

SOME WORDS OF ADVICE ON DFT AND ALL THAT
NICOLA MARZARI, EPFL



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

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

“...Some form of approximation is essential, and this would mean the construction of tables. The tabulation function of one variable requires a page, of two variables a volume and of three variables a library; but 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 at which to tabulate this function, but 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)

Reduced density matrices

$$\gamma_1(r'_1, r_1) =$$

$$N \int \dots \int \Psi(r'_1, r_2, r_3, r_4, \dots, r_N) \Psi^*(r_1, r_2, r_3, r_4, \dots, r_N) dr_2 dr_3 dr_4 \dots dr_N$$

$$\gamma_2(r'_1, r'_2, r_1, r_2) =$$

$$\frac{N(N-1)}{2} \int \dots \int \Psi(r'_1, r'_2, r_3, r_4, \dots, r_N) \Psi^*(r_1, r_2, r_3, r_4, \dots, r_N) dr_3 dr_4 \dots dr_N$$

The exact energy functional is known!

$$E = \int \left[\left(-\frac{1}{2} \nabla_1^2 + V_{ext}(r_1) \right) \gamma_1(r'_1, r_1) \right]_{r'_1=r_1} dr_1 + \iint_{r_{12}} \frac{1}{r_{12}} \gamma_2(r_1, r_2, r_1, r_2) dr_1 dr_2$$

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
- $E = \text{kinetic} + \text{external pot.} + \text{el.-el.}$
- 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 !

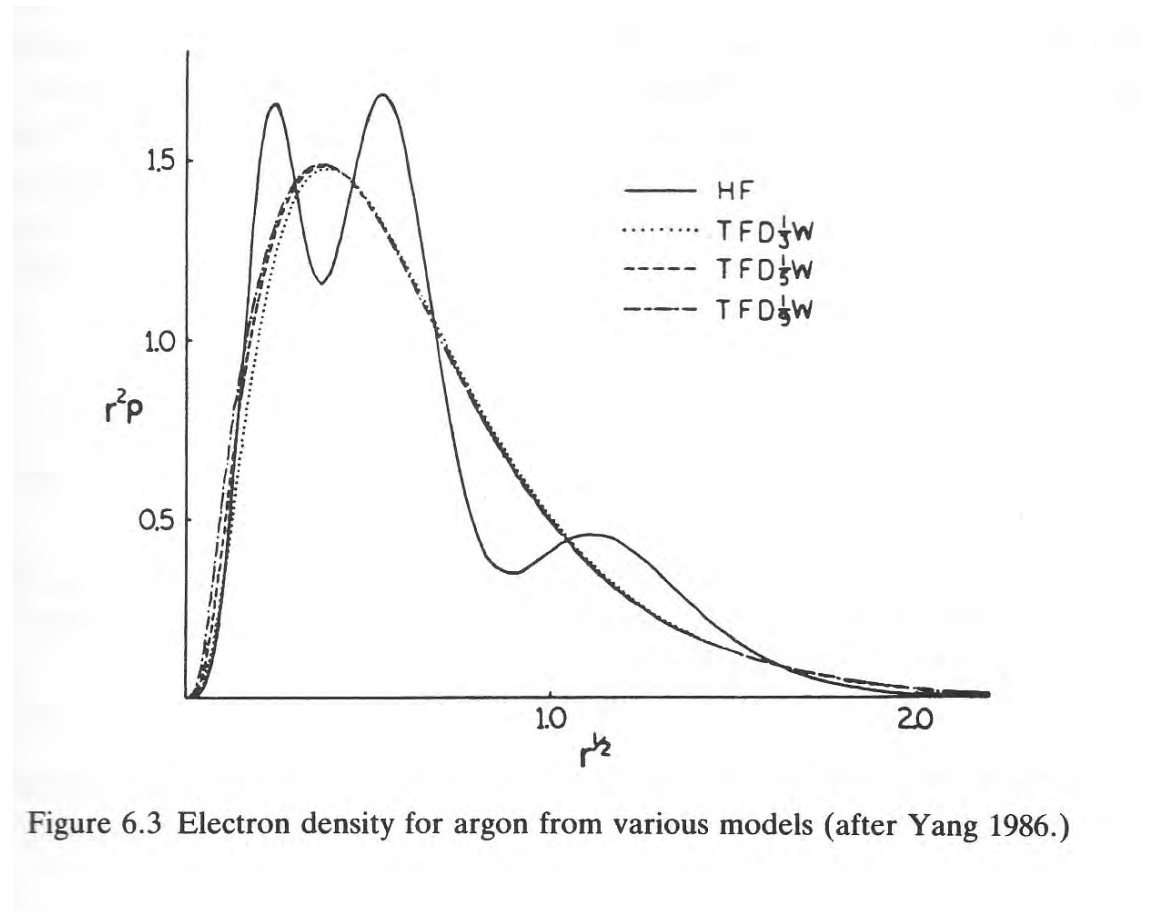


Figure 6.3 Electron density for argon from various models (after Yang 1986.)

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: $V_{\text{ext}} \iff n$

The universal functional $F[\rho]$

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

The universal functional F is well defined:

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

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)

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

From DFT (density) to Kohn-Sham DFT (fake electrons)

- **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 + mystery

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

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

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)

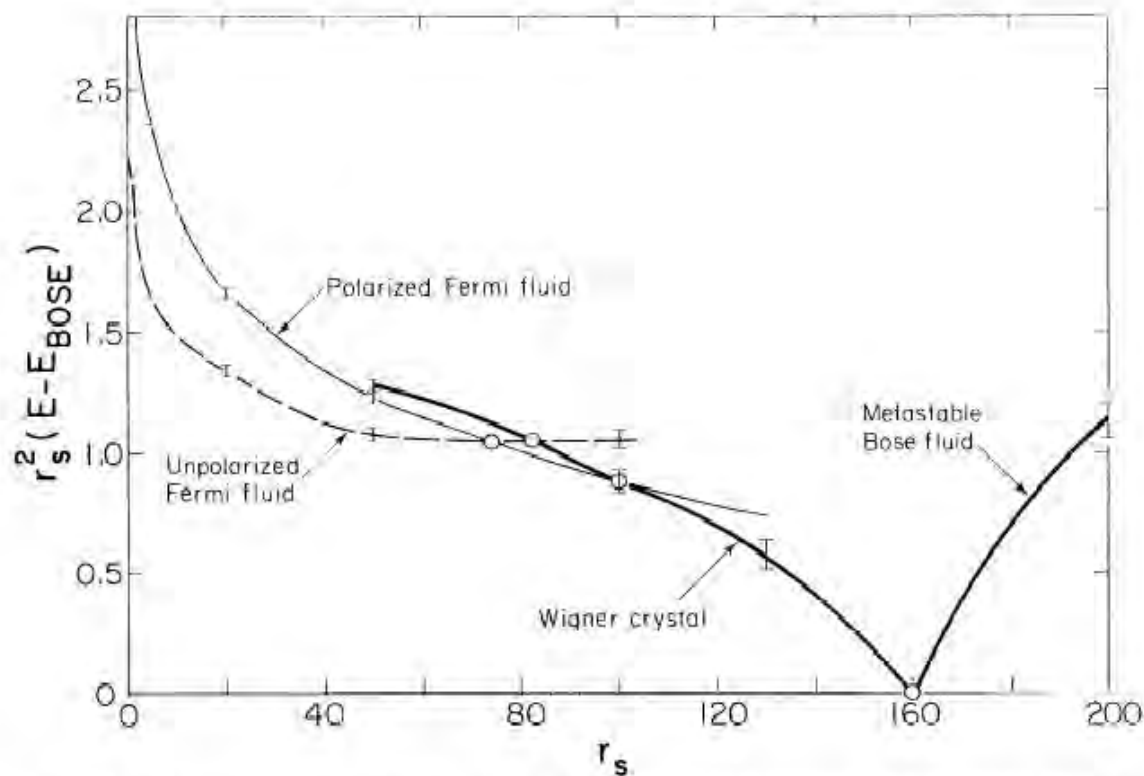


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^{-2} in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid 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!

