Why is DFT like tinder ?

Nicola Marzari, EPFL

THE RISE OF SIMULATION SCIENCE

2013 Chemistry Prize

Taking the Experiment to Cyberspace

Photo © Harvard University

Martin Karplus

Martin Karplus, U.S. and Austrian citizen. Born 1930 in Vienna, Austria.

Photo: S. Fisch

Michael Levitt

Michael Levitt, U.S., British and Israeli citizen. Born 1947 in Pretoria,

Photo: Wikimedia Commons

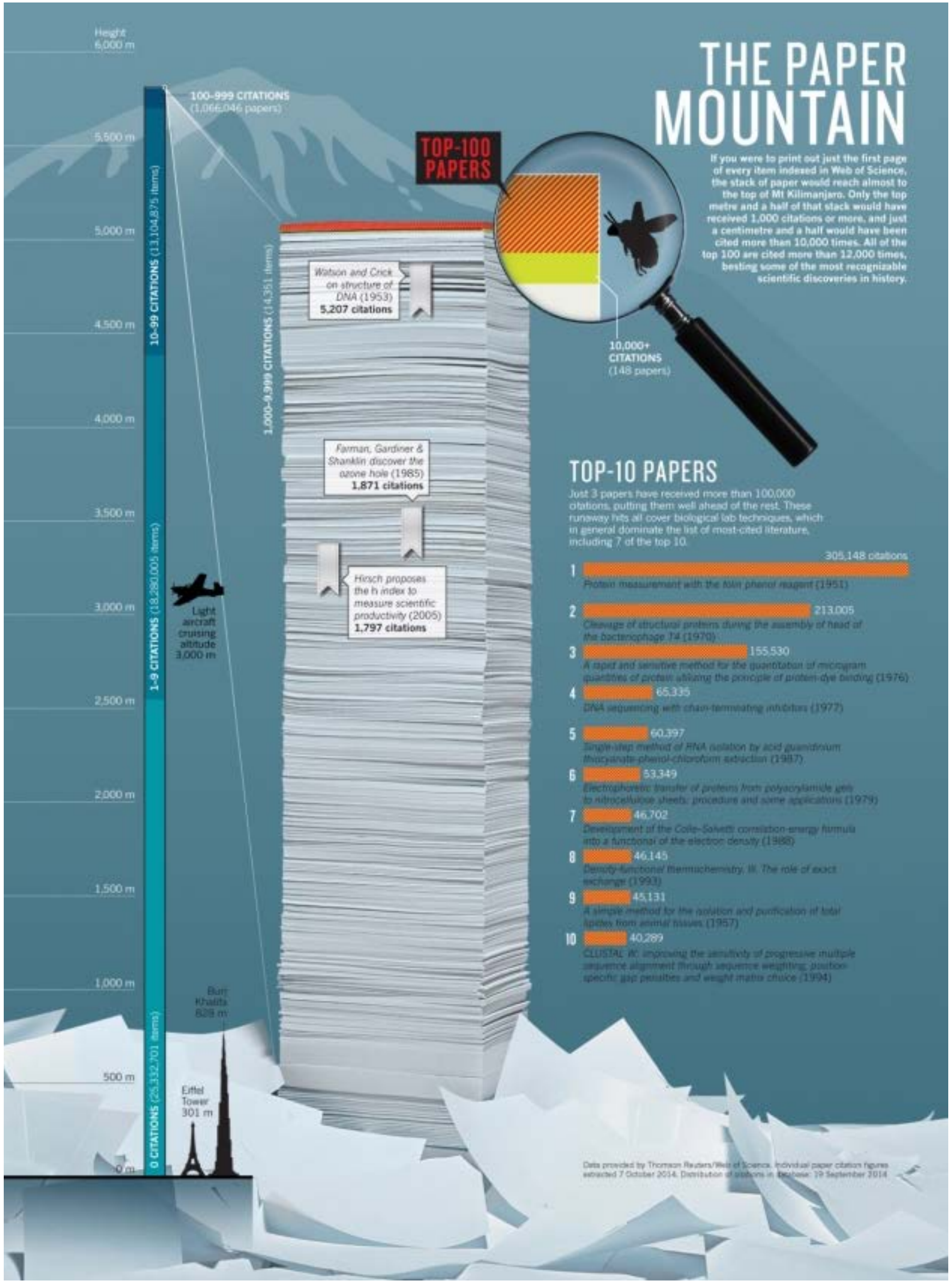
Arieh Warshel

Arieh Warshel, U.S. and Israeli citizen. Born 1940 in Kibbutz Sde-

"The prize focuses on how to evaluate the variation in the energy of the real system in a accurate and efficient way […]. The Car–Parrinello approach is the leading strategy along this line."

"Simulations are so realistic that they predict the outcome of traditional experiments."

From www.nobelprize.org/nobel_prizes/chemistry/laureates/2013/



If you were to print out just the first page of every item indexed in Web of Science, the stack of paper would reach almost to the top of Mt Kilimanjaro. Only the top metre and a half of that stack would have received 1,000 citations or more, and just a centimetre and a half would have been cited more than 10,000 times. All of the top 100 are cited more than 12,000 times, besting some of the most recognizable scientific discoveries in history.

TOP-10 PAPERS

Just 3 papers have received more than 100,000 citations, putting them well ahead of the rest. These runaway hits all cover biological lab techniques, which in general dominate the list of most-cited literature, including 7 of the top 10.

1 305,148 citations *Protein measurement with the folin phenol reagent* (1951)
2 213,005 *Cleavage of structural proteins during the assembly of head of the bacteriophage T4* (1970)
3 155,530 *A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding* (1976)
4 65,335 *DNA sequencing with chain-terminating inhibitors* (1977)
5 60,397 *Single-step method of RNA isolation by acid guanidinium thiocyanate-phenol-chloroform extraction* (1987)
6 53,349 *Electrophoretic transfer of proteins from polyacrylamide gels to nitrocellulose sheets: procedure and some applications* (1979)
7 46,702 *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density* (1988)
8 46,145 *Density-functional thermochemistry. III. The role of exact exchange* (1993)
9 45,131 *A simple method for the isolation and purification of total lipides from animal tissues* (1957)
10 40,289 *CLUSTAL W: improving the sensitivity of progressive multiple sequence alignment through sequence weighting, position-specific gap penalties and weight matrix choice* (1994)

Data provided by Thomson Reuters/Web of Science. Individual paper citation figures extracted 7 October 2014. Distribution of citations in database: 19 September 2014

NATURE,
October 2014

THE TOP 100 PAPERS:

12 papers on DFT in the top-100 most cited papers in the entire scientific literature, ever.

AROSA (GRISONS), 27th DECEMBER 1925

At the moment I am struggling with a new atomic theory. I am very optimistic about this thing and expect that if I can only... solve it, it will be very beautiful.

Erwin Schrödinger

Schrödinger equation and the complexity of the many-body Ψ

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + \sum_i V_{ext}\left(\vec{r}_i\right) + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}\right]\psi(\vec{r}_1,\ldots,\vec{r}_n) = E_{el}\psi(\vec{r}_1,\ldots,\vec{r}_n)$$

Schrödinger equation and the complexity of the many-body Ψ

$$\psi(\vec{r}_1, \dots, \vec{r}_n)$$

"... the full specification of a single wave function of neutral iron is a function of 78 variables. It would be rather crude to restrict to 10 the number of values of each variable … even so, full tabulation would require 10^{78} entries."

Douglas R Hartree

Charles G. Darwin, *Biographical Memoirs of Fellows of the Royal Society*, 4, 102 (1958)

Variational Principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E[\Psi] \geq E_0$$

If $E[\Psi] = E_0$, then Ψ is the ground state wavefunction, and viceversa…

Hartree Equations

The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written as the product of single orbitals (i.e. we are working with independent electrons)

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2)\cdots\varphi_n(\vec{r}_n)$$

$$\left[-\frac{1}{2}\nabla_i^2+V_{ext}(\vec{r}_i)+\sum_{j\neq i}\int|\phi_j(\vec{r}_j)|^2\,\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j\right]\phi_i(\vec{r}_i)=\varepsilon\phi_i(\vec{r}_i)$$

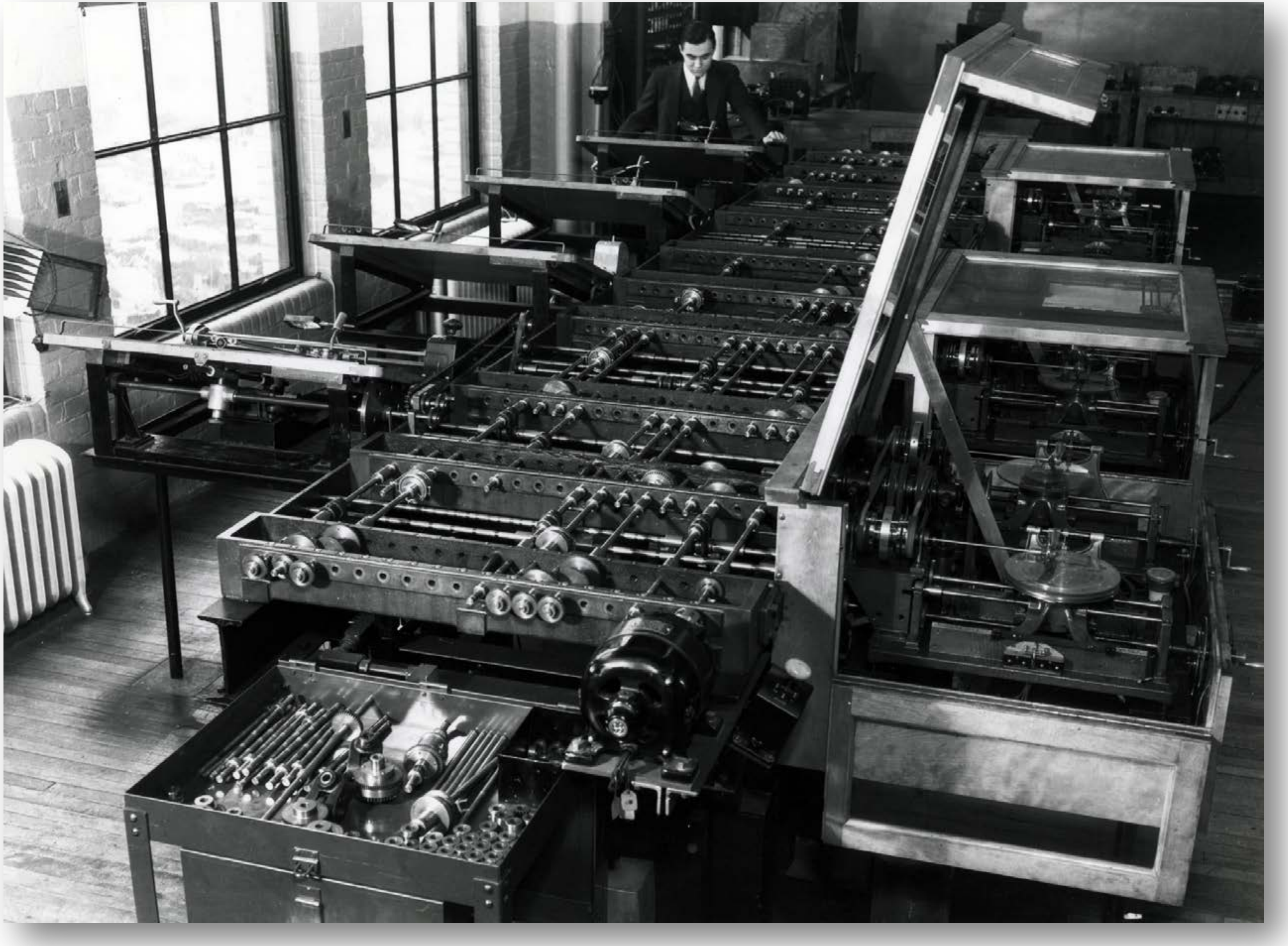
Spin-Statistics

- All elementary particles are either fermions (half-integer spins) or bosons (integer)
- A set of identical (indistinguishable) fermions has a wavefunction that is antisymmetric by exchange

$$\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_j,\ldots,\vec{r}_k,\ldots,\vec{r}_n)=-\psi(\vec{r}_1,\vec{r}_2,\ldots,r_k,\ldots,\vec{r}_j,\ldots,\vec{r}_n)$$

- For bosons it is symmetric

The top supercomputer in the 1920s



As We May Think – *Atlantic Monthly* Jul 1945

The advanced arithmetical machines of the future […] **will perform complex arithmetical computations at exceedingly high speeds, and they will record results in such form as to be readily available for distribution or for later further manipulation.**

Only then will mathematics be practically effective in bringing the **growing knowledge of atomistics to the useful solution of the advanced problems** of chemistry, metallurgy, and biology.

A memex is a device in which an individual stores all his books, records, and communications, and which is mechanized so that it may be consulted with exceeding speed and flexibility. It is an **enlarged intimate supplement** to his memory.

It consists of a desk, and while it can presumably be operated from a distance, it is primarily the piece of furniture at which he works. On the top are slanting translucent screens, on which material can be projected for convenient reading. There is a keyboard, and sets of buttons and levers.

Wholly new forms of encyclopedias will appear, ready made with a mesh of associative trails running through them.

The chemist, struggling with the synthesis of an organic compound, **has all the chemical literature before him in his laboratory, with trails following the analogies** of compounds, and side trails to their physical and chemical behavior.

Reduced density matrices

$$\gamma_1\left(r_1', r_1\right) =$$

$$N\int \ldots \int \Psi\left(r_1', r_2, r_3, r_4, \ldots, r_N\right)\Psi^*\left(r_1, r_2, r_3, r_4, \ldots, r_N\right) dr_2\, dr_3\, dr_4 \ldots dr_N$$

$$\gamma_2\left(r_1', r_2', r_1, r_2\right) =$$

$$\frac{N(N-1)}{2}\int \ldots \int \Psi\left(r_1', r_2', r_3, r_4, \ldots, r_N\right)\Psi^*\left(r_1, r_2, r_3, r_4, \ldots, r_N\right) dr_3\, dr_4 \ldots dr_N$$

The exact energy functional is known!

$$E = \int \left[\left(-\frac{1}{2}\nabla_1^2 + V_{ext}\left(r_1\right) \right) \gamma_1\left(r_1', r_1\right) \right]_{r_1' = r_1} dr_1 + \iint \frac{1}{r_{12}} \gamma_2\left(r_1, r_2, r_1, r_2\right) dr_1\, dr_2$$

But: N-representability problem!

