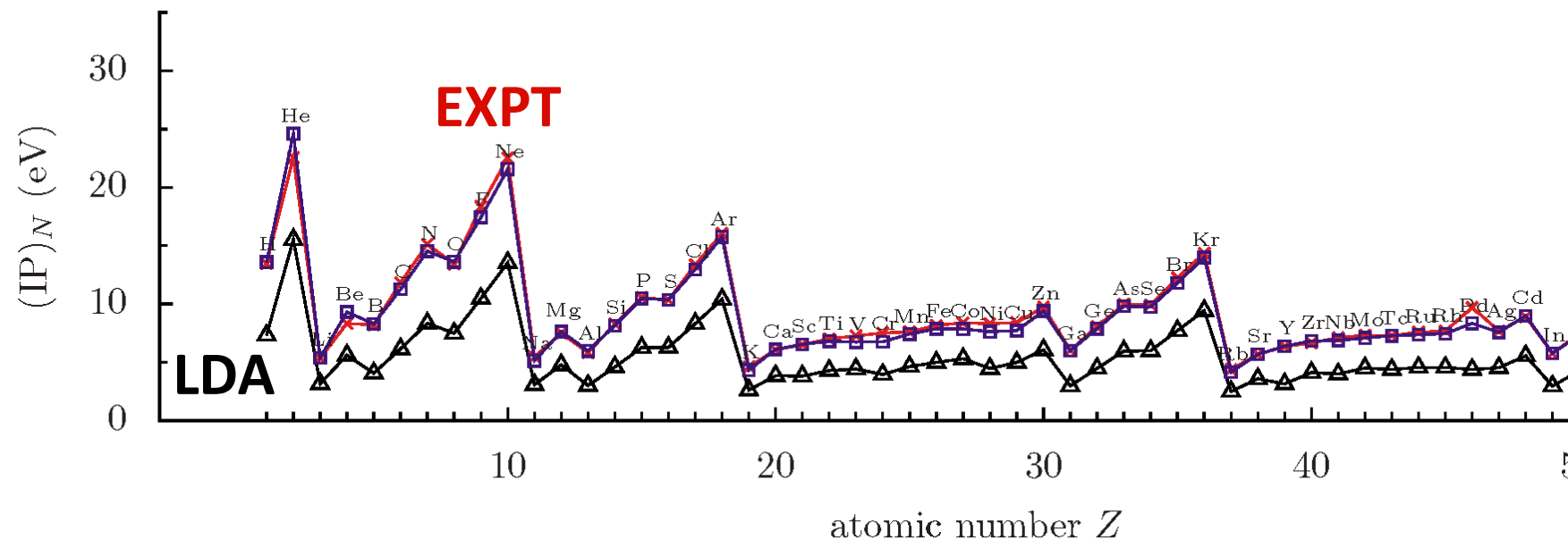
$$+ \underbrace{t'_2 \sum_{\langle\langle ij \rangle\rangle \alpha} c_{i\alpha}^\dagger c_{j\alpha}}_{2^{nd} NN} + \underbrace{it_2'' \sum_{\langle\langle ij \rangle\rangle \alpha\beta} u_{ij} (\mathbf{s} \times \mathbf{d}_{ij}^0)_{\alpha\beta}^z c_{i\alpha}^\dagger c_{j\beta}}_{\text{in-plane SOC}},$$

$$H_{J3KM} = H_{KM} + \lambda \tilde{H}_{2^{nd} NL}$$

What's wrong with DFT ?

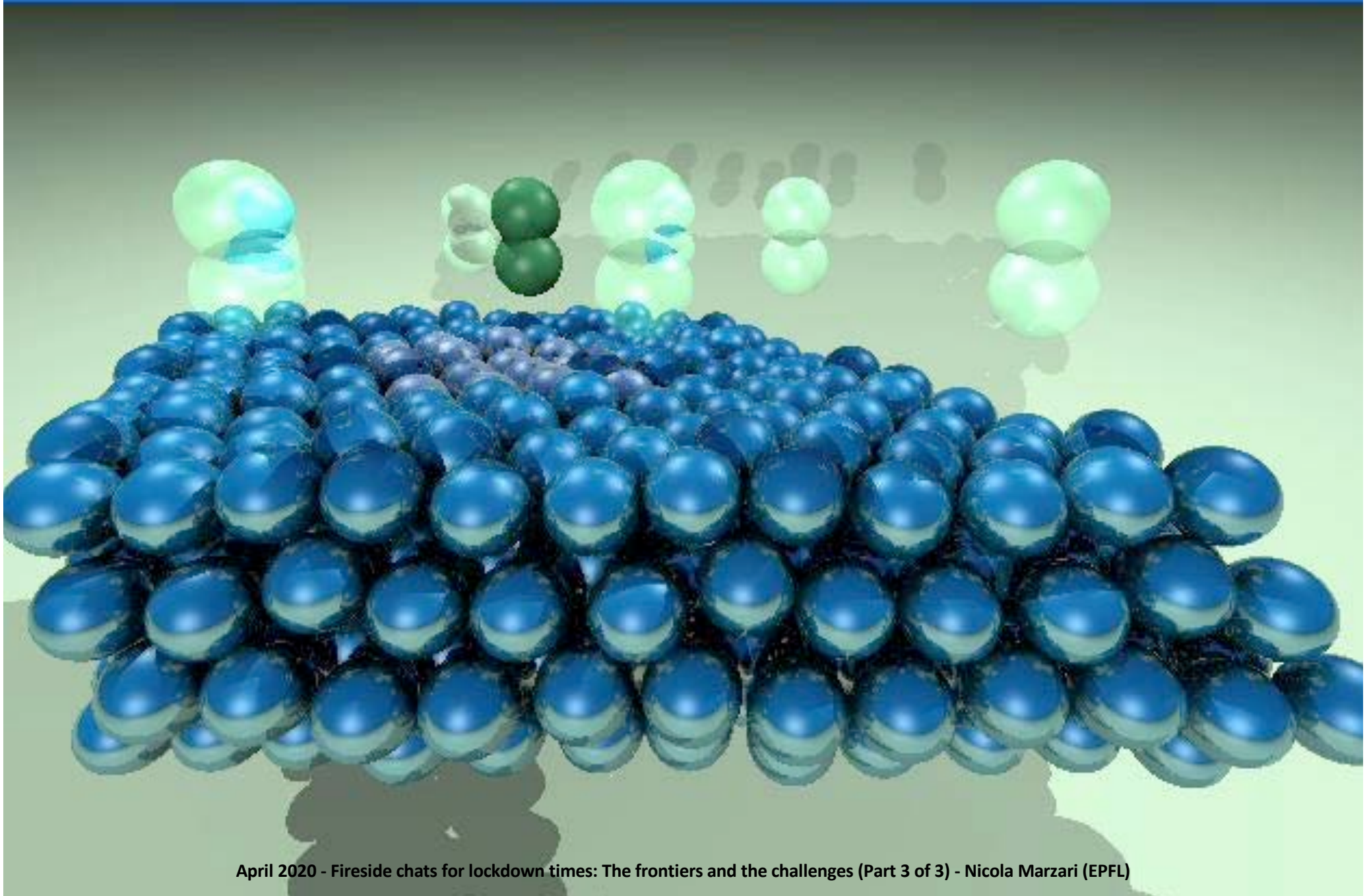
- **In its practice, it is approximate**
- **It is a static theory (of the charge density)**

Notable failures I: Photoemission spectra (at least IP from HOMO – should be exact)