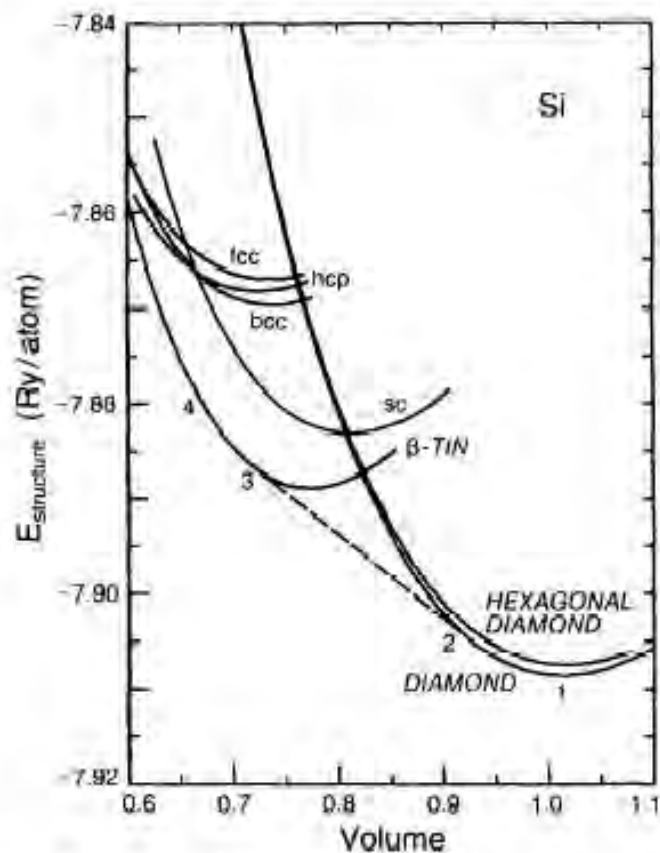
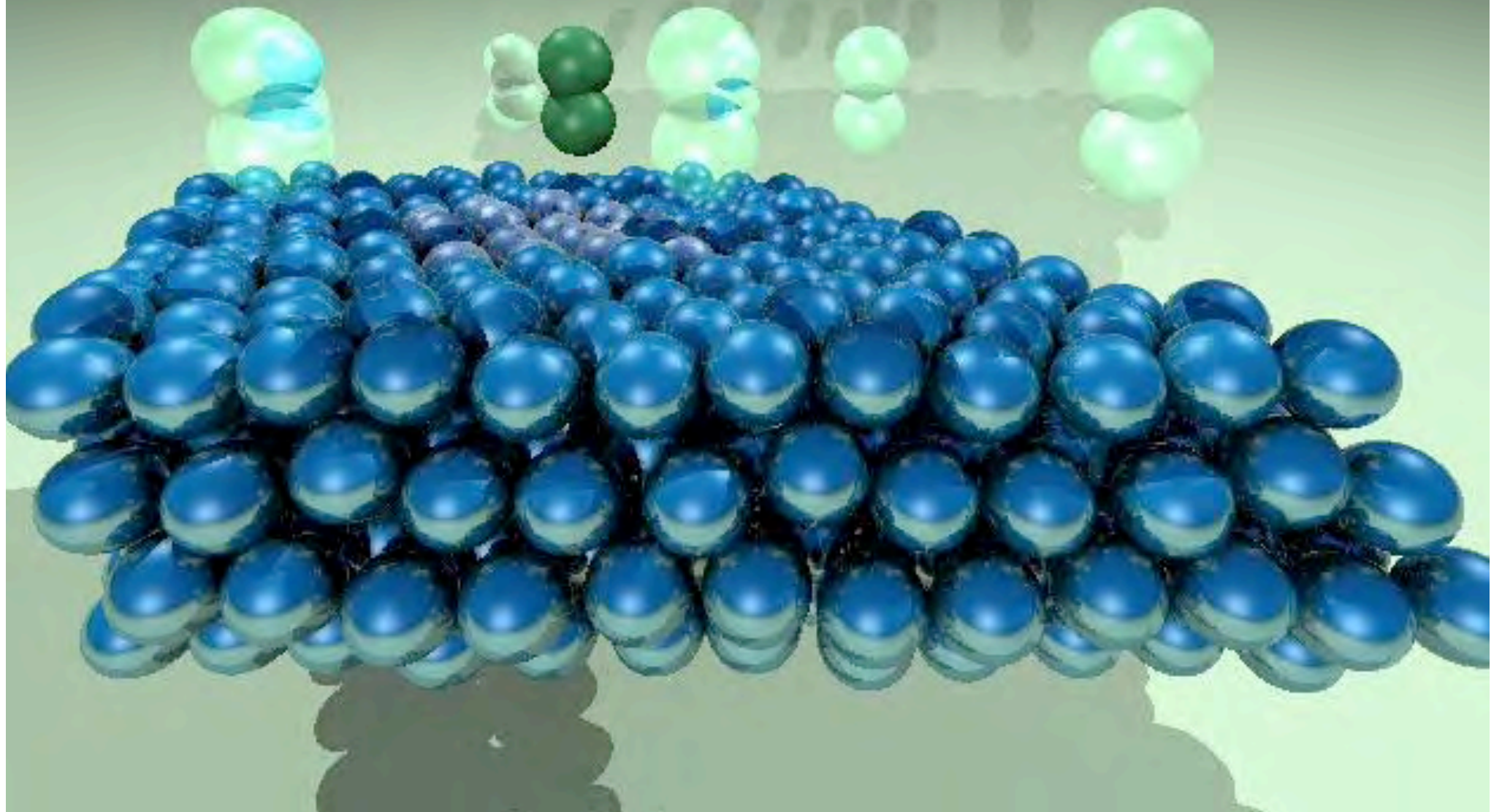


FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β -tin phase ($c/a=0.552$).

Yin and
Cohen,
PRL 1980,
PRB 1982

- **What's wrong, then?**
- **Some possible solutions**
- **Getting some (dynamical) action**

Notable failures I: Charge transfer



Beautiful, but perverse

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

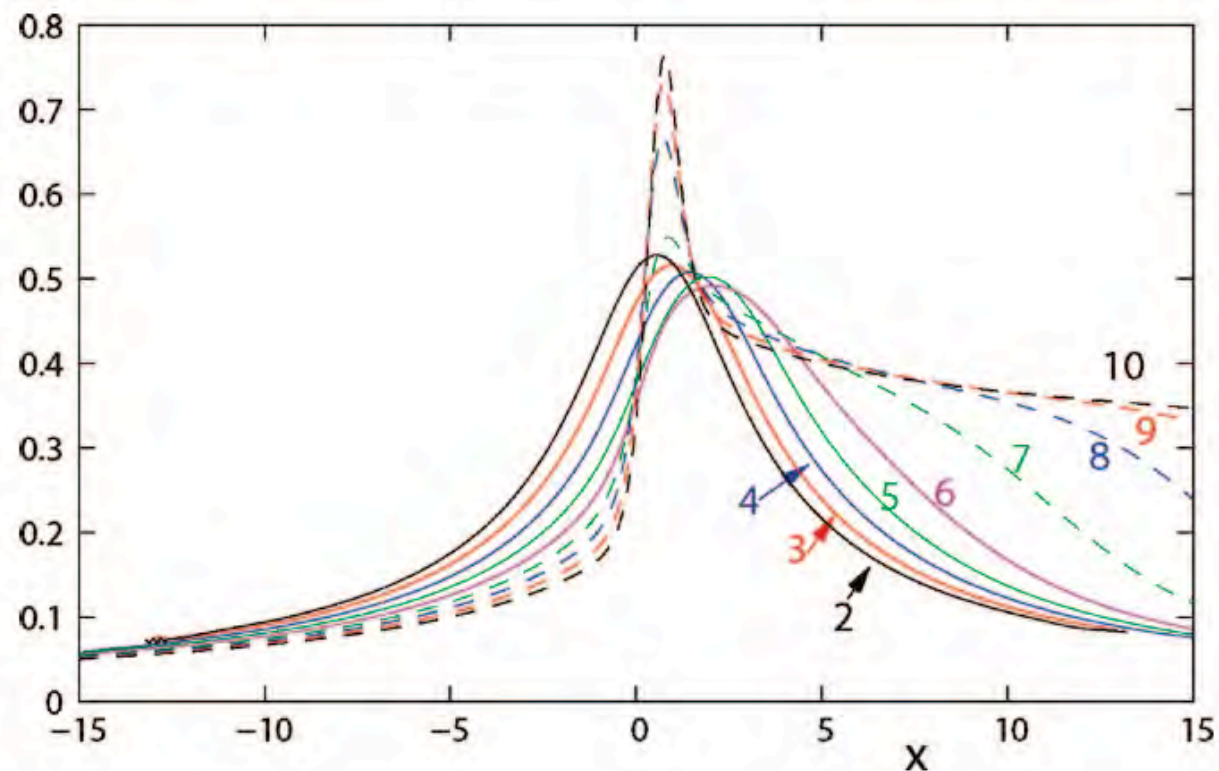
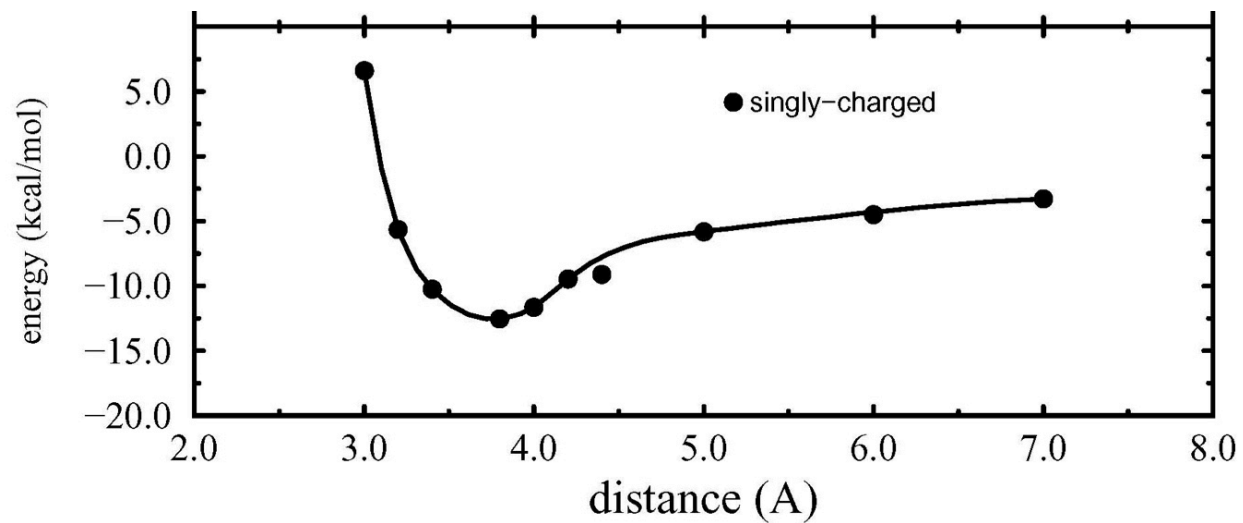
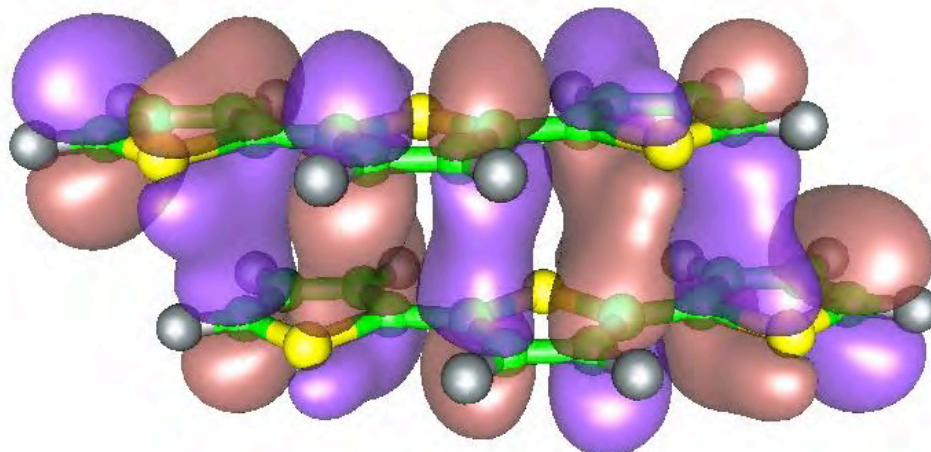