Density-functional theory

- The external potential V_{ext} and the number N of electrons completely define the quantum problem
- The wavefunctions are – in principle – uniquely determined, via the Schrödinger Equation
- All system properties follow from the wavefunctions
- The energy (and everything else) is thus a functional of V_{ext} and N

Fermi’s intuition

- Let’s try to find out an expression for the energy as a function of the charge density
- E = kinetic + external pot. + el.-el.
- Kinetic is the tricky term: how do we get the curvature of a wavefunction from the charge density ?
- Answer: local-density approximation

Local-density approximation

- We take the kinetic energy density at every point to correspond to the kinetic energy density of the non-interacting homogenous electron gas

$$T(\vec{r}) = A n^{\frac{5}{3}}(\vec{r})$$

$$E_{Th-Fe}[n] = A\int n^{\frac{5}{3}}(\vec{r})\,d\vec{r} + \int n(\vec{r})V_{ext}(\vec{r})\,d\vec{r} + \frac{1}{2}\iint \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

It’s a poor man Hartree…

- The idea of an energy functional is not justified
- It scales linearly, and we deal with 1 function of three coordinates !

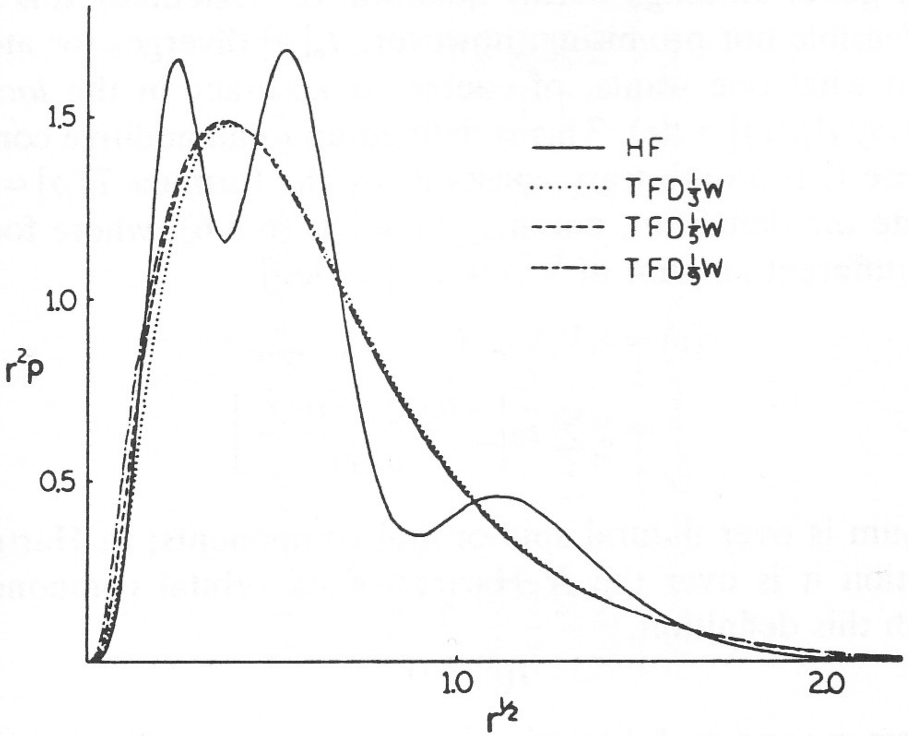


Figure 6.3 Electron density for argon from various models (after Yang 1986.)

First Hohenberg-Kohn theorem

The density as the basic variable: the external potential V_{ext} determines uniquely the charge density, and the charge density determines uniquely the external potential V_{ext}.

1-to-1 mapping: $V_{ext} \Leftrightarrow n$

The universal functional *F*[ρ]

The ground state density determines the potential of the Schrödinger equation, and thus the wavefunction.

The universal functional F is well defined:

$$F[n(\vec{r})] = \left\langle \Psi \middle| \hat{T} + \hat{V}_{e-e} \middle| \Psi \right\rangle$$

Second Hohenberg-Kohn theorem

The variational principle – we have a *new Schrödinger's-like equation*, expressed in terms of the charge density only

$$E_v[n(\vec{r})] = F[n(\vec{r})] + \int n(\vec{r}) V_{ext}(\vec{r}) d\vec{r} \geq E_0$$

(*n* determines its groundstate wavefunction, that can be taken as a trial wavefunction in this external potential)

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} + \hat{V}_{e-e} + V_{ext} | \Psi \rangle = \int n(\vec{r}) V_{ext}(\vec{r}) + F[n]$$

The non-interacting unique mapping

- **The Kohn-Sham system:** a reference system is introduced (the Kohn-Sham electrons)
- These electrons do not interact, and live in an external potential (the Kohn-Sham potential) such that their ground-state charge density is identical to the charge density of the interacting system

The Kohn-Sham mapping

F decomposed in non-interacting kinetic + Hartree + mistery

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})],$$

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^\star(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] +$$

$$+E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})\ d\mathbf{r}$$

Ground State of the Electron Gas by a Stochastic Method

D. M. Ceperley
National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

B. J. Alder
Lawrence Livermore Laboratory, University of California, Livermore, California 94550

(Received 16 April 1980)

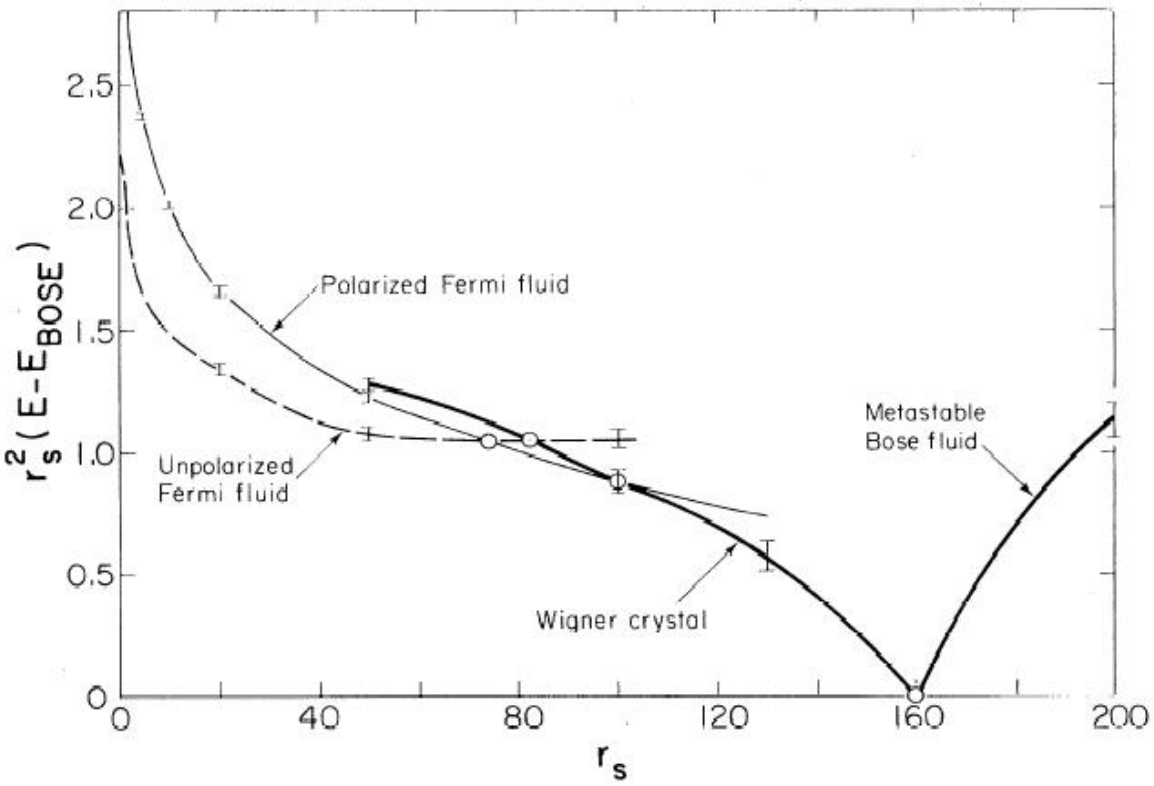


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s = 75$. The polarized (ferromagnetic) Fermi fluid is stable between $r_s = 75$ and $r_s = 100$, the Fermi Wigner crystal above $r_s = 100$, and the normal paramagnetic Fermi fluid below $r_s = 75$.

It works!

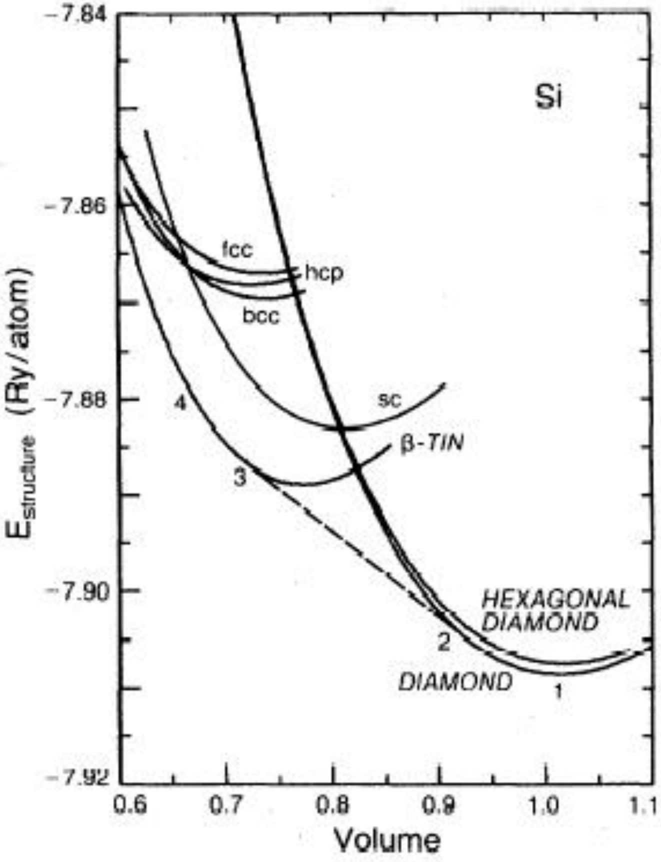


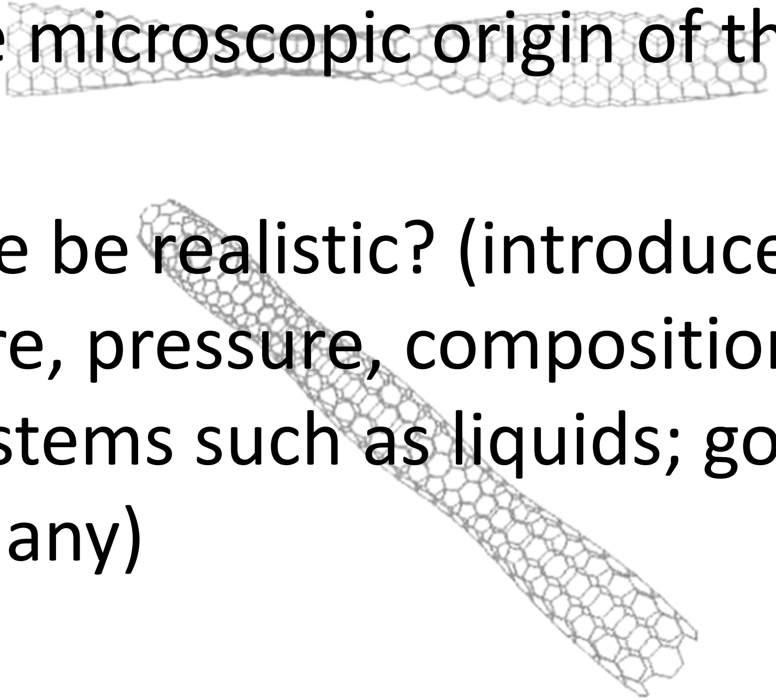
FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β-tin phase ($c/a=0.552$).

Summary on xc
(energy – see late for spectral)

- LDA (local density approximation)
- GGA (generalized gradient approximation): BP88, PW91, PBEsol, BLYP, …
- Meta-GGAs: Laplacian (SCAN)
- WDA (weighted density approximation – good, not much used)
- Bayesian-optimized functionals (BEEF)
- DFT + Hubbard; hybrids (B3LYP, PBE0PBE, HSE) - part of Fock exchange

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

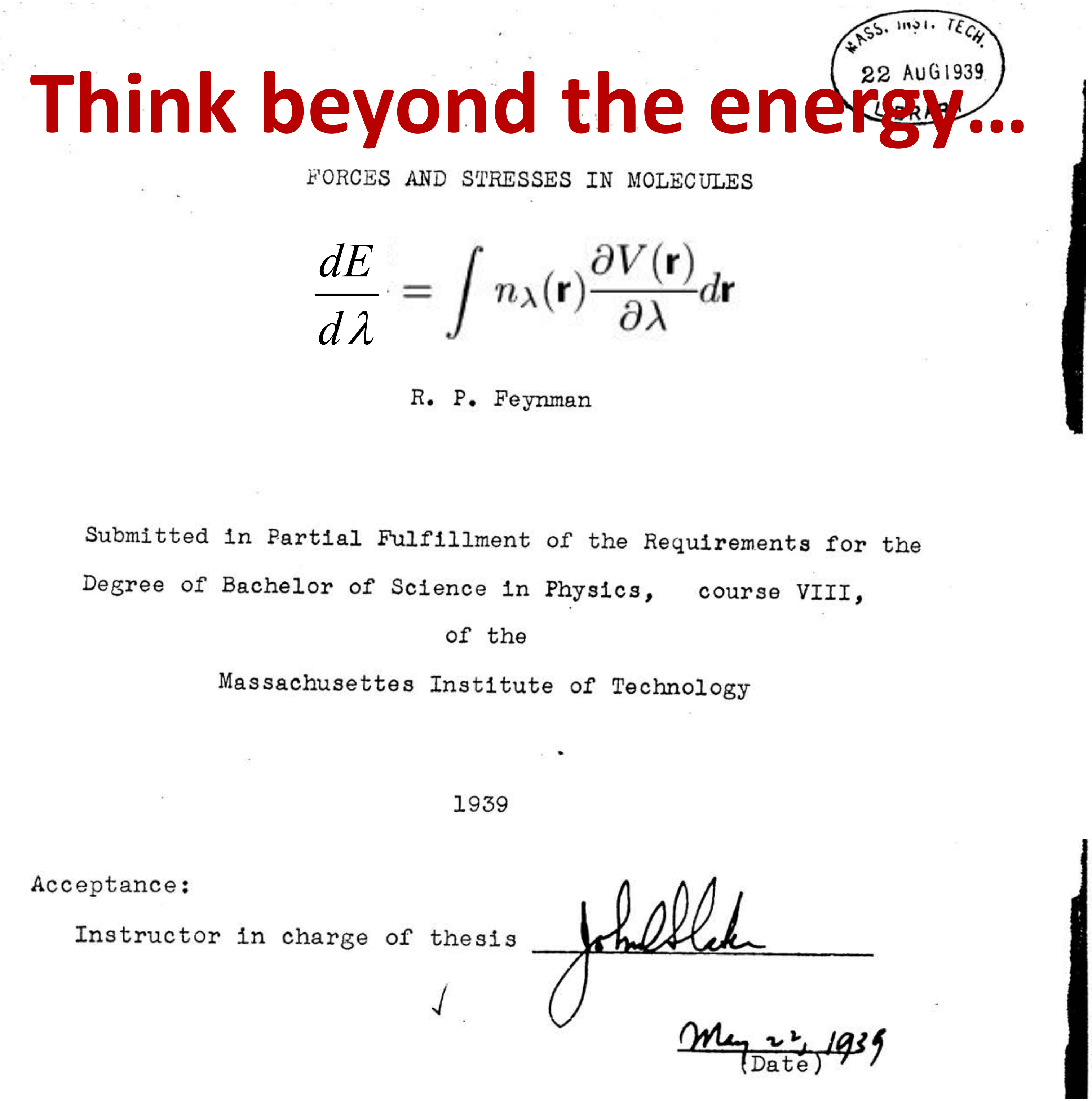
- **From total energy to thermodynamics**
  - temperature, pressure, chemical potentials and partial pressures, electrochemical potential, pH
- **From DFT to real electrons**
  - many-body perturbation theory
  - quantum Monte Carlo
  - DMFT, cluster DMFT, DCA

