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

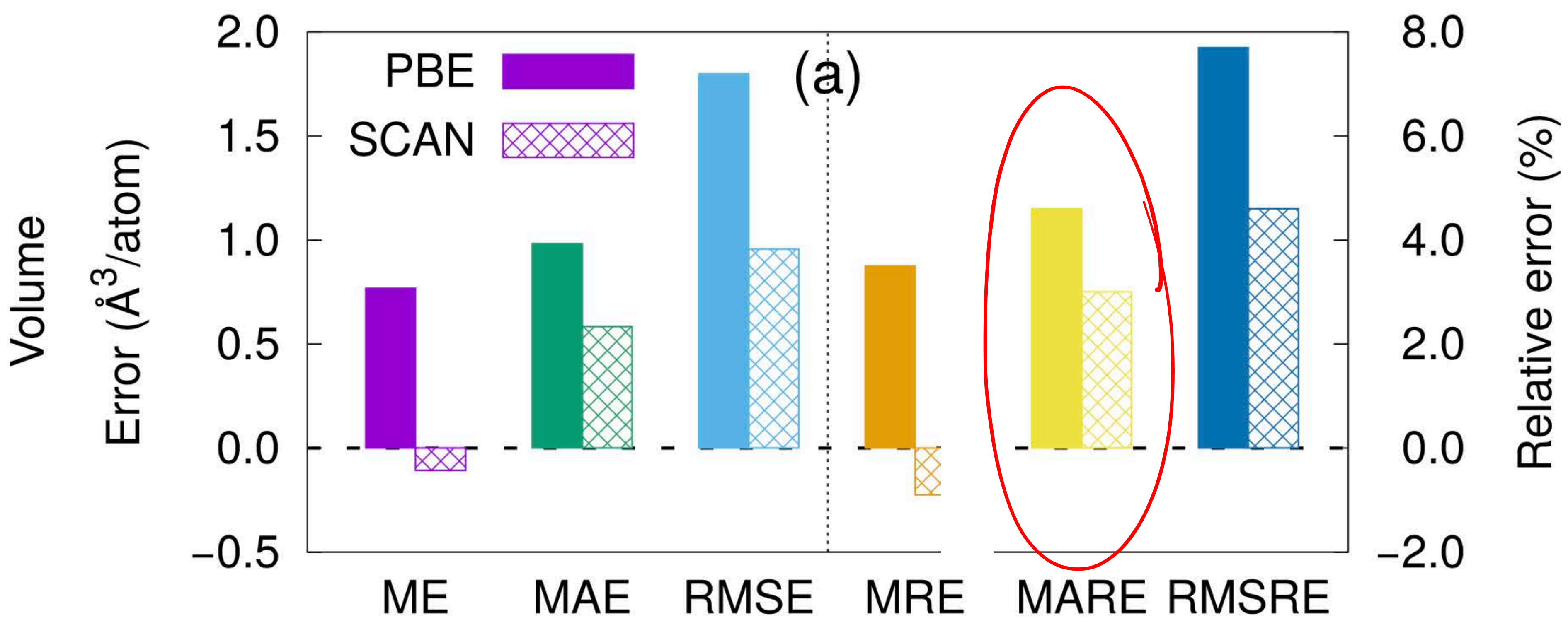
- **From DFT to real electrons**
  - many-body perturbation theory
  - quantum Monte Carlo
  - DMFT, cluster DMFT, DCA

Examples

- **Length, time, phase and composition sampling**
  - linear scaling, multiscale,
  - metadynamics, sketch-map
  - minima hopping, random-structure searches

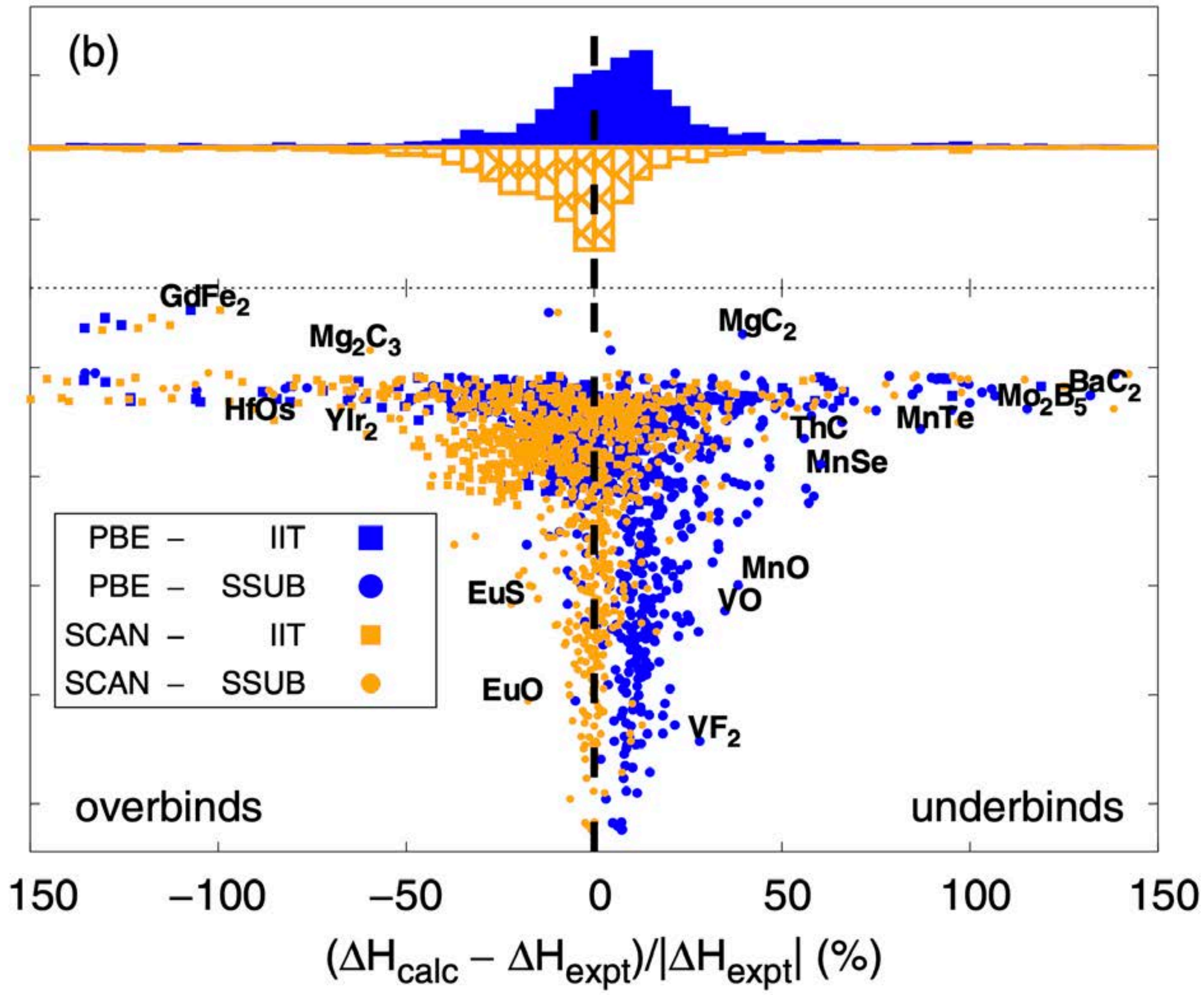
- **Complex properties**
  - phase diagrams
  - spectroscopies and microscopies: IR, Raman, XPS, XANES, NMR, EPR, ARPES, STM, TEM…
  - transport: ballistic, Keldysh, Boltzmann

Easy: equilibrium volume



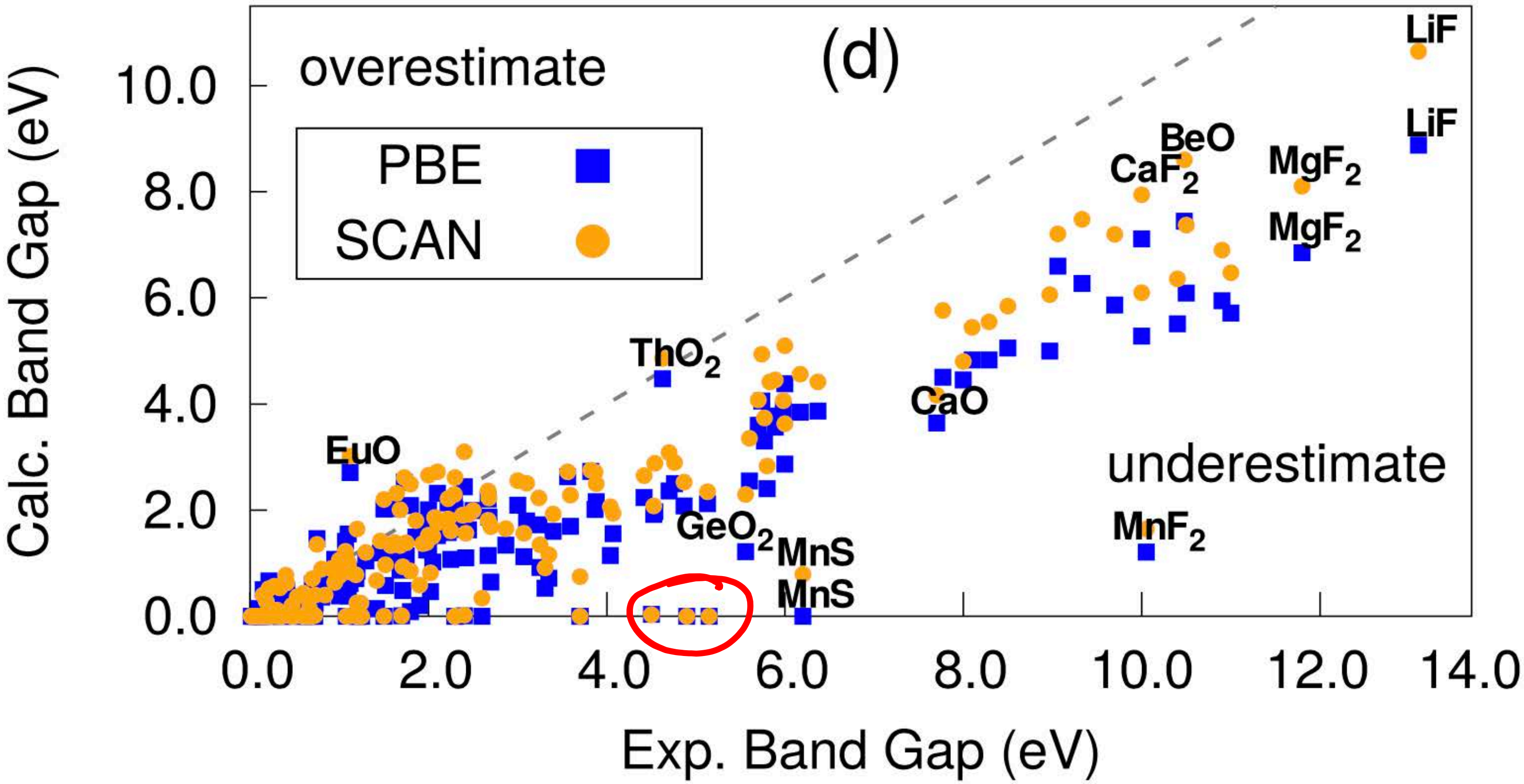
Eric B. Isaacs and Chris Wolverton, Phys. Rev. Materials 2, 06380 (2018)

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

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

$$-\frac{dE}{d\vec{R}}$$

R. P. Feynman

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

1939

Acceptance:

Instructor in charge of thesis John Slater

May 22, 1939
(Date)

Helmann-Feynman theorem

$\lambda = \vec{R}$

$\lambda = \vec{\mathcal{E}}$

$\hat{T} + \hat{V}$

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

$$\frac{d}{d\lambda}\langle\psi|\psi\rangle = 0$$

$$\left\langle \frac{\partial\psi}{\partial\lambda}\right| H |\psi\rangle + \left\langle\psi\right| \frac{\partial H}{\partial\lambda} |\psi\rangle +$$

$$+ \langle\psi| H \left|\frac{\partial\psi}{\partial\lambda}\right\rangle = \epsilon\left(\cancel{\left\langle\frac{\partial\psi}{\partial\lambda}\middle|\psi\right\rangle + \left\langle\psi\middle|\frac{\partial\psi}{\partial\lambda}\right\rangle}\right) +$$

$$+ \left\langle\psi\right|\frac{\partial H}{\partial\lambda}\left|\psi\right\rangle$$

Linear-response theory

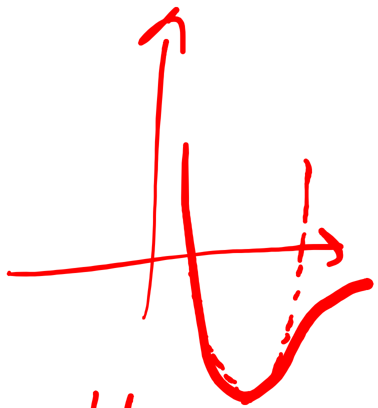
Perturbation (external potential):

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

Response (charge density):

LINEAR RESPONSE

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



Hellmann-Feynman Theorem:

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

$\omega = \sqrt{\frac{k}{m}}$ $\quad \frac{1}{2} k \Delta x^2$

Total Energy:

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

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

Linear-response theory

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

$$\Downarrow$$

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

$$\Downarrow$$

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

$$\Downarrow$$

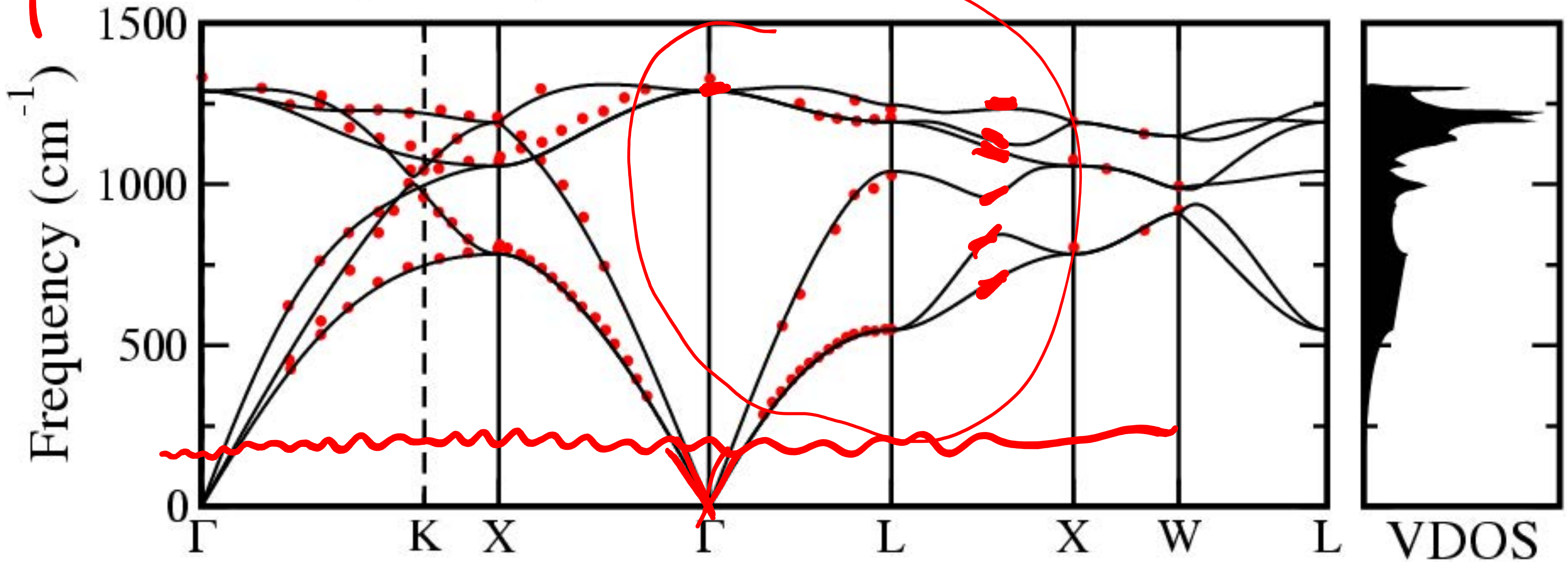
$$\Delta n(\mathbf{r}) = 2\sum \psi_v^*(\mathbf{r})\,\Delta\psi_v(\mathbf{r})\,\theta(\epsilon_F - \epsilon_v)$$

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

8065 cm^{-1} = 1 eV   RT $\simeq \frac{1}{40}$ eV

Phonons and temperature

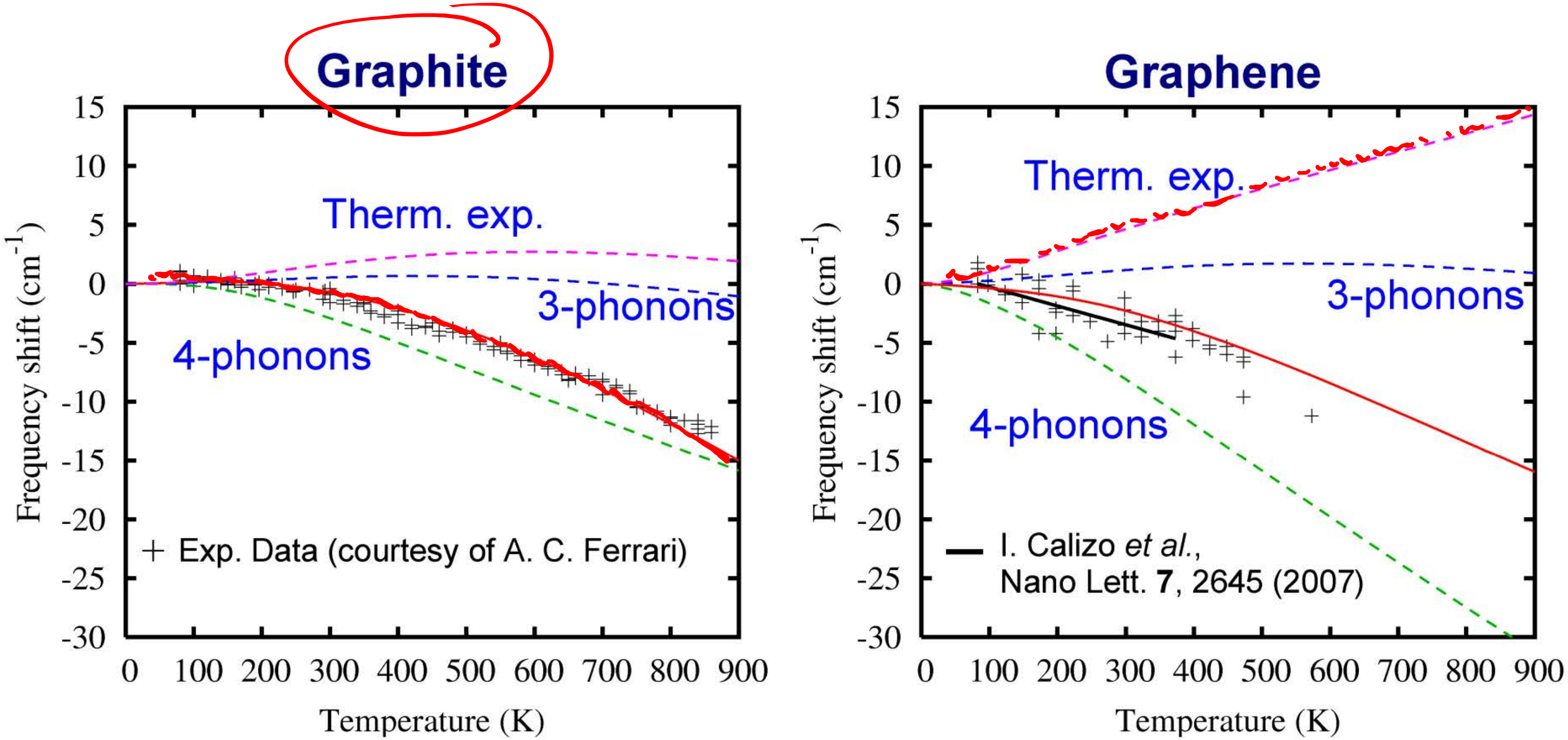
DIAMOND



- 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
		B δ_{BTE}	B δ_{BTE}
$(B_{12}H_{12})^{2-}$		-14.9[a]	(-14.9)
$(B_{11}CH_{12})^{-}$	Ortho	-16.3[b]	-16.2
	Meta	-13.3[b]	-11.7
	Antipodal	-6.9[b]	-5.4
		C δ_{TMS}	Cδ_{TMS}
$(B_{11}CH_{12})^{-}$		54.6[c]	(54.6)

[a]In CD_3CN solvent, Ref. [18].
[b]In hexadeuterioacetone, Ref. [19].
[c]Ref. [20].