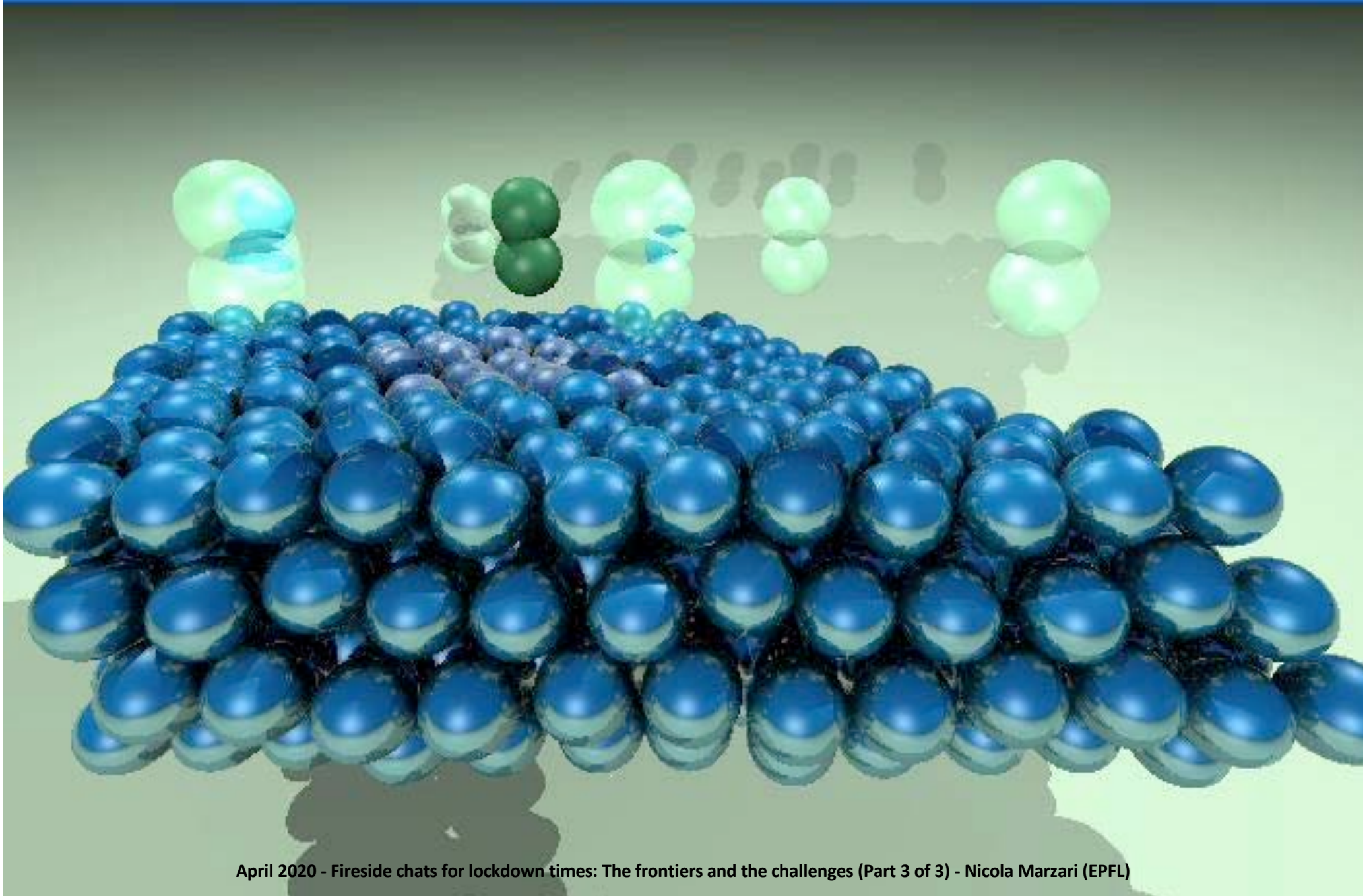


I. Dabo et al. Phys. Rev. B 82 115121 (2010)

Notable failures II: Charge transfer



Notable failures II: Charge transfer



Notable failures III: beautiful, but perverse

J. Chem. Theory Comput., Vol. 5, No. 4, 2009 775

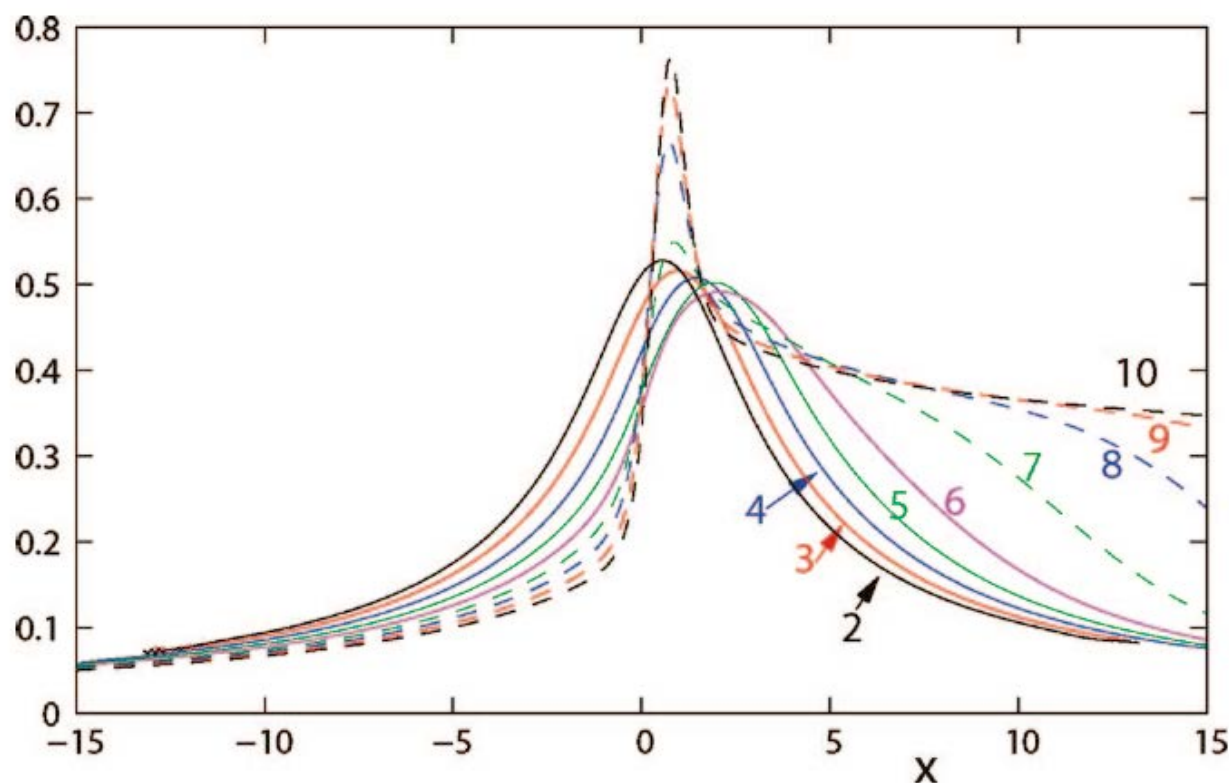
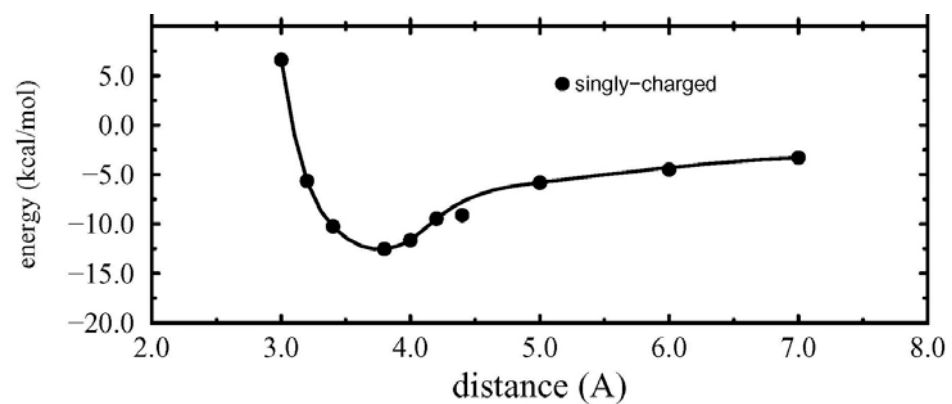
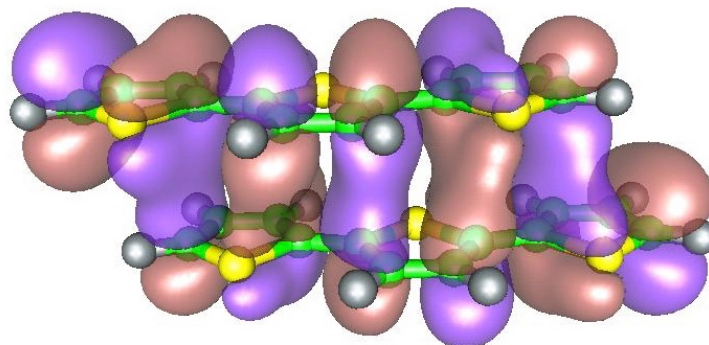


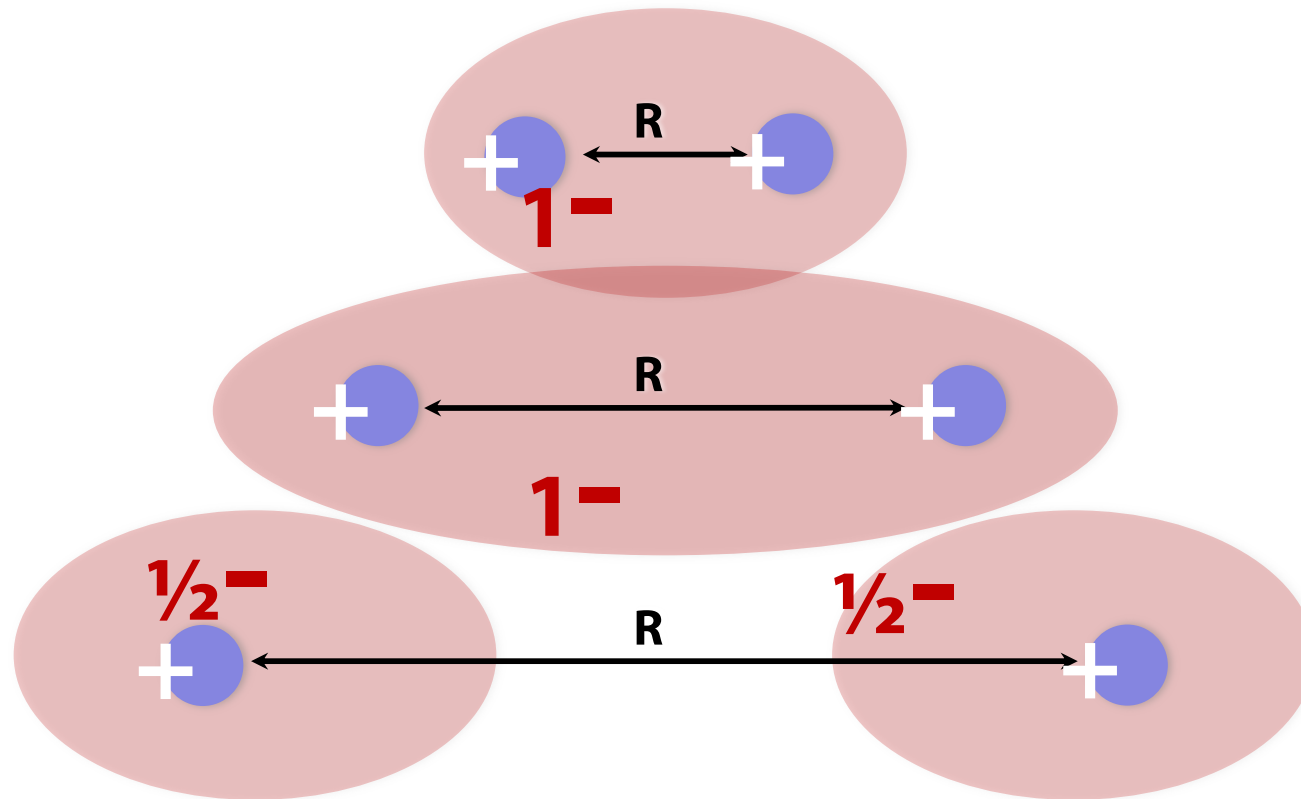
Figure 7. Hartree-exchange-correlation potential, $v_{\text{Hxc}}(x)$ for our LiH model ($c = 2.8$); the values of interatomic separation R are indicated.