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

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
Massachusettes Institute of Technology

1939

Acceptance:

Instructor in charge of thesis John Slater

May 22, 1939
(Date)

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:

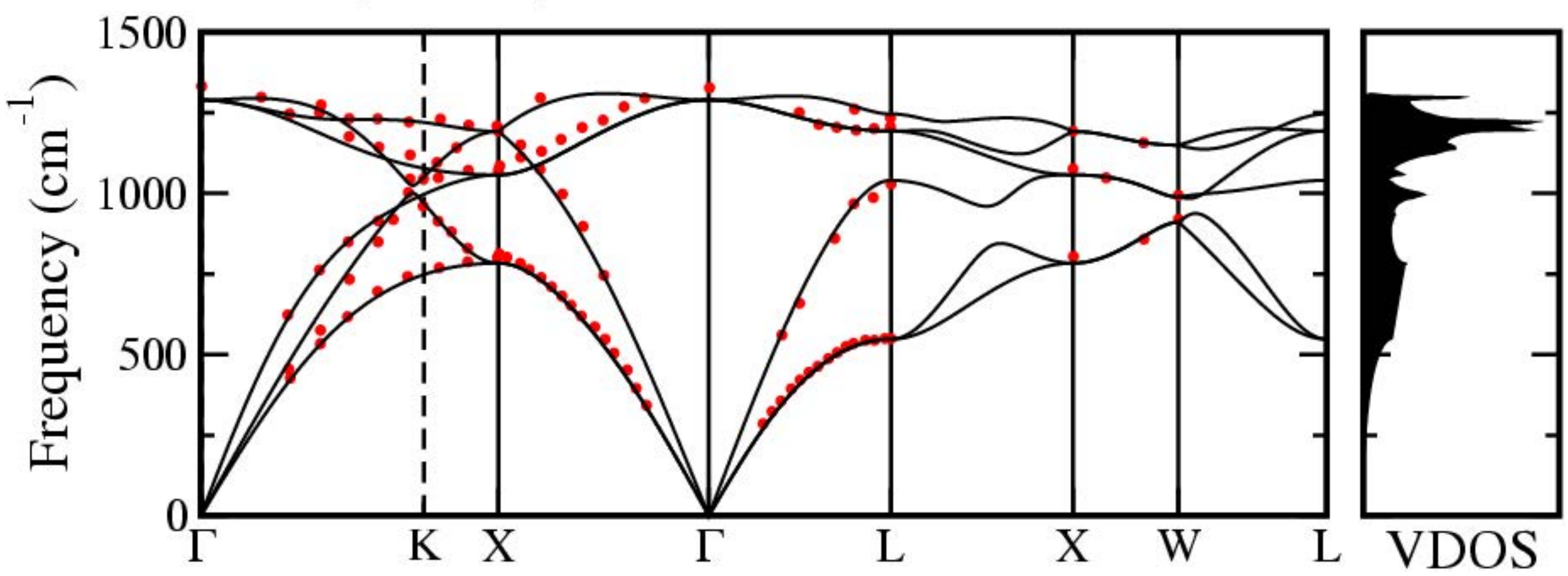
$$\frac{dE}{d\lambda} = \int n_\lambda(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

Total Energy:

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

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

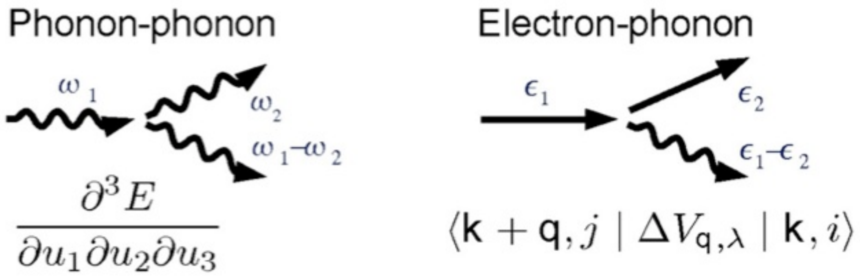
Phonons and temperature



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

MULTISCALE, MULTIPHYSICS

1. Vibrational properties from density-functional theory (electrons from many-body perturbation theory)
2. Carriers' scattering rates from density-functional perturbation theory (www.quantum-espresso.org)



$$\frac{\partial^3 E}{\partial u_1 \partial u_2 \partial u_3} \qquad \langle \mathbf{k}+\mathbf{q}, j \mid \Delta V_{\mathbf{q},\lambda} \mid \mathbf{k}, i \rangle$$

3. Wannier interpolations (www.wannier.org, epw.org.ac.uk)
4. Transport properties from Boltzmann's equation

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

MULTISCALE, MULTIPHYSICS

FIRST-PRINCIPLES EXPTS (Efetov and Kim)

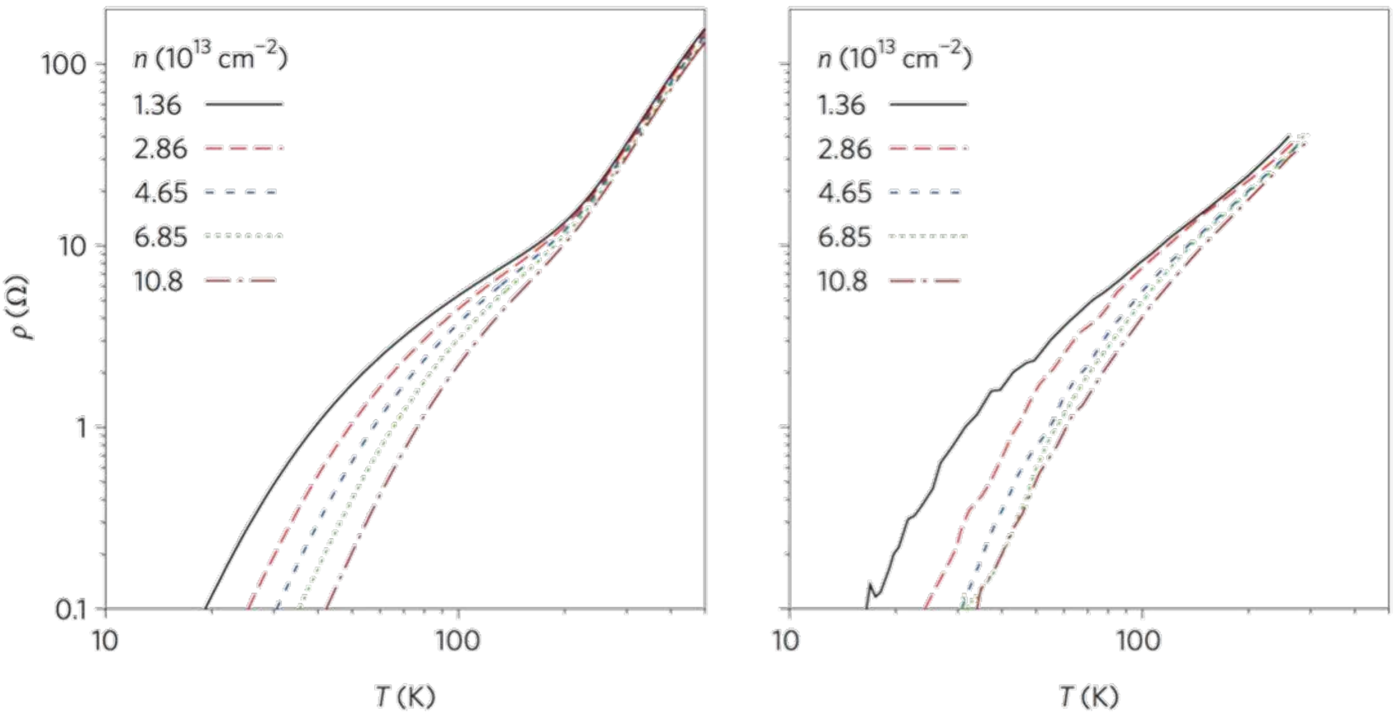
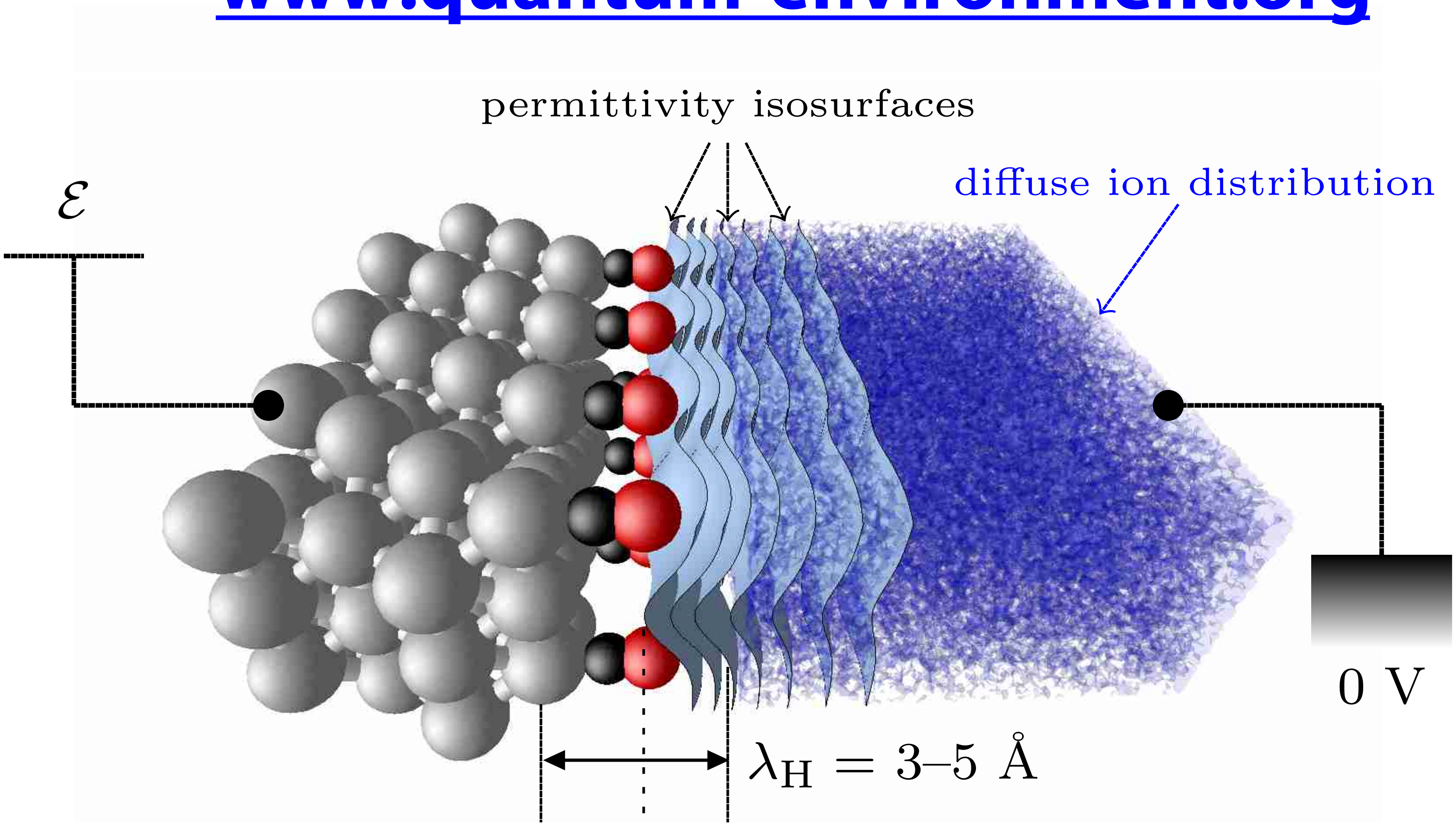


Figure 1 | Electrical resistivity of graphene as a function of temperature and doping (ρ, electrical resistivity; T, temperature; n, carrier density). Left panel: first-principles results obtained using a combination of density-functional perturbation theory, many-body perturbation theory and Wannier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

www.quantum-environment.org



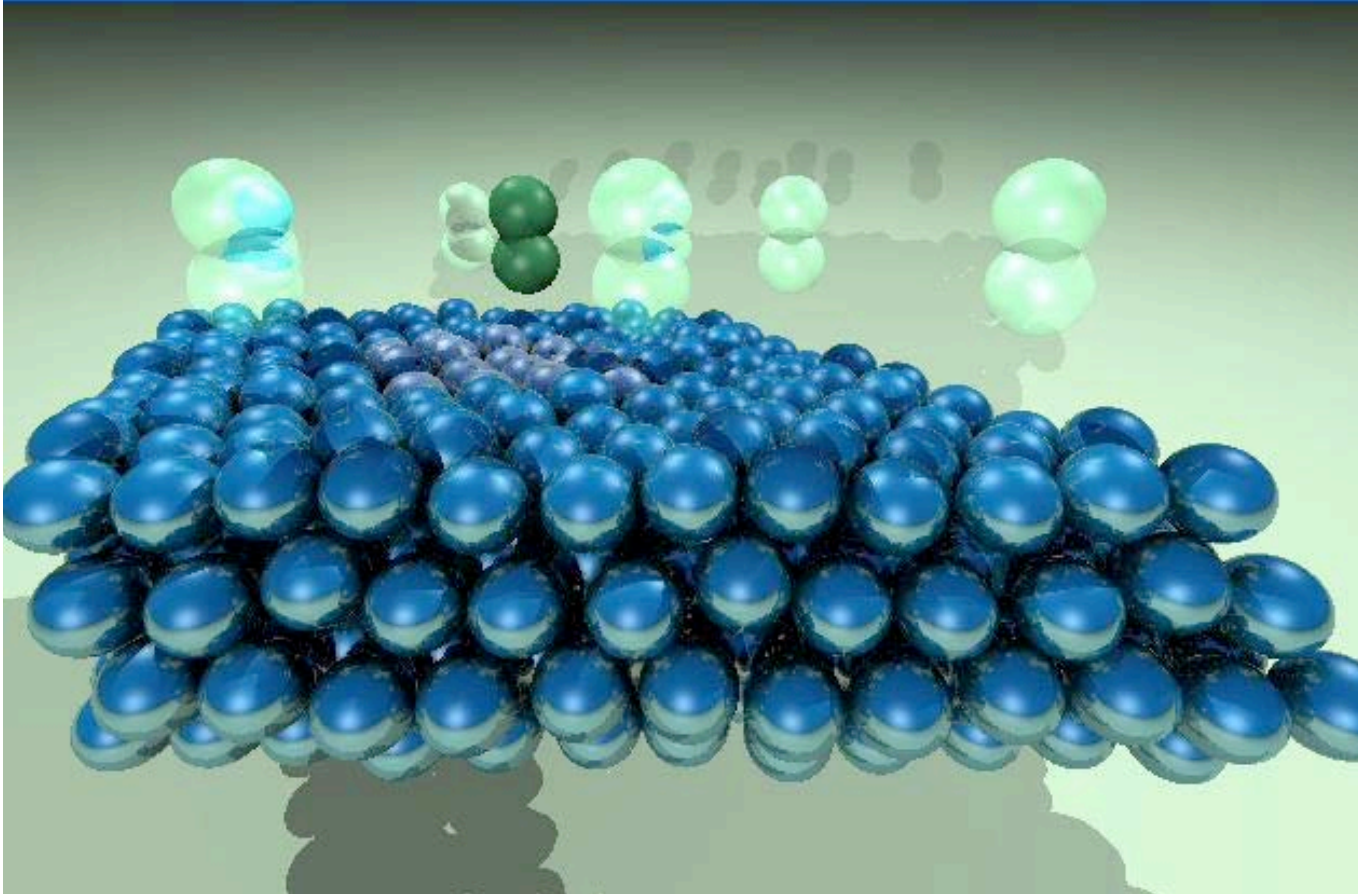
I. Dabo, N. Bonnet, Y. Li and N. Marzari, *"Ab-initio Electrochemical Properties of Electrode Surfaces"*, in Fuel Cell Science: Theory, Fundamentals and Bio-Catalysis, A. Wiecowski and J. Norskov Eds., John Wiley and Co. (2011).