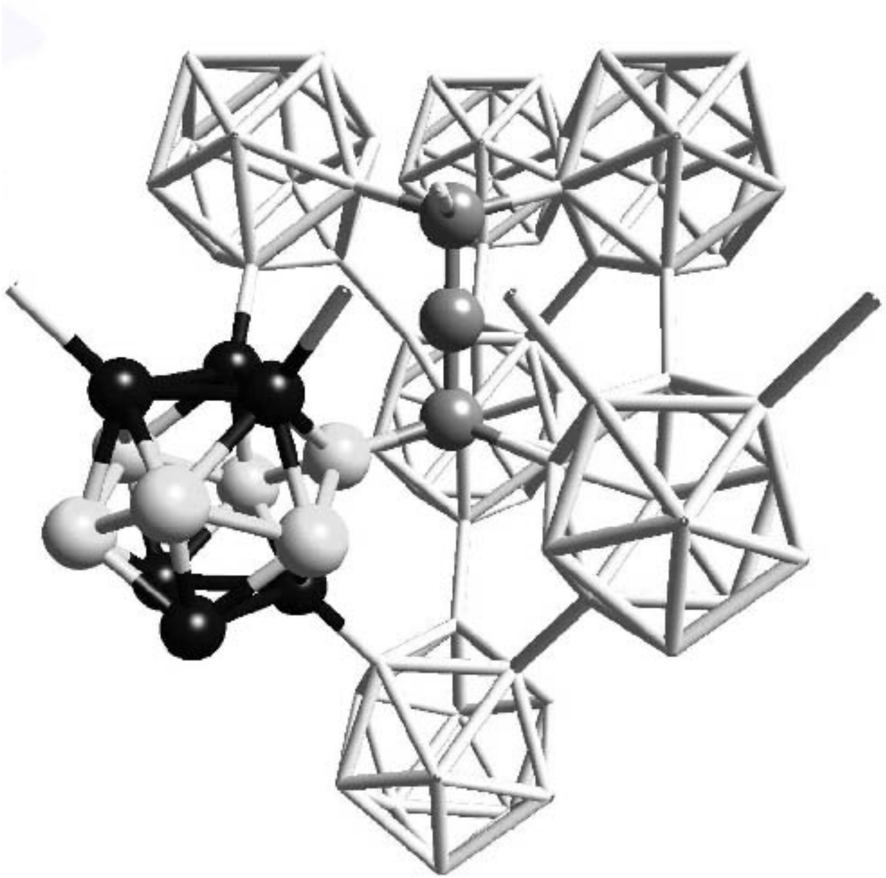
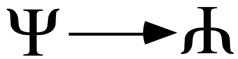


FIG. 1. Atomic structure of B_4C. The black atoms are on the so-called polar sites, bonded to neighboring icosahedra. The white atoms form a puckered hexagon and are in equatorial sites. The grey atoms form the chain, to which the equatorial atoms are bonded.

Sampling excitations

Electronic

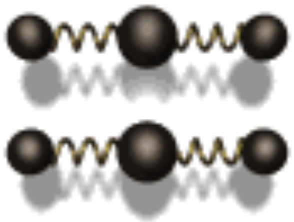
Occupation



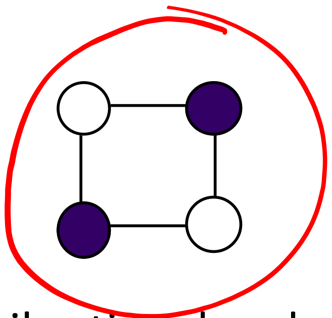
Magnetic (electron spin)

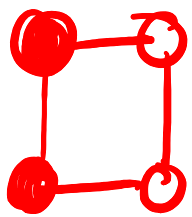
$\uparrow \longrightarrow \downarrow$

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

$\frac{1}{k_B T}$

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

$$Q = \sum_i \exp[-\beta\, E_i]$$ → Partition Function

$$F = -\beta \ln[Q]$$ → Free energy (Helmholtz)

$$S = -k_B \sum_i P_i \ln(P_i)$$ → Entropy

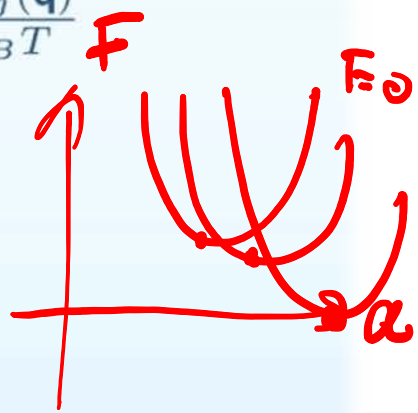
For the vibrational free energy, analytically!

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:

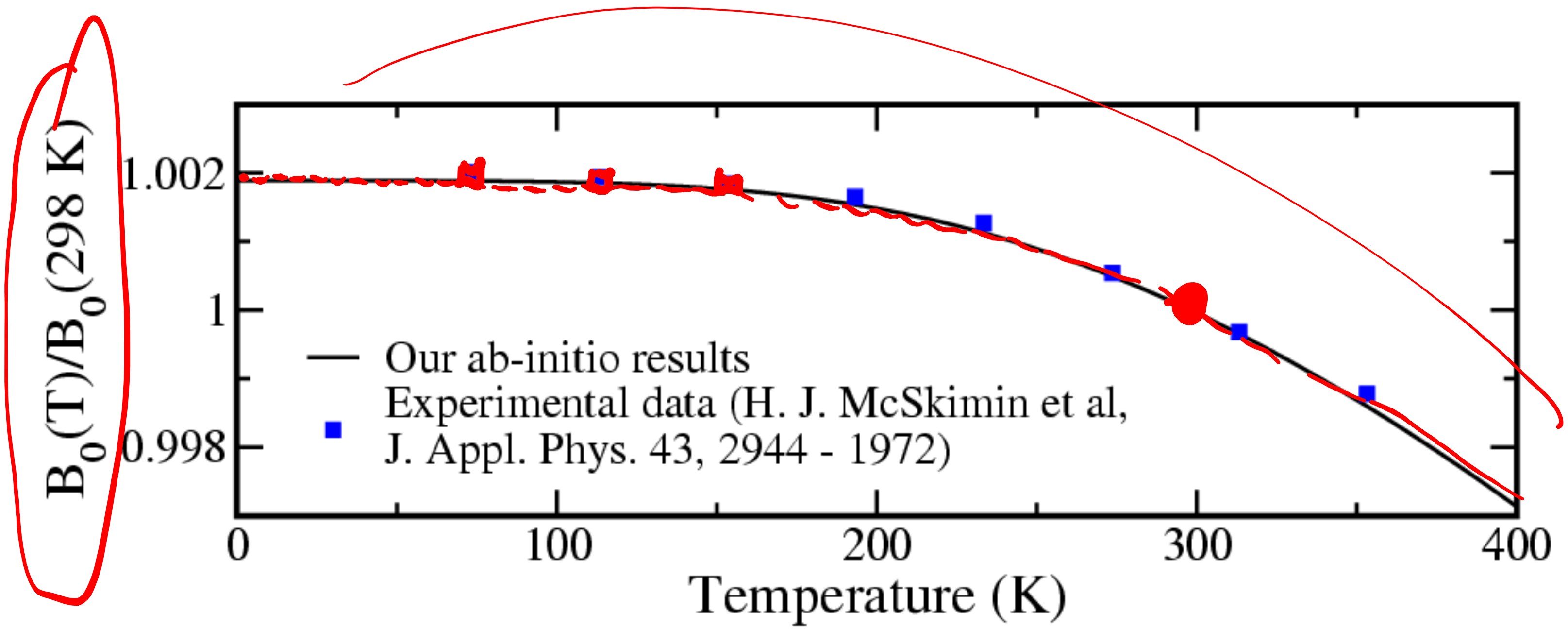
$$Z_{total} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j} = \frac{1}{\prod_{\mathbf{q},j} 2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

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

$\omega_{q,j}(\{a_i\})$

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

Thermomechanics (bulk modulus of diamond)

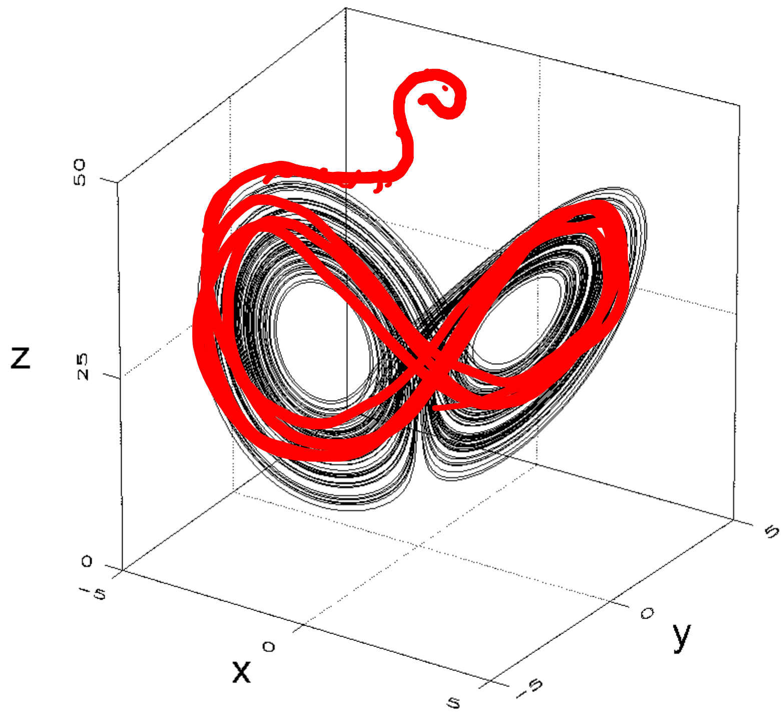


Otherwise, thermodynamical averages

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

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

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



F.P.

Molecular dynamics

H-F DFT

$$m_i \frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i(\vec{r}) = -\vec{\nabla} V(\vec{r}) \longrightarrow \begin{matrix} \vec{r}(t) \\ \vec{v}(t) \end{matrix}$$

TAYLOR EXP.

FORWARD

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

BACKWARD

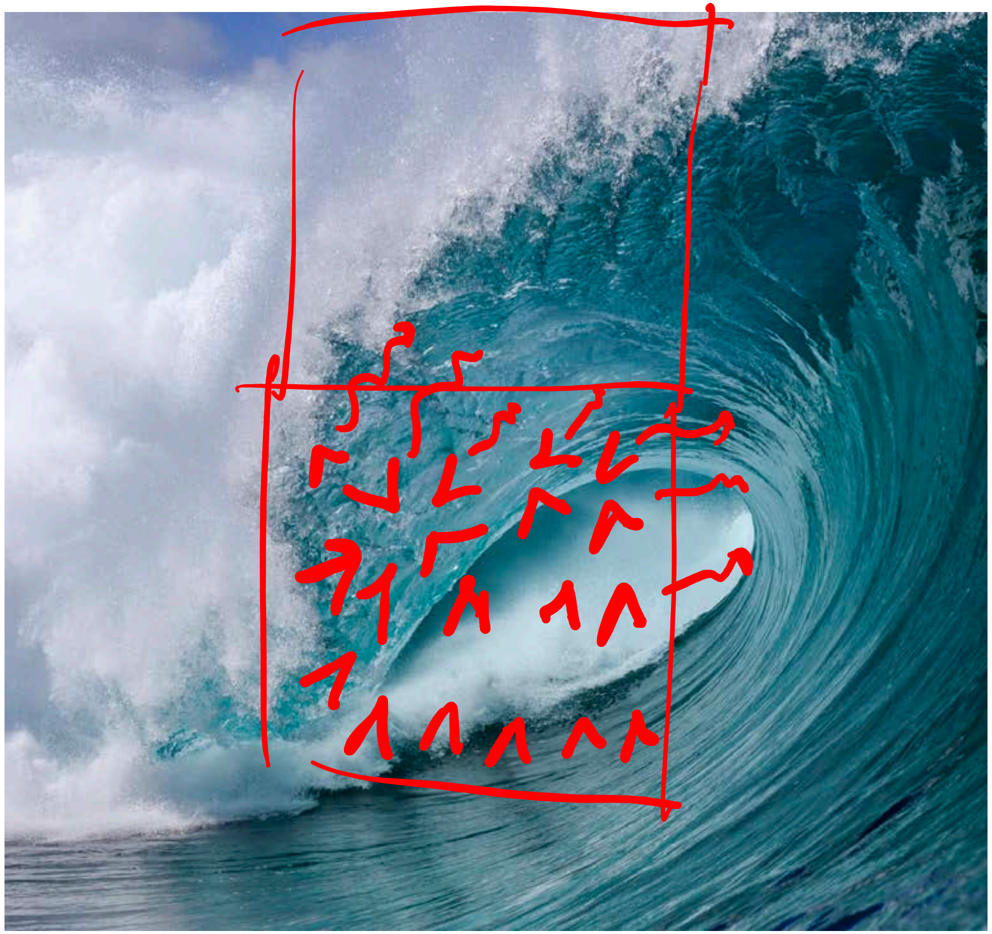
$$\mathbf{r}(t-\Delta t) = \mathbf{r}(t) - \cancel{\mathbf{v}(t)\Delta t} + (1/2)\mathbf{a}(t)\Delta t^2 - \cancel{(1/6)\mathbf{b}(t)\Delta t^3} + O(\Delta t^4)$$

+

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

$\vec{F}/m$

A drop to drink



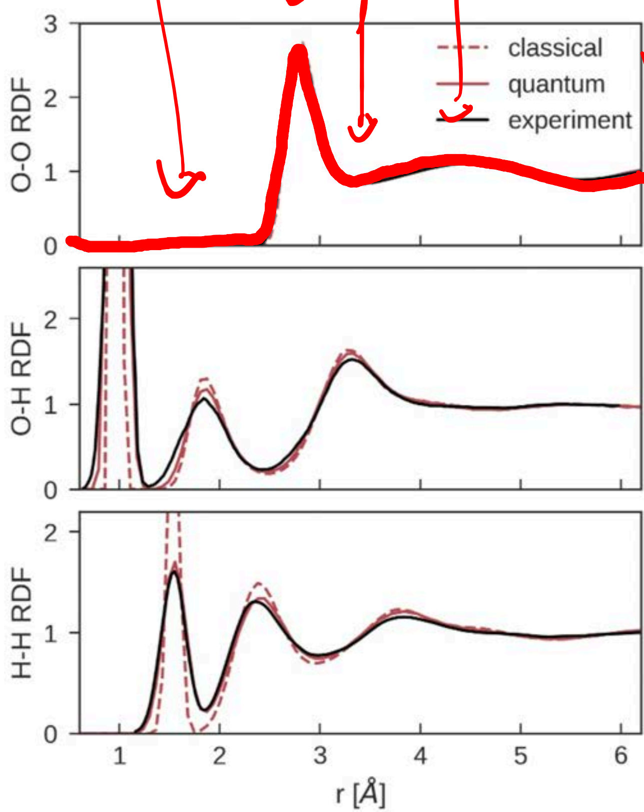
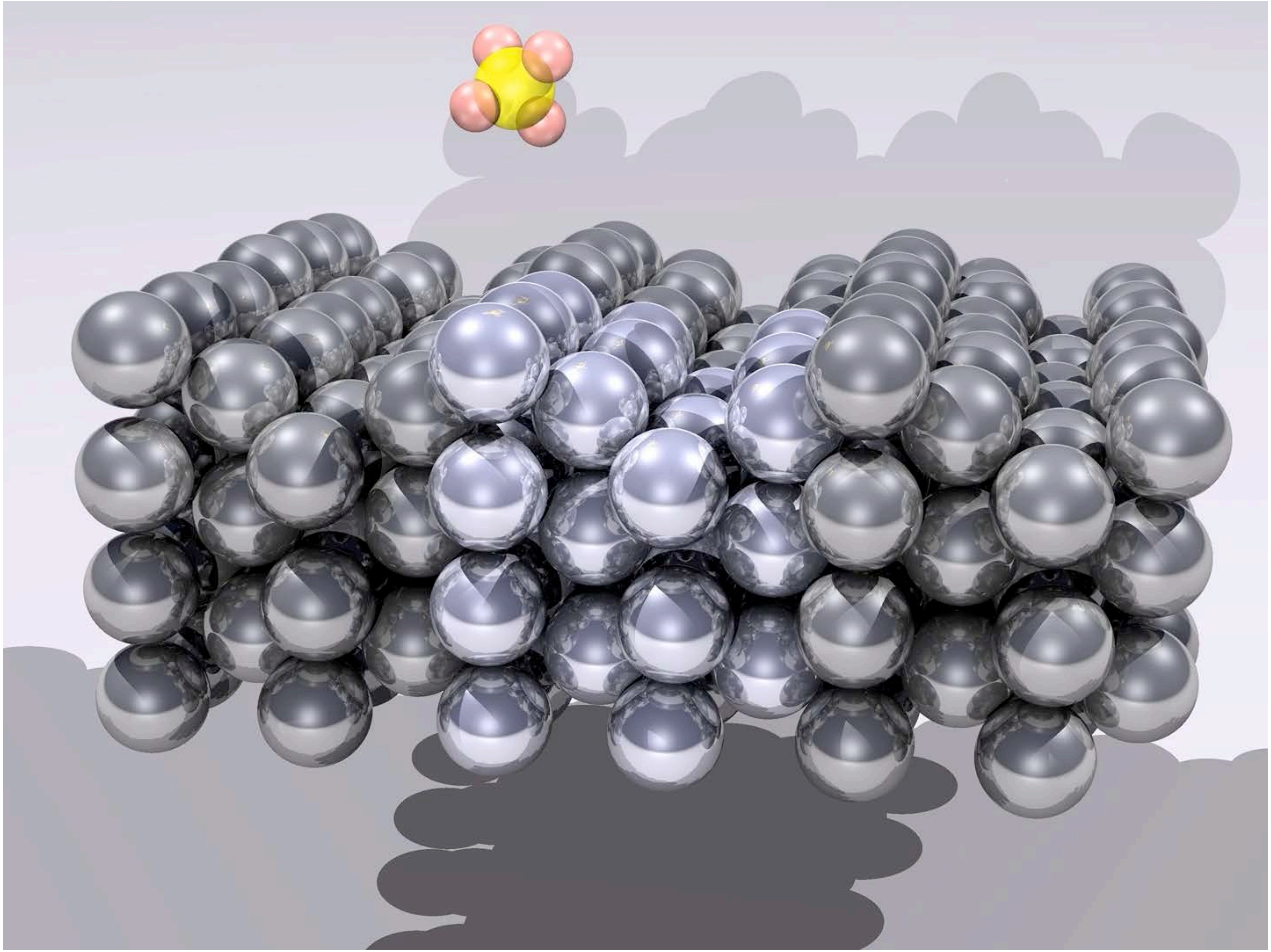


Fig. 2. Oxygen–oxygen, oxygen–hydrogen, and hydrogen–hydrogen RDFs at 300 K and experimental density computed via (PI)MD simulations in the constant number of particles, volume, and temperature (NVT) ensemble using the NN potential. The experimental O–O RDF was obtained from ref. 37, and the experimental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

$\Sigma A \frac{1}{N}$

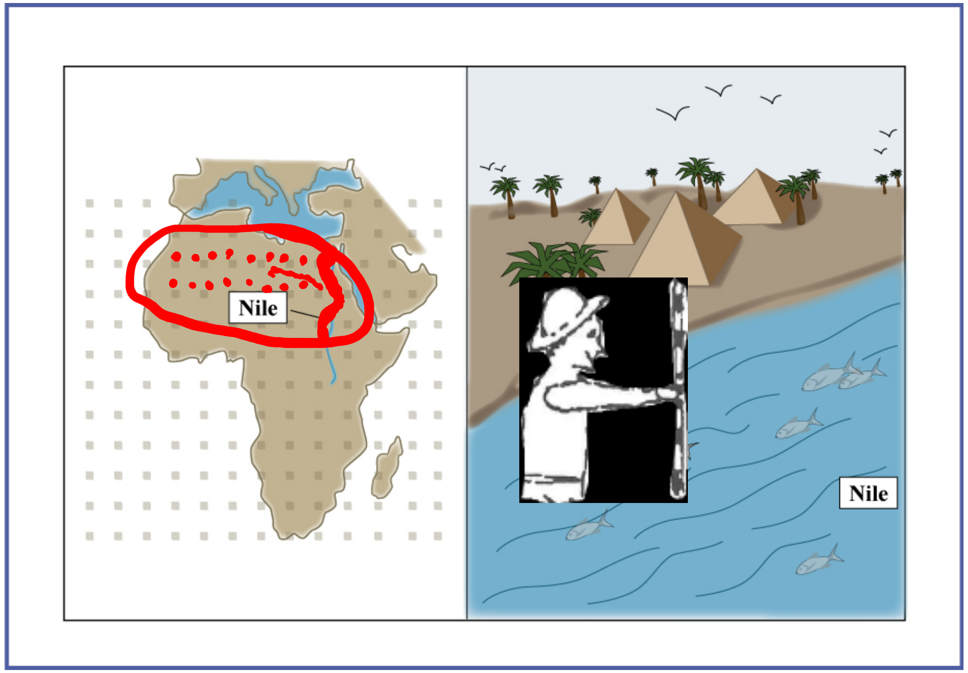
$$\langle A \rangle = \frac{\int A \exp(-\beta E)\, d\vec{r}\, d\vec{p}}{\int \exp(-\beta E)\, d\vec{r}\, d\vec{p}}$$