Notable failures IV: Delocalization of electrons/holes



D. A. Scherlis and N. Marzari, JPCB (2004), JACS (2005)

Notable failures V: H_2^+ dissociation limit



$$\hat{H} = -\frac{1}{2}\vec{\nabla}^2 + V_{\text{ext}}(\vec{r})$$

Schrödinger

$$\hat{H}_{KS} = -\frac{1}{2}\vec{\nabla}^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$$

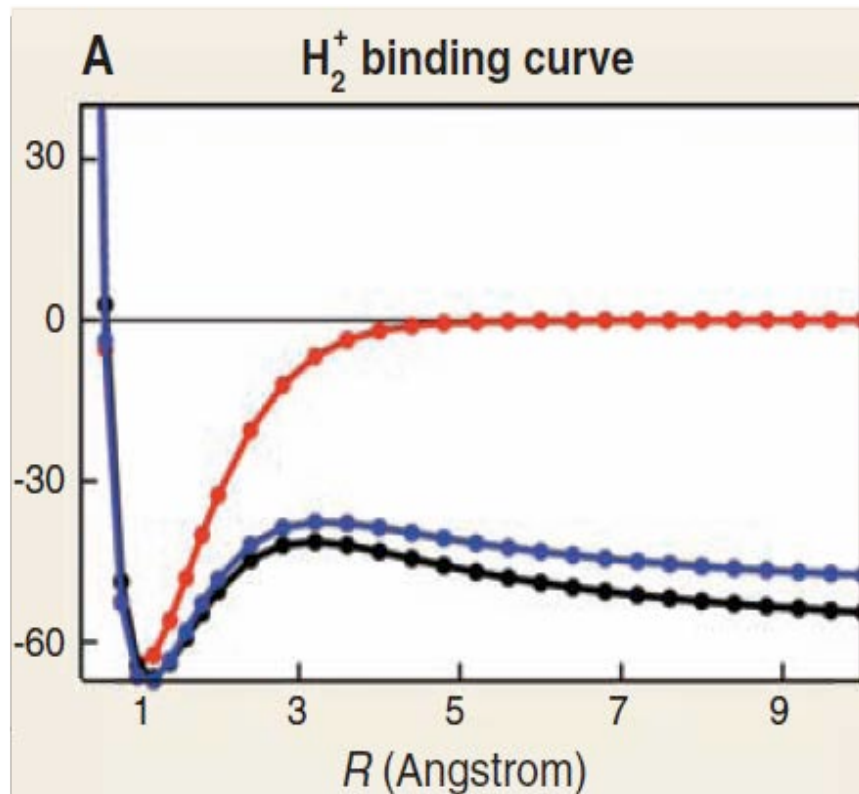
Kohn-Sham

So, it doesn't work even for one electron

HF

B3LYP

LDA



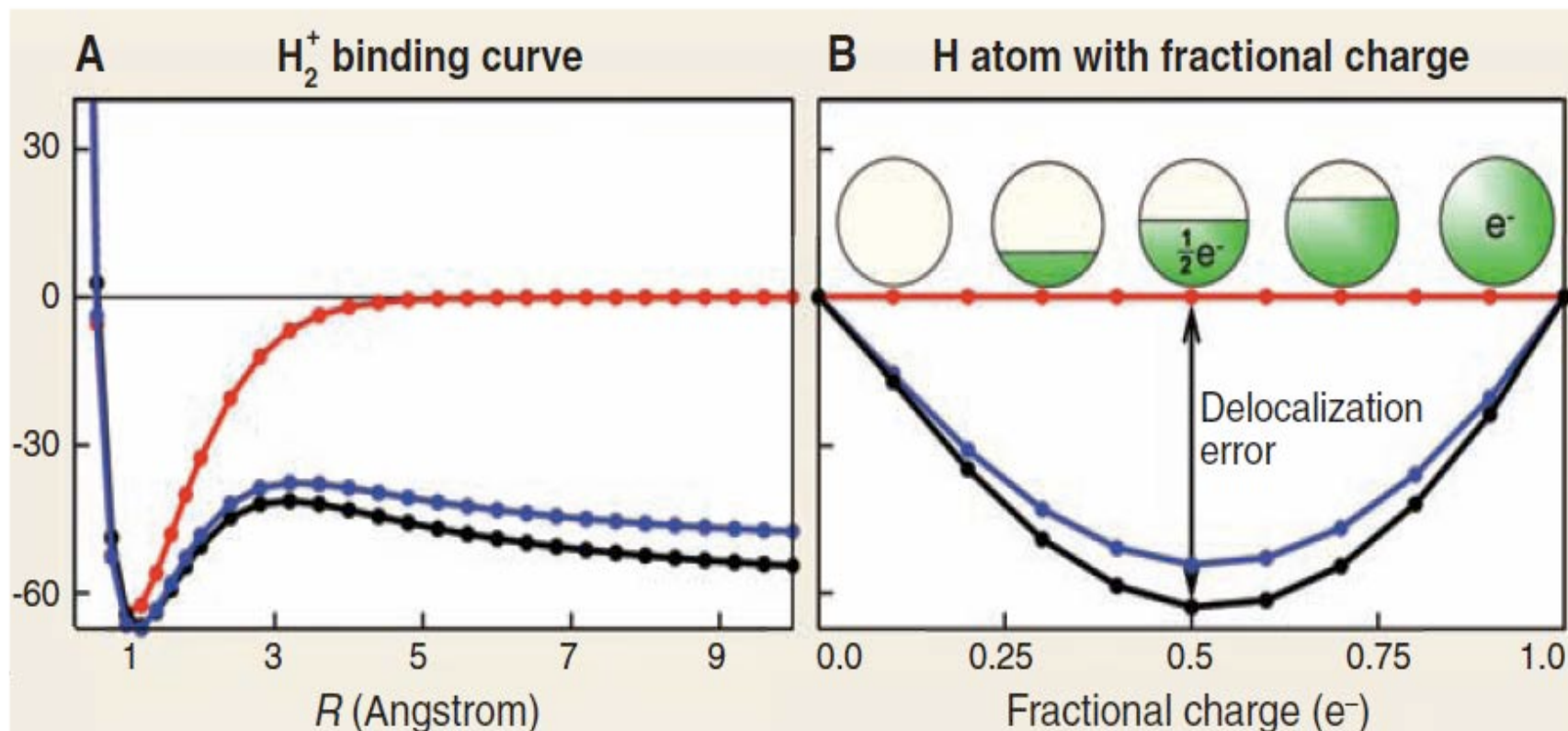
A.J. Cohen, P. Mori-Sanchez, W. Yang, Science (2008)

So, it doesn't work even for one electron

HF

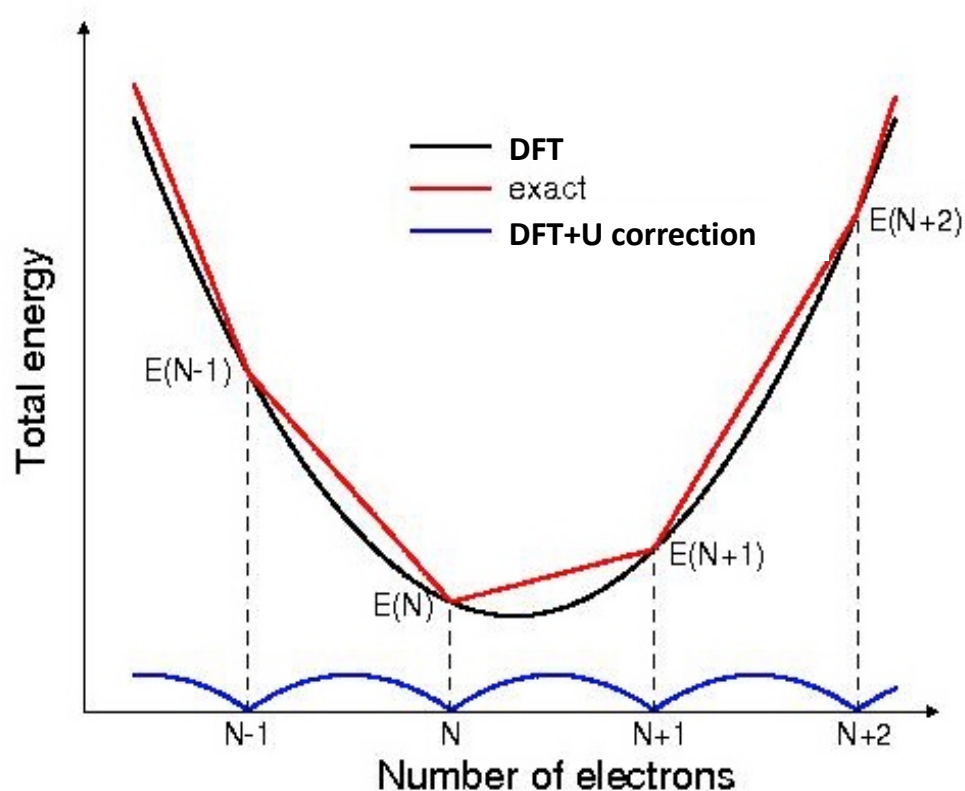
B3LYP

LDA



A.J. Cohen, P. Mori-Sanchez, W. Yang, Science (2008)