O. Andreussi, I. Dabo and N. Marzari, “Revised self-consistent continuum solvation in electronic structure calculations”, J. Chem. Phys. 136, 064102 (2012).

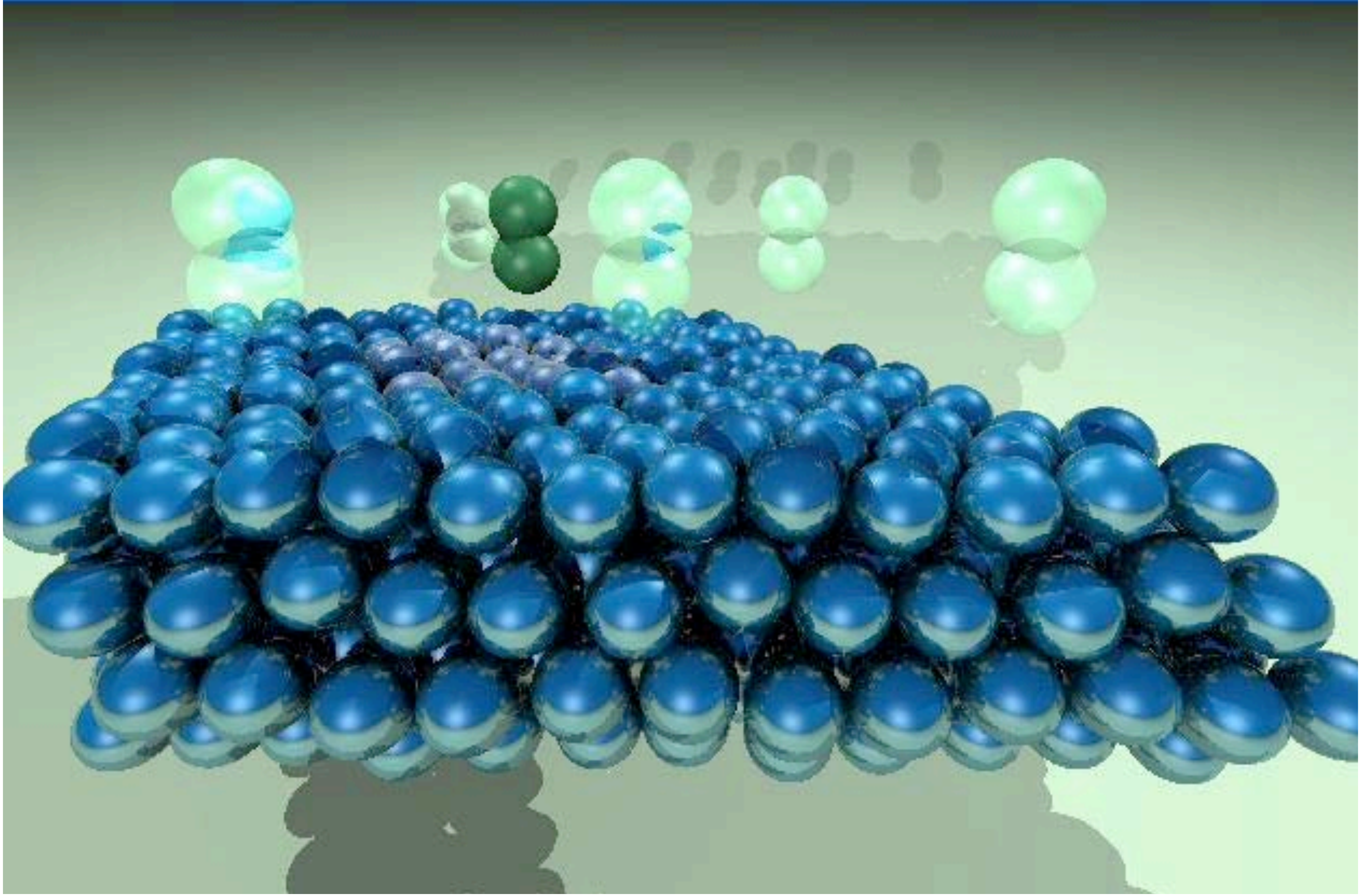
What's wrong with DFT ?

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

Notable failures I: Charge transfer



Notable failures I: Charge transfer



Notable failures II: Beautiful, but perverse

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

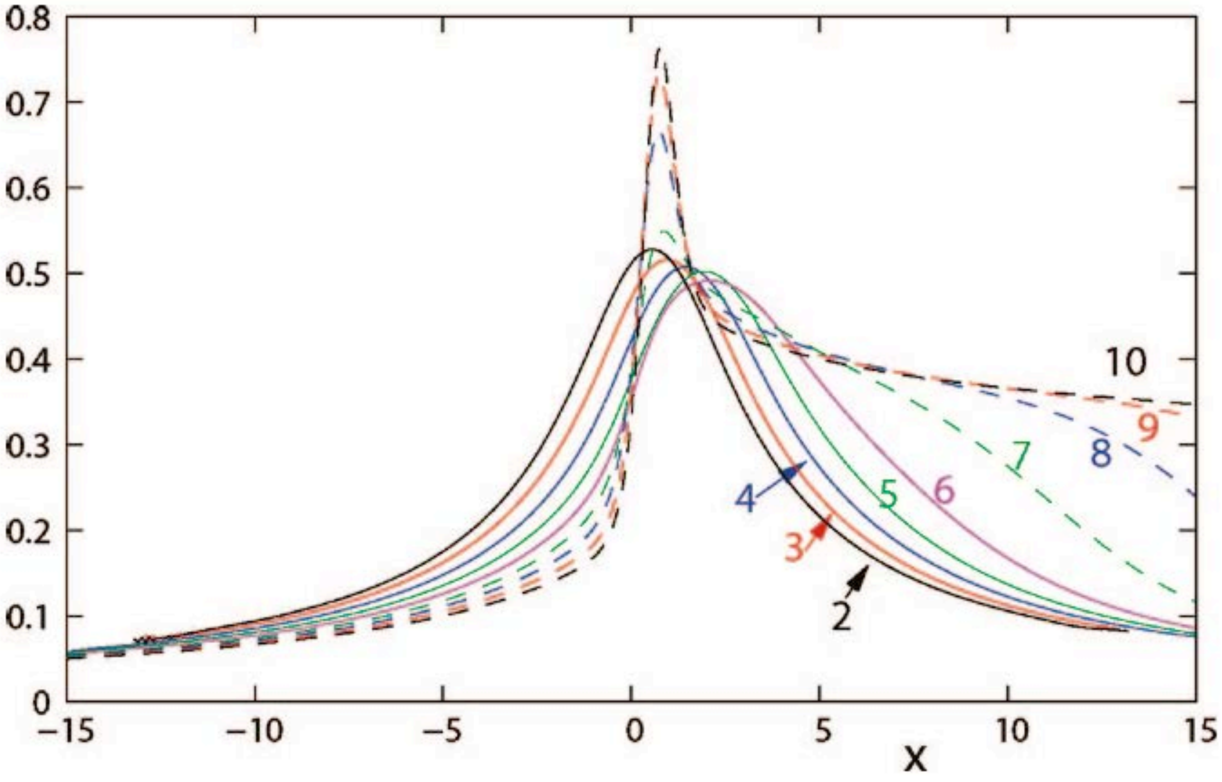
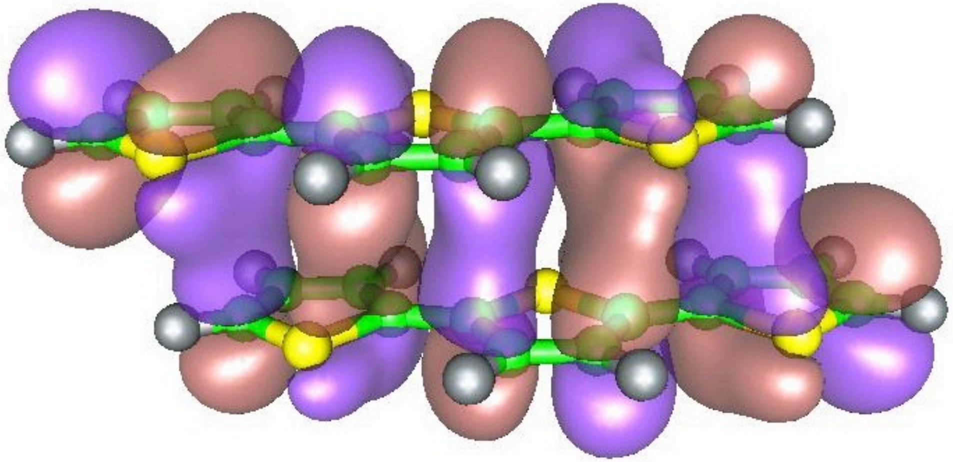
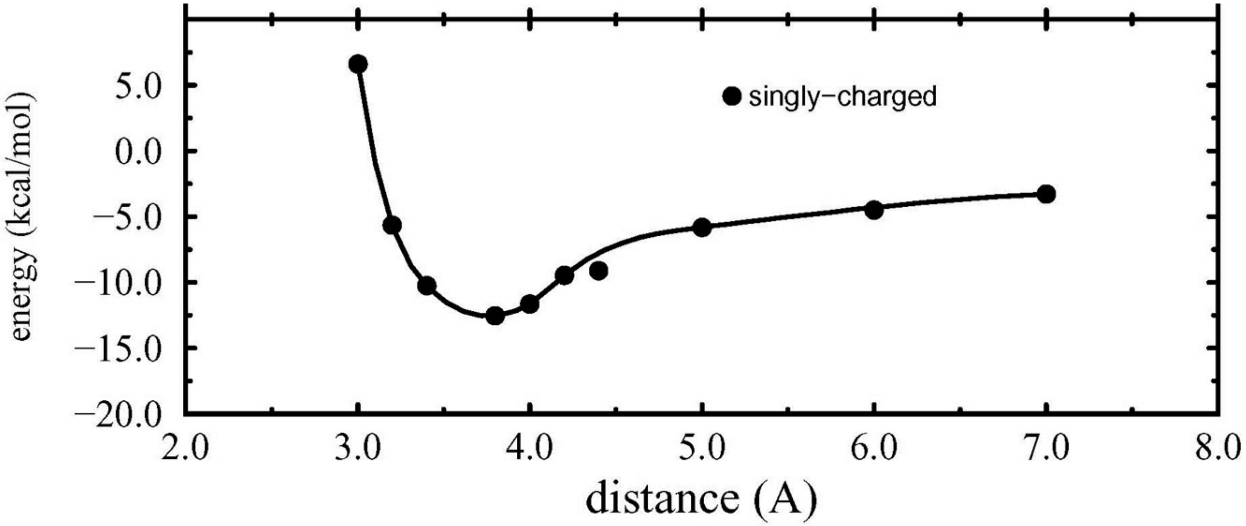


Figure 7. Hartree-exchange-correlation potential, $v_{Hxc}(x)$ for our LiH model ($c = 2.8$); the values of interatomic separation R are indicated.