Figure 7. Hartree-exchange-correlation potential, $v_{\text{Hxc}}(x)$ for our LiH model ($c = 2.8$); the values of interatomic separation R are indicated.

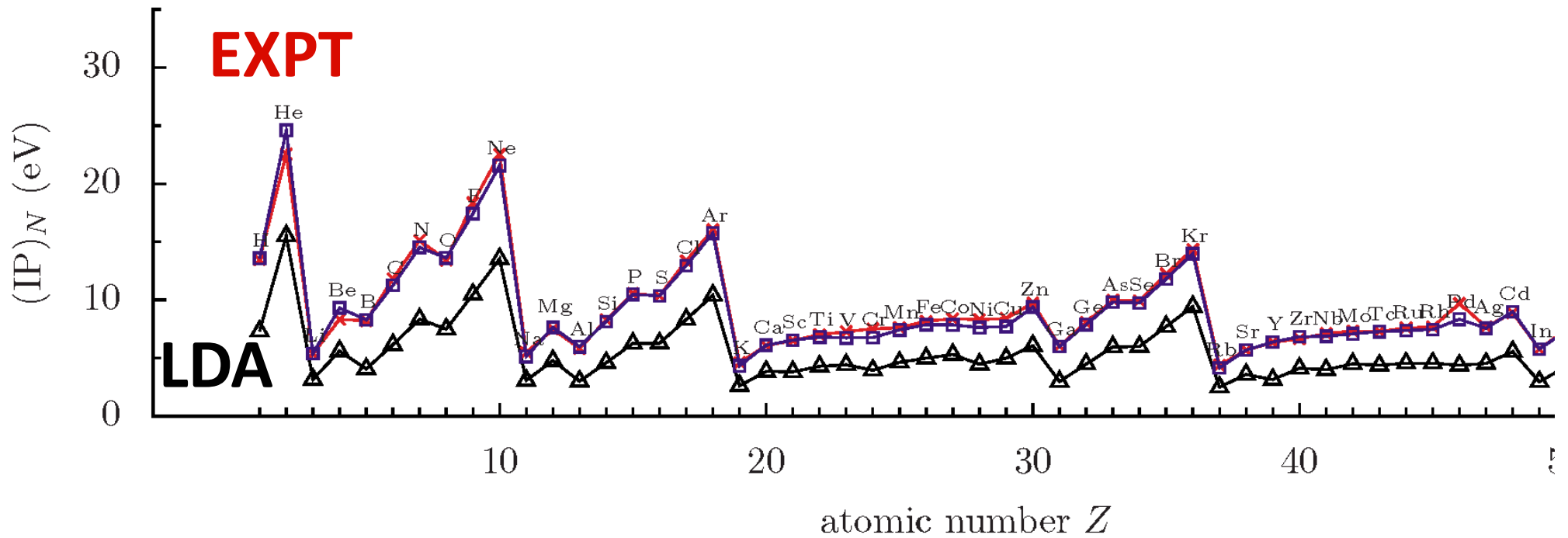
Neepa Maitra JCTC 2009, Helbig and Rubio JCP 2009

Notable failures II: Delocalization of electrons/holes



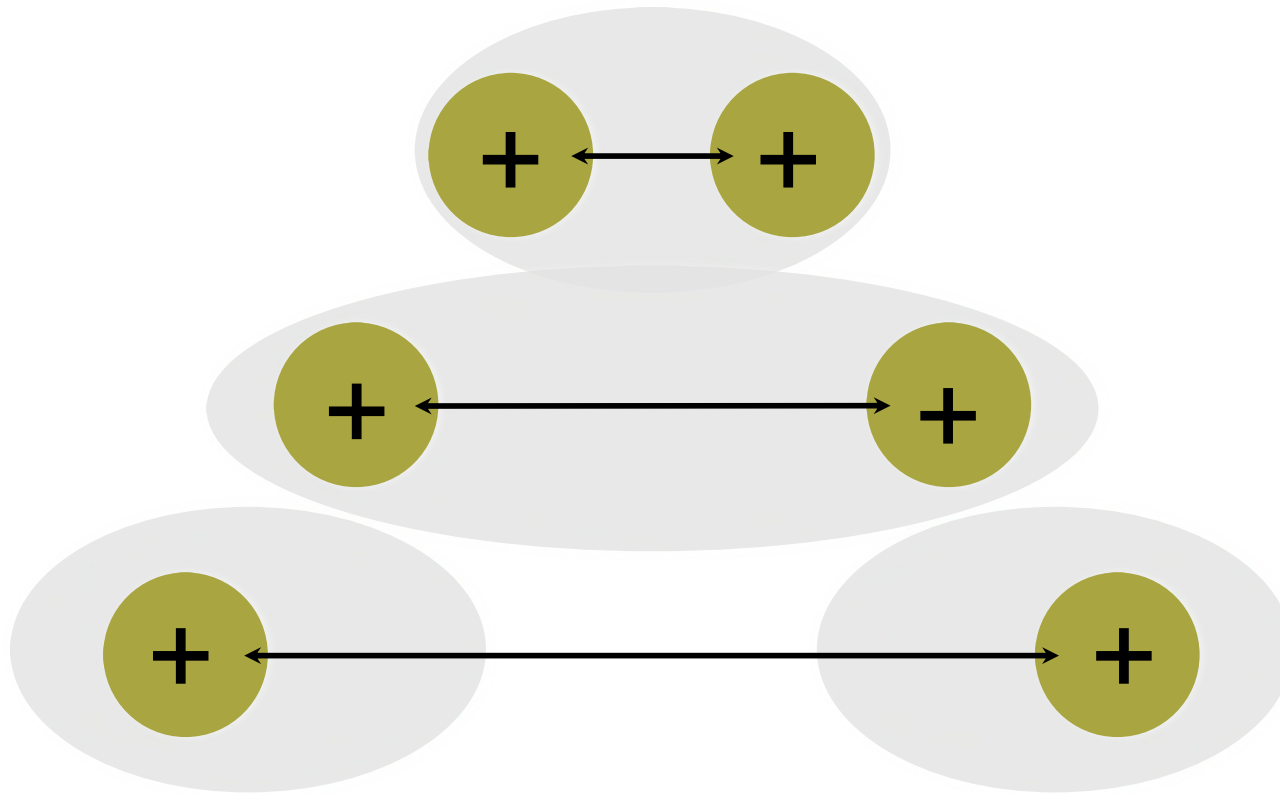
D. A. Scherlis and N. Marzari, JPCB (2004), JACS (2005)