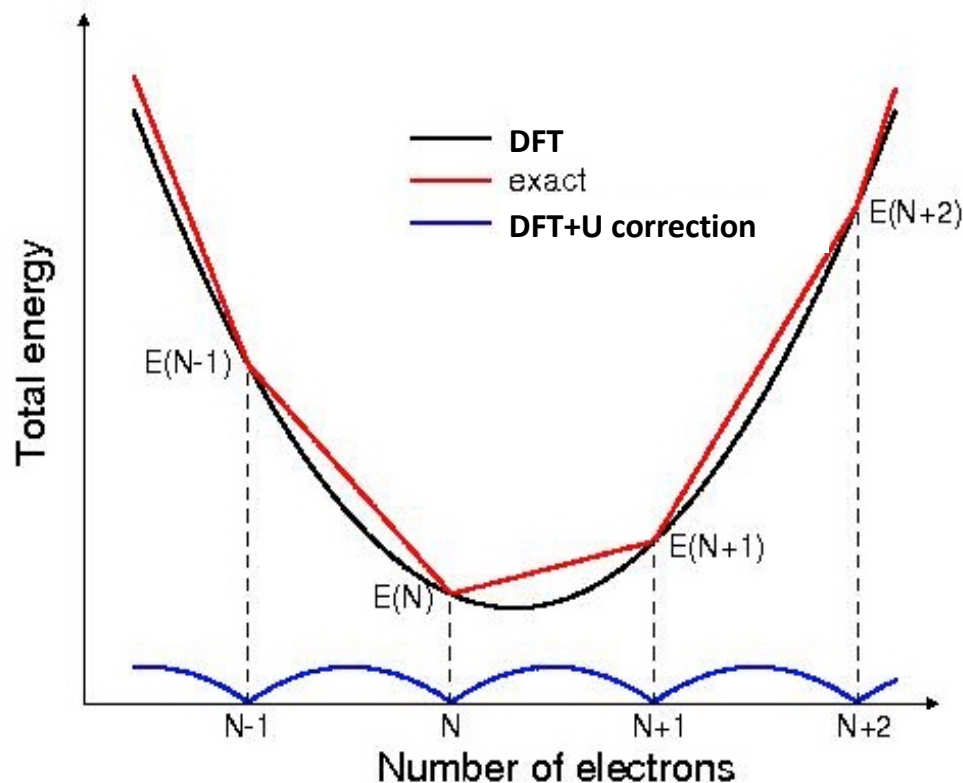
A DFT + Hubbard U approach



- The energy functional has an unphysical curvature
- the exact solution is piecewise linear

A DFT + Hubbard U approach

$$\frac{U}{2} \sum_{I,\sigma} \sum_{mm'} [n_{mm'}^{I\sigma} (\delta_{m'm} - n_{m'm}^{I\sigma})]$$



- The energy functional has an unphysical curvature
- the exact solution is piecewise linear
- a +U correction reproduces the exact solution

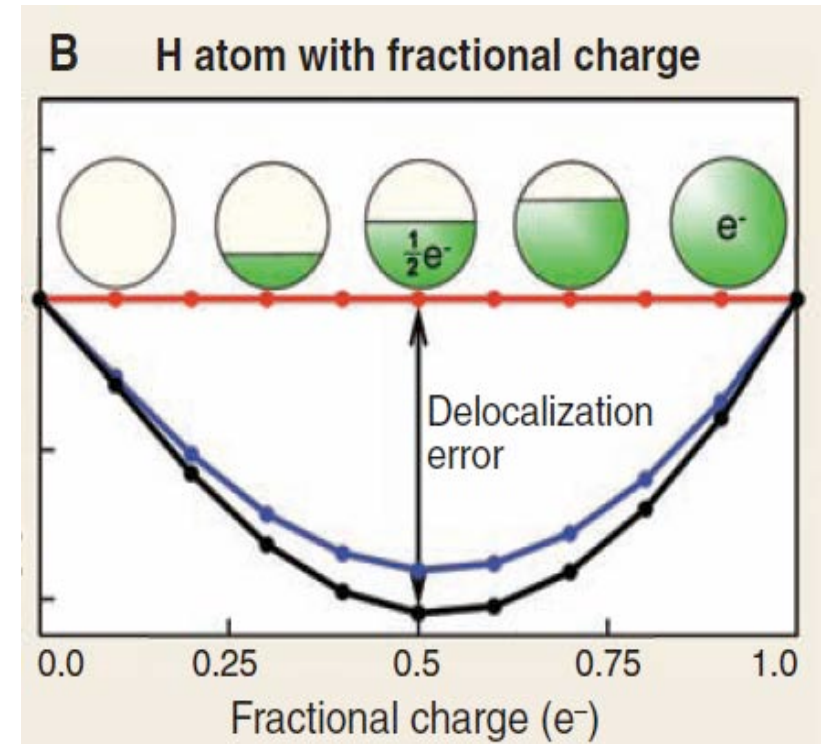
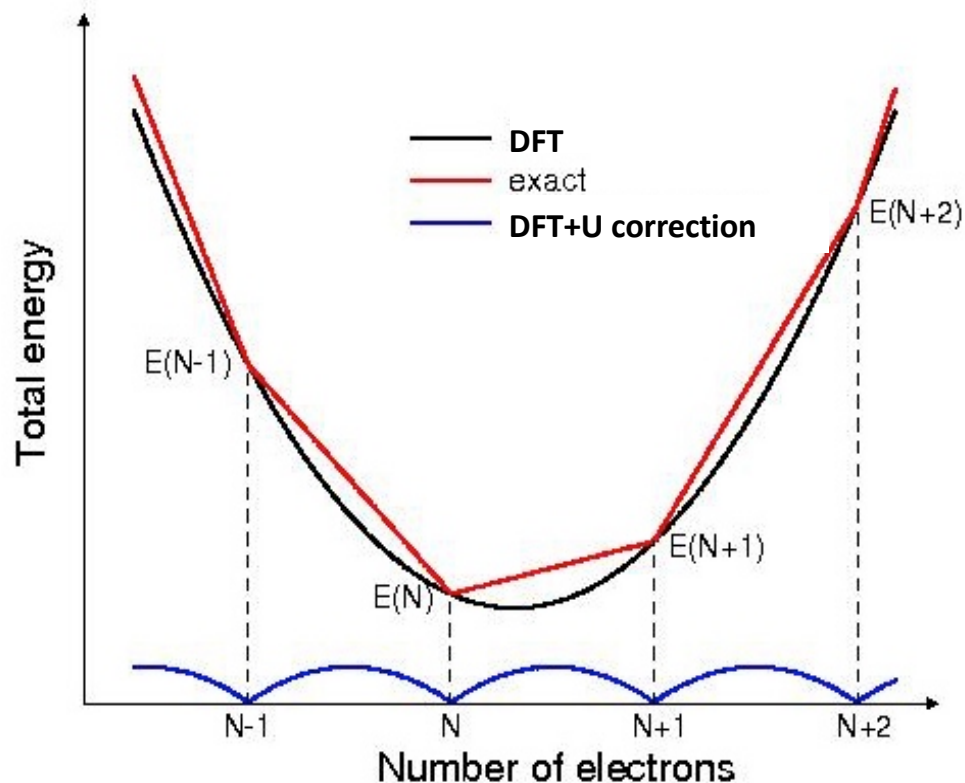
U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

LRT U: M. Cococcioni (PhD 2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

$$U = \frac{d^2 E^{LDA}}{d(n^{Id})^2} - \frac{d^2 E_0^{LDA}}{d(n^{Id})^2}$$

A DFT + Hubbard U approach

$$\frac{U}{2} \sum_{I,\sigma} \sum_{mm'} [n_{mm'}^{I\sigma} (\delta_{m'm} - n_{m'm}^{I\sigma})]$$