Neepa Maitra JCTC 2009, Helbig and Rubio JCP 2009

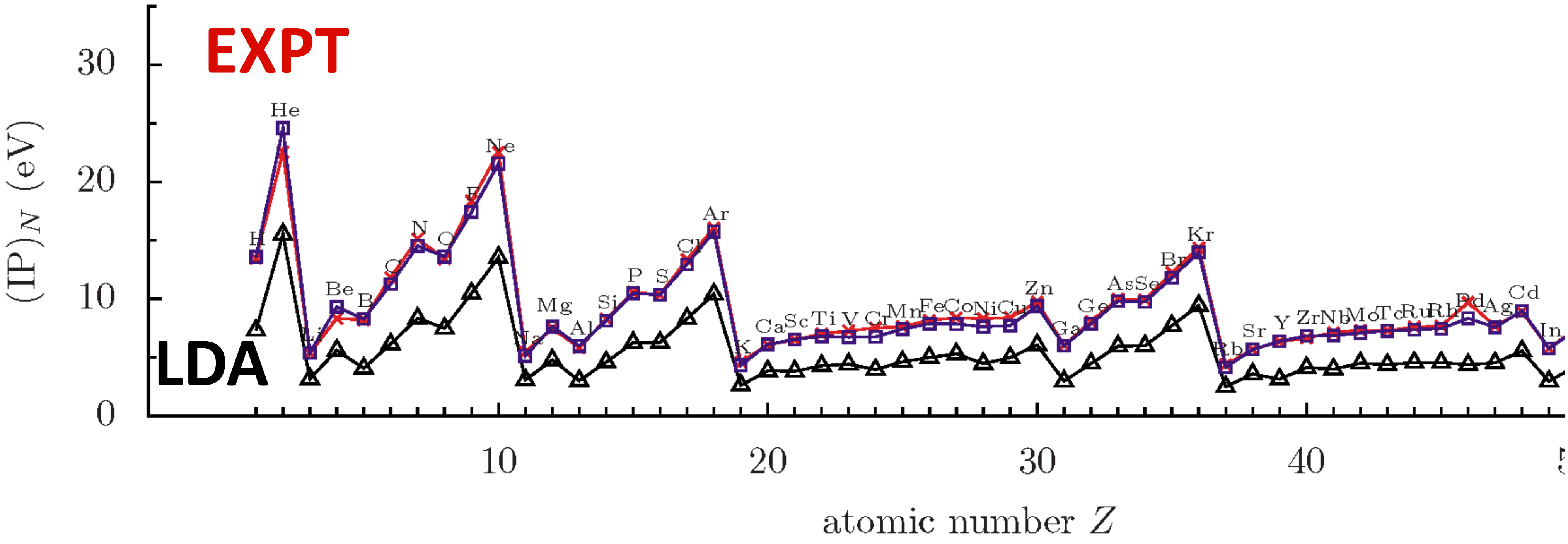
Notable failures III: Delocalization of electrons/holes





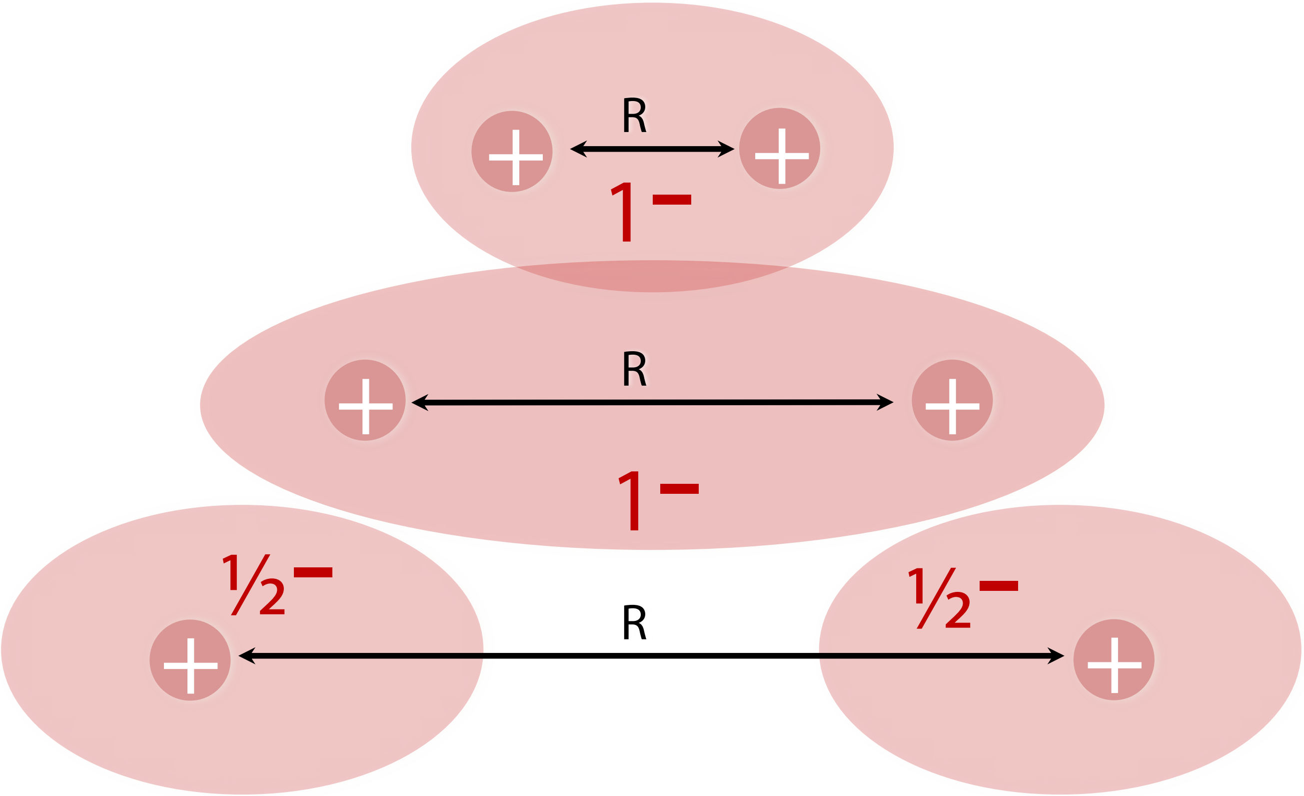
D. A. Scherlis and N. Marzari, JPCB (2004), JACS (2005)

Notable failures IV: Photoemission spectra (IP from HOMO – should be exact)



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

Notable failures V: H_2^+ dissociation limit

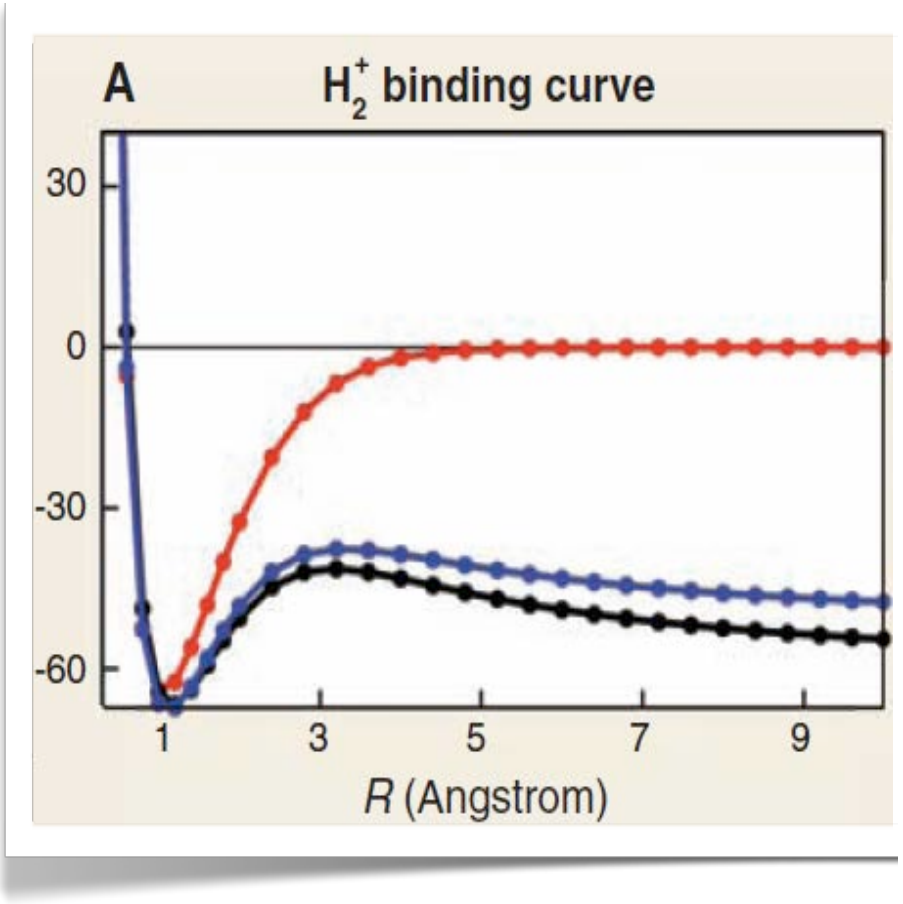


$$\hat{H} = -\frac{1}{2}\vec{\nabla}^2 + V_{\text{ext}}(\vec{r})$$ **Schrödinger**

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

So, it doesn't work even for one electron

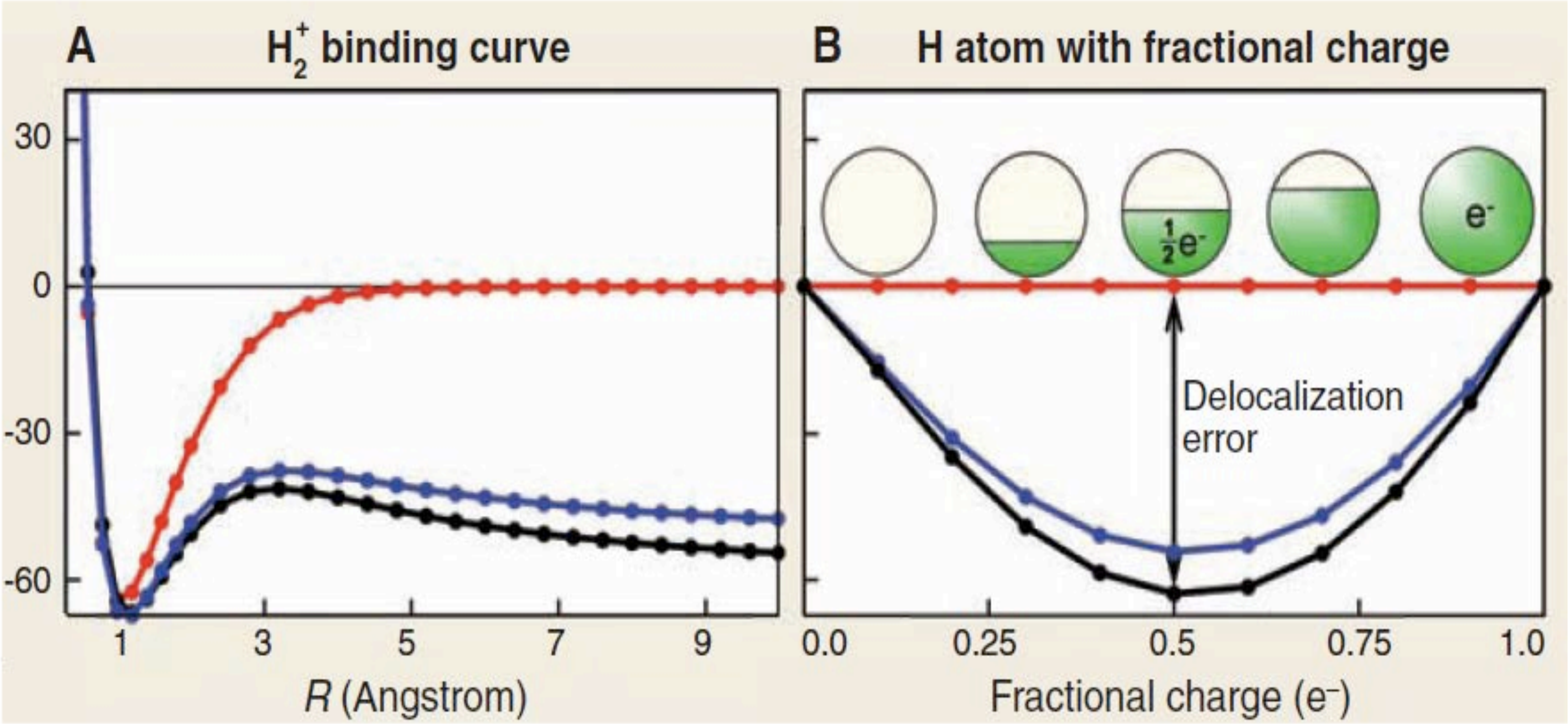
HF **B3LYP** **LDA**



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

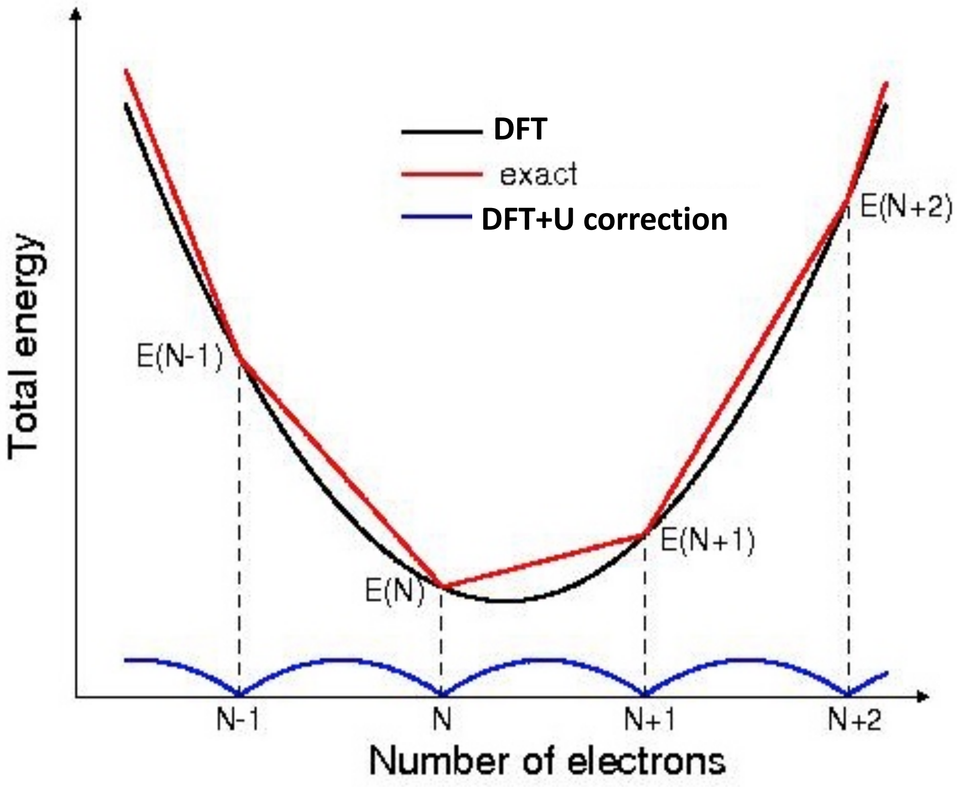
So, it doesn't work even for one electron