Metropolis algorithm
(by Arianna and Marshall Rosenbluth)

$$P_{i\to j} = 1 \quad \textbf{when} \quad E_j < E_i$$

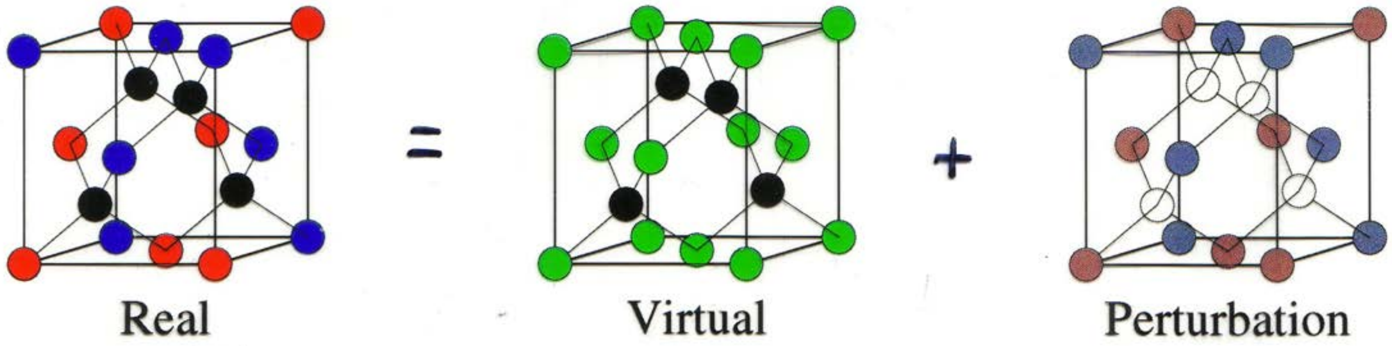
$$P_{i\to j} = \exp(-\beta(E_j - E_i)) \quad \textbf{when} \quad E_j > E_i$$

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



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

Thermodynamics of substitutional alloys



Perturbation (external potential):

→ SEMIDIFF. PSEUDO

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

Total energy:

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

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

Monte Carlo simulations :

$\langle x \rangle = \langle x \rangle(\Delta\mu)$

$x(\mu)$

$\Downarrow$

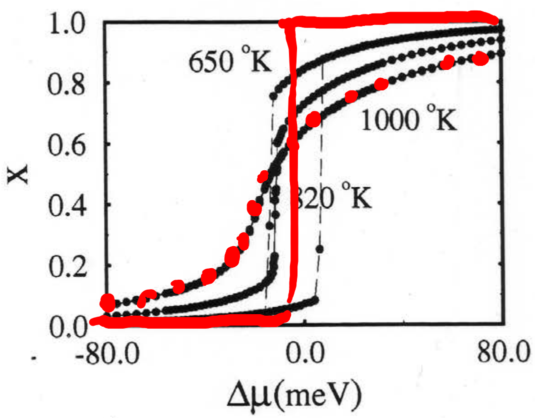
$\mu(x)$

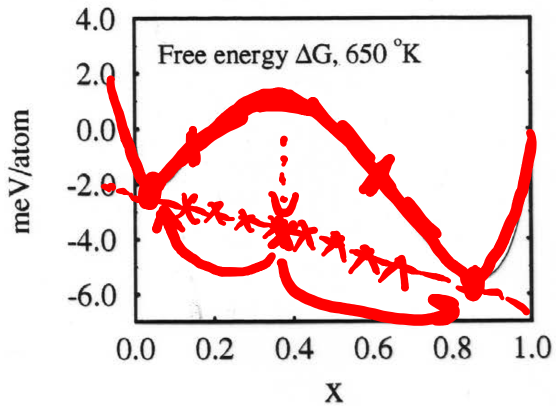
$G \quad \int \frac{dE}{dN}$

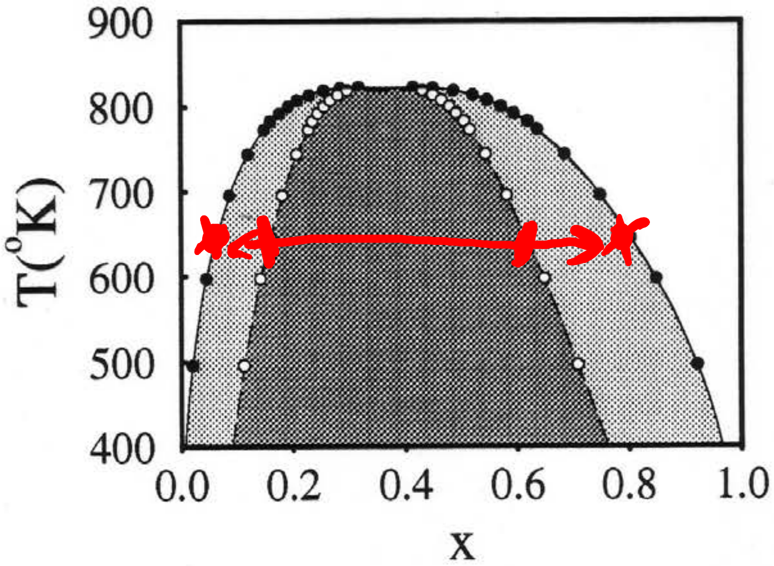
$G(x) = \int \Delta\mu(\xi) d\xi$:

common tangent

$\Downarrow$



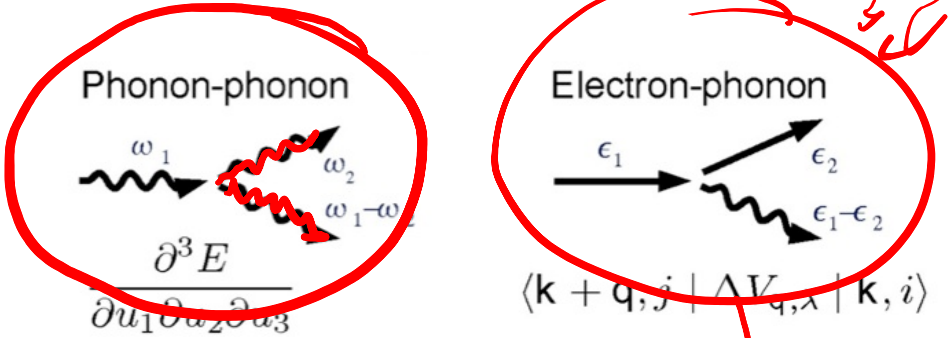




Nicola Marzari, Stefano de Gironcoli, and Stefano Baroni, Phys. Rev. Lett. 72, 4001

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

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

Resistivity in doped graphene

FIRST-PRINCIPLES EXPTS (Efetov and Kim) 2010

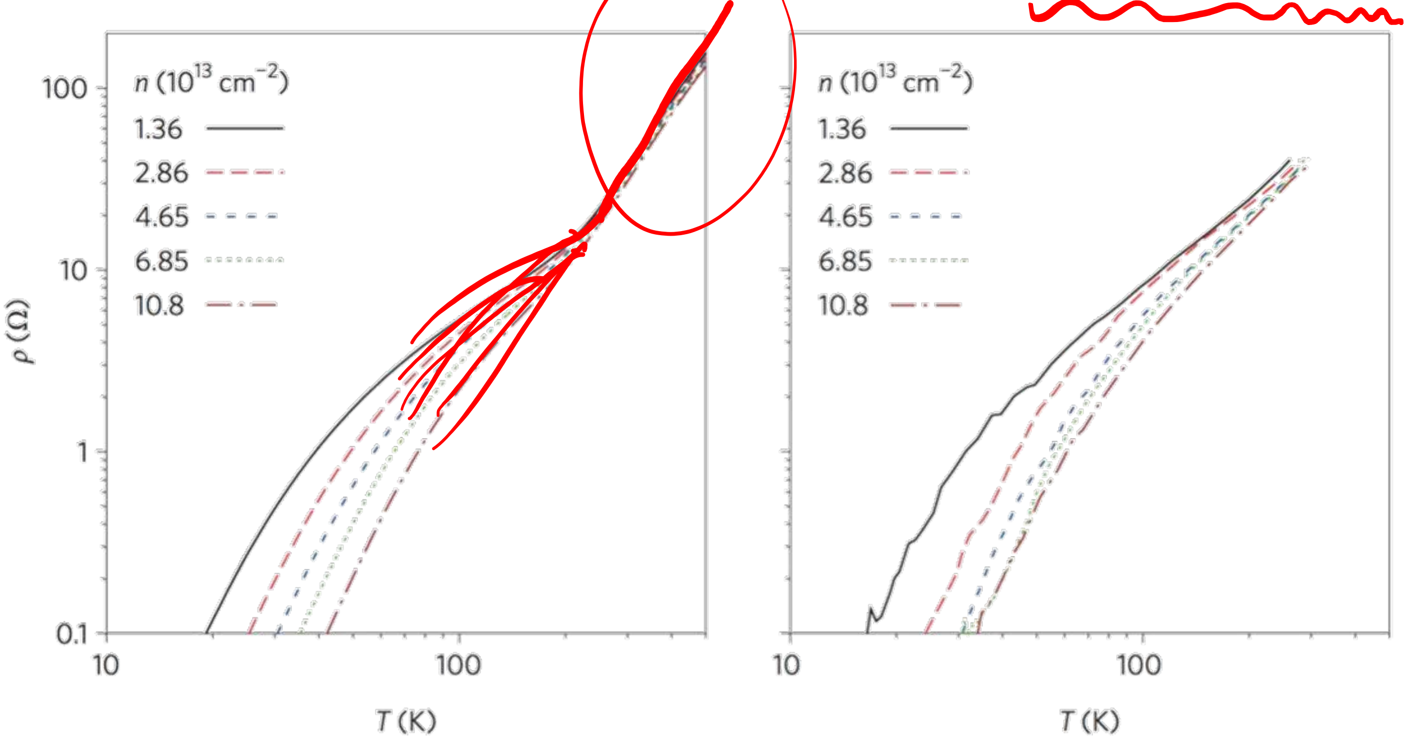
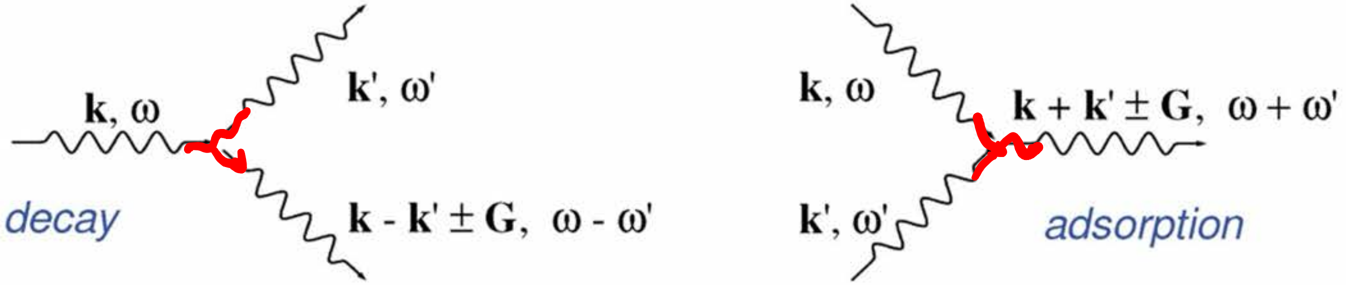


Figure 1 | Electrical resistivity of graphene as a function of temperature and doping (ρ, electrical resistivity; T, temperature; n, carrier density). Left panel: first-principles results obtained using a combination of density-functional perturbation theory, many-body perturbation theory and Wannier 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

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

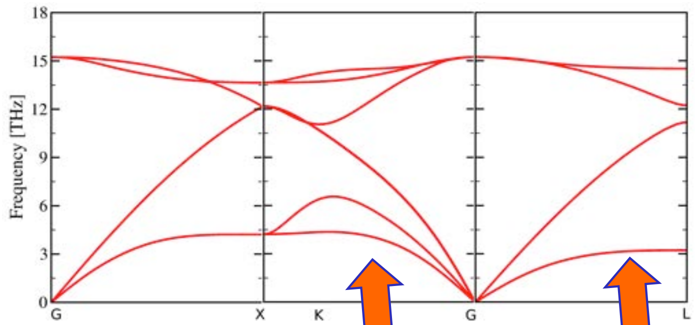
τ

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

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

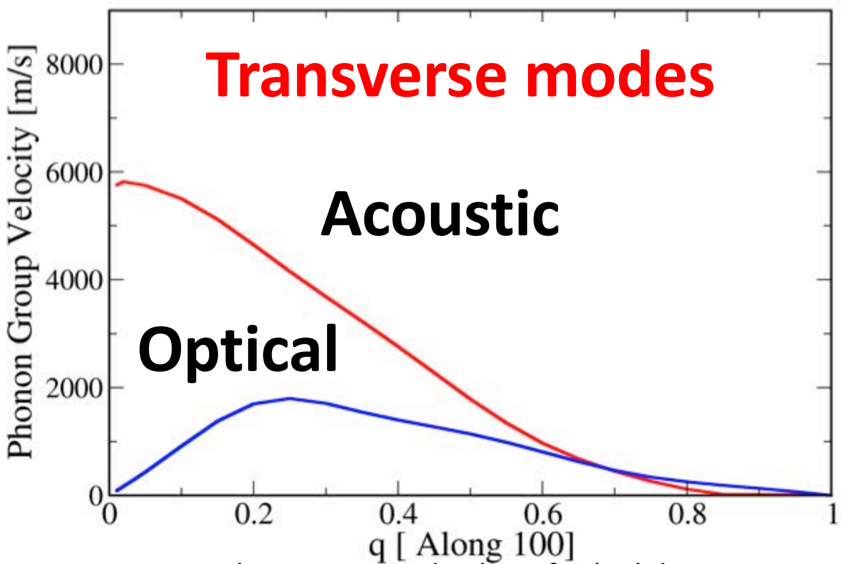
$$\boxed{\frac{\partial^3 E}{\partial u_\nu(\mathbf{0})\partial u_\mu(\boldsymbol{q})\partial u_\eta(-\boldsymbol{q})}}$$ calculated using DFPT and the *2n+1* theorem

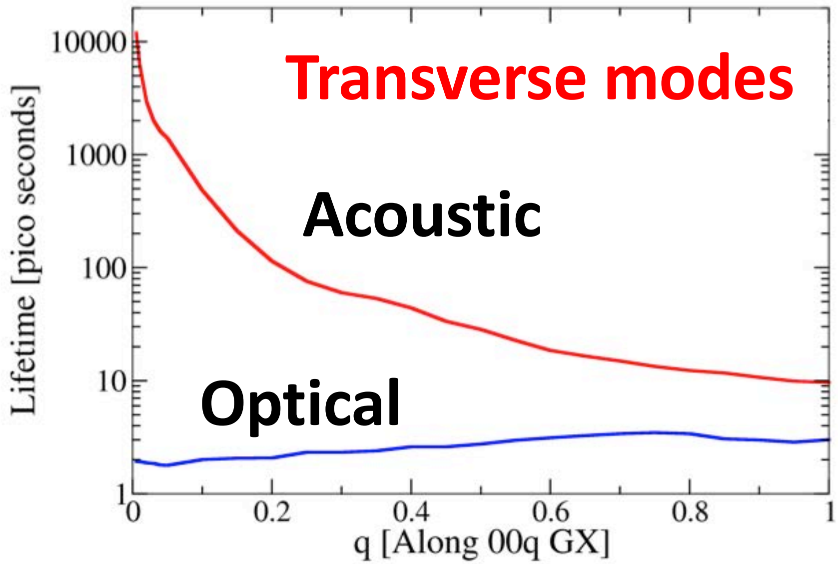
Thermal conductivity (SMRTA)



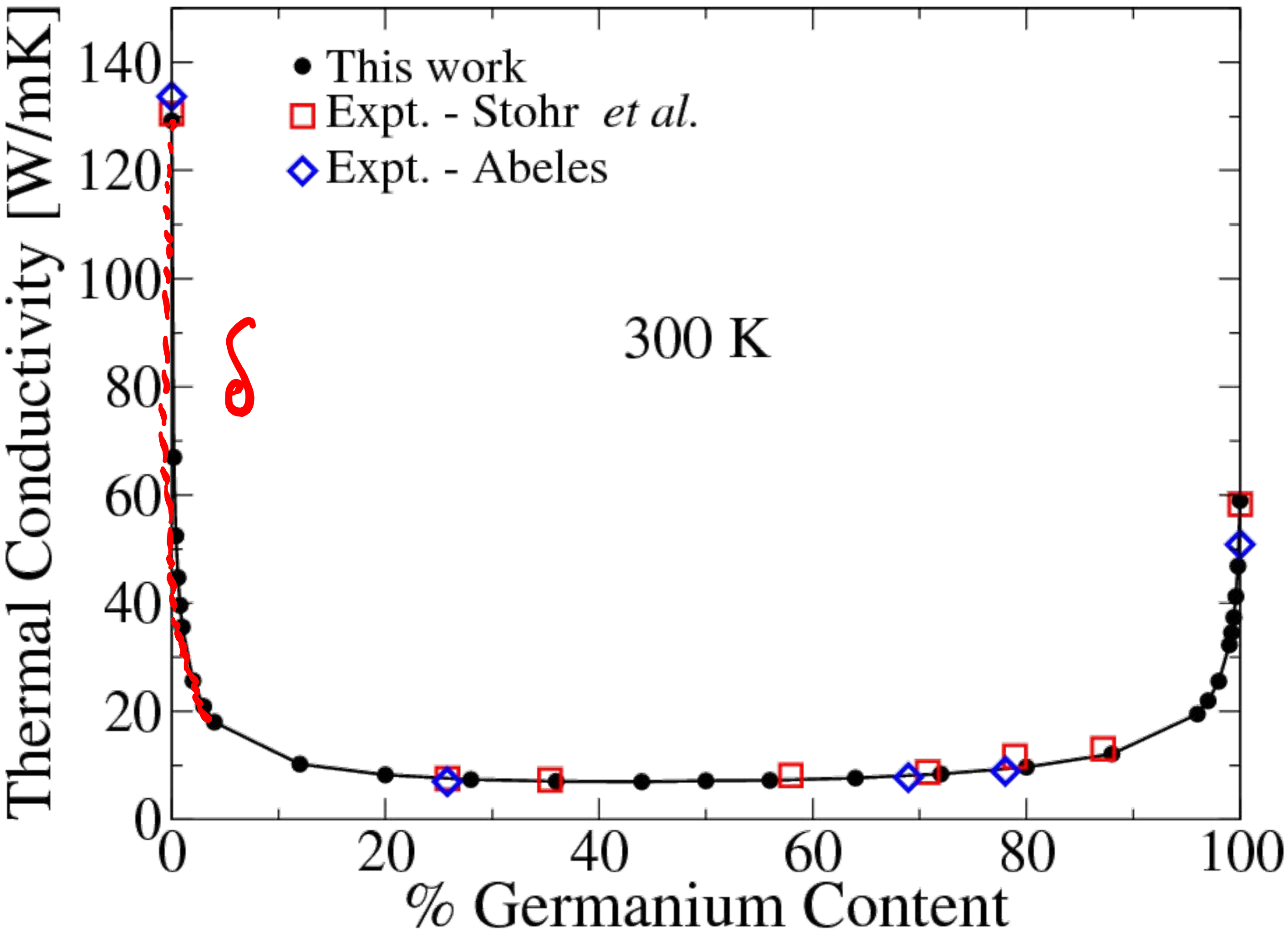
$$\frac{1}{\tau} = \frac{1}{\tau_{sc}} + \frac{1}{\tau_{iso}}$$