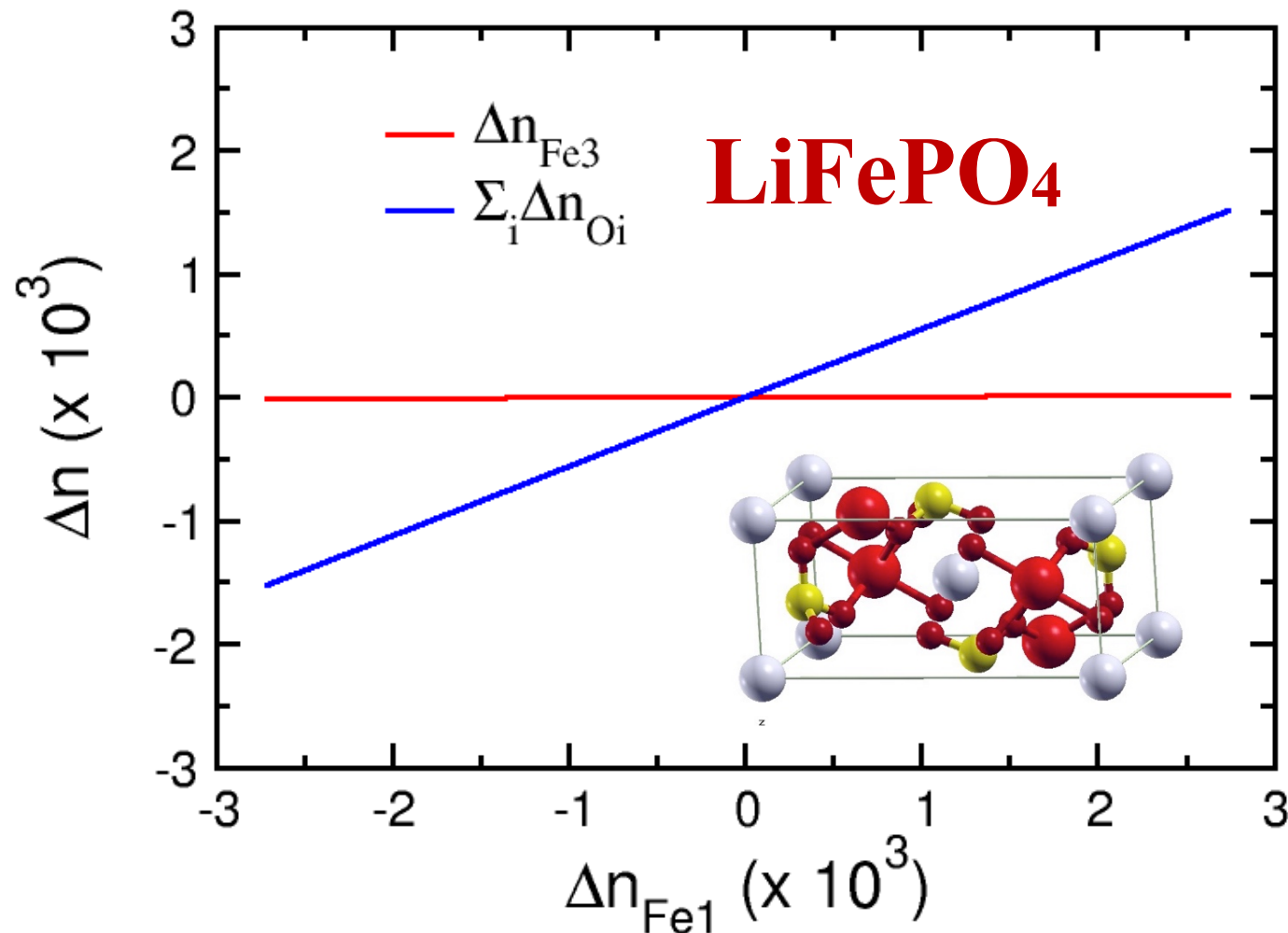


U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

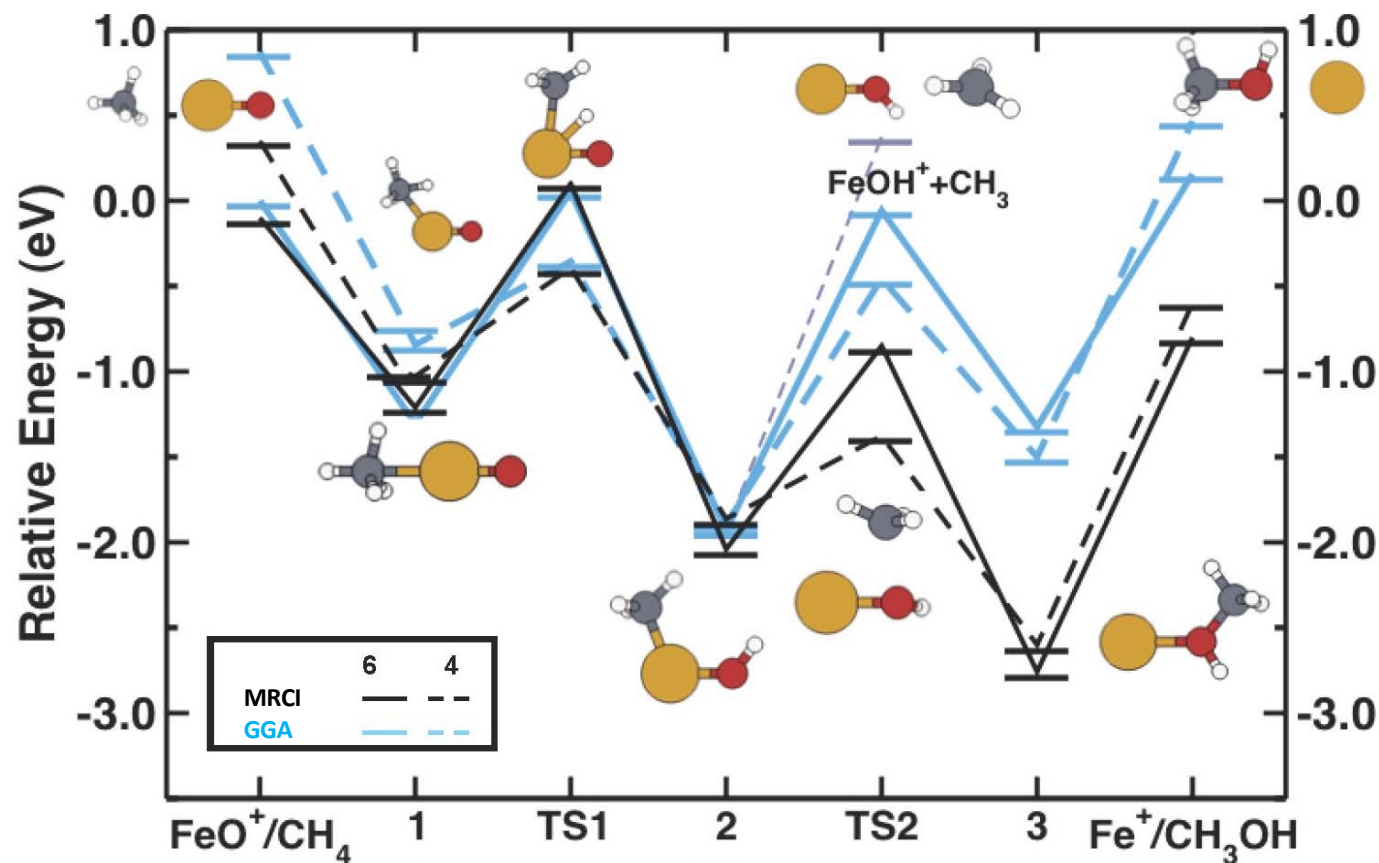
LRT U: M. Cococcioni (PhD 2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

DFT + U has nothing to do with correlation !

$$\frac{U}{2} \sum_{I,\sigma} \sum_{mm'} [n_{mm'}^{I\sigma} (\delta_{m'm} - n_{m'm}^{I\sigma})]$$