HF B3LYP LDA



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

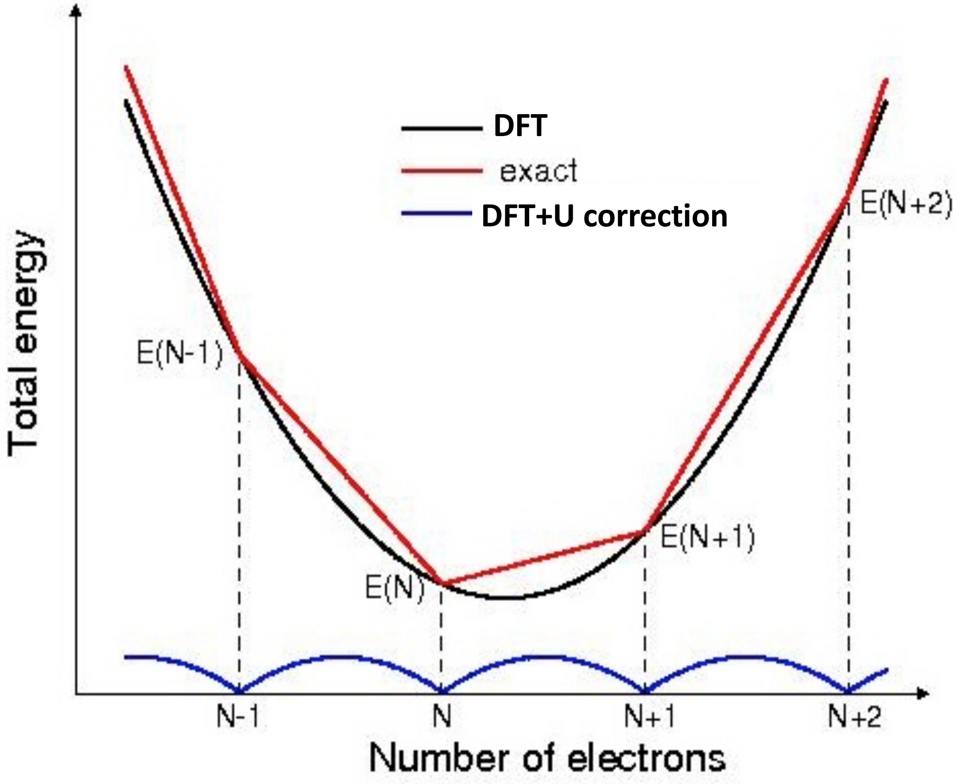
A DFT + Hubbard U approach



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

A DFT + Hubbard U approach

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



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

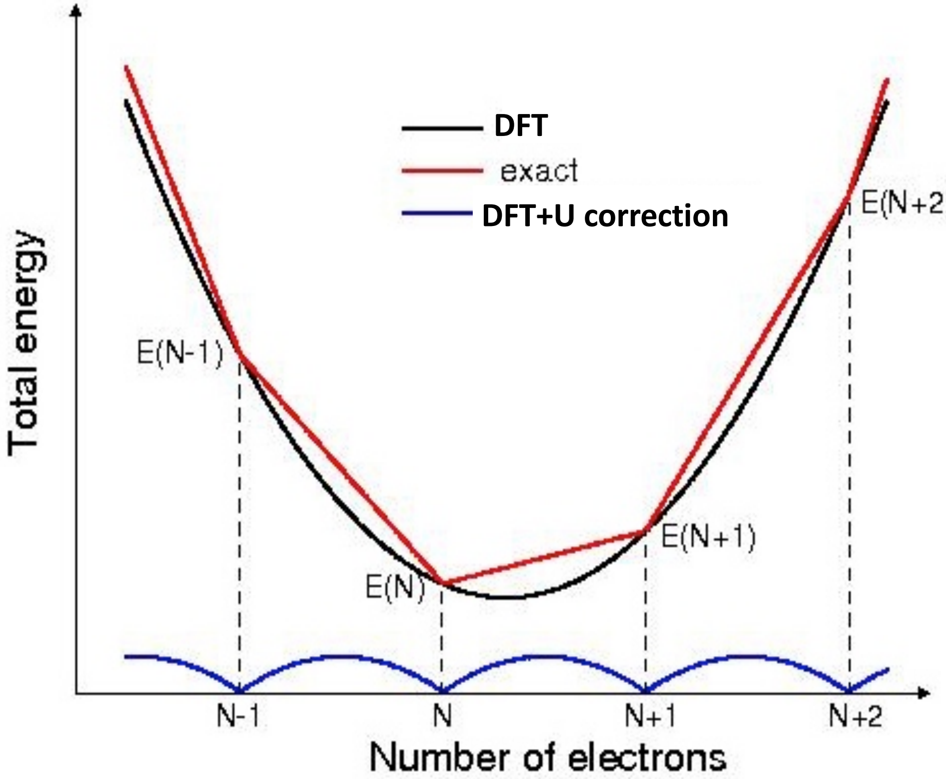
$$\boxed{U=\frac{d^2E^{LDA}}{d(n^{Id})^2}-\frac{d^2E_0^{LDA}}{d(n^{Id})^2}}$$

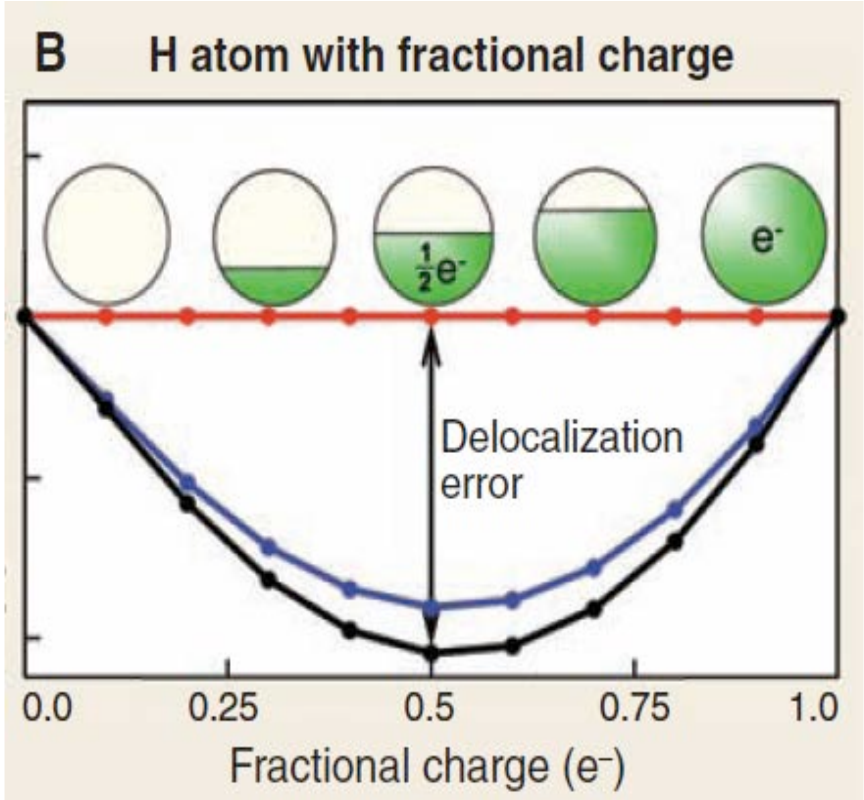
U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

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

A DFT + Hubbard U approach

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

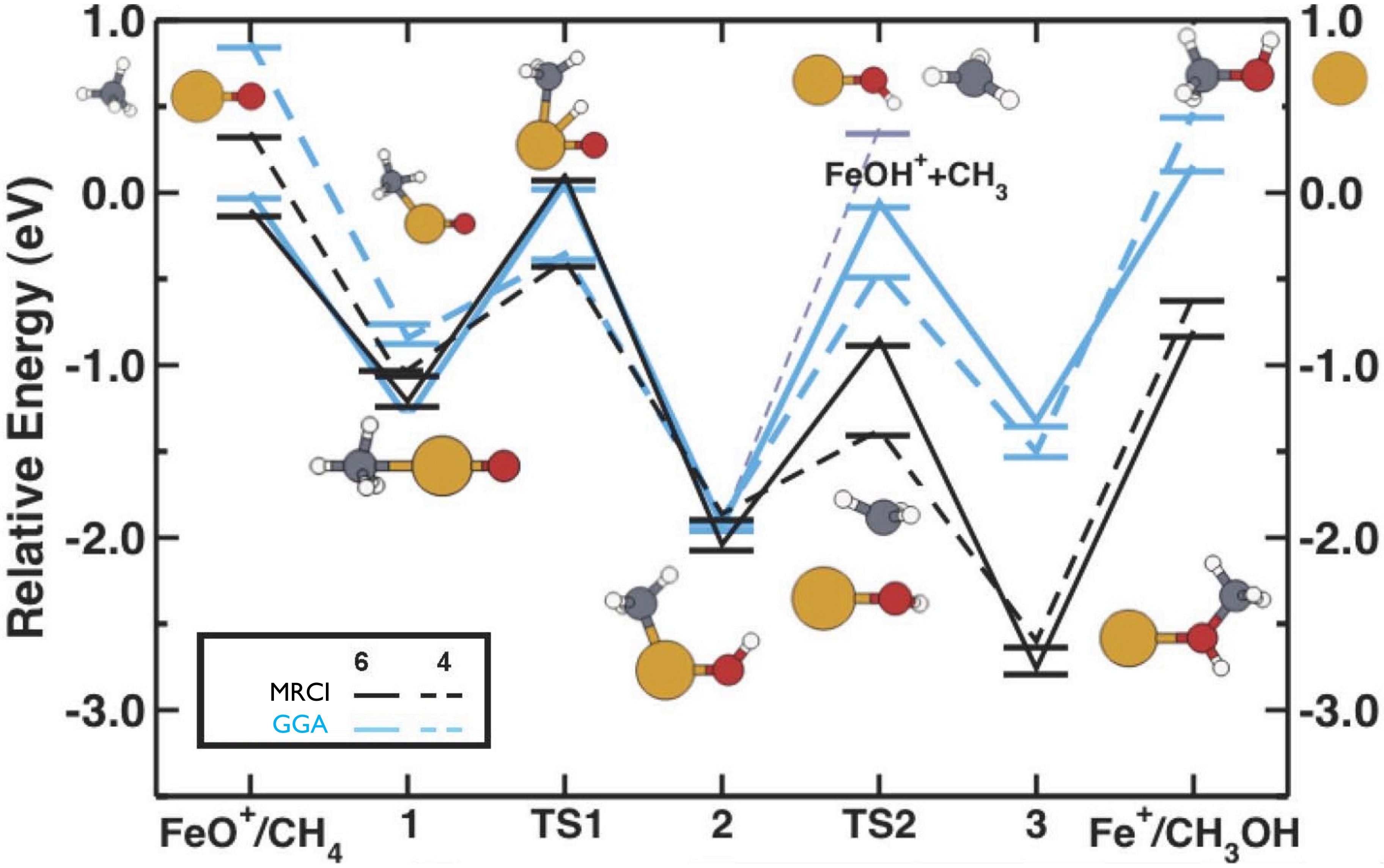




U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

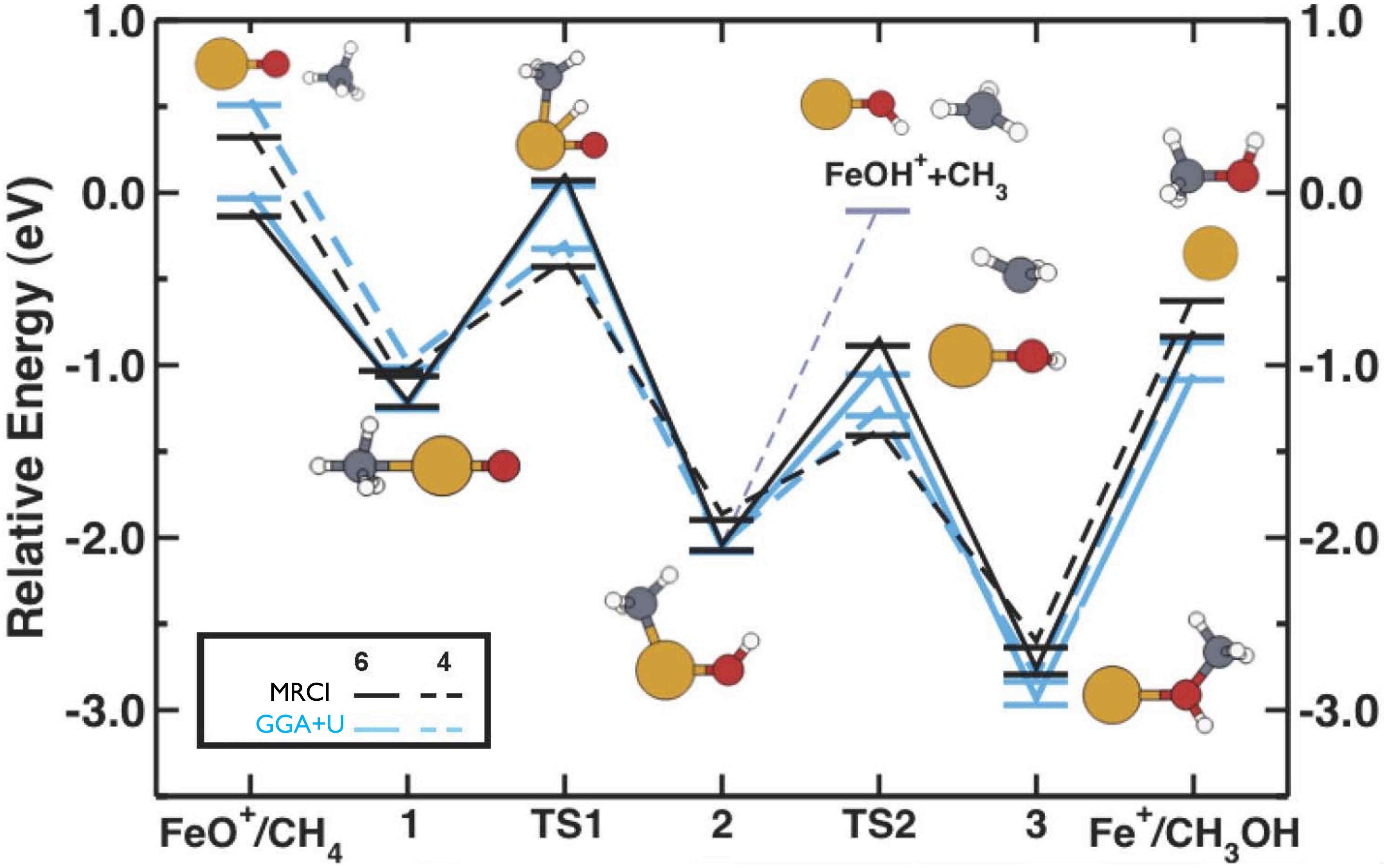
LRT U: M. Cococcioni (PhD 2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

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

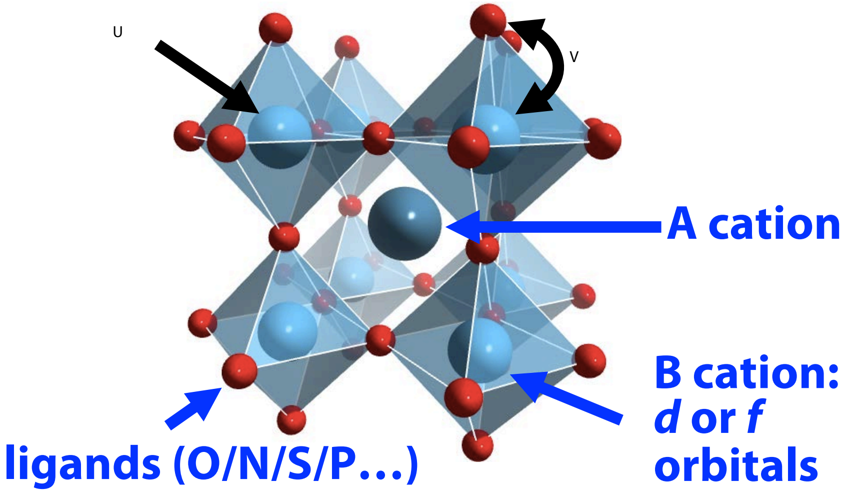


H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, Phys. Rev. Lett. (2006)
H.J. Kulik and N. Marzari, JCP 129 134314 (2008)