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



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

Notable failures IV: H_2^+ dissociation limit



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

Schrödinger

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

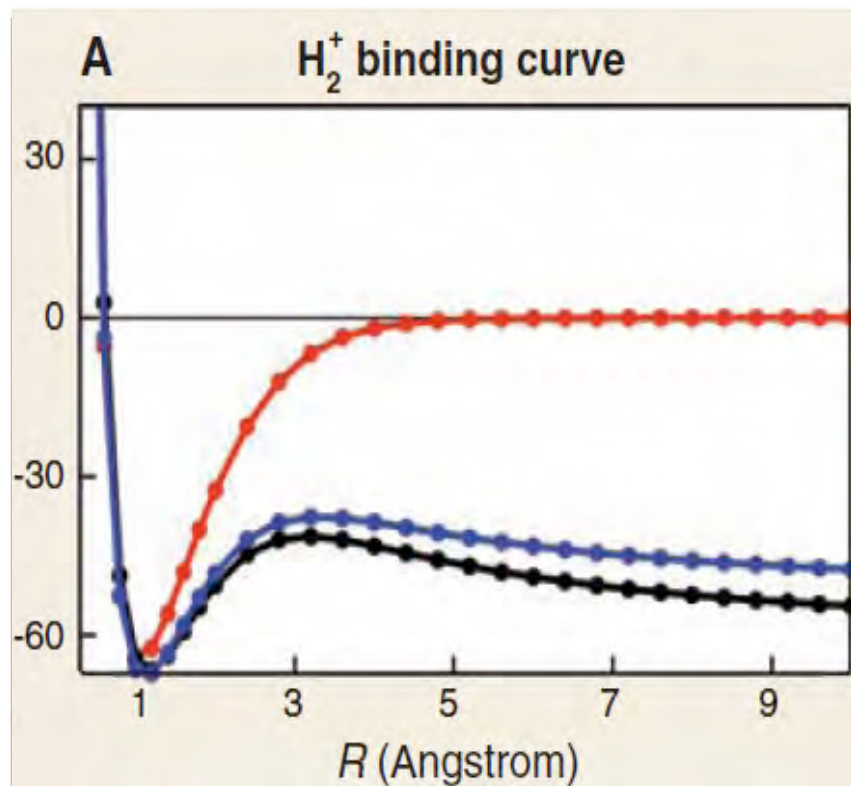
Kohn-Sham

It doesn't work even for one electron!

HF

B3LYP

LDA



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

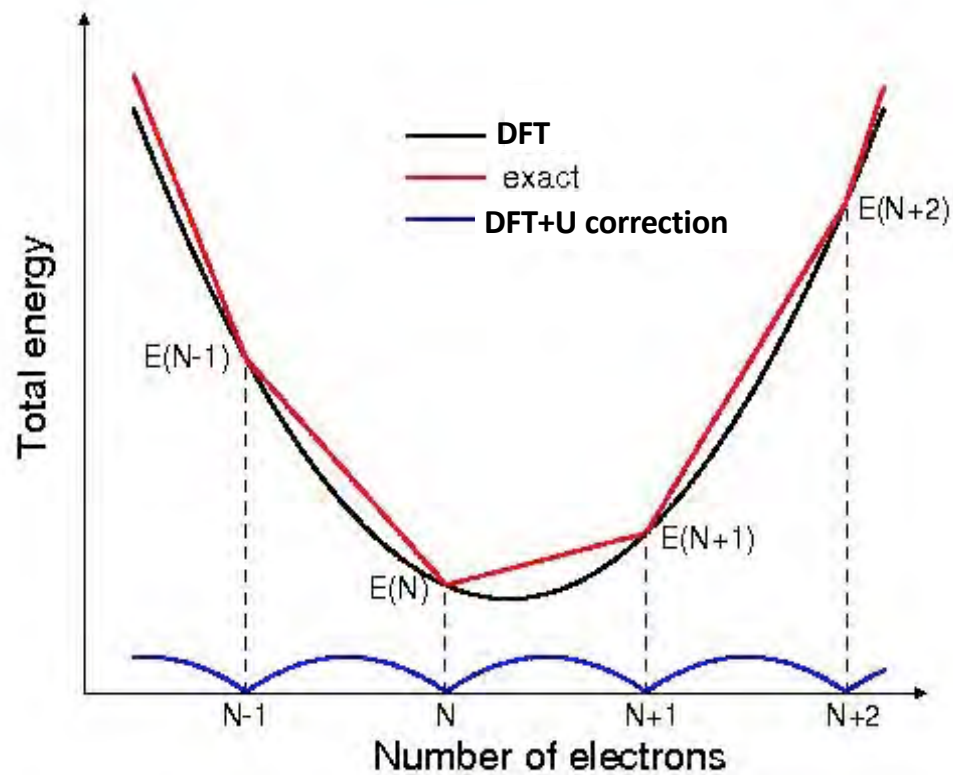
The image is a reproduction of the famous fresco 'The Creation of Adam' by Michelangelo. It depicts Adam on the left, reclining on a rock, and God on the right, reclining on a red cushion. The two figures' hands are just inches apart, creating a sense of tension. A speech bubble is overlaid on the image, containing text in a handwritten style. The background shows a landscape with hills and a blue sky.

ADAM, TAKE NOTES:

- LINEARIZATION
- SCREENING
- LOCALIZATION

DFT+U AS A FIRST EXAMPLE OF LINEARIZATION+SCREENING

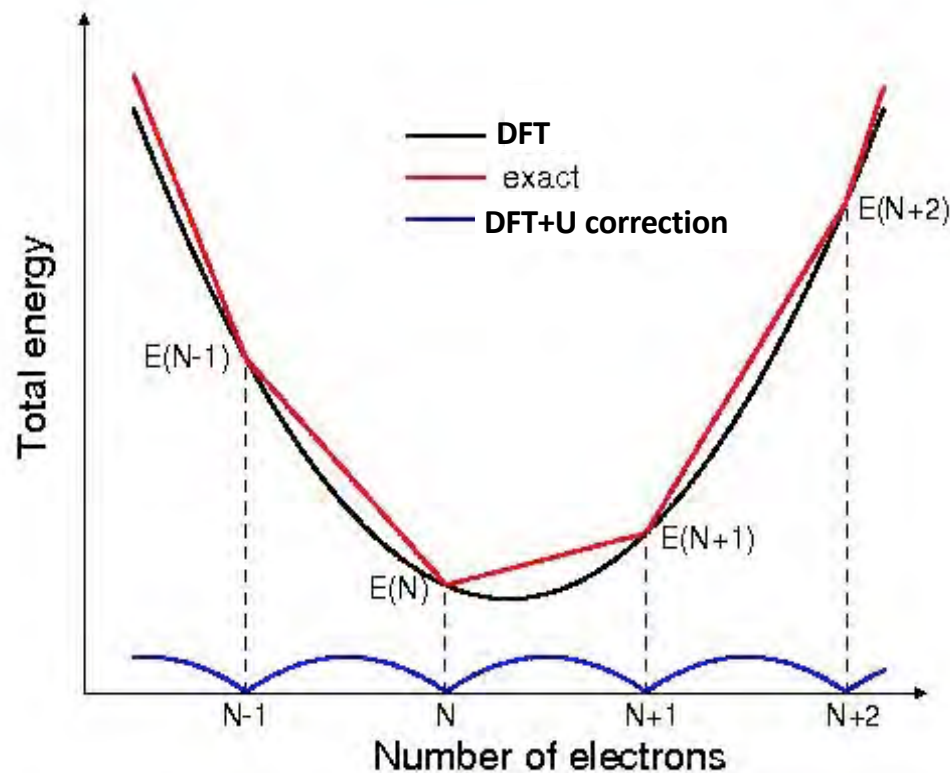
A DFT + Hubbard U approach



- 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

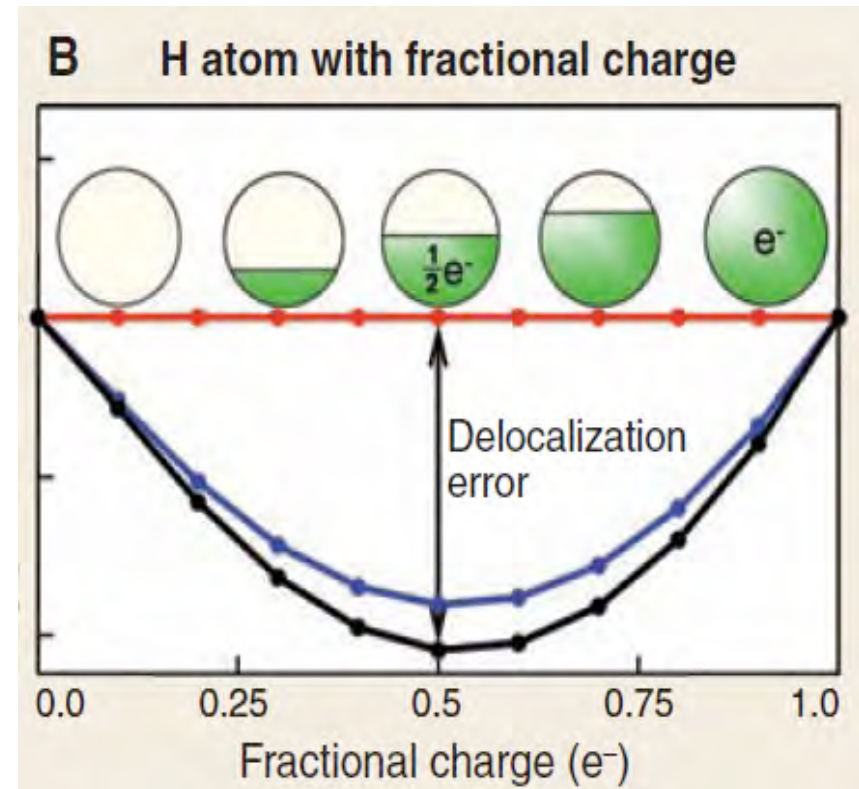
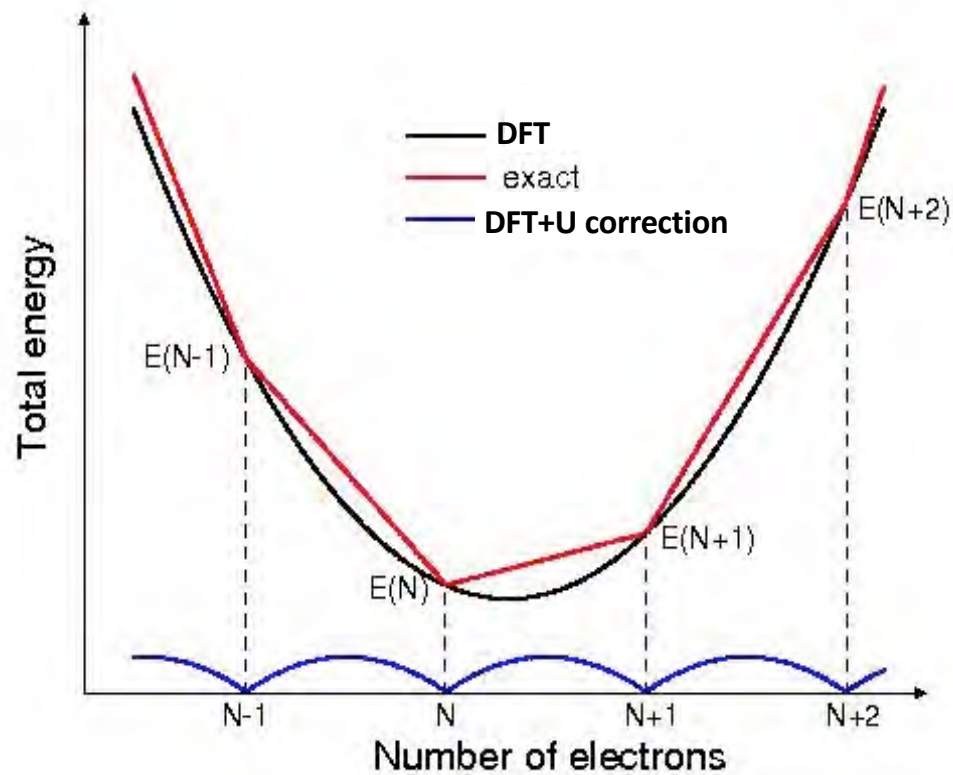
U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