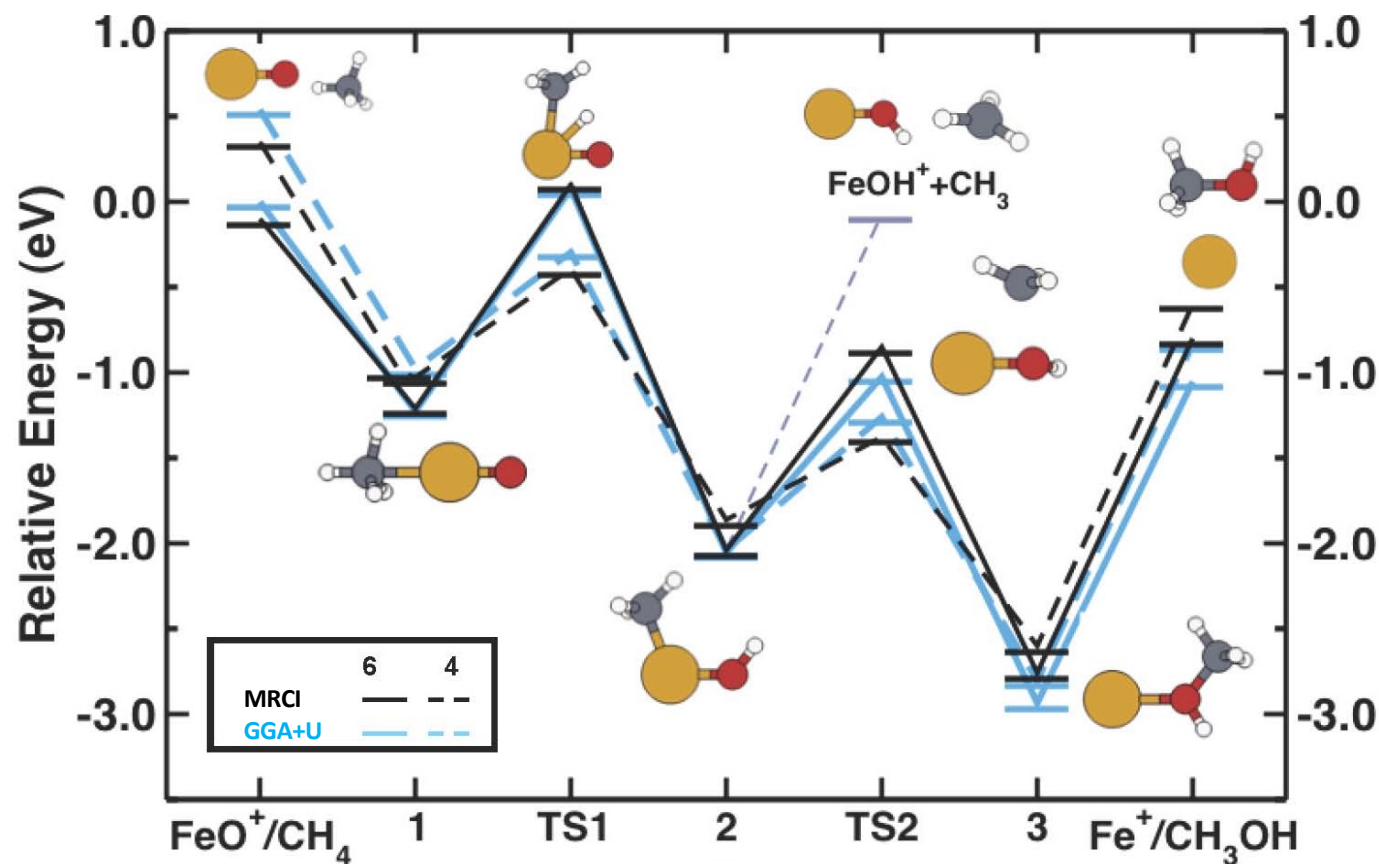


Methane on FeO^+ : GGA vs MRCI



H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, *Phys. Rev. Lett.* (2006)
H.J. Kulik and N. Marzari, *JCP* 129 134314 (2008)

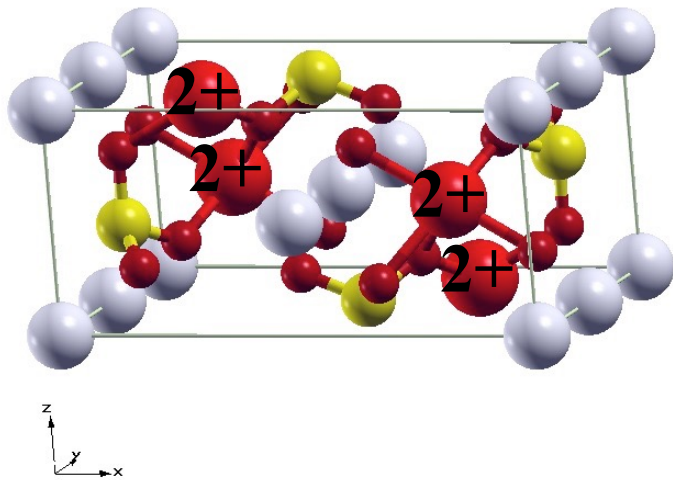
Methane on FeO^+ : GGA+U vs MRCI



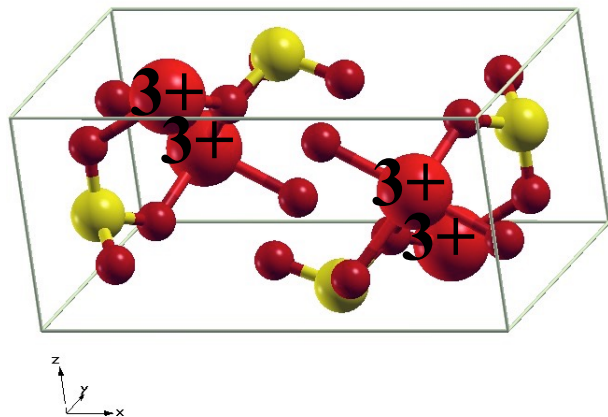
H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, *Phys. Rev. Lett.* (2006)
H.J. Kulik and N. Marzari, *JCP* 129 134314 (2008)

Mixed-valence olivines for battery cathodes

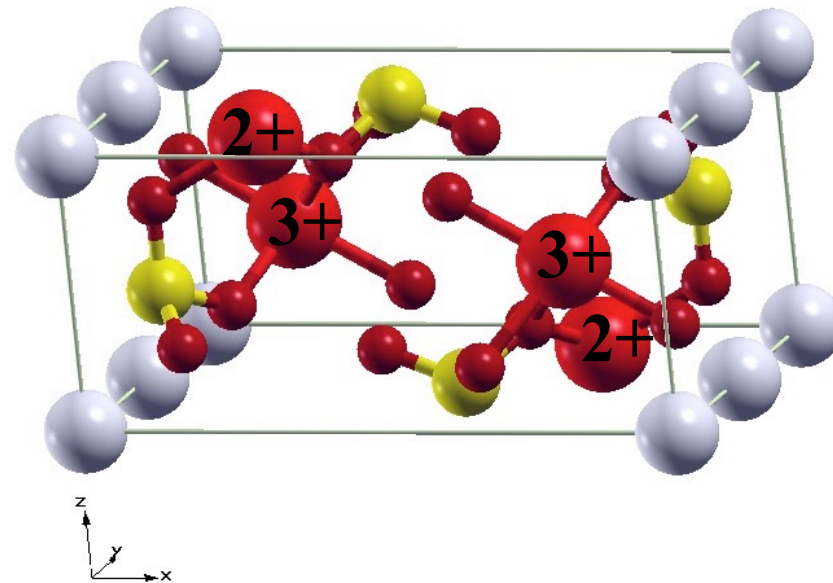
LiMPO₄



MPO₄



Li_{0.5}MPO₄



Li_xFePO₄: from PBE to scf DFT+U+V

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 3.5
PBE	-126	2.73
PBE+U	159	4.06
PBE+U _{scf}	189	3.83
PBE+U _{scf} +V _{scf}	128	3.48

	LiFePO ₄		Li _{0.5} FePO ₄		FePO ₄	
Method	2+	3+	2+	3+	2+	3+
PBE	6.22		6.11	6.08		5.93
PBE+U	6.19		6.19	5.68		5.65
PBE+U _{scf}	6.21		5.74	6.19		5.70
PBE+U _{scf} +V _{scf}	6.22		6.22	5.77		5.76

The image is a reproduction of Michelangelo's famous fresco, 'The Creation of Adam'. It depicts Adam reclining on the left, reaching towards God who is reclining on the right, surrounded by other figures. A speech bubble is superimposed over the central gap between the two figures.

That was good,
Adam. Can you make
it more general?

OBJECTIVE: SPECTRAL FUNCTIONALS

- **Spectral properties with a functional theory**
- It's actually not very difficult, but cannot be done with DFT: a functional of the **local, static density** gives you only the energy
- A functional of the **local spectral density** $\rho(\mathbf{r},\omega)$ provides also the correct energy levels
- In a quasi-particle approximation, this spectral functional depends discretely on **the orbital densities** $\rho(\mathbf{r},i)$

KOOPMANS' COMPLIANT SPECTRAL FUNCTIONALS

For every orbital the expectation value

$$\epsilon_i = \langle \varphi_i | \hat{H}^{\text{DFT}} | \varphi_i \rangle$$

does not depend on the occupation of the orbital

I. Dabo, M. Cococcioni, and N. Marzari, arXiv:0910.2637 (2009)

I. Dabo et al., Phys. Rev. B 82, 115121 (2010)

LINEARIZATION (FIRST, AT FROZEN ORBITALS)

add linear Koopmans


$$E^{\text{KI}} = E^{\text{DFT}} + \sum_i \left[- \int_0^{f_i} \langle \varphi_i | \hat{H}^{\text{DFT}} | \varphi_i \rangle + f_i \int_0^1 \langle \varphi_i | \hat{H}^{\text{DFT}} | \varphi_i \rangle \right]$$


remove ~quadratic Slater

I. Dabo et al., Phys. Rev. B 82, 115121 (2010)
G. Borghi et al., Phys. Rev. B 90, 075135 (2014)

SCREENING TO ACCOUNT FOR ORBITAL RELAXATIONS

$$E^{\text{KI}} = E^{\text{DFT}} + \sum_i \underbrace{\alpha_i}_{\text{orbital-dependent screening coefficient}} \left[- \int_0^{f_i} \langle \varphi_i | \hat{H}^{\text{DFT}} | \varphi_i \rangle + f_i \int_0^1 \langle \varphi_i | \hat{H}^{\text{DFT}} | \varphi_i \rangle \right]$$

I. Dabo et al., Phys. Rev. B 82, 115121 (2010)
N. Colonna et al., JCTC in press (2018), and arXiv

ORBITAL-DENSITY DEPENDENT

Explicitly, the KI Koopmans' functional adds to the base functional

$$E^{\text{KI}} = E^{\text{DFT}} + \sum_i \alpha_i \left[\left(E_{\text{Hxc}}[\rho - \rho_i] - E_{\text{Hxc}}[\rho] \right) + f_i \left(E_{\text{Hxc}}[\rho - \rho_i + n_i] - E_{\text{Hxc}}[\rho - \rho_i] \right) \right]$$