FROM ON-SITE TO INTER-SITE

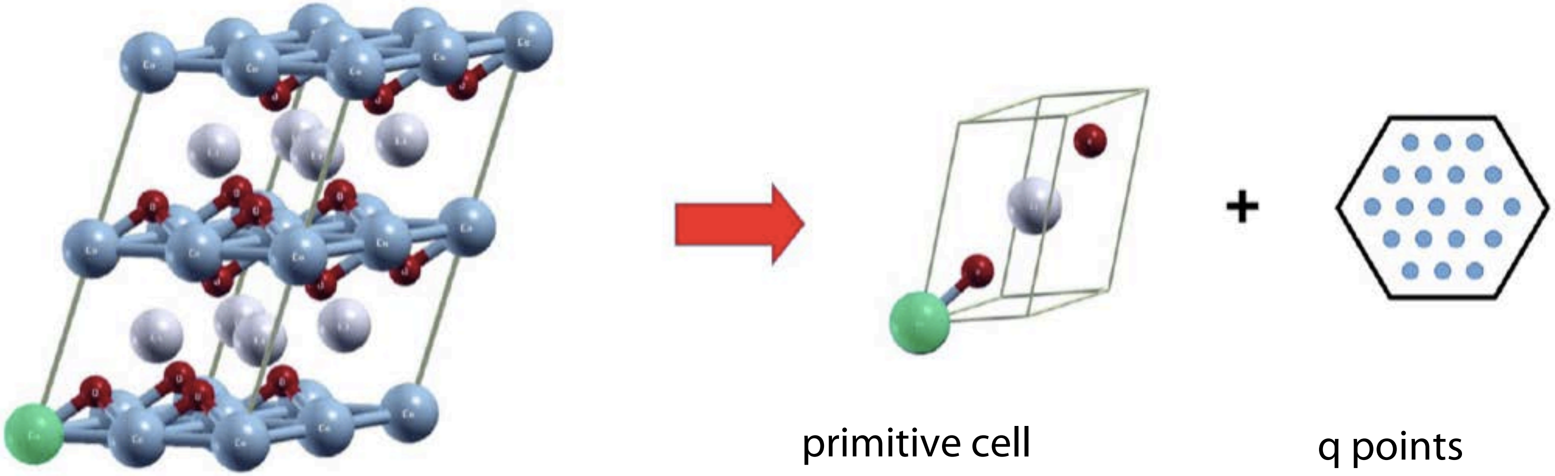
$$E_{\mathrm{Hub}} = \sum_{I,\sigma} \frac{U^I}{2} \mathrm{Tr}\left[(\mathbf{1} - \mathbf{n}^{II\sigma})\mathbf{n}^{II\sigma}\right] - \sum_{I,J,\sigma}^{*} \frac{V^{IJ}}{2} \mathrm{Tr}\left[\mathbf{n}^{IJ\sigma}\mathbf{n}^{JI\sigma}\right]$$

on-site interactions **inter-site interactions**



- **Hubbard U favors integer occupations of electronic d states (0 or 1)**
- **Hubbard V favors fractional occupations (hybridization between d and p states)**

U AND V FROM DFPT: AUTOMATIC, INEXPENSIVE



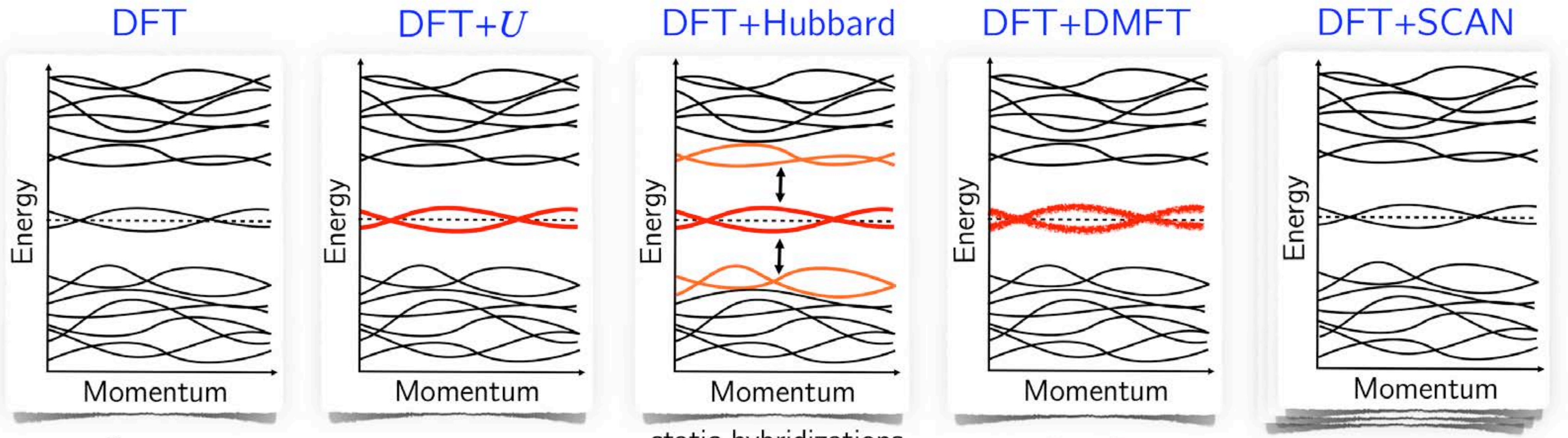
primitive cell

q points

$$\Delta^{J} n^{I} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_{I}-\mathbf{R}_{J})} \Delta^{\mathbf{q}} n^{I}$$

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

METHODS' PANORAMA



DFT: all states treated on the same footing (inexpensive)

DFT+U: **correlated states** are treated statically (inexpensive)

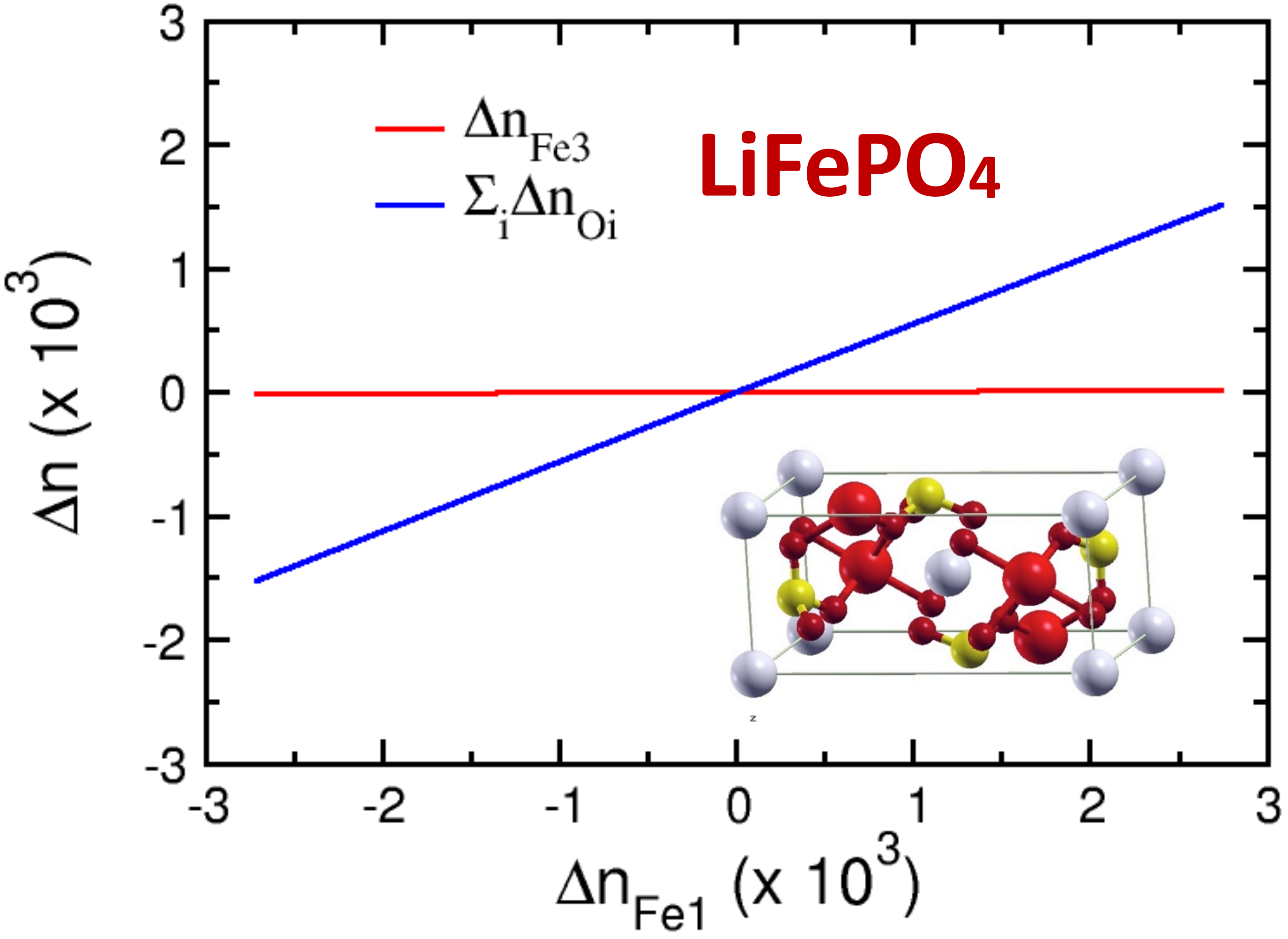
DFT+Hubbard: static hybridizations with **ligand states**, crucial for covalency (inexpensive)

DFT+DMFT: **correlated states** are treated dynamically (very expensive)

DFT+SCAN: large supercells, ensemble average of configurations (expensive)

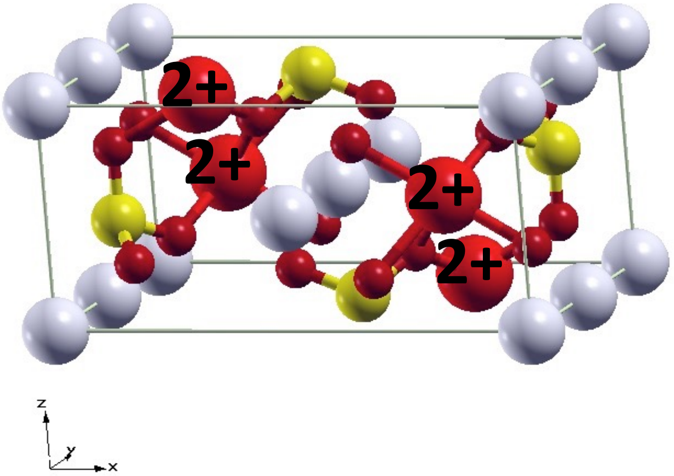
DFT + U has nothing to do with correlation !