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



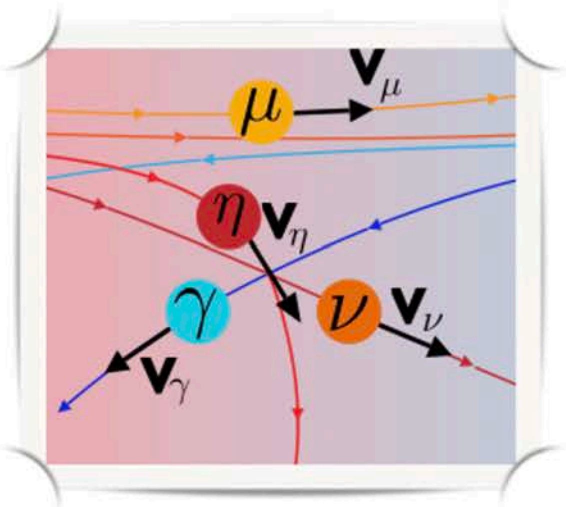


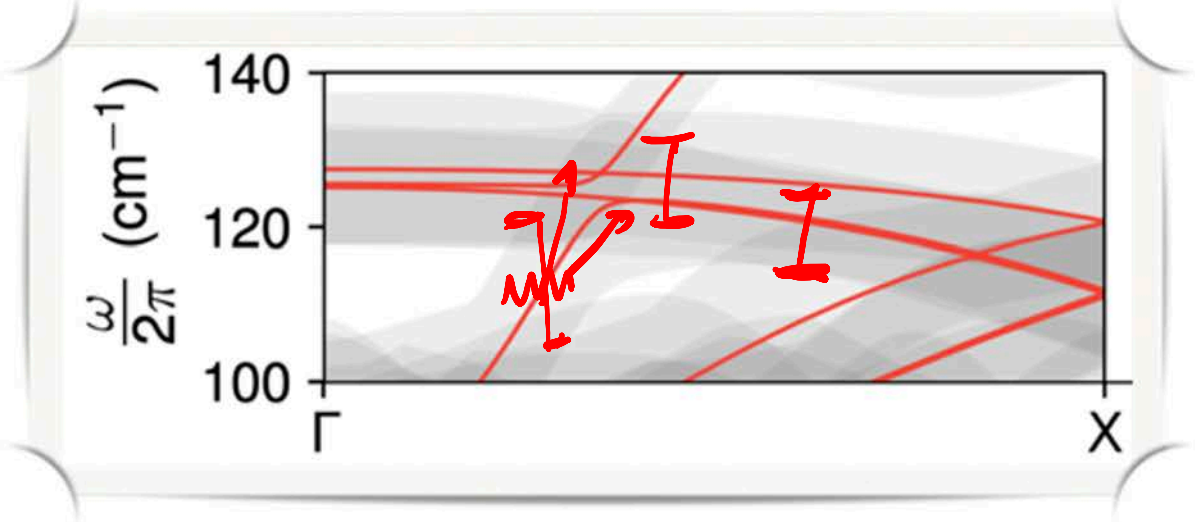
Composition dependence in SiGe alloys



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

Generalized Wigner Boltzmann

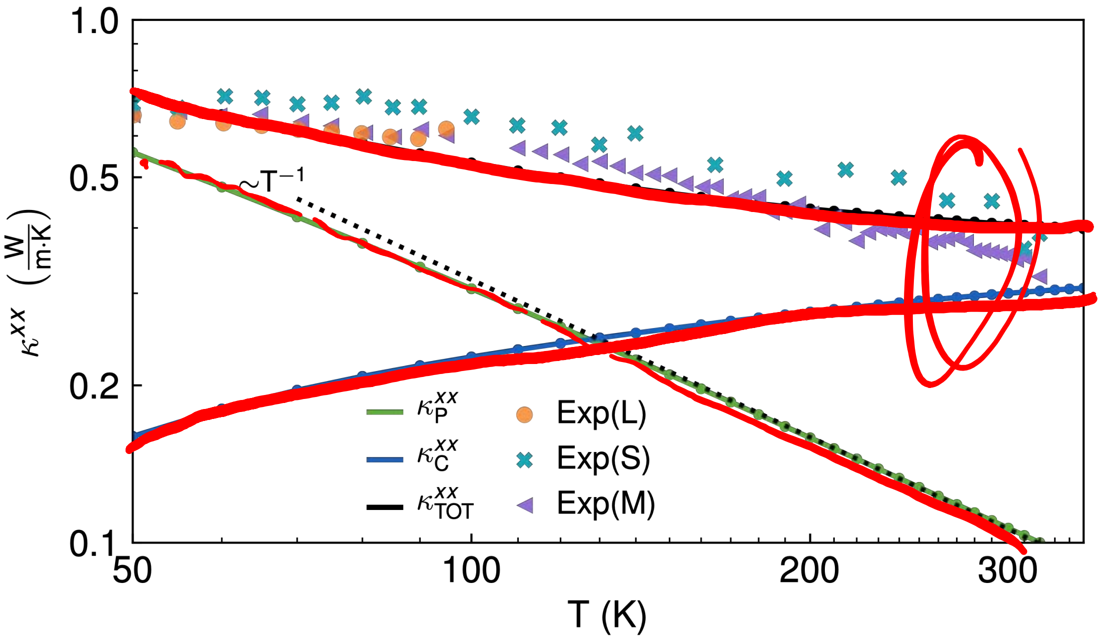




Simoncelli, Marzari, Mauri, Nature Physics (2019)

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

Total K = Peierls + coherences



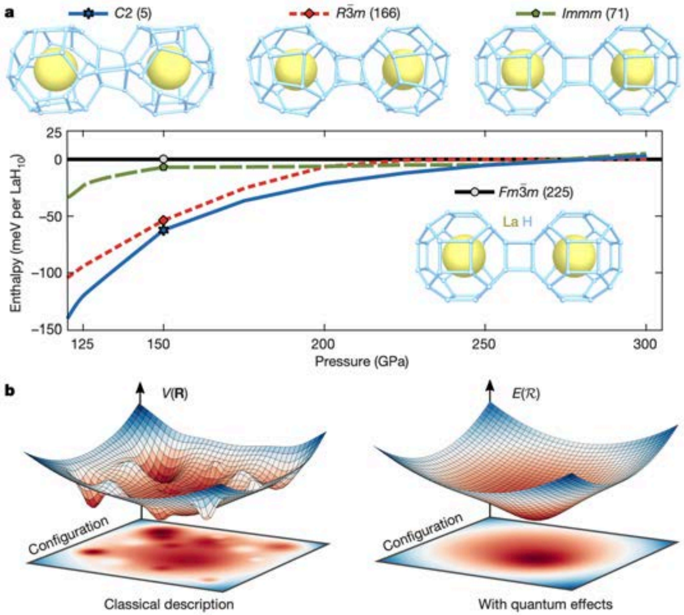
Article

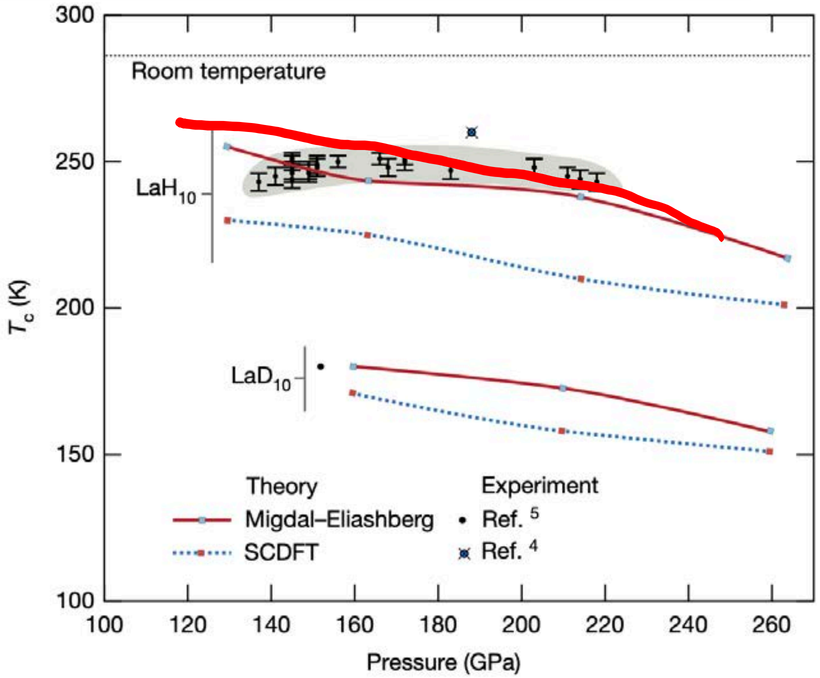
Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride

https://doi.org/10.1038/s41586-020-1955-z
Received: 24 July 2019
Accepted: 14 November 2019
Published online: 5 February 2020

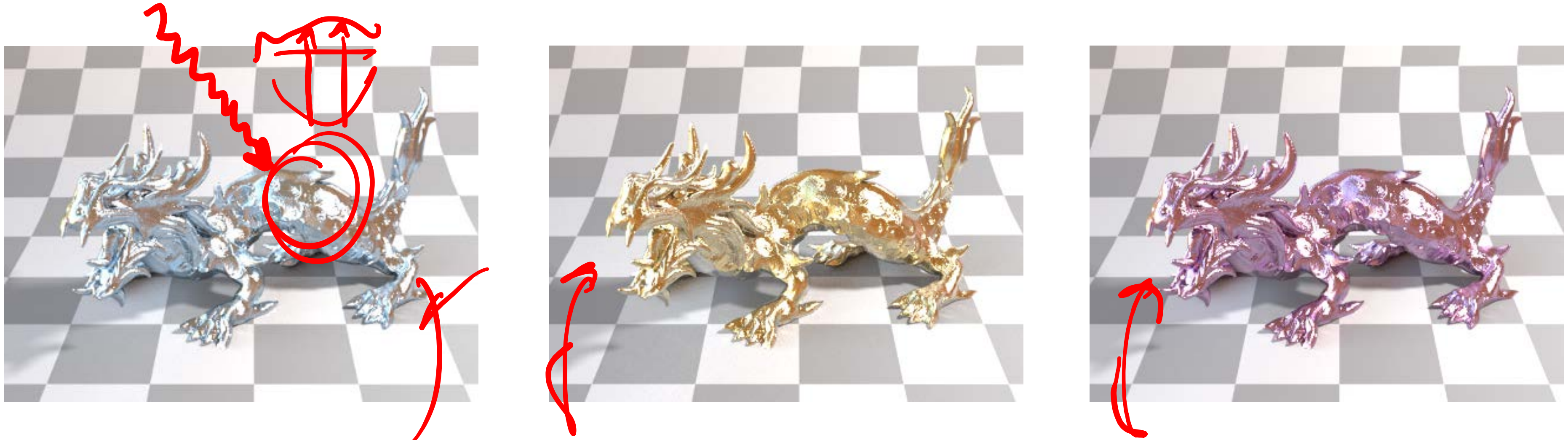
Ion Errea[1,2,3], Francesco Belli[1,2], Lorenzo Monacelli[4], Antonio Sanna[5], Takashi Koretsune[6], Terumasa Tadano[7], Raffaello Bianco[2], Matteo Calandra[8], Ryotaro Arita[9,10], Francesco Mauri[4,11] & José A. Flores-Livas[4]*

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



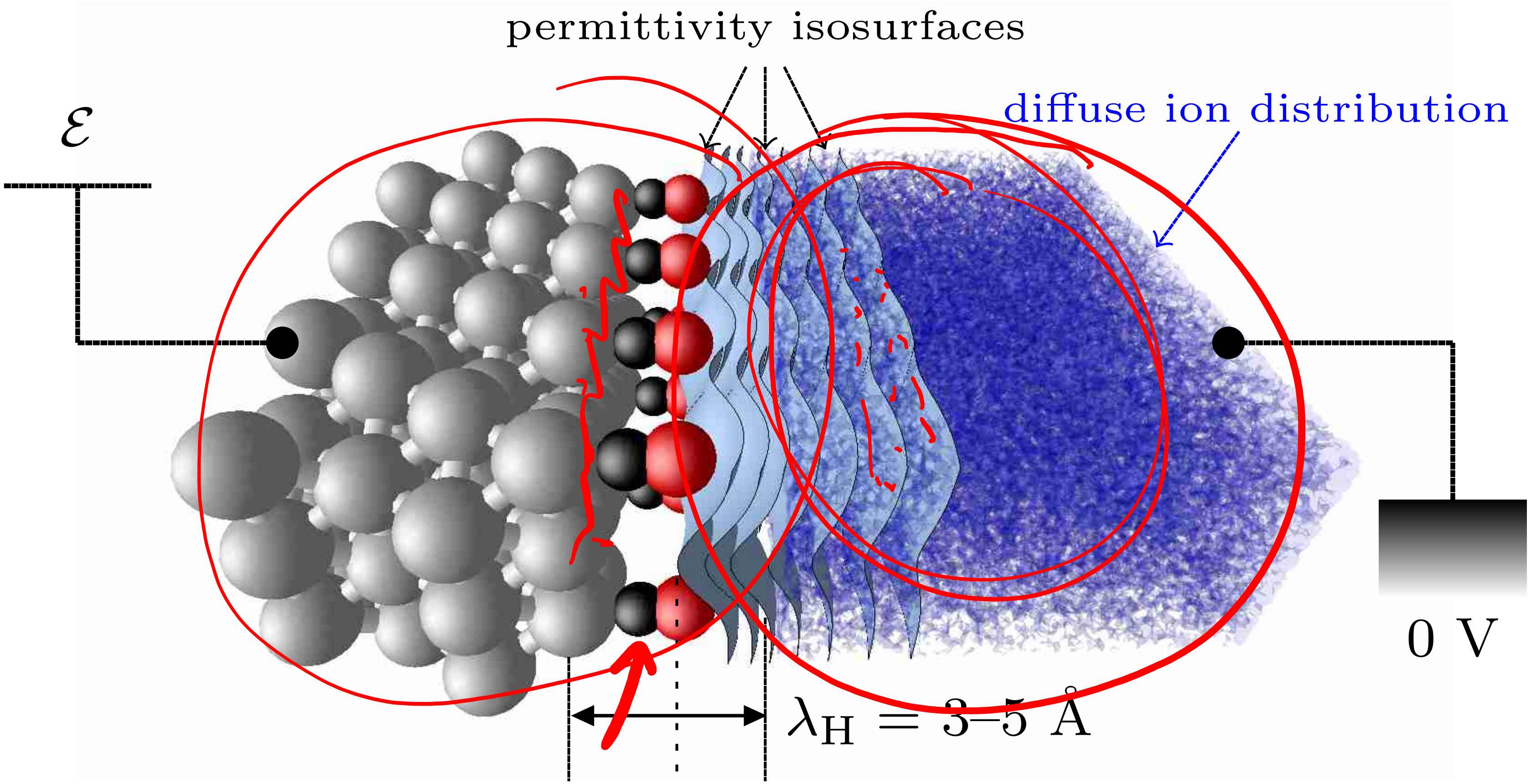


A FUN EXAMPLE



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

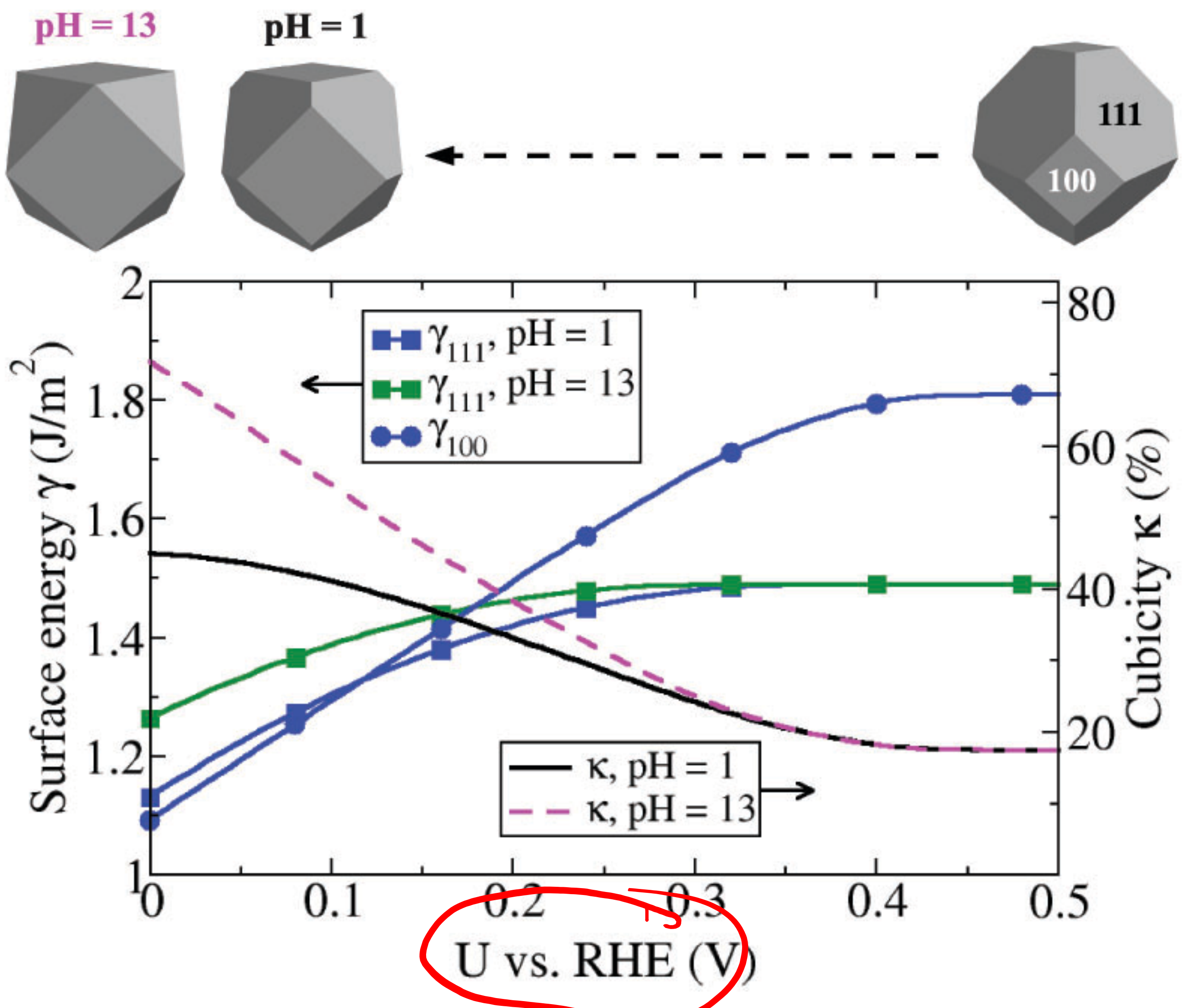
Multi-scale/physics: electrochemistry



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. Norskov (2011).

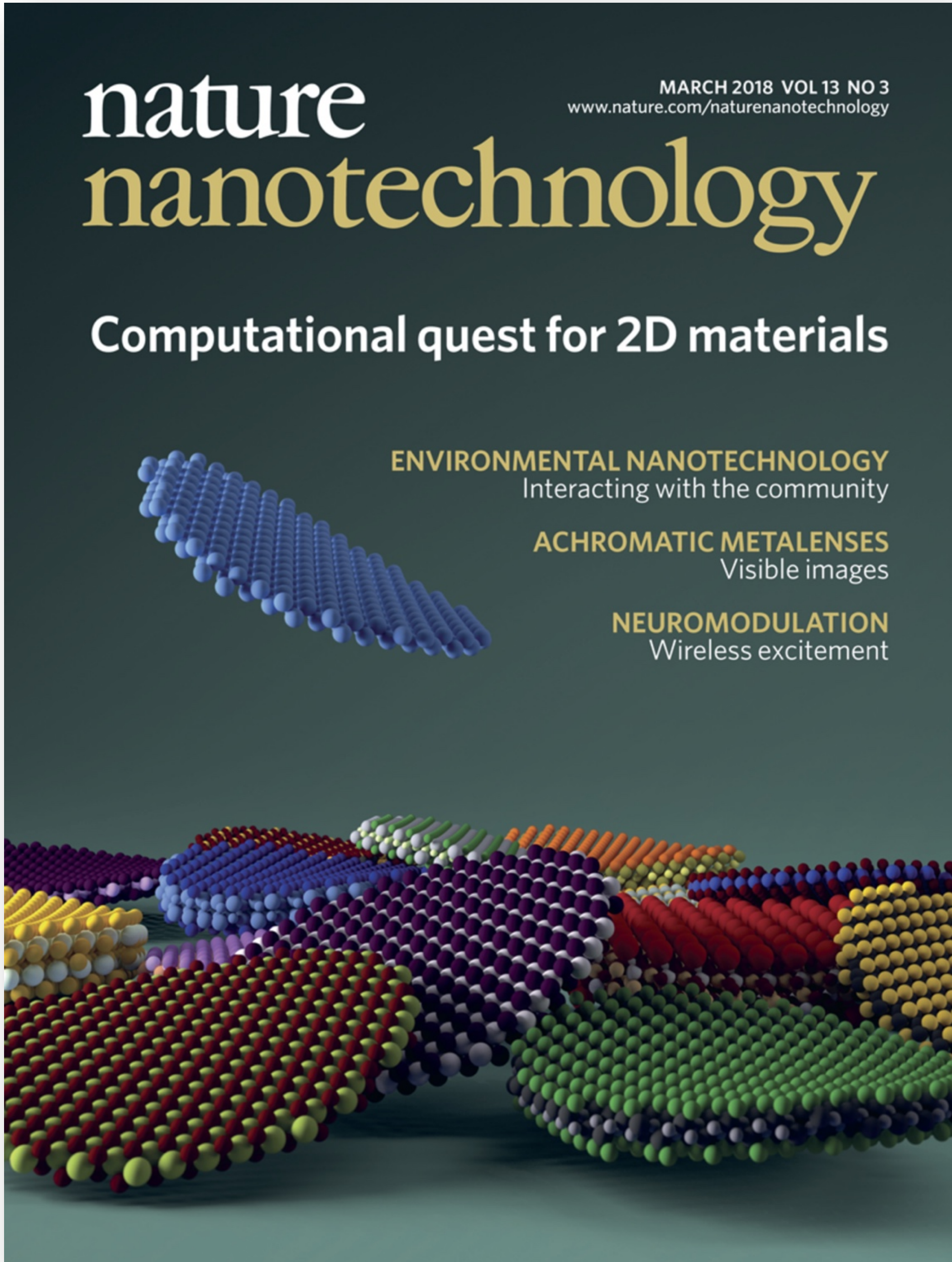
O. Andreussi, I. Dabo and N. Marzari, "Revised self-consistent continuum solvation in electronic structure calculations", J. Chem. Phys. 136, 064102 (2012). www.quantum-environment.org