ρ_i orbital density at filling f_i

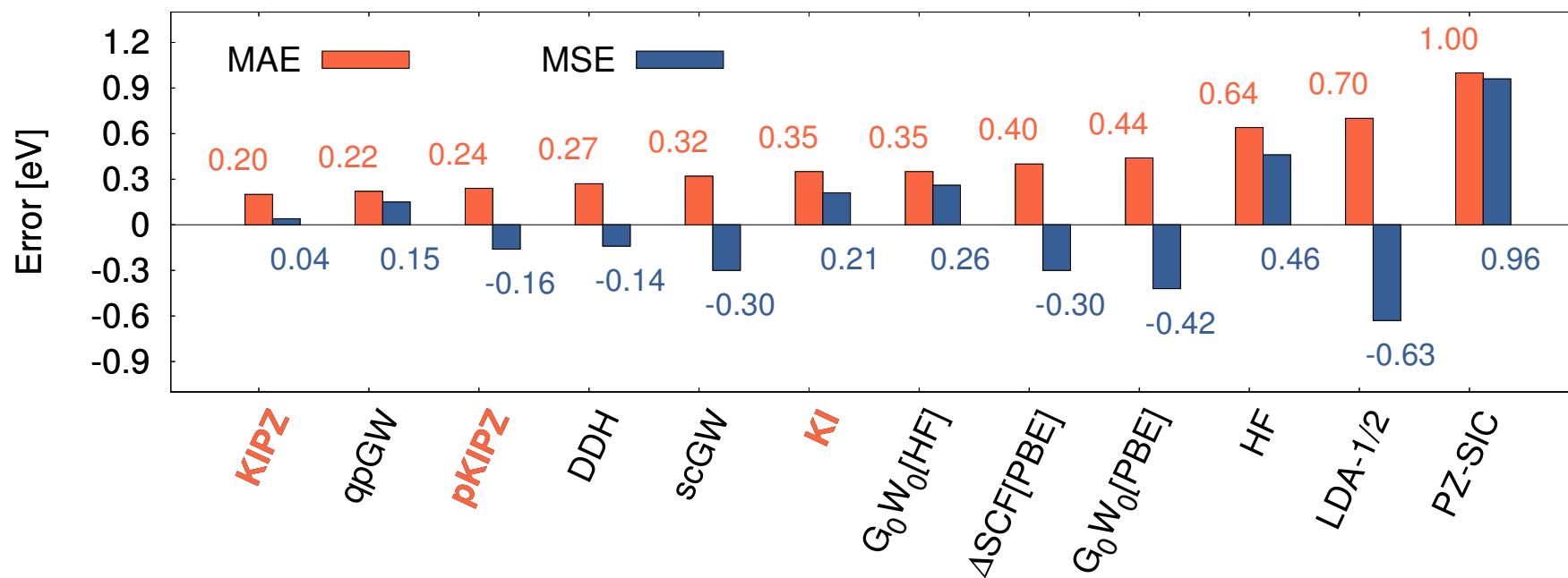
n_i orbital density at integer filling

KIPZ adds a screened PZ self-interaction term

$$E^{\text{KIPZ}} = E^{\text{KI}} - \sum_i \alpha_i f_i E_{\text{Hxc}}[n_i]$$

G. Borghi et al., Phys. Rev. B 90, 075135 (2014); Phys. Rev. B 91, 155112 (2015)

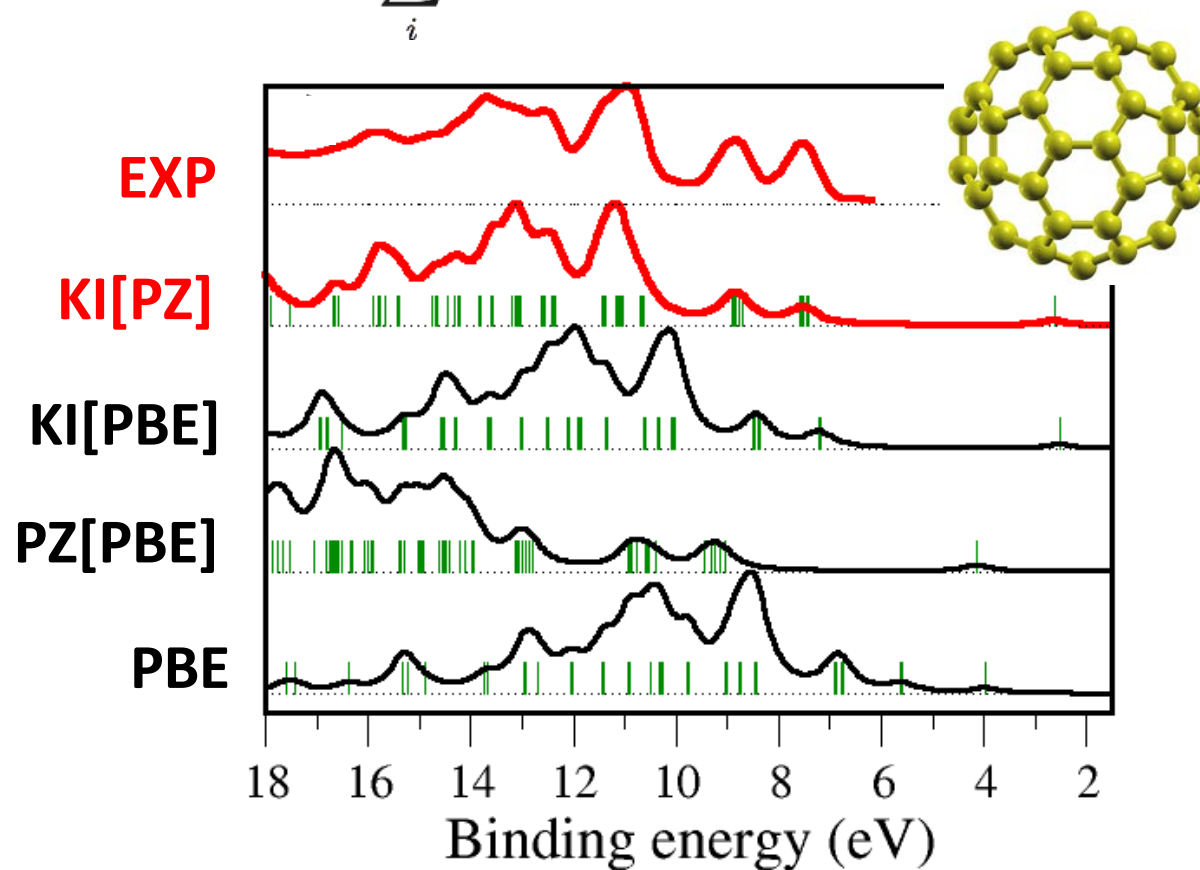
GW100 TEST SET



N. Colonna et al., JCTC in press (2018)

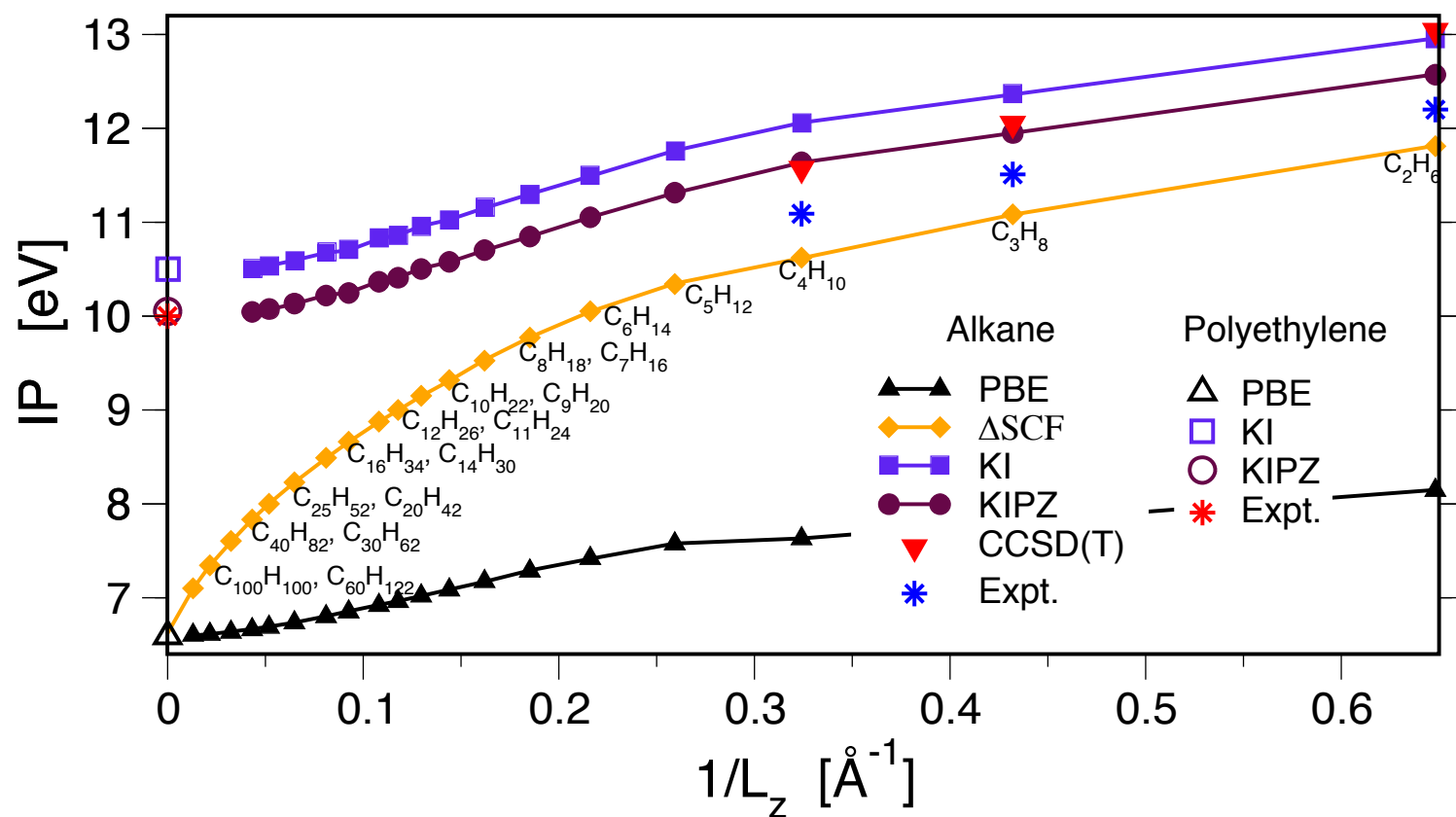
UPS (fullerene)