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

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

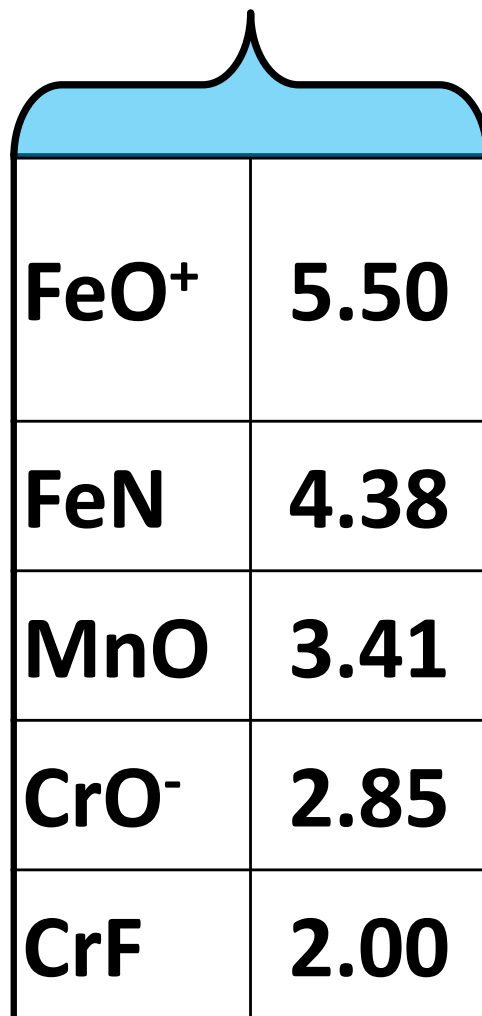


U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, Sutton and coworkers PRB (1995)

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

Isoelectronic FeO⁺ series

$6\Sigma^+$



FeO ⁺	5.50
FeN	4.38
MnO	3.41
CrO ⁻	2.85
CrF	2.00

Isoelectronic FeO⁺ series

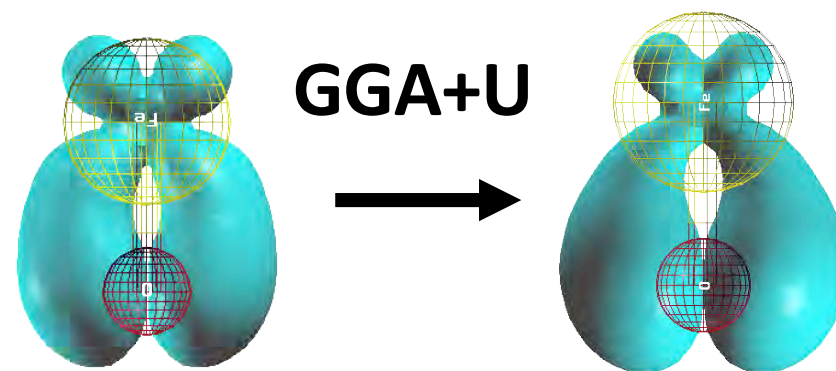
$6\Sigma^+$

FeO⁺	5.50
FeN	4.38
MnO	3.41
CrO⁻	2.85
CrF	2.00

Structural Parameters: FeO⁺

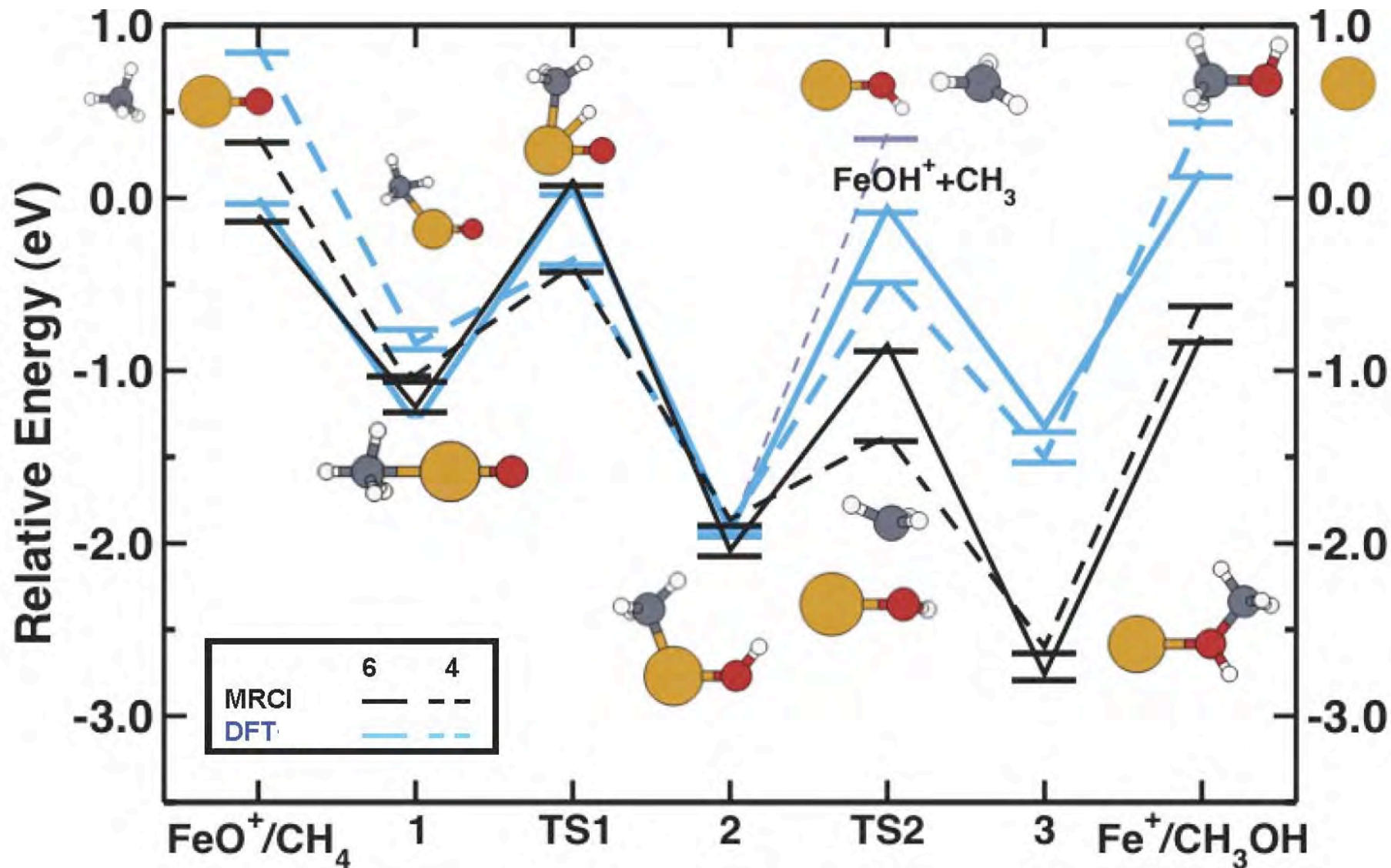
Method	6FeO^+			4FeO^+		
	R_e	ω_e	$\omega_e x_e$	R_e	ω_e	$\omega_e x_e$
GGA	1.62	901	328	1.56	1038	332
GGA+U	1.66	749	432	1.75	612	172
CCSD(T)	1.66	724	434	1.70	633	188