Wulff construction, nanoparticle shape



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

COMPUTATIONAL EXFOLIATION OF ALL KNOWN INORGANIC MATERIALS

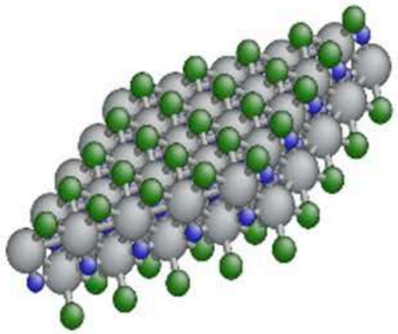


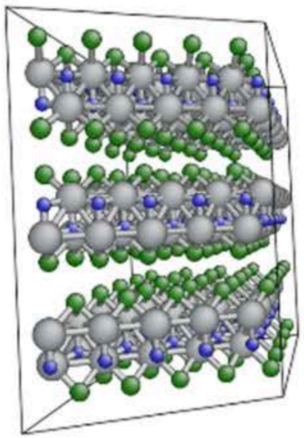
HIGH-THROUGHPUT COMPUTATIONAL EXFOLIATION

Exfoliation

External databases (ICSD, COD)

Geometrically layered





VdW-DFT electronic structure, binding energies

Characterization

Electronic

Magnetic

Mechanical

Applications

High e/h mobility

Topological

CDW, spintronics

Plasmonics

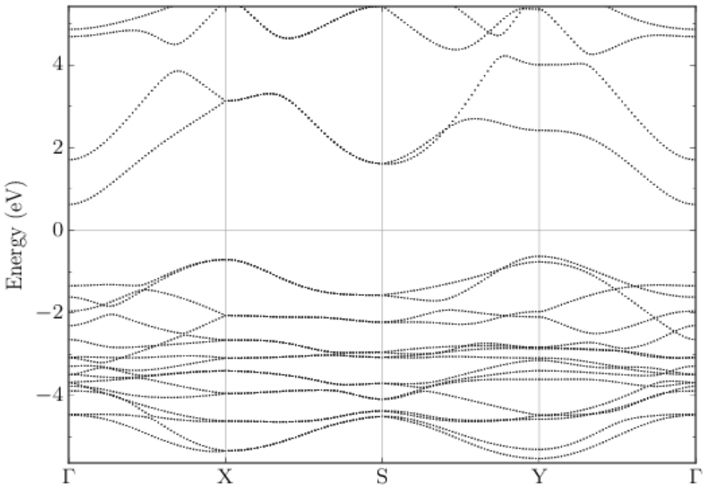
Photocatalysis

Membranes

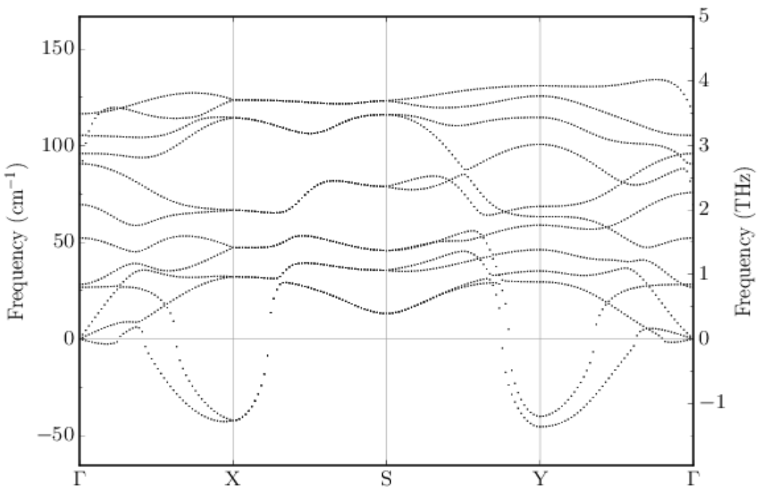
....

See also: S. Lebègue *et al.*, PRX (2013); R. Hennig *et al.*, PRL (2017) and E. Reed *et al.*, Nano Letters (2017), K. Choudhary, F. Tavazza, et al. Sci. Rep. (2017), and K. Thygesen, 2D Materials (2018)

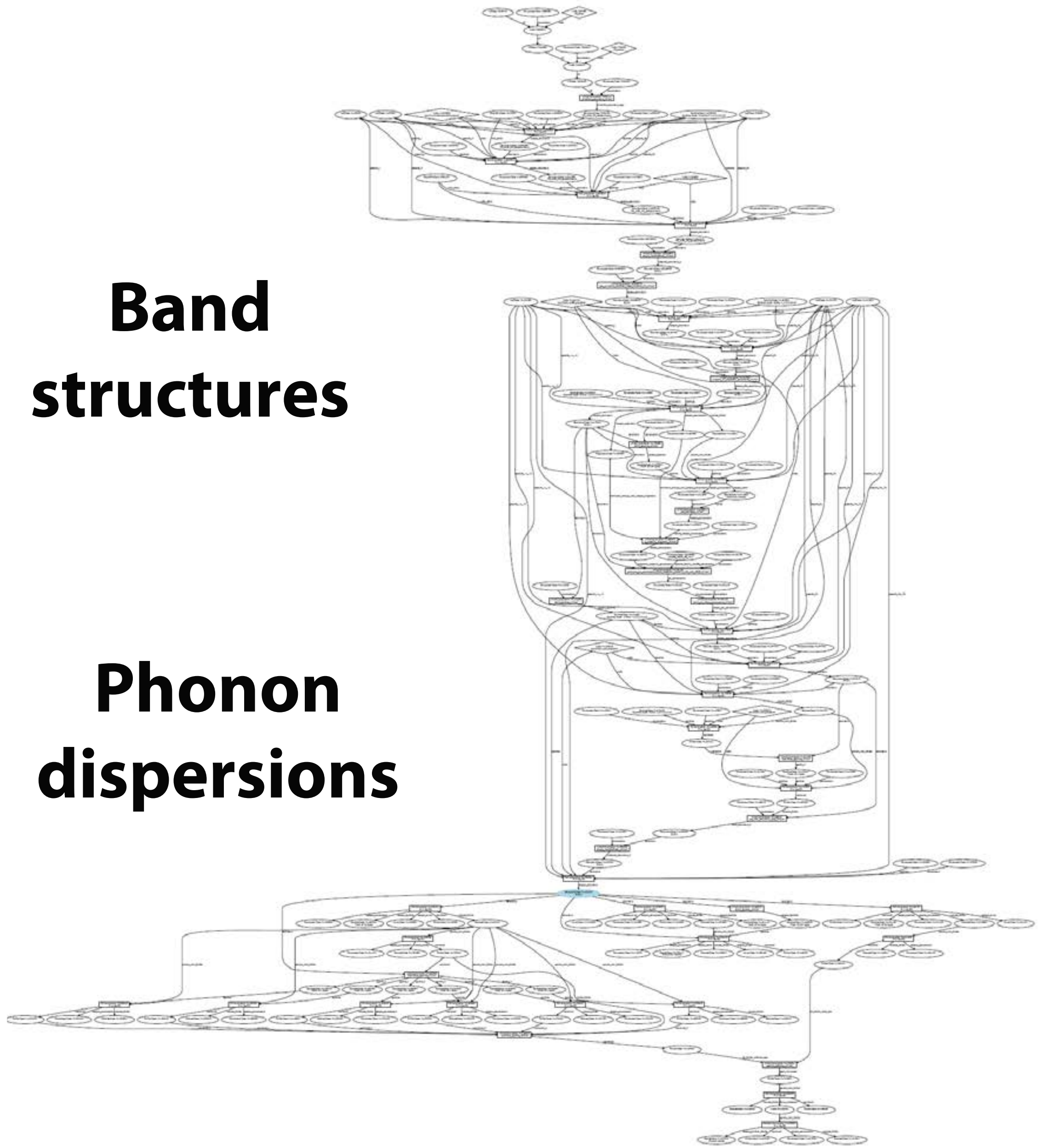
ALL AUTOMATED WITH AiiDA (http://aiida.net)



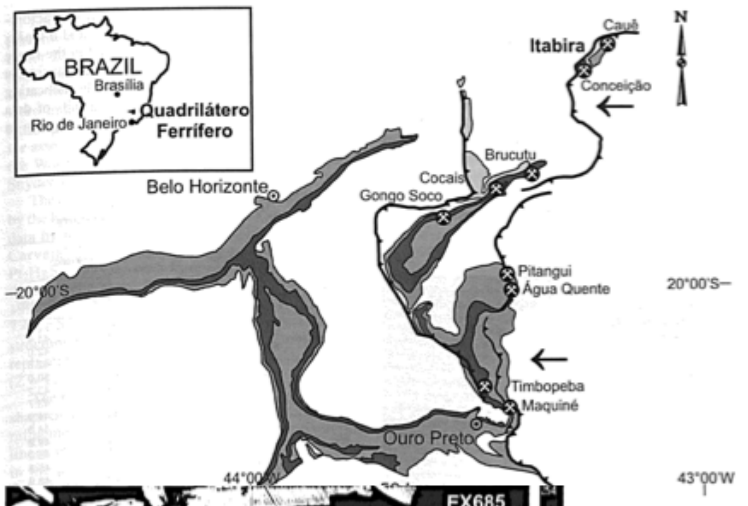
Band structures

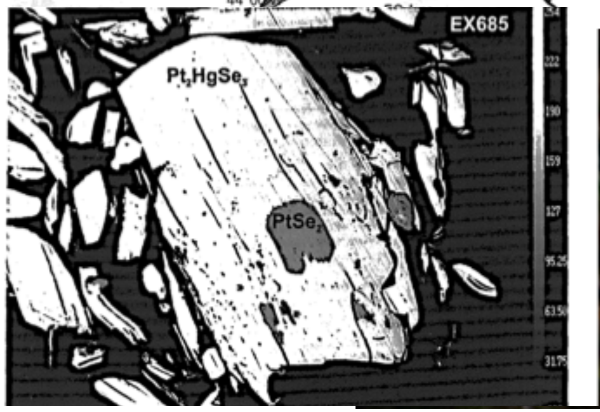


Phonon dispersions



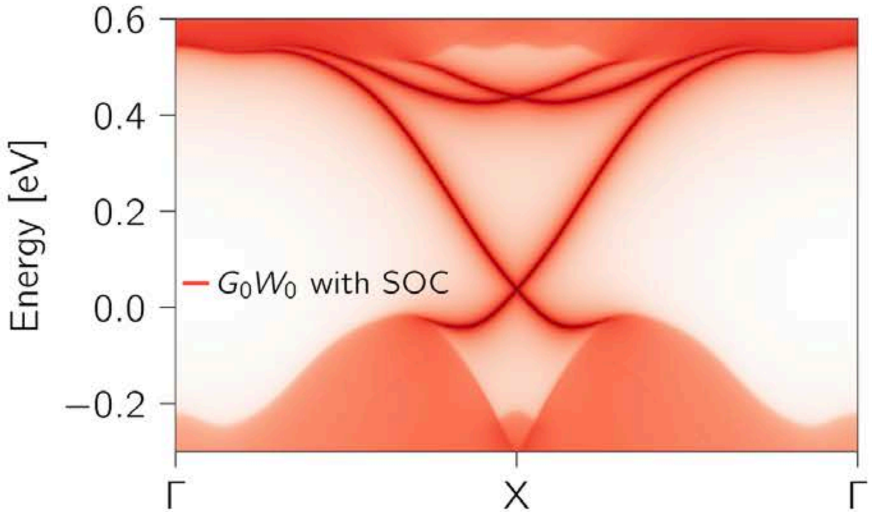
THE DISCOVERY OF JACUTINGAITE





THE DISCOVERY OF JACUTINGAITE

Monolayer: room-temperature Kane-Mele quantum spin Hall insulator – G_0W_o with S.O.C.

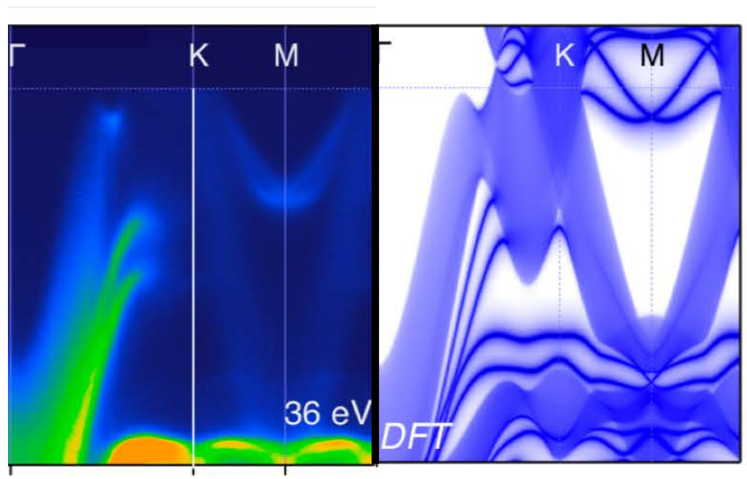


A. Marrazzo et al., Phys. Rev. Lett. 120, 117701 (2018)

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

$$+ t_2' \underbrace{\sum_{\langle\langle ij \rangle\rangle \alpha} c^{\dagger}_{i\alpha} c_{j\alpha}}_{2^{nd}\mathrm{NN}} + it_2'' \underbrace{\sum_{\langle\langle ij \rangle\rangle \alpha\beta} u_{ij} (\mathbf{s} \times \mathbf{d}^{0}_{ij})^{z}_{\alpha\beta} c^{\dagger}_{i\alpha} c_{j\beta}}_{\text{in-plane SOC}},$$

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)

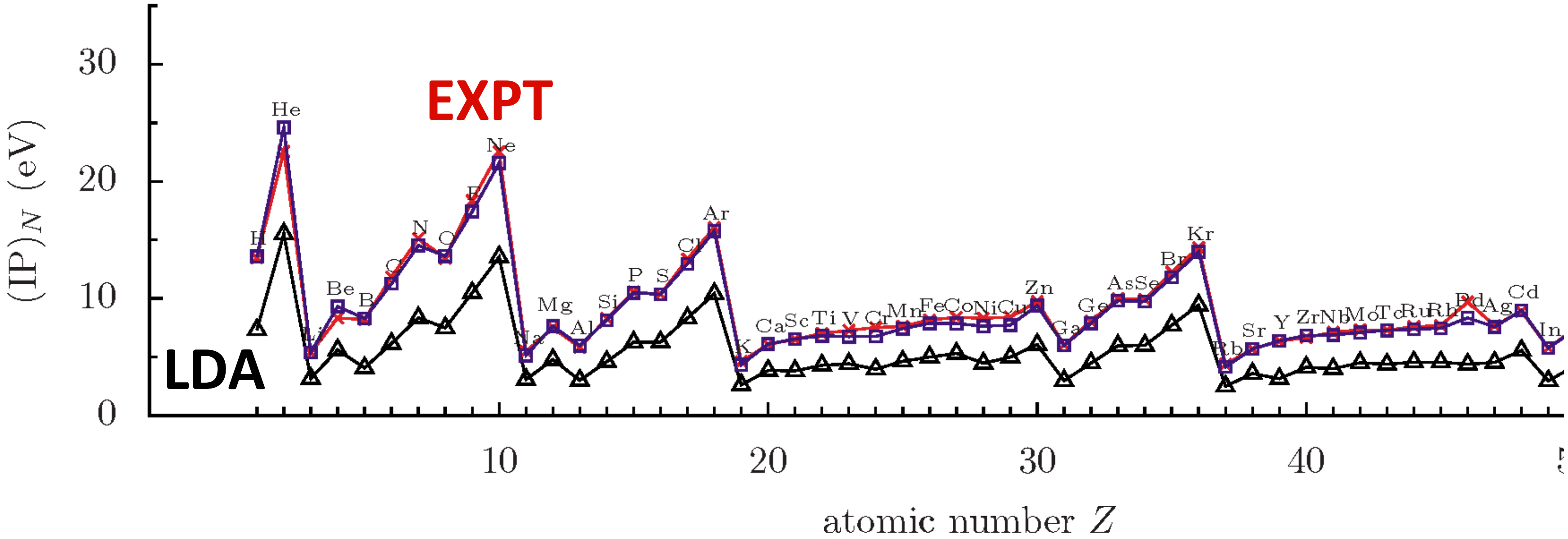
$$H_{J3KM} = H_{KM} + \lambda \tilde{H}_{2^{nd}NL}$$

What’s wrong with DFT ?

- **In its practice, it is approximate**

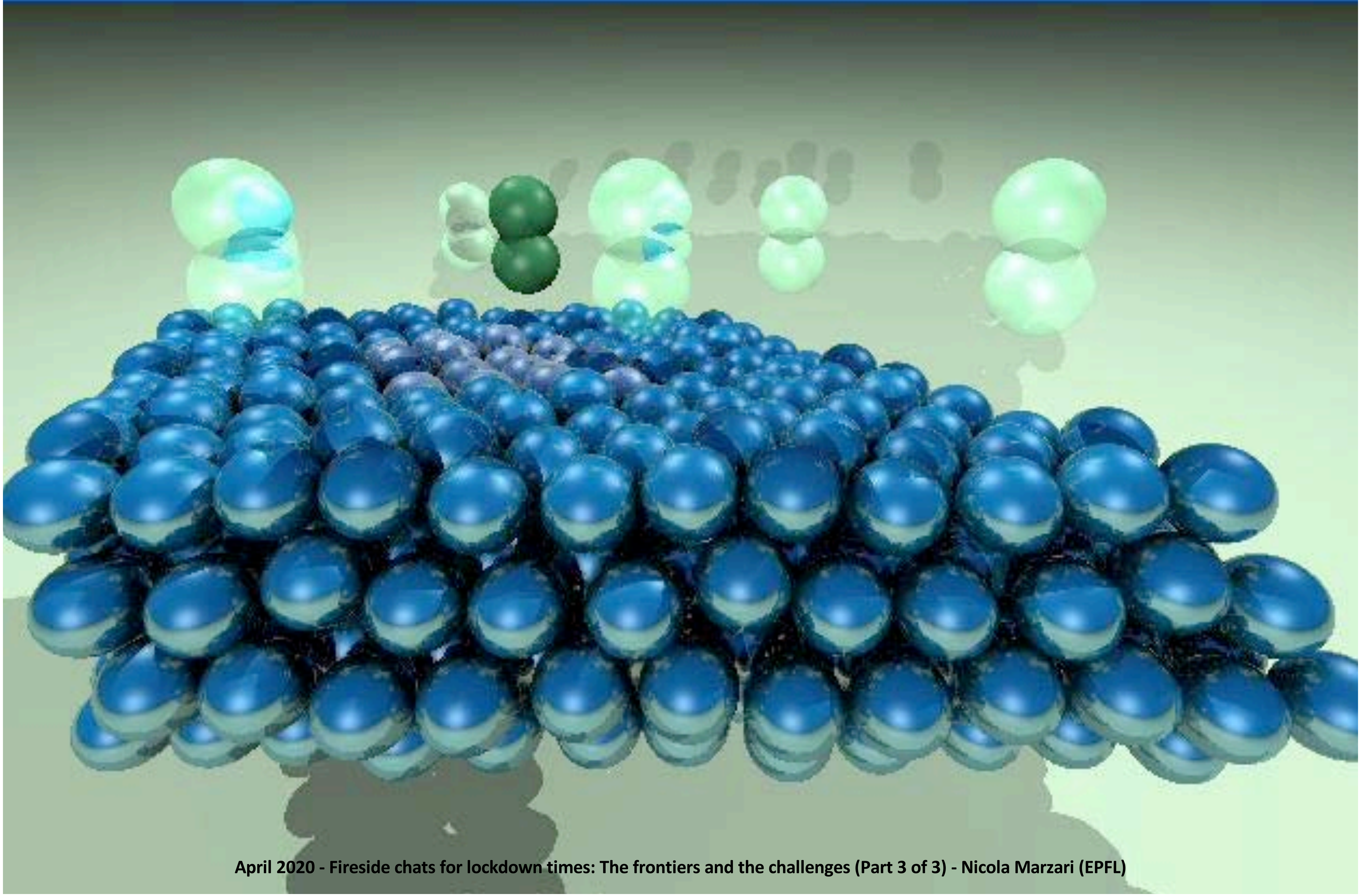
- **It is a static theory (of the charge density)**