$$I(\omega) = \sum_i |\langle \varphi_f | \hat{H}_{\text{int}} | \varphi_i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \hbar\omega)$$

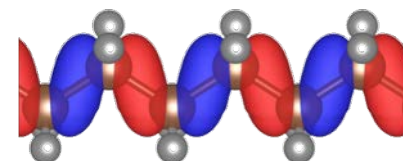


L. Nguyen, G. Borghi, A. Ferretti, I. Dabo, N. Marzari, *Phys. Rev. Lett.* 114, 166405 (2015)

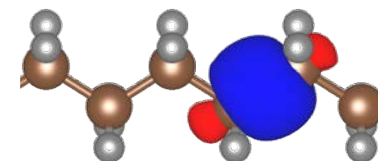
SOLID-STATE LIMIT



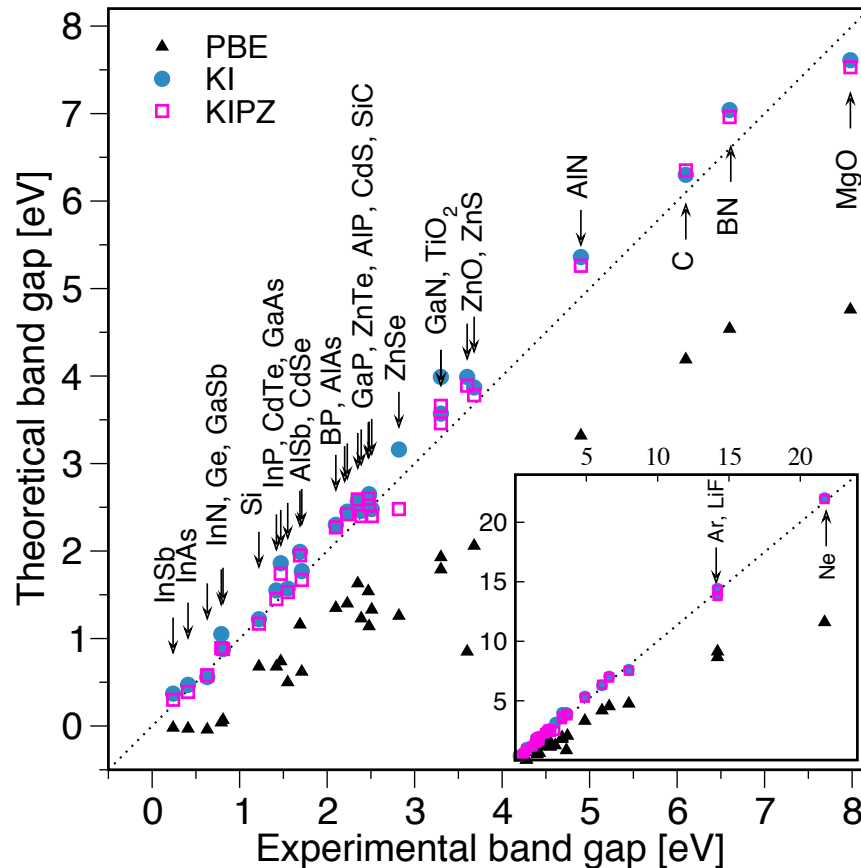
Canonical orbital



**Variational
(minimizing)
orbital**



BAND GAPS AND IPs (30 SOLIDS)



MAE (eV)	Gap	IP
PBE	2.54	1.09
G_0W_0	0.56	0.39
QSGW	0.18	0.49
KI	0.27	0.19
KIPZ	0.22	0.21

GW: W. Chen and A. Pasquarello PRB 92 041115 (2015); Koopmans: L. Nguyen, N. Colonna, A. Ferretti, and N. Marzari, PRX (2018)

Linearity + screening + localization

- **Linearity** as a foundation (orbital energies independent from their occupation), plus **screening**, plus **localization**.
- Beyond-DFT orbital-density formulation
- Functional theory of both energies and spectral properties
- **Can we substitute diagrammatic approaches like GW or DMFT with spectral functionals?**

Resonance with many ideas, from...

1. Short-range hybrid functionals (Scuseria, many)
2. Range-separated hybrids (Kronik, Baer, Neaton)
3. Self-consistent hybrids (Galli)
4. Many-body self-interaction free (Weitao Yang)

KI functional applied to:

- **HOMO/LUMO → ensemble-DFT (Krischer-Kronik 2013)**
- **Maximally-localized Wannier functions → Koopmans-Wannier method (Lin-Wan Wang, 2015)**

Why is DFT like tinder ?

It's a  Match!

Why is DFT like tinder?

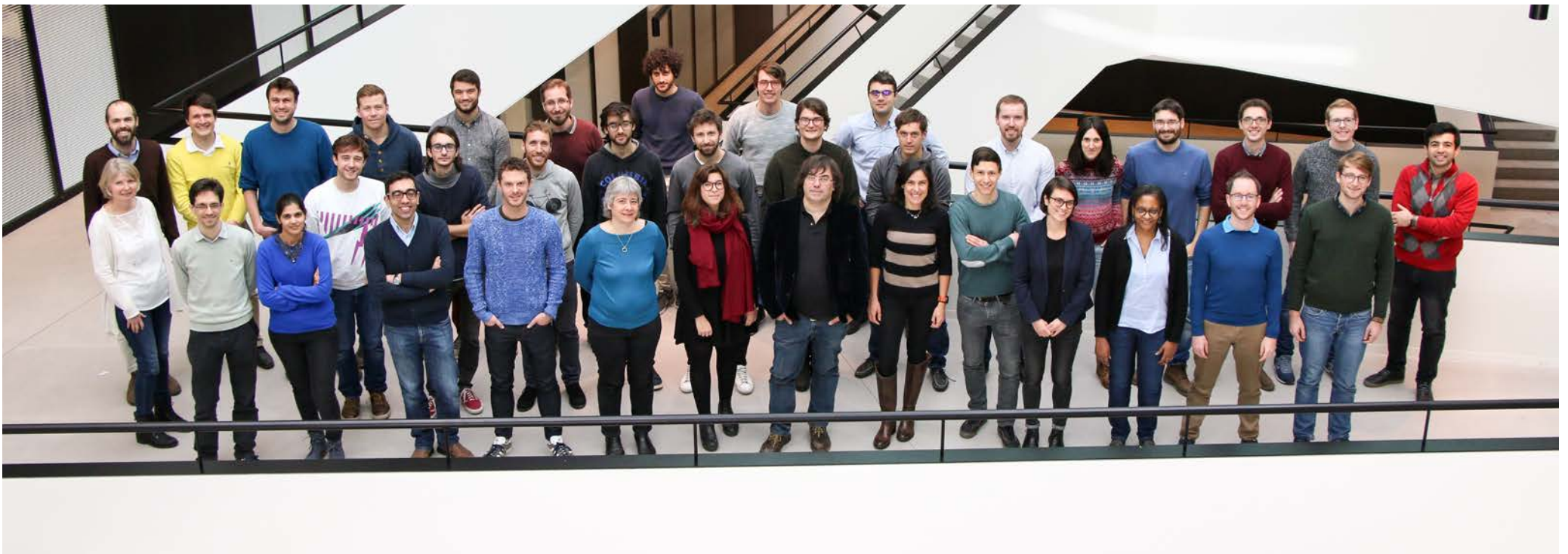
- I. It's very popular! Everyone does it**
- II. It's fast and easy, and requires no thinking**
- III. You can swipe functionals left until you find the one that works for you, for a while**

N. Marzari, *Materials modelling: The frontiers and the challenges*, Nature Materials 15, 381 (2016)

Acknowledgements

The people I learnt from – Mauro Ferrari, Alfonso Baldereschi, Stefano Baroni, Alessandro de Vita, Mike Payne, David Vanderbilt, Roberto Car

<http://theosrv1.epfl.ch/Main/People>



*About your cat, Mr. Schrödinger -
I have good news, and bad news.*