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

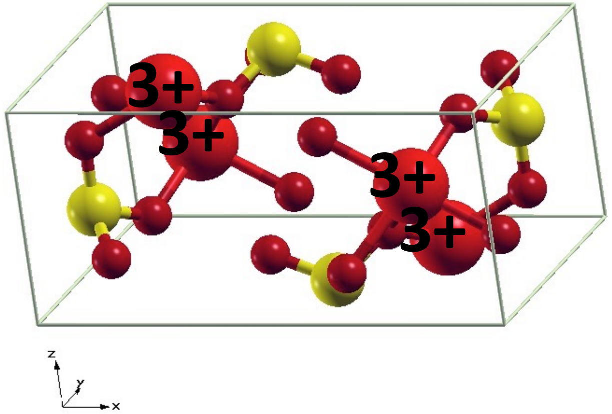


Mixed-valence Fe/Mn/Co olivines for battery cathodes

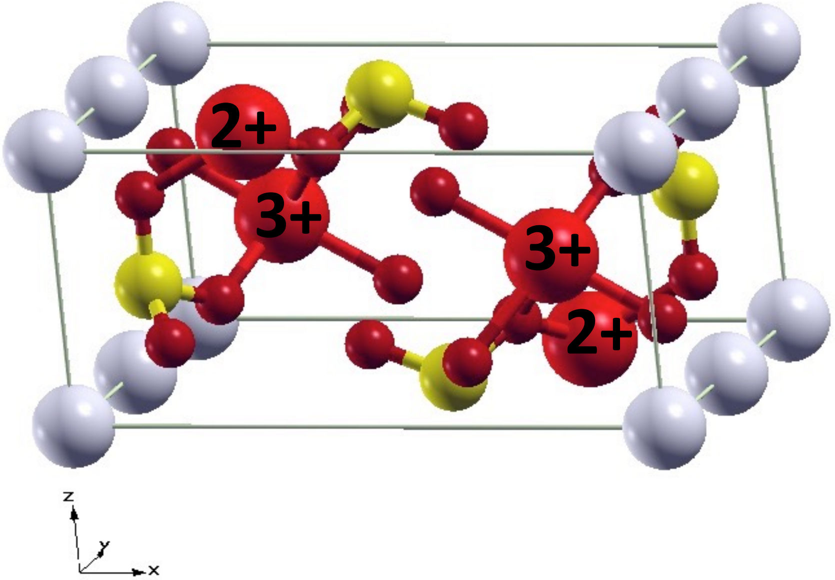
$LiMPO_4$



MPO_4



$Li_{0.5}MPO_4$

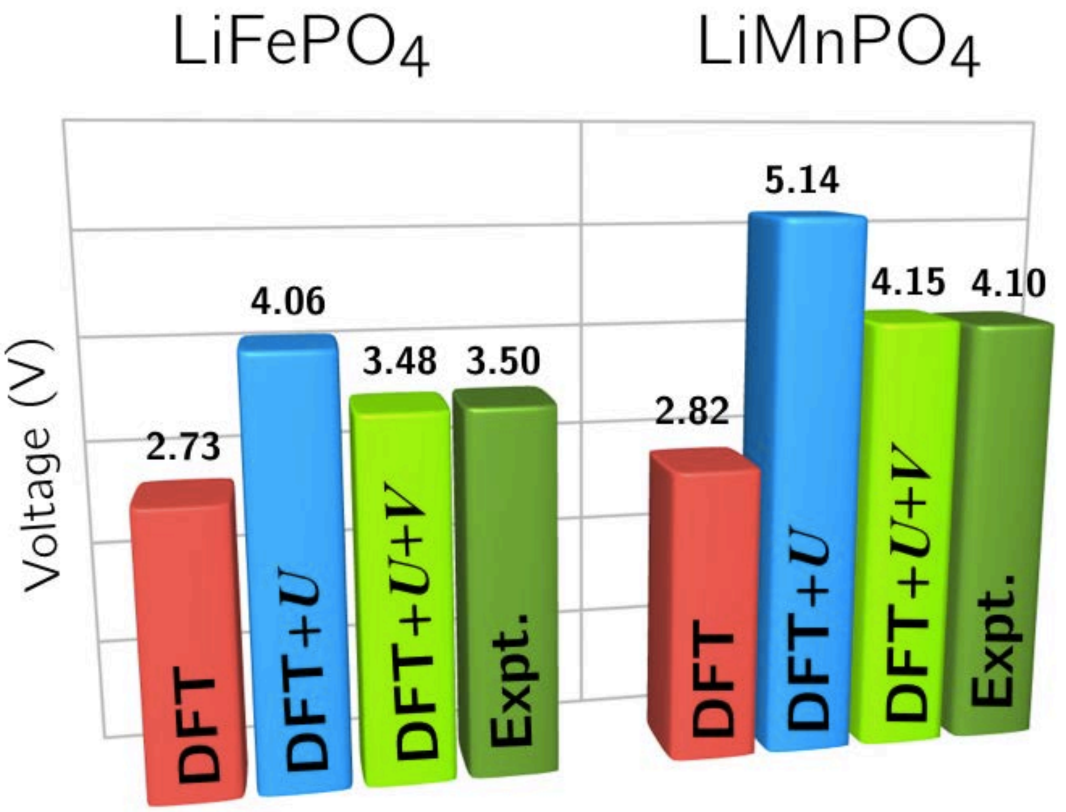


Li_xFePO_4: from PBE to scf DFT+U+V

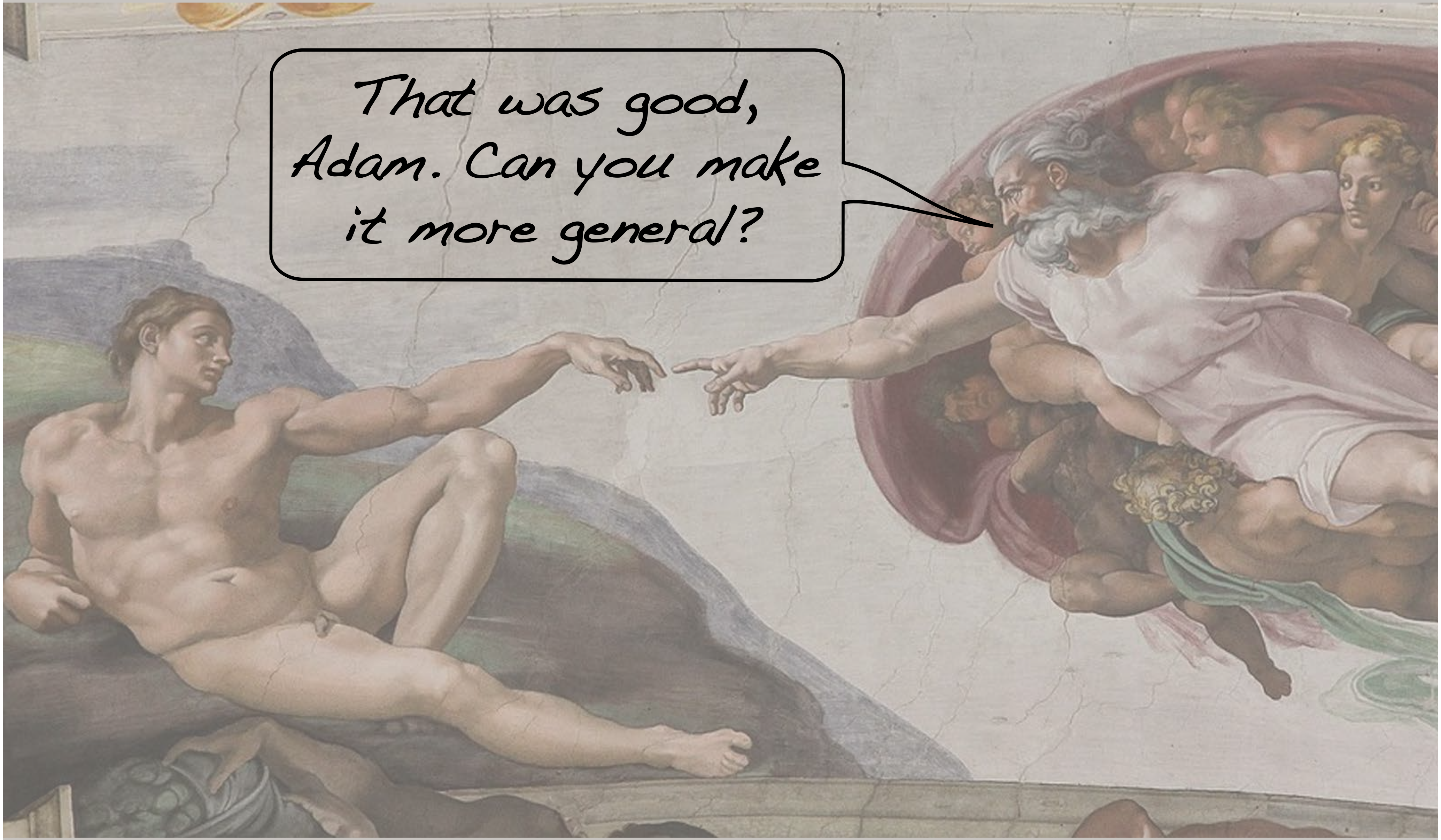
Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 3.5
PBE	-126	2.73
PBE+U	159	4.06
PBE+U_{scf}	189	3.83
PBE+U_{scf}+V_{scf}	128	3.48

	$LiFePO_4$		$Li_{0.5}FePO_4$		$FePO_4$	
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

MIXED-VALENCE OLIVINES FOR BATTERY CATHODES



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


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

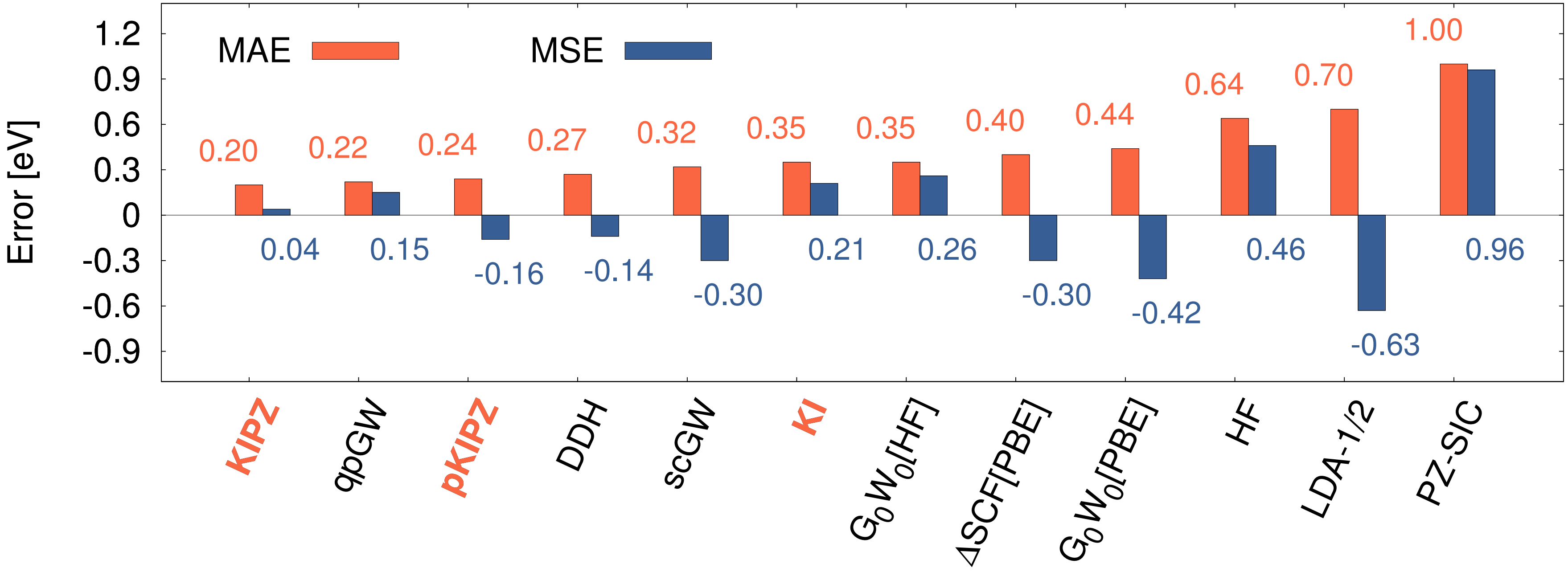
In a quasi-particle approximation, this spectral functional depends discretely on **the orbital densities** ρ**(r,i)**

LINEARIZATION

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

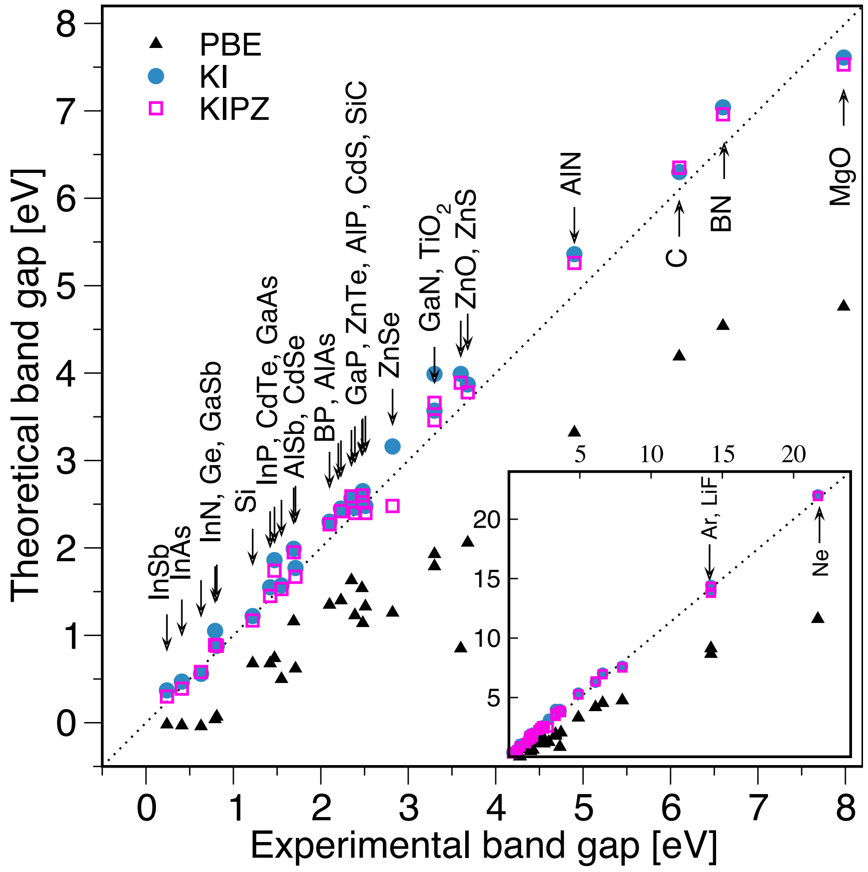
I. Dabo et al., Phys. Rev. B 82, 115121 (2010)
G. Borghi et al., Phys. Rev. B 90, 075135 (2014)

GW100 TEST SET



N. Colonna et al., JCTC (2018)

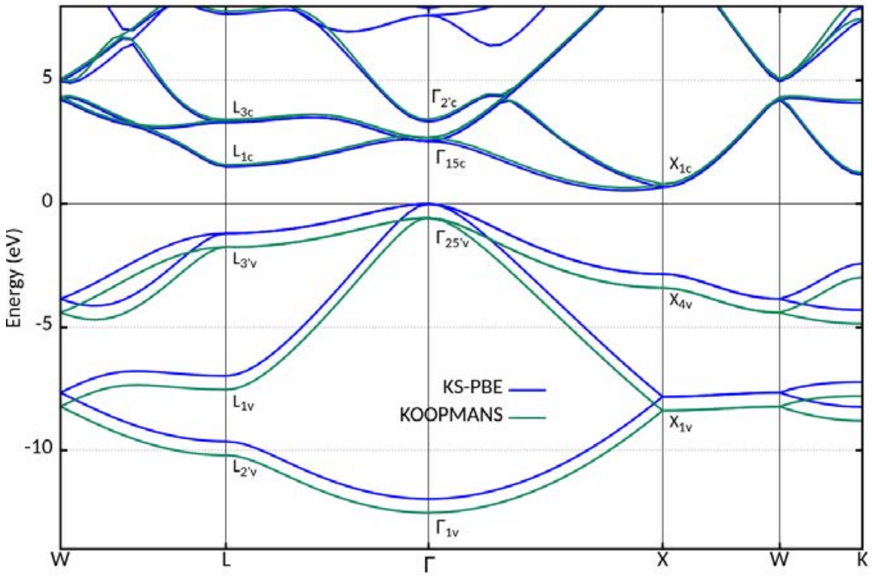
BAND GAPS AND IPs (30 SOLIDS)



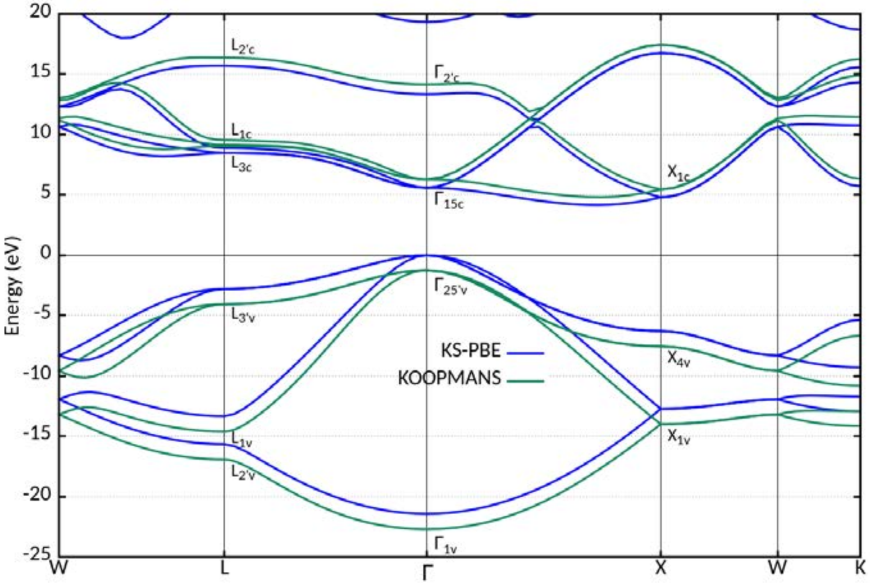
MAE (eV)	Gap	IP
PBE	**2.54**	**1.09**
G_0W_0	**0.56**	**0.39**
QSGW	**0.18**	**0.49**
KI	**0.27**	**0.19**
KIPZ	**0.22**	**0.21**

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

BAND STRUCTURES (KI)



PBE	G_0W_0	$QSG\widetilde{W}$	KI	Exp(-ZPR)
0.68	1.17	1.30	1.22	1.22



PBE	G_0W_0	$QSG\widetilde{W}$	KI	Exp(-ZPR)
4.19	5.59	5.90	5.98	5.88

De Gennaro, Colonna, and Marzari (in preparation).

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)

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