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

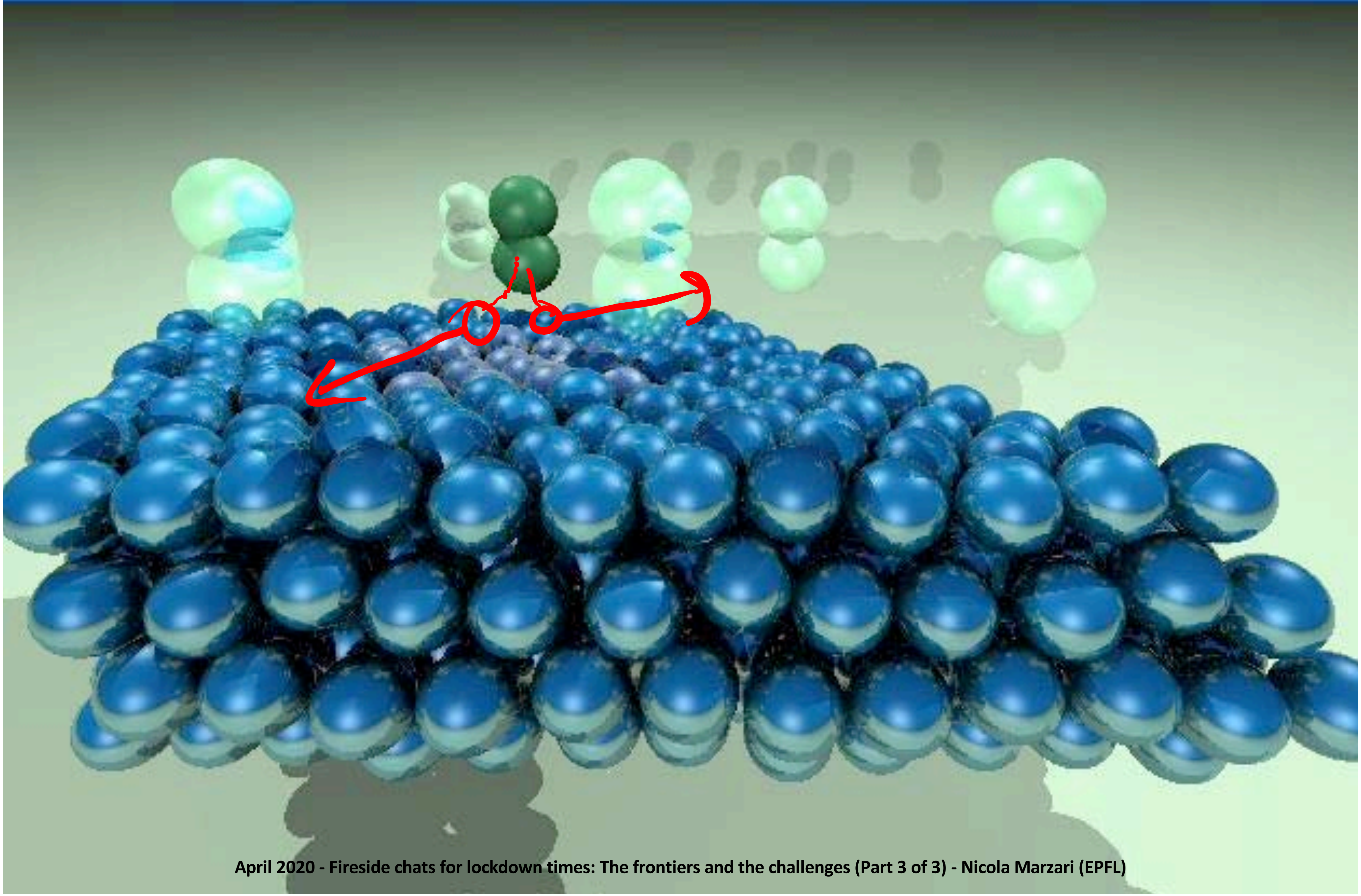


I. Dabo et al. Phys. Rev. B 82 115121 (2010)

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**

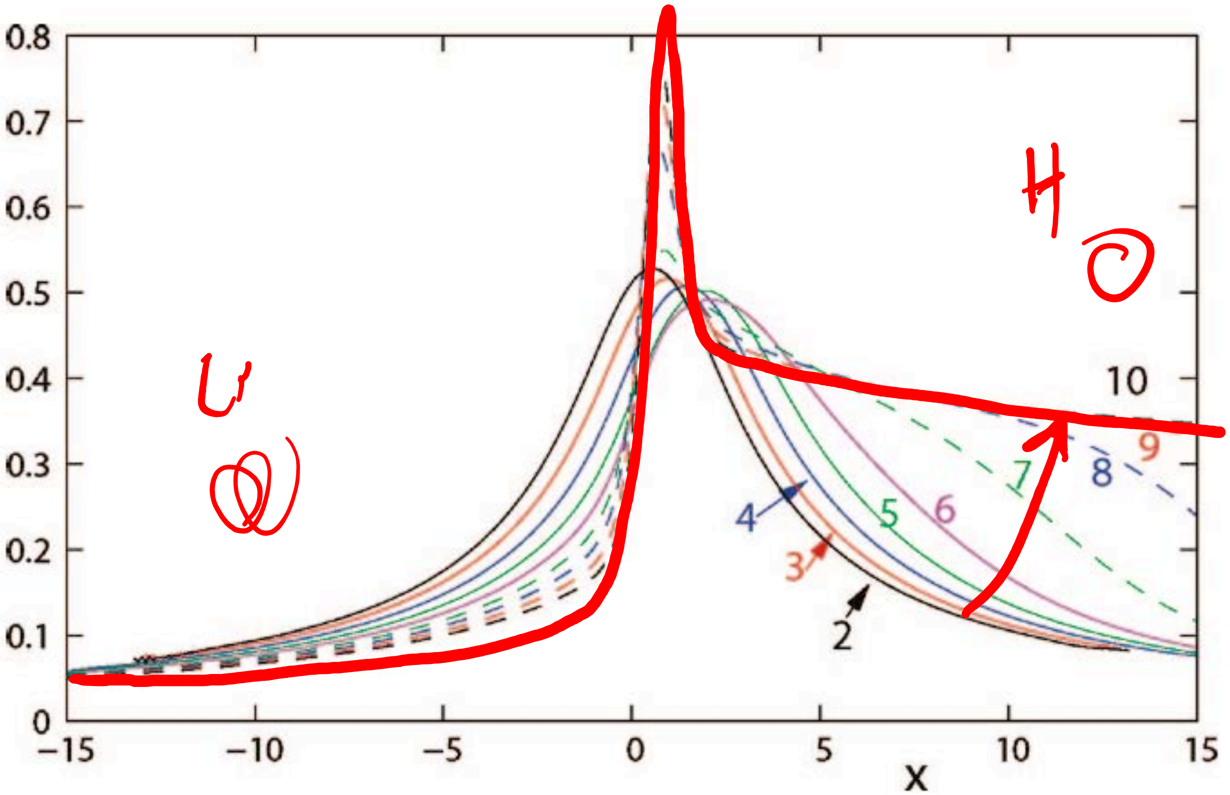
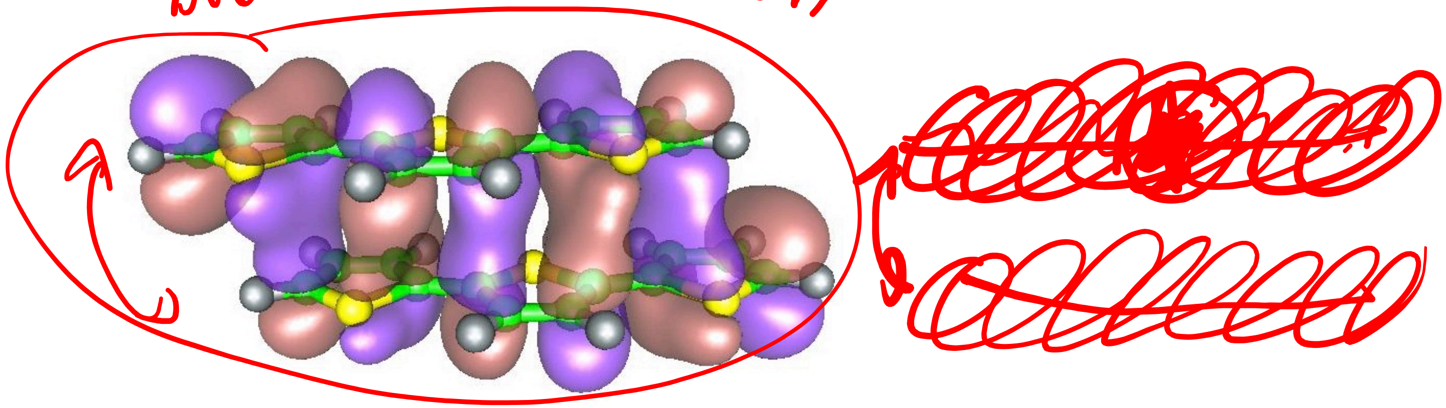


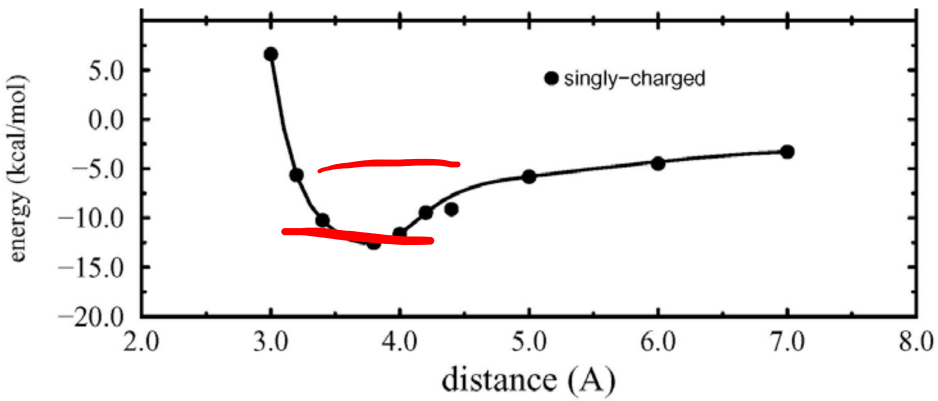
Figure 7. Hartree-exchange-correlation potential, $v_{Hxc}(x)$ for our LiH model ($c = 2.8$); the values of interatomic separation R are indicated.

Neepa Maitra JCTC 2009, Helbig and Rubio JCP 2009

Notable failures IV: Delocalization of electrons/holes

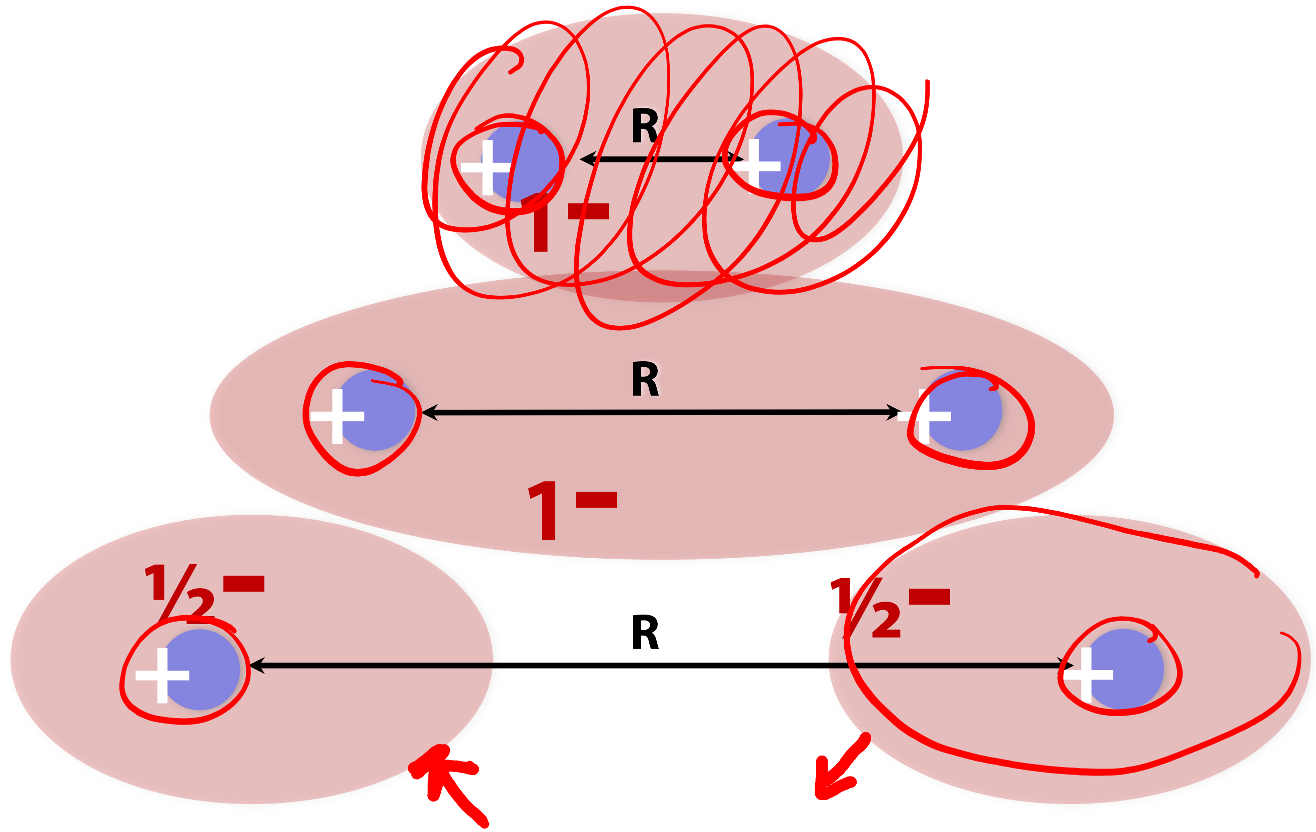
DELOCAL HOLE DFT (GGA)





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

Notable failures V: H_2^+ dissociation limit



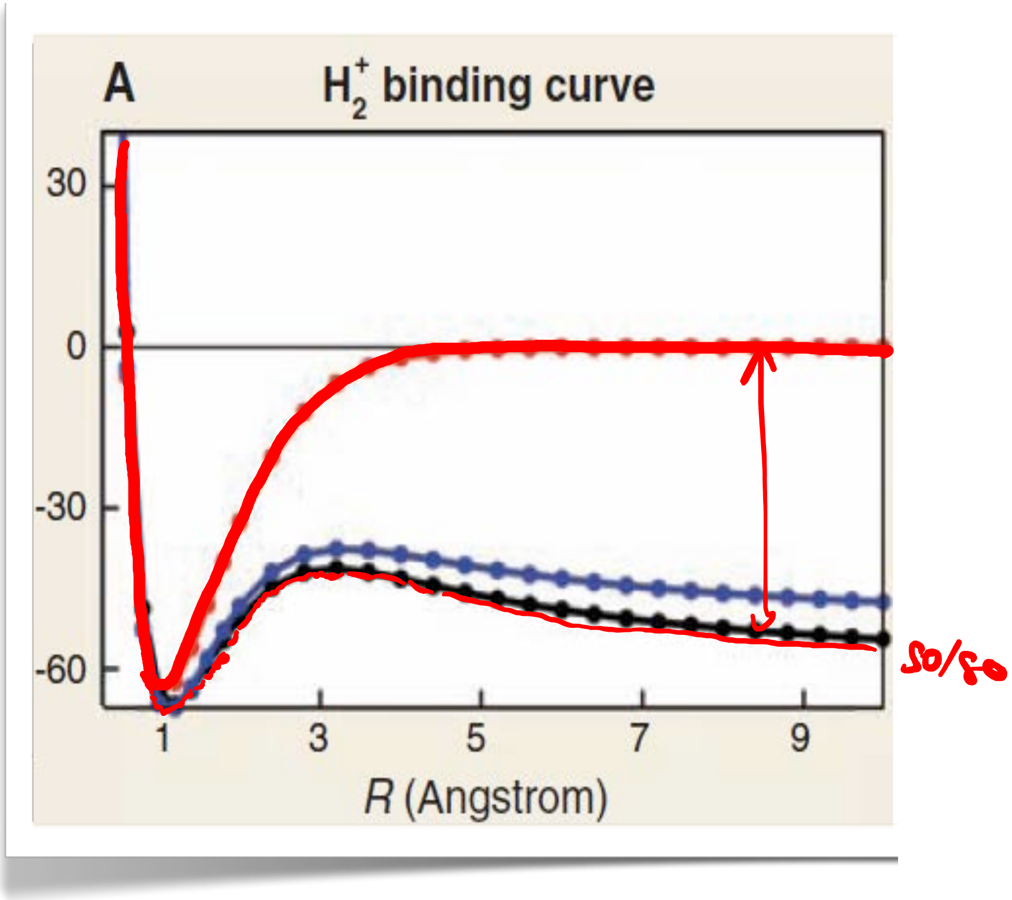
LEFT-RIGHT

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

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

So, it doesn't work even for one electron

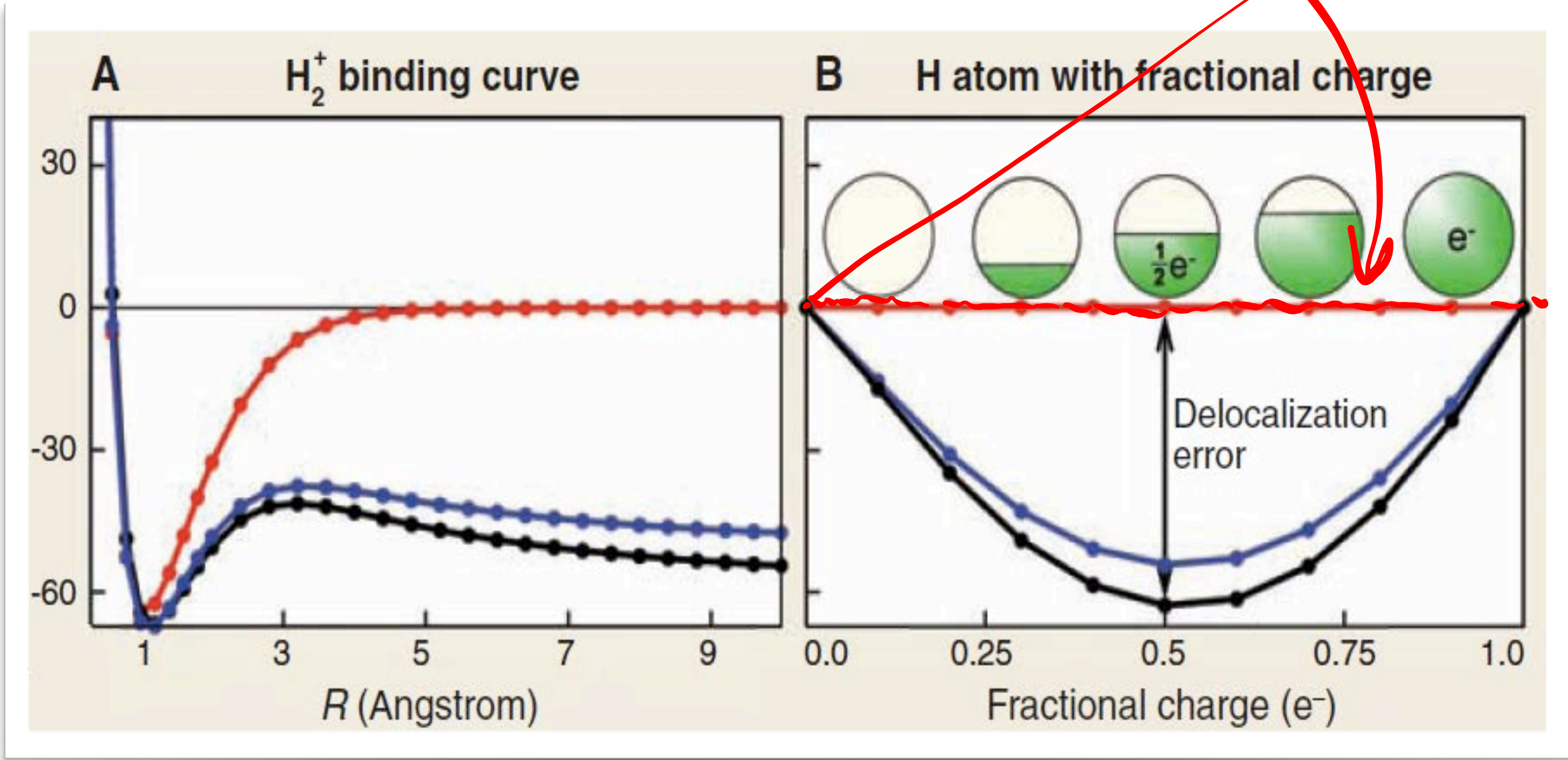
HF B3LYP LDA



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

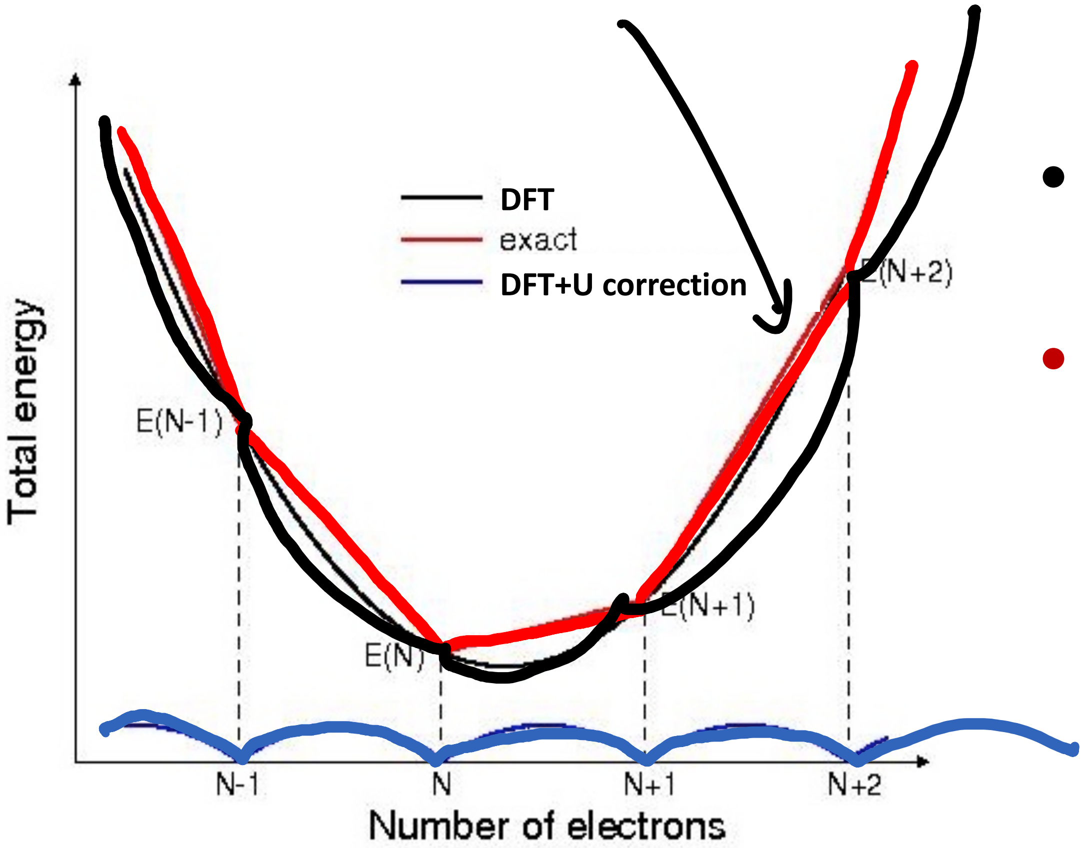
So, it doesn't work even for one electron