Delocalized minority spin bond of 4FeO^+



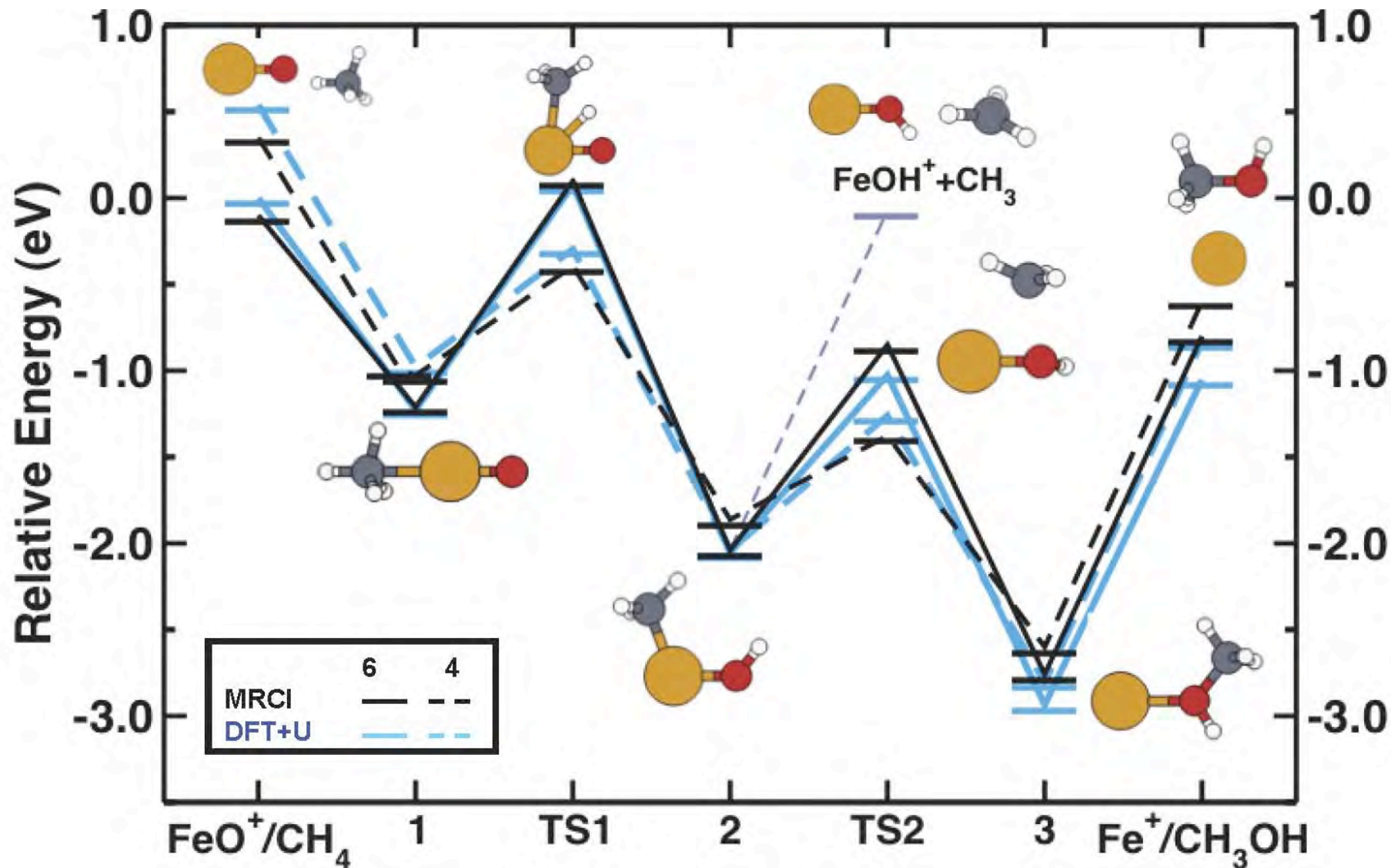
H.J. Kulik, M. Cococcioni, D.A. Scherlis,
and N. Marzari, Phys. Rev. Lett. (2006)

Methane on FeO⁺: GGA vs MRCI



H.J. Kulik and N. Marzari, JCP 129 134314 (2008)

Methane on FeO⁺: GGA+U vs MRCI



H.J. Kulik and N. Marzari, JCP 129 134314 (2008)

From on-site to intersite: DFT+U+V

$$\sum_{I,\sigma} \frac{U^I}{2} \text{Tr} \left[n^{II\sigma} (1 - n^{II\sigma}) \right] - \sum_{IJ,\sigma} \frac{V^{IJ}}{2} \text{Tr} \left[n^{IJ\sigma} n^{JI\sigma} \right]$$

$$n_{mm'}^{IJ\sigma} = \sum_{k,\nu} f_{k\nu}^{\sigma} \langle \psi_{k\nu}^{\sigma} | \Phi_{m'}^J \rangle \langle \Phi_m^I | \psi_{k\nu}^{\sigma} \rangle$$

V. L. Campo and M. Cococcioni, JPCM 22, 055602 (2010)

Seesawing TM dioxides: Mn, Fe, Co

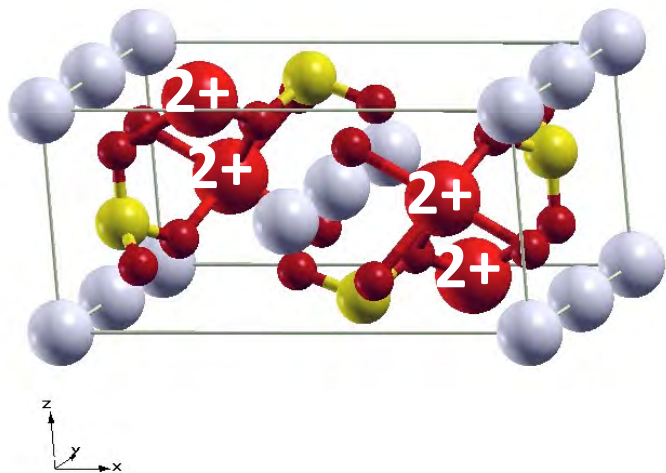
Bond angles

State	DFT	+U	+U _{r₀}	+V	Expt.
⁴ B ₁ MnO ₂	128	180	140	143	135 ± 5
³ B ₁ FeO ₂	138	180	155	156	150 ± 10
² Σ _g ⁺ CoO ₂	158	180	180	180	180

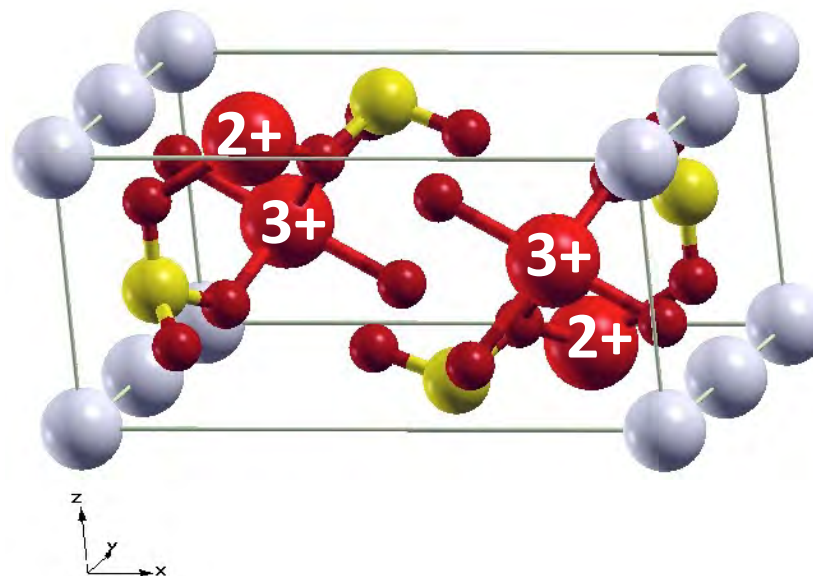
H. J. Kulik and N. Marzari, JCP 134 094103 (2011)

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

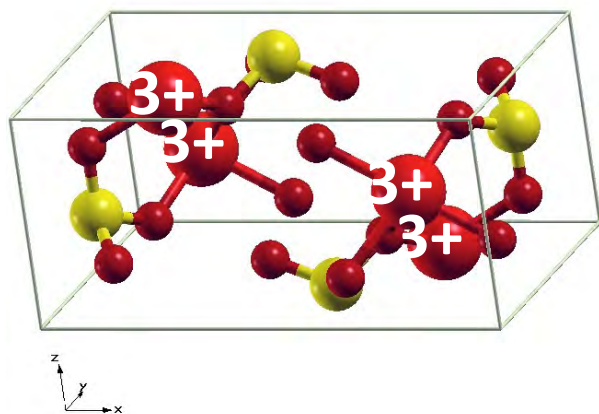
LiMPO₄



Li_{0.5}MPO₄



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

	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

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

Method	LiFePO ₄		Li _{0.5} FePO ₄		FePO ₄	
	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