HF B3LYP LDA



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

A DFT + Hubbard U approach



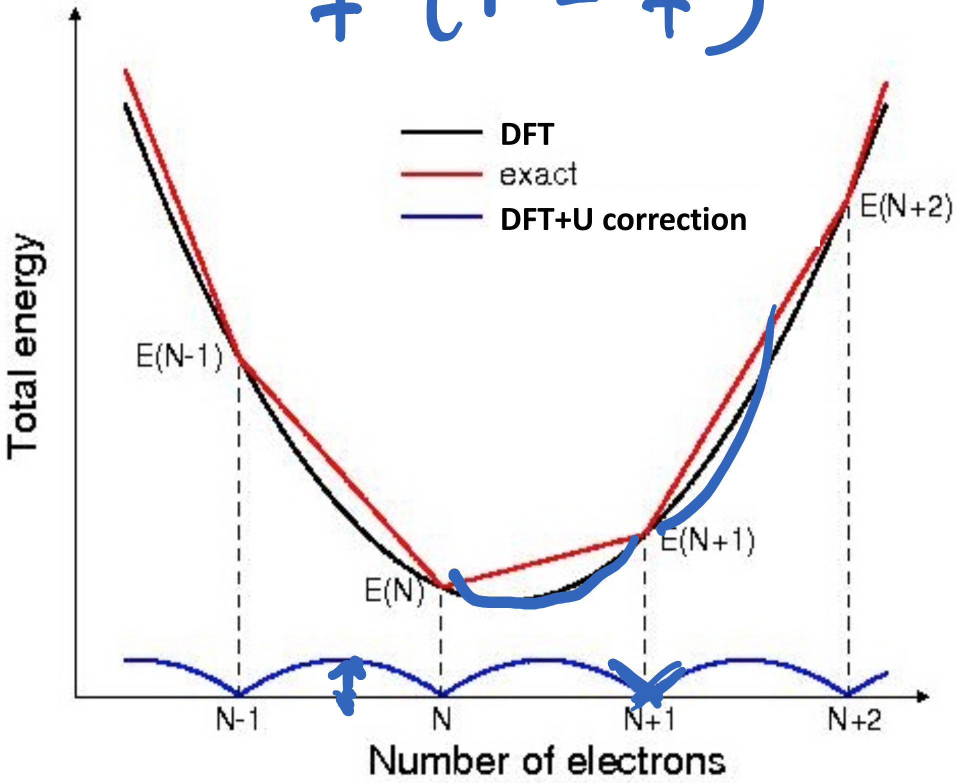
- The energy functional has an unphysical curvature
- the exact solution is piecewise linear

A DFT + Hubbard U approach

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

H.M.

$f(1-f)$



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

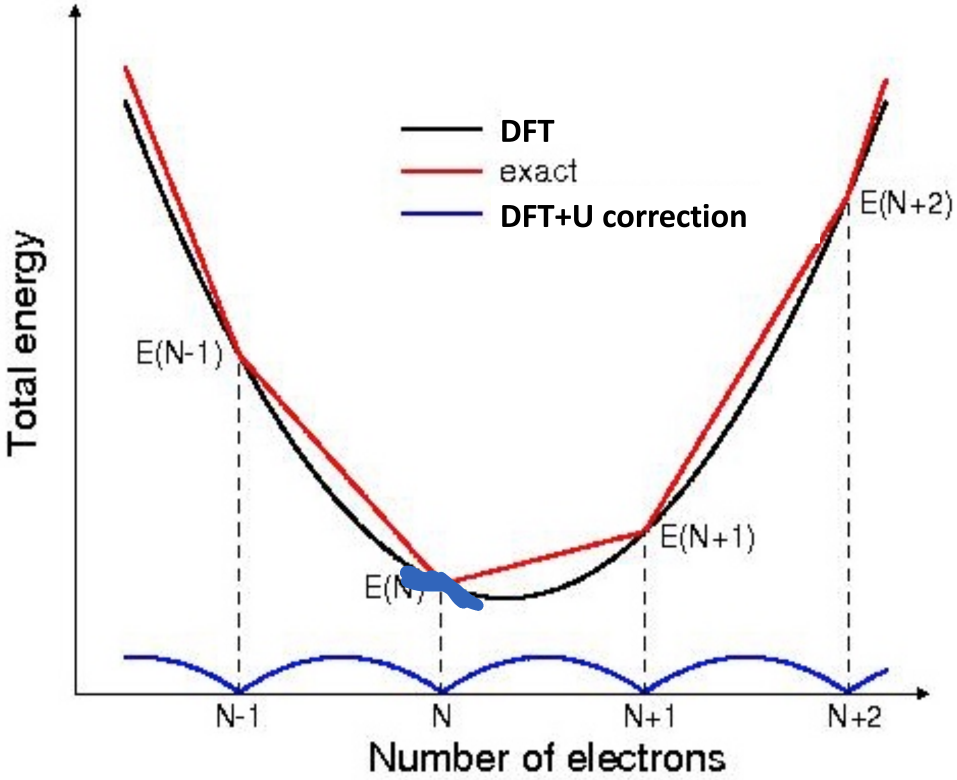
$$\boxed{U=\frac{d^2E^{LDA}}{d(n^{Id})^2}-\frac{d^2E_0^{LDA}}{d(n^{Id})^2}}$$

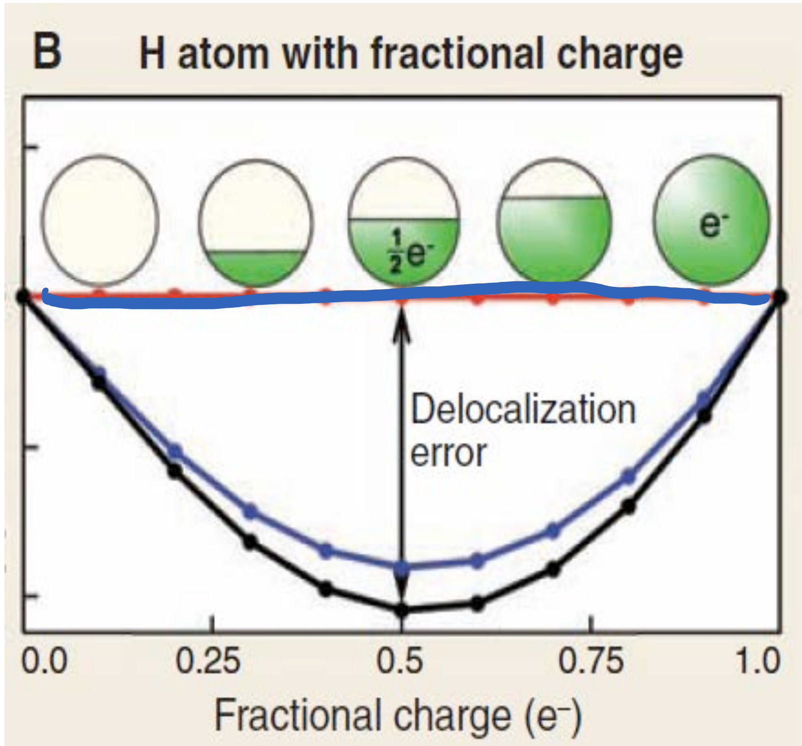
U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

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

A DFT + Hubbard U approach

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



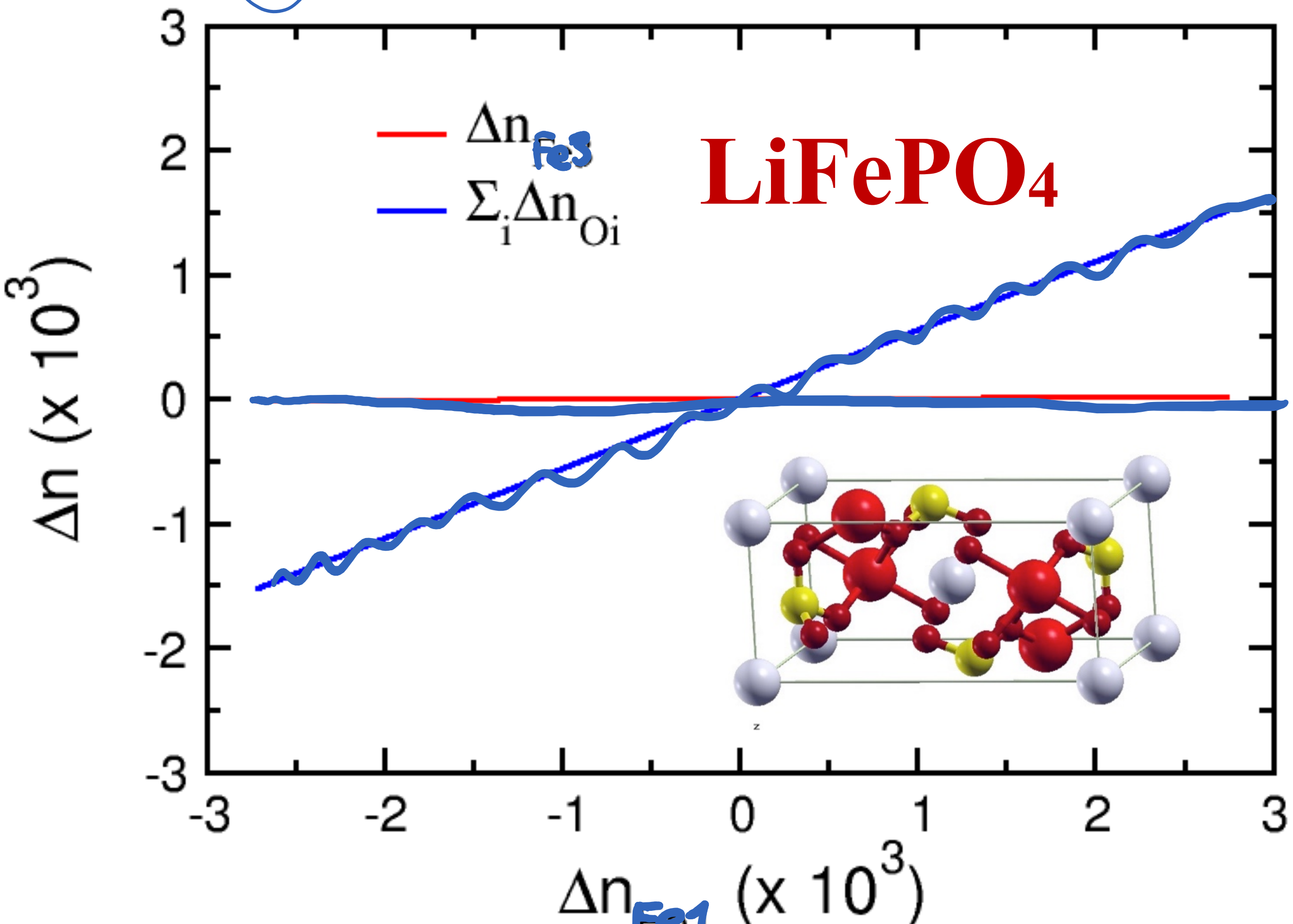


U and rotationally-invariant U: **V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)**

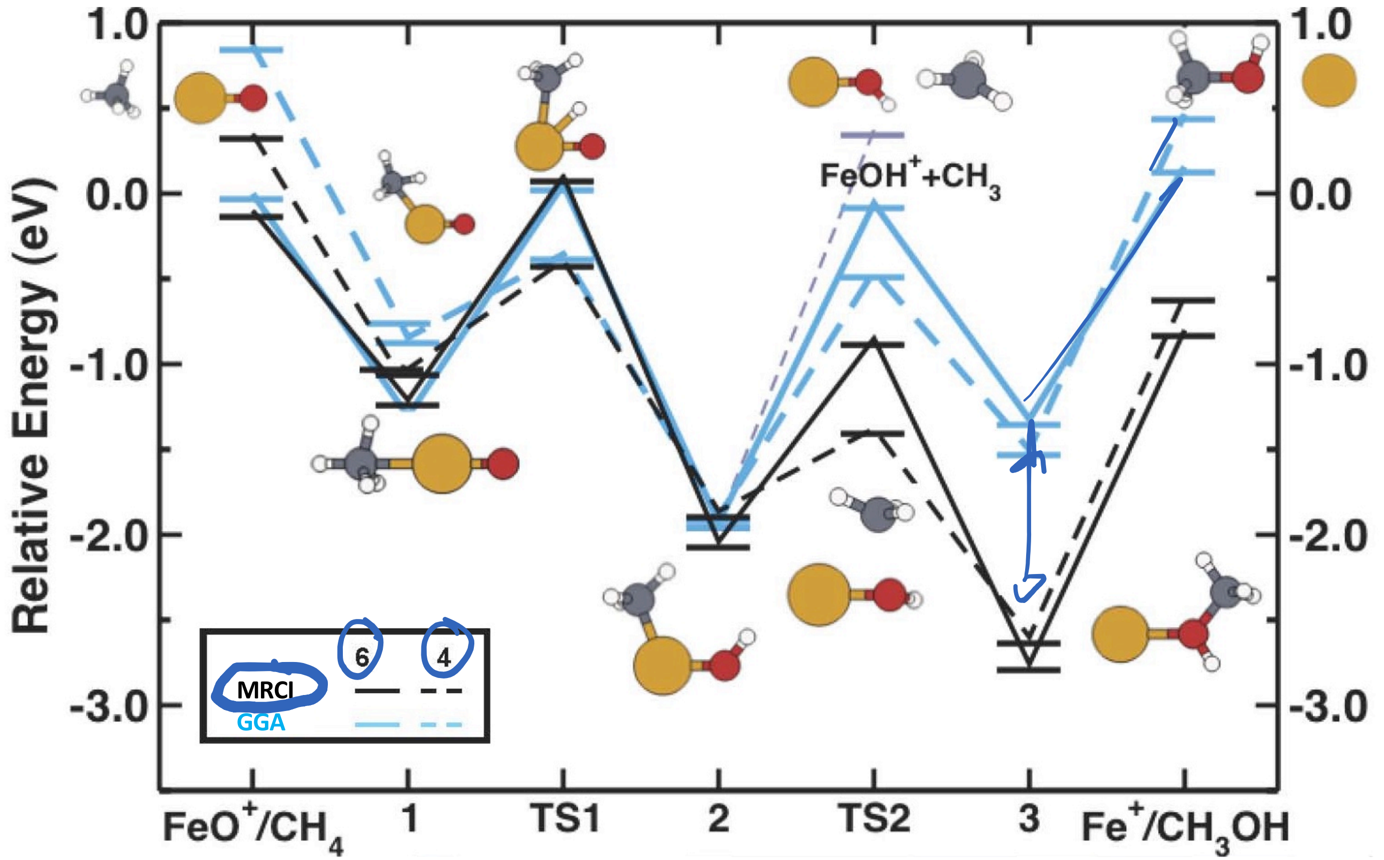
LRT U: **M. Cococcioni (PhD 2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)**

DFT + U has nothing to do with correlation !

$$\frac{U}{2}\sum_{I,\sigma}\sum_{mm'}\left[\overset{f}{n_{mm'}^{I\sigma}}\overset{(1-f)}{\left(\delta_{m'm}-n_{m'm}^{I\sigma}\right)}\right]$$

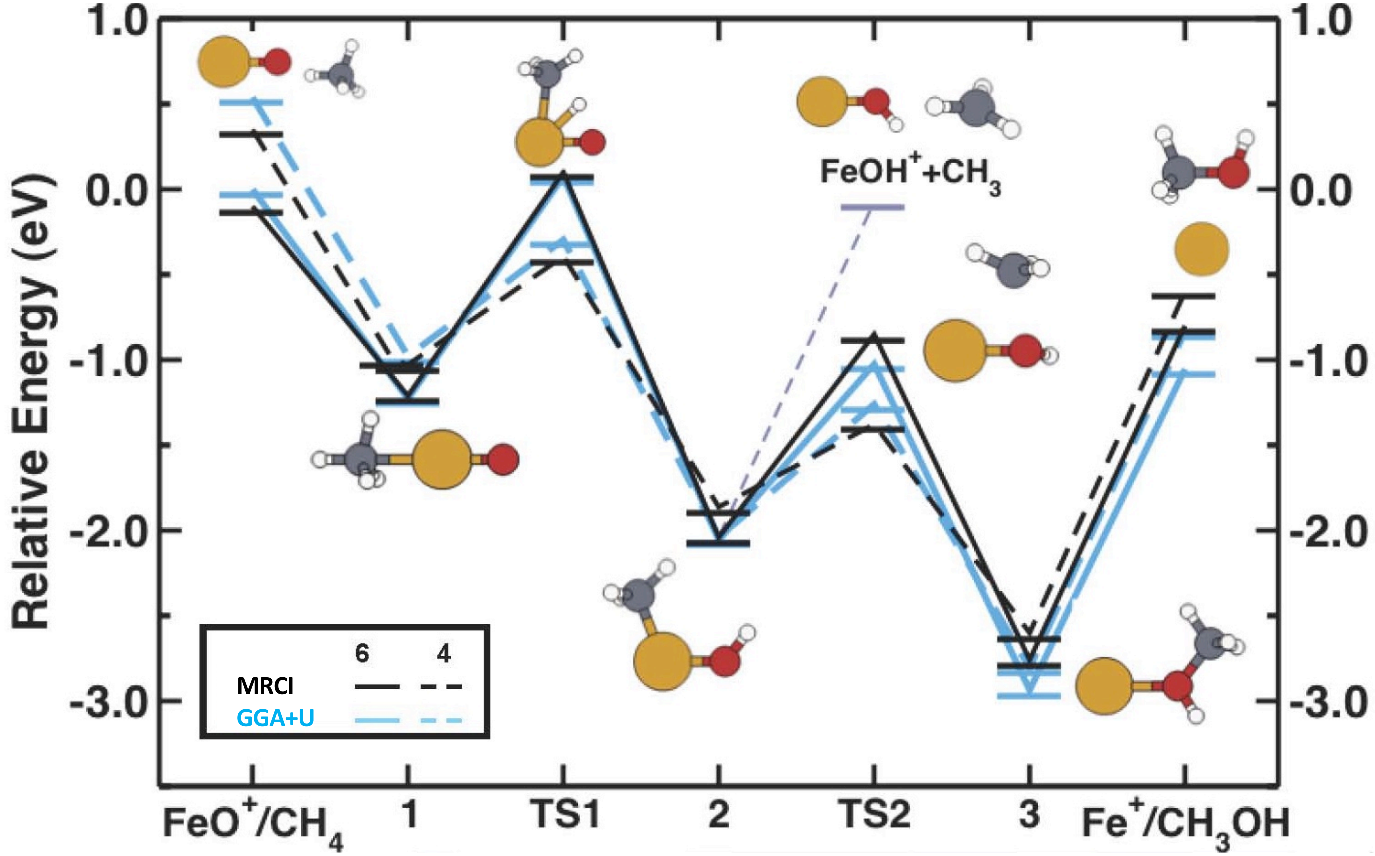


Methane on FeO^+: GGA vs MRCI



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)

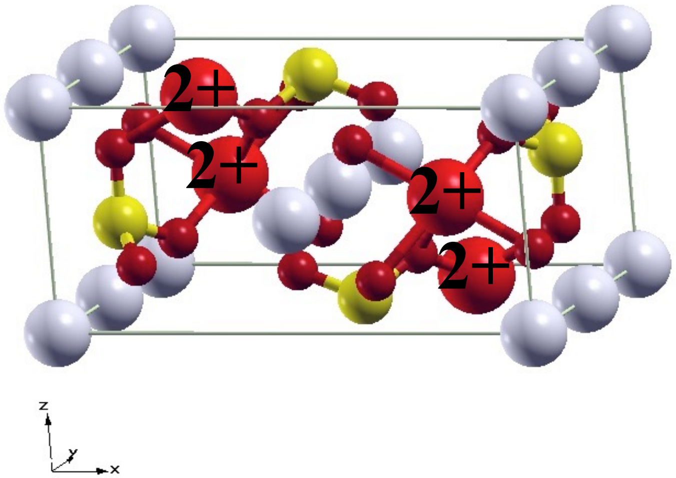
Methane on FeO^+: GGA+U vs MRCI



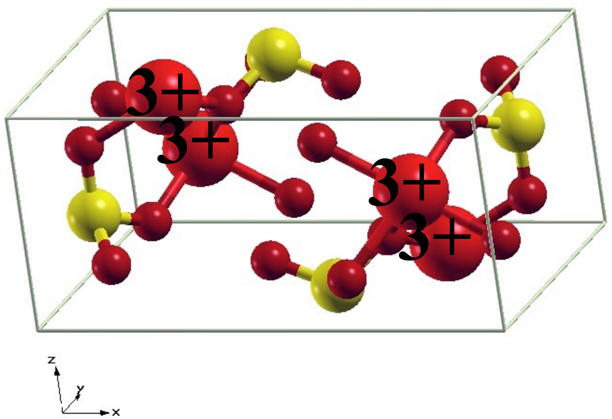
H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, Phys. Rev. Lett. (2006)
H.J. Kulik and N. Marzari, JCP 129 134314 (2008)

Mixed-valence olivines for battery cathodes

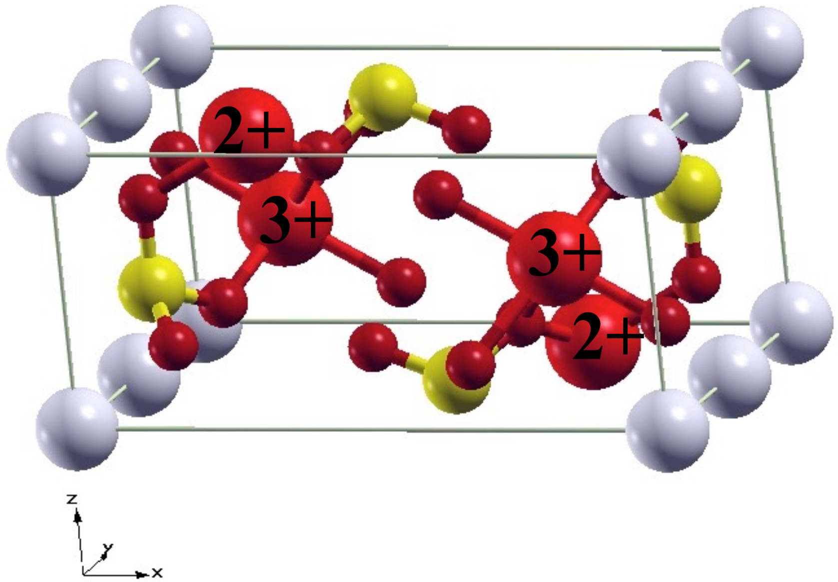
$LiMPO_4$



MPO_4



$Li_{0.5}MPO_4$



Li_xFePO_4: 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


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** ρ**(r,ω))** provides also the correct energy levels
- In a quasi-particle approximation, this spectral functional depends discretely on **the orbital densities** ρ**(r,i)**

KOOPMANS' COMPLIANT SPECTRAL FUNCTIONALS

For every orbital the expectation value

$$\boxed{\varepsilon_i = \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle}$$

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)

$$E^{\mathrm{KI}} = E^{\mathrm{DFT}} + \sum_i \Big[\underbrace{- \int_0^{f_i} \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle}_{\text{remove \textasciitilde quadratic Slater}} \overbrace{+ f_i \int_0^1 \langle \varphi_i | \eta \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle}^{\text{add linear Koopmans}} \Big]$$

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

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

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

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

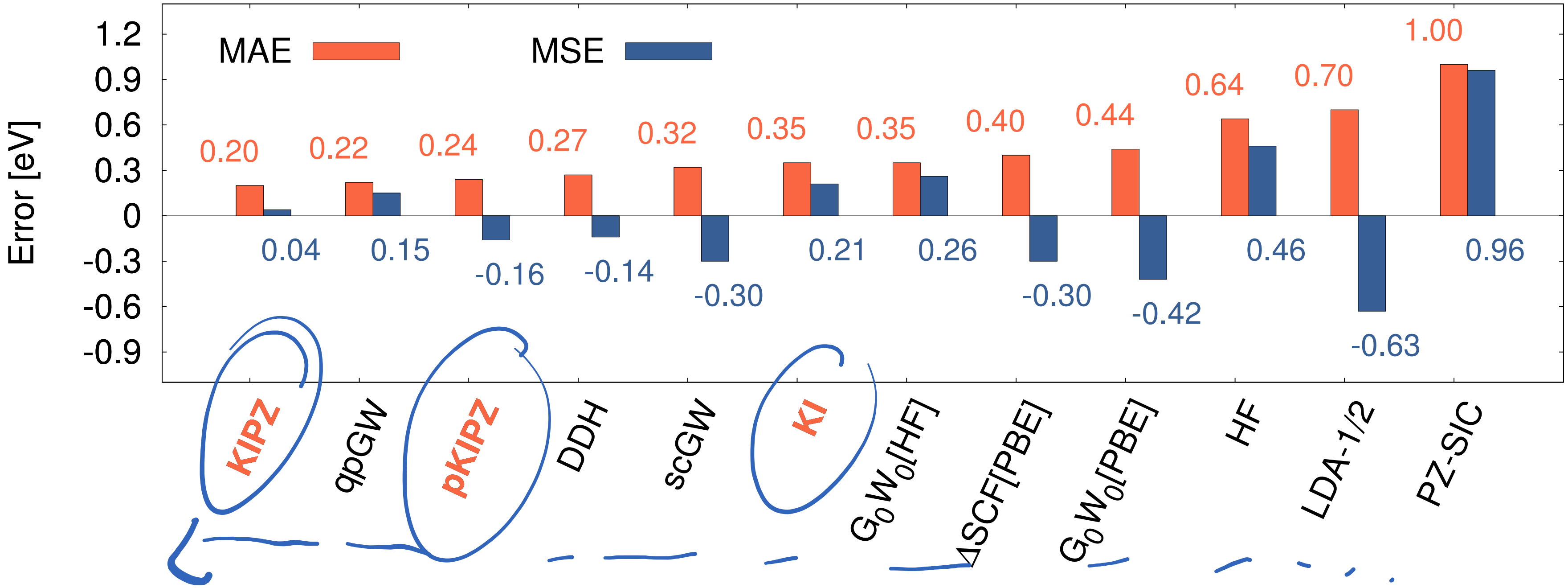
ρ_i orbital density at filling f_i
n_i orbital density at integer filling

KIPZ adds a screened PZ self-interaction term

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

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

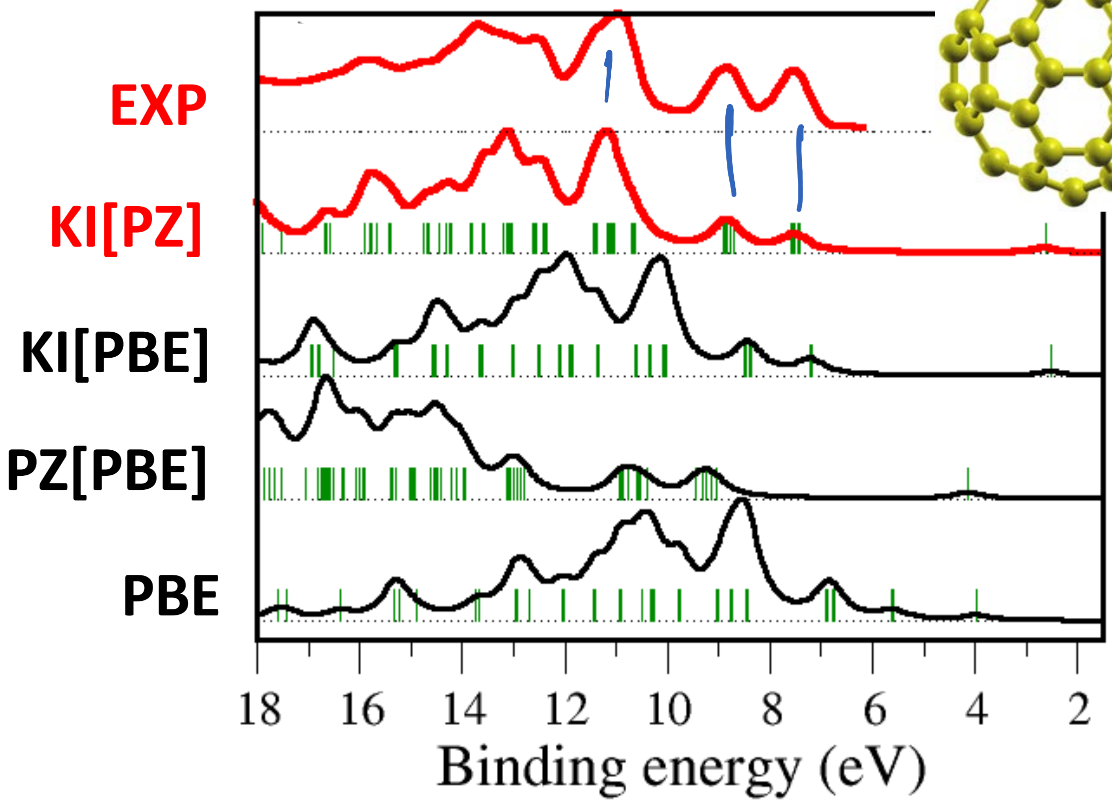
GW100 TEST SET

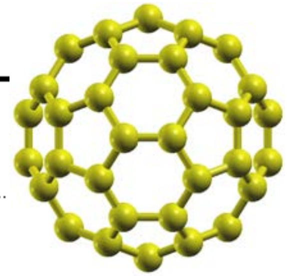


N. Colonna et al., JCTC in press (2018)

UPS (fullerene)

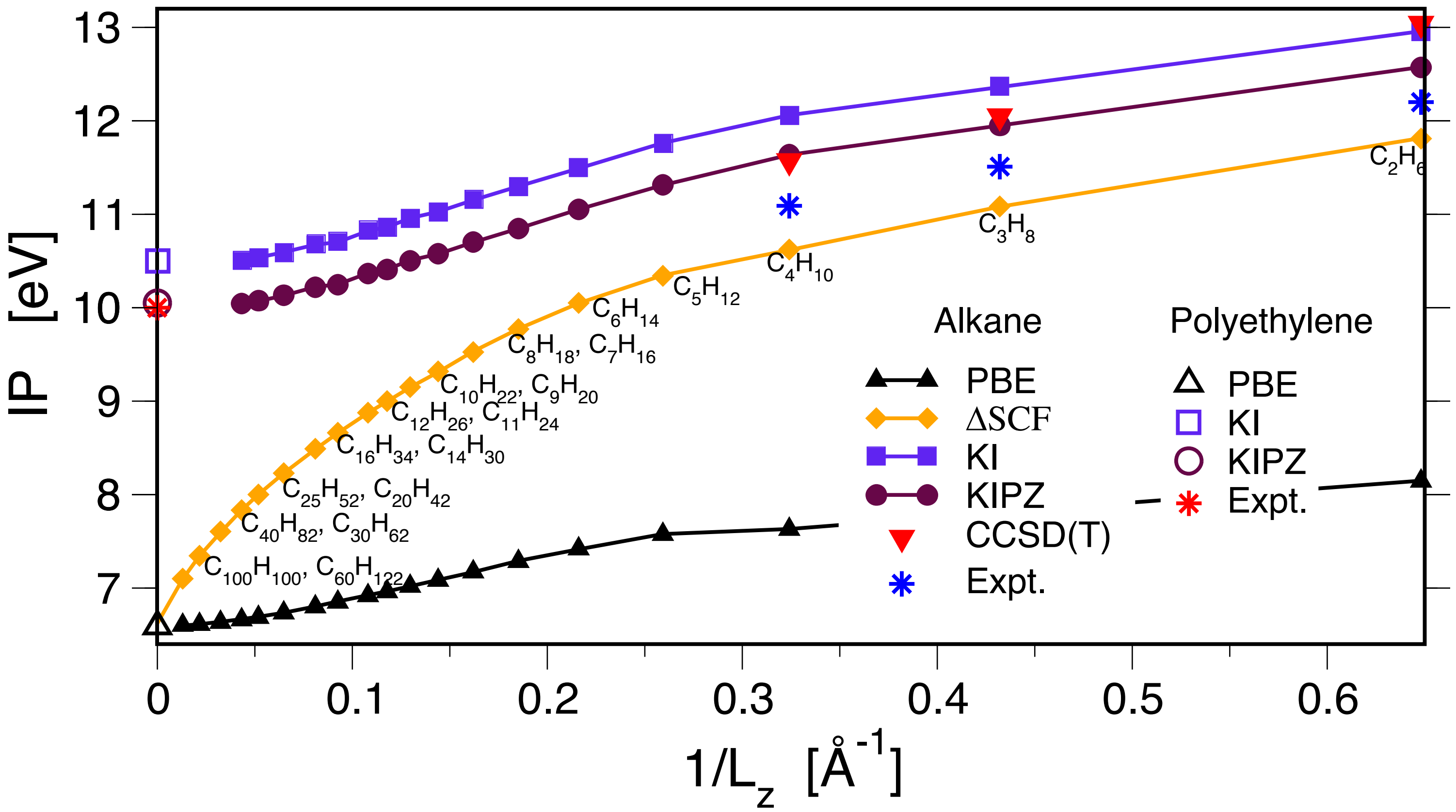
$$I(\omega) = \sum_i |\langle\varphi_f|\hat{H}_{\rm int}|\varphi_i\rangle|^2 \delta(\epsilon_f - \epsilon_i - \hbar\omega)$$



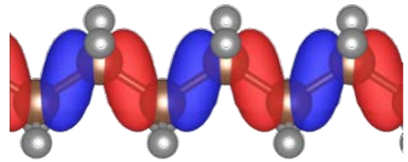


L. Nguyen, G. Borghi, A. Ferretti, I. Dabo, N. Marzari, Phys. Rev. Lett. 114, 166405 (2015)

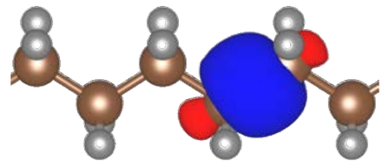
SOLID-STATE LIMIT



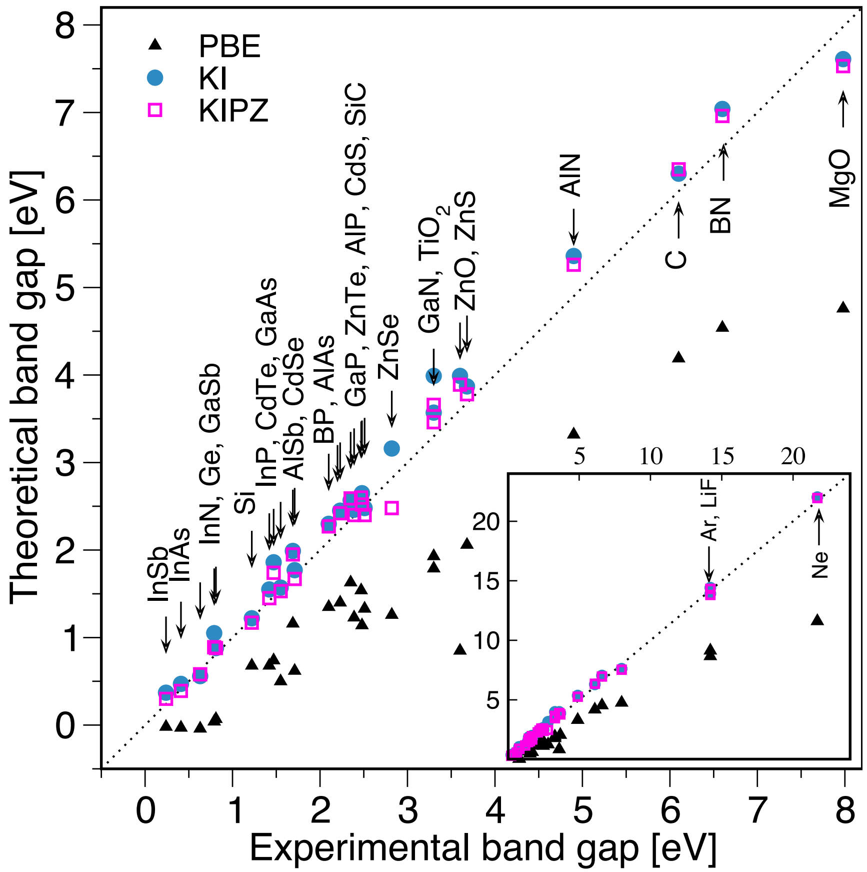
Canonical orbital



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 (Kreisler-Kronik 2013)**
- **Maximally-localized Wannier functions → Koopmans-Wannier method (Lin-Wan Wang, 2015)**

Why is DFT like tinder ?

Why is DFT like tinder?

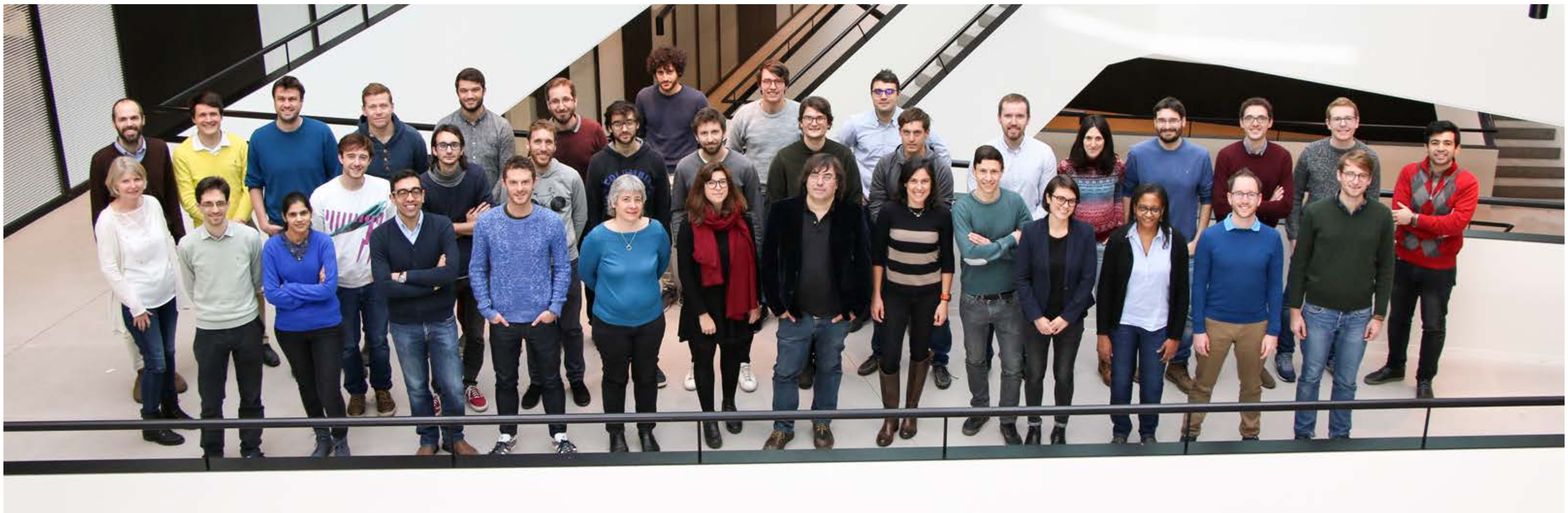
I. It's very popular! Everyone does it
II. It's fast and easy, and requires no thinking
III. You can swipe functionals left until you find the one that works for you, for a while

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://theossrv1.epfl.ch/Main/People



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