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

Method	LiFePO ₄		Li _{0.5} FePO ₄		FePO ₄	
	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

Li_xMnPO₄: from PBE to scf DFT+U+V

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 4.1
PBE	63	2.82
PBE+U	212	4.31
PBE+U _{scf}	126	5.14
PBE+U _{scf} +V _{scf}	206	4.15

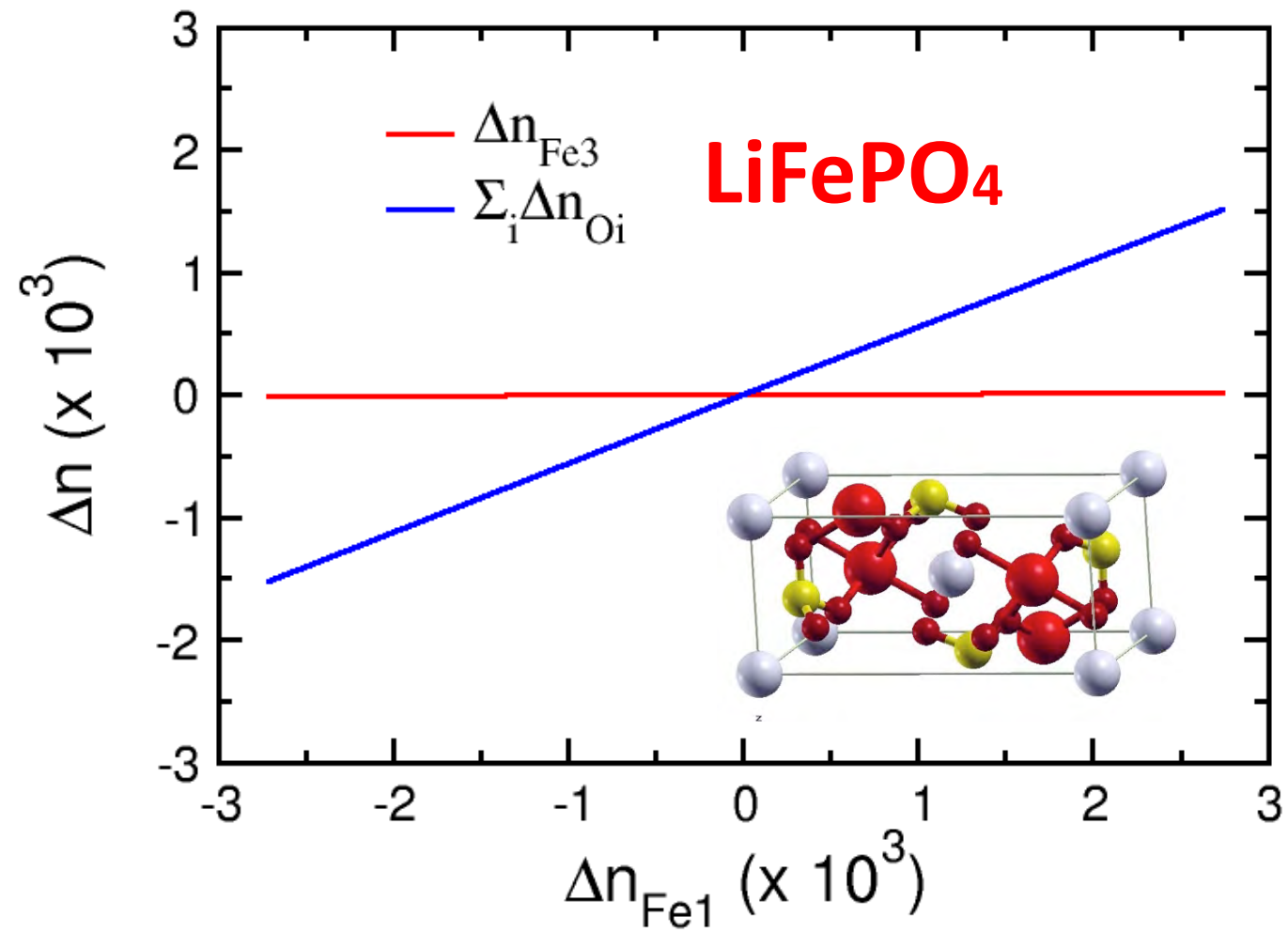
Li_xMnPO₄: from PBE to scf DFT+U+V

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 4.1
PBE	63	2.82
PBE+U	212	4.31
PBE+U _{scf}	126	5.14
PBE+U _{scf} +V _{scf}	206	4.15

Method	LiMnPO ₄		Li _{0.5} MnPO ₄		MnPO ₄	
	2+	3+	2+	3+	2+	3+
PBE	5.30		5.19	5.17		5.11
PBE+U	5.19		5.11	5.05		4.96
PBE+U _{scf}	5.18		5.11	5.07		4.98
PBE+U _{scf} +V _{scf}	5.23		5.22	4.99		4.99

DFT + U has nothing to do with correlation !!

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



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The image shows a section of the famous fresco 'The Creation of Adam' by Michelangelo. On the left, Adam is reclining on a rock, his body perfectly proportioned and muscular. On the right, God is shown in a dynamic, twisting pose, reaching out with his right hand towards Adam's outstretched left hand. The space between their hands is the focal point. A speech bubble is overlaid on the upper part of the image, containing text that reads: "That was good, Adam. Can you make it more general?".

*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 $\rho(\mathbf{r},i)$**

M. Gatti, V. Olevano, L. Reining, and I. V. Tokatly, PRL 99, 057401 (2007)

A. Ferretti, I. Dabo, M. Cococcioni, and N. Marzari, PRB 89, 195134 (2014)

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)


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

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

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


orbital-dependent
screening coefficient

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

N. Colonna et al., *JCTC* 14, 2549 (2018)

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

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

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

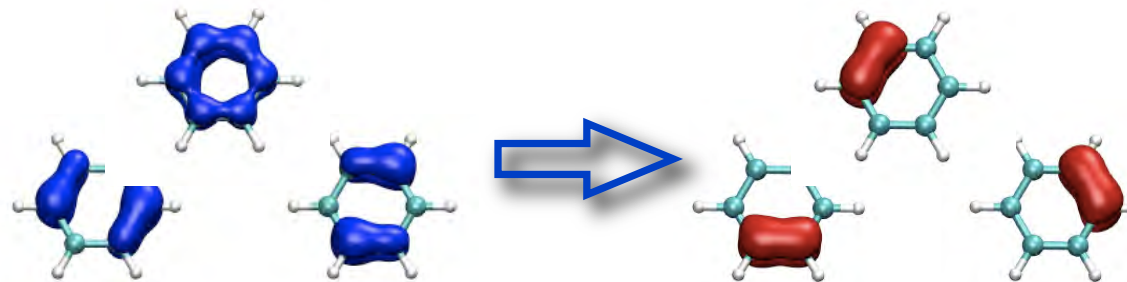
KIPZ adds a screened PZ self-interaction term

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

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

NOT UNITARY INVARIANT

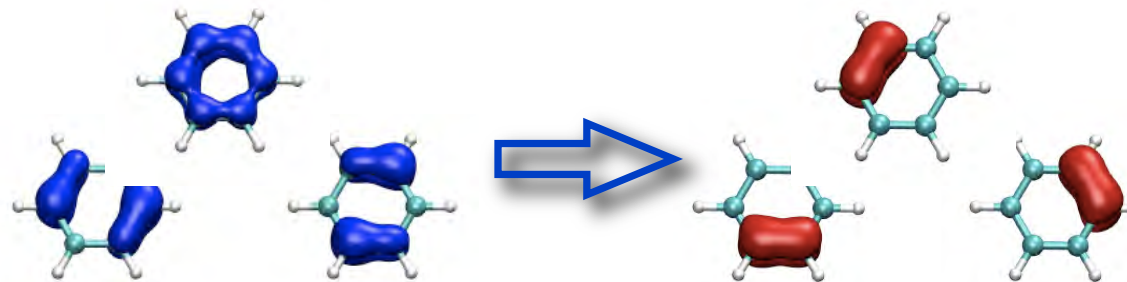
The functionals are minimized by localized *variational* orbitals



G. Borghi, C-H. Park, N. L. Nguyen, A. Ferretti, and NM, Phys. Rev. B 91, 155112 (2015)

NOT UNITARY INVARIANT

The functionals are minimized by localized *variational* orbitals

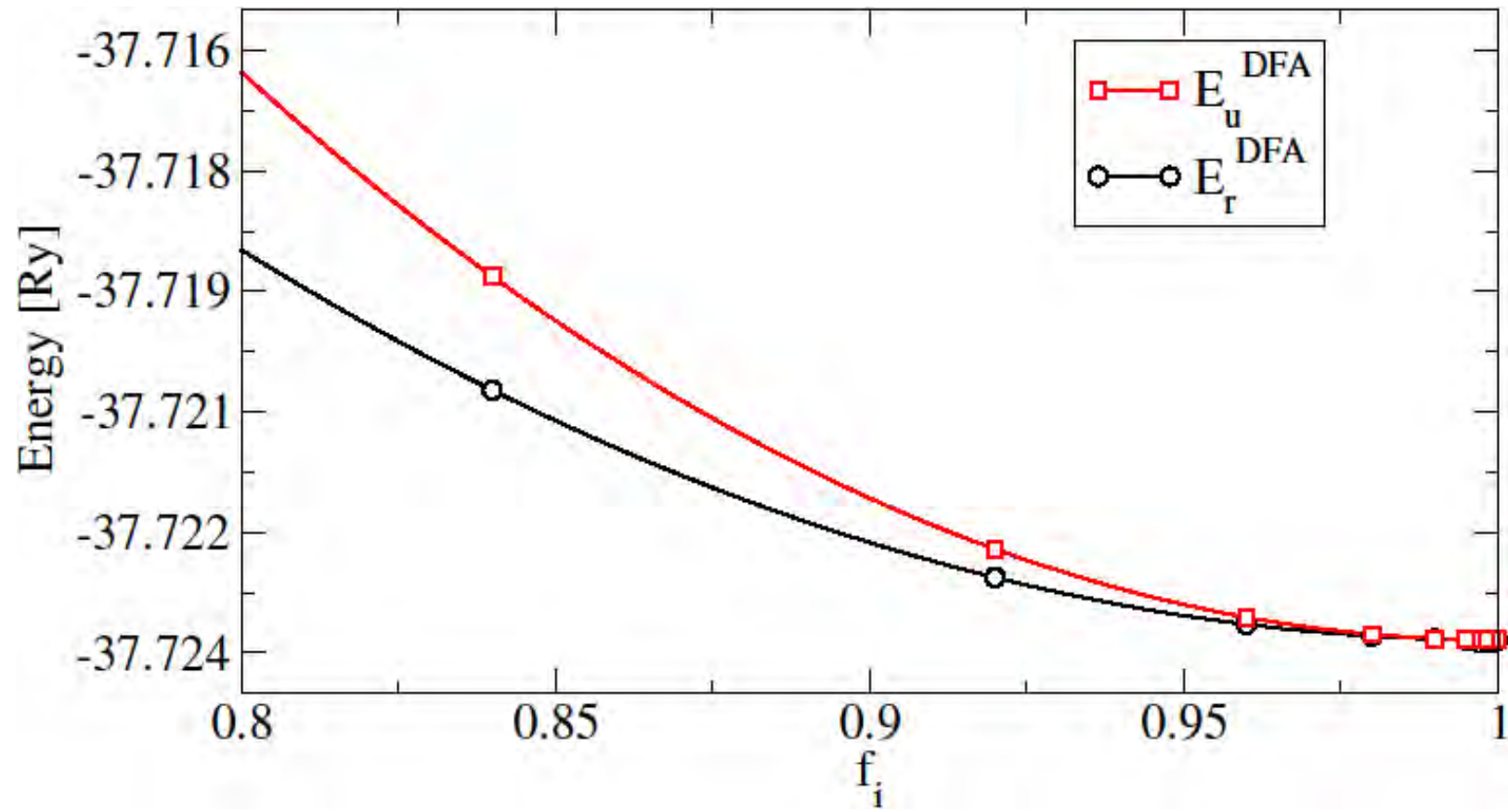


G. Borghi, C-H. Park, N. L. Nguyen, A. Ferretti, and NM, Phys. Rev. B 91, 155112 (2015)

$$\min_{\{\psi'_{\sigma i}\}} E_{\text{SIC}}[\{\psi'_{\sigma i}\}] = \min_{\{\psi_{\sigma i}\}} \left(\min_{\{O_{\sigma}\}} E_{\text{SIC}}[\{\psi_{\sigma i}\}, \{O_{\sigma}\}] \right)$$

N. Marzari, D. Vanderbilt, and M. C. Payne, Phys. Rev. Lett. 79, 1337 (1997)

SCREENING



SCREENING

Expansion of Koopmans additional terms as a function of occupation

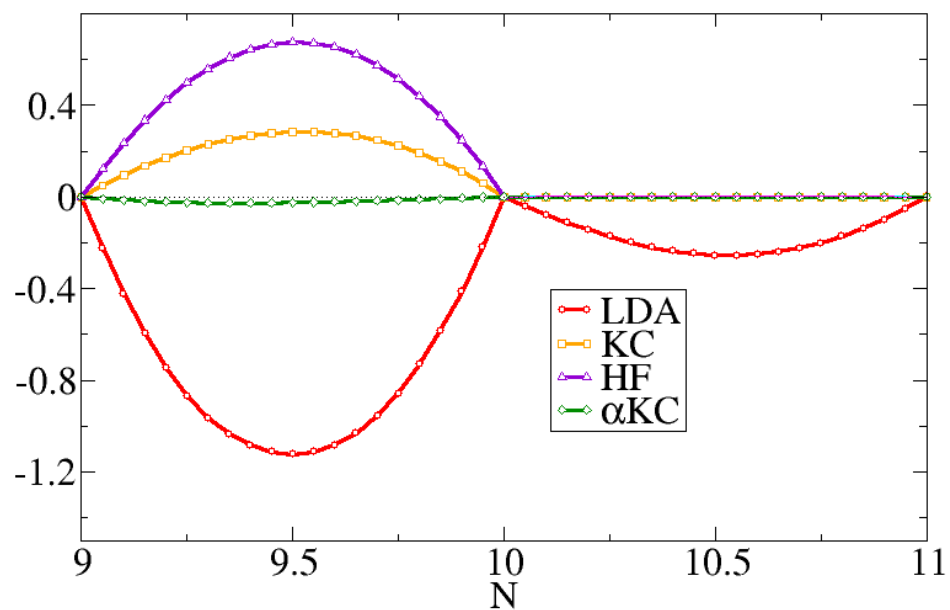
$$\frac{1}{2} f_i(1 - f_i) \int d\mathbf{r} d\mathbf{r}' n_i(\mathbf{r}) [f_{Hxc}]_{(\mathbf{r}, \mathbf{r}')} n_i(\mathbf{r}')$$

$$\frac{1}{2} f_i(1 - f_i) \int d\mathbf{r} d\mathbf{r}' n_i(\mathbf{r}) [\tilde{\epsilon}^{-1} f_{Hxc}]_{(\mathbf{r}, \mathbf{r}')} n_i(\mathbf{r}') \quad \tilde{\epsilon}^{-1} = I + f_{Hxc} \chi$$

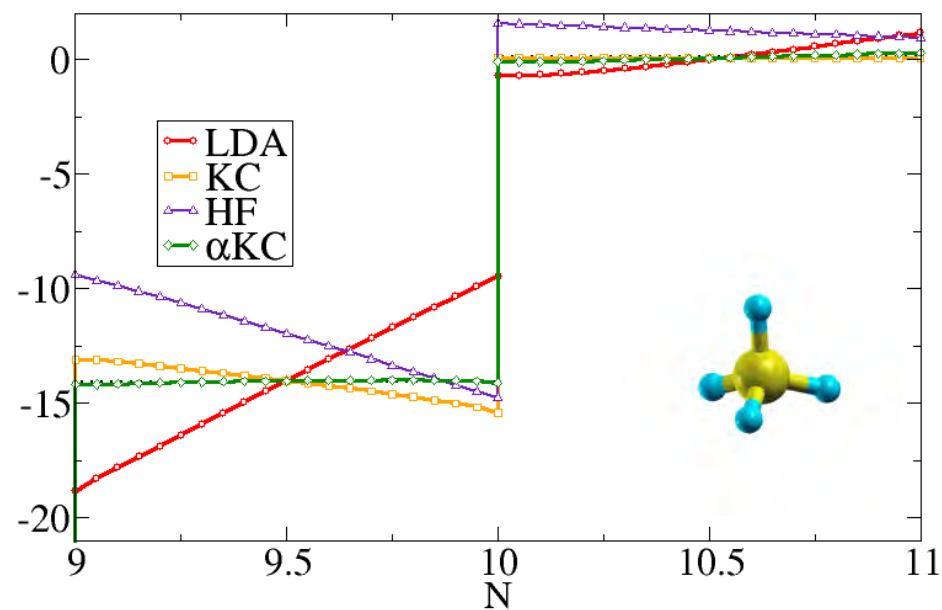
$$\alpha_i = \frac{\Pi_i^{(2), rKI}}{\Pi_i^{(2), uKI}} = 1 + \frac{\int d\mathbf{r} d\mathbf{r}' n_i(\mathbf{r}) [f_{Hxc} \chi f_{Hxc}]_{(\mathbf{r}, \mathbf{r}')} n_i(\mathbf{r}')}{\int d\mathbf{r} d\mathbf{r}' n_i(\mathbf{r}) f_{Hxc}(\mathbf{r}, \mathbf{r}') n_i(\mathbf{r}')} = 1 + \beta_i$$

ENERGIES AND EIGENVALUES

Energy deviation from linearity



HOMO



ORGANIC MOLECULES

	IP	EA	Gap
scfGW	0.31	0.29	0.28
KI	0.45	0.22	0.32
KIPZ	0.25	0.17	0.20

IP, EA from opposite of HOMO, LUMO

GW: Blase et al., Phys. Rev. B 83, 115103 (2011)

Koopmans: Nguyen et al., PRL 114, 166405 (2015)

ORGANIC MOLECULES

	IP	EA	Gap
scfGW	0.31	0.29	0.28
KI	0.45	0.22	0.32
KIPZ	0.25	0.17	0.20

TRANSITION METAL COMPLEXES

	IP
G_0W_0[PBE0]	0.21
KI	0.39
KIPZ	0.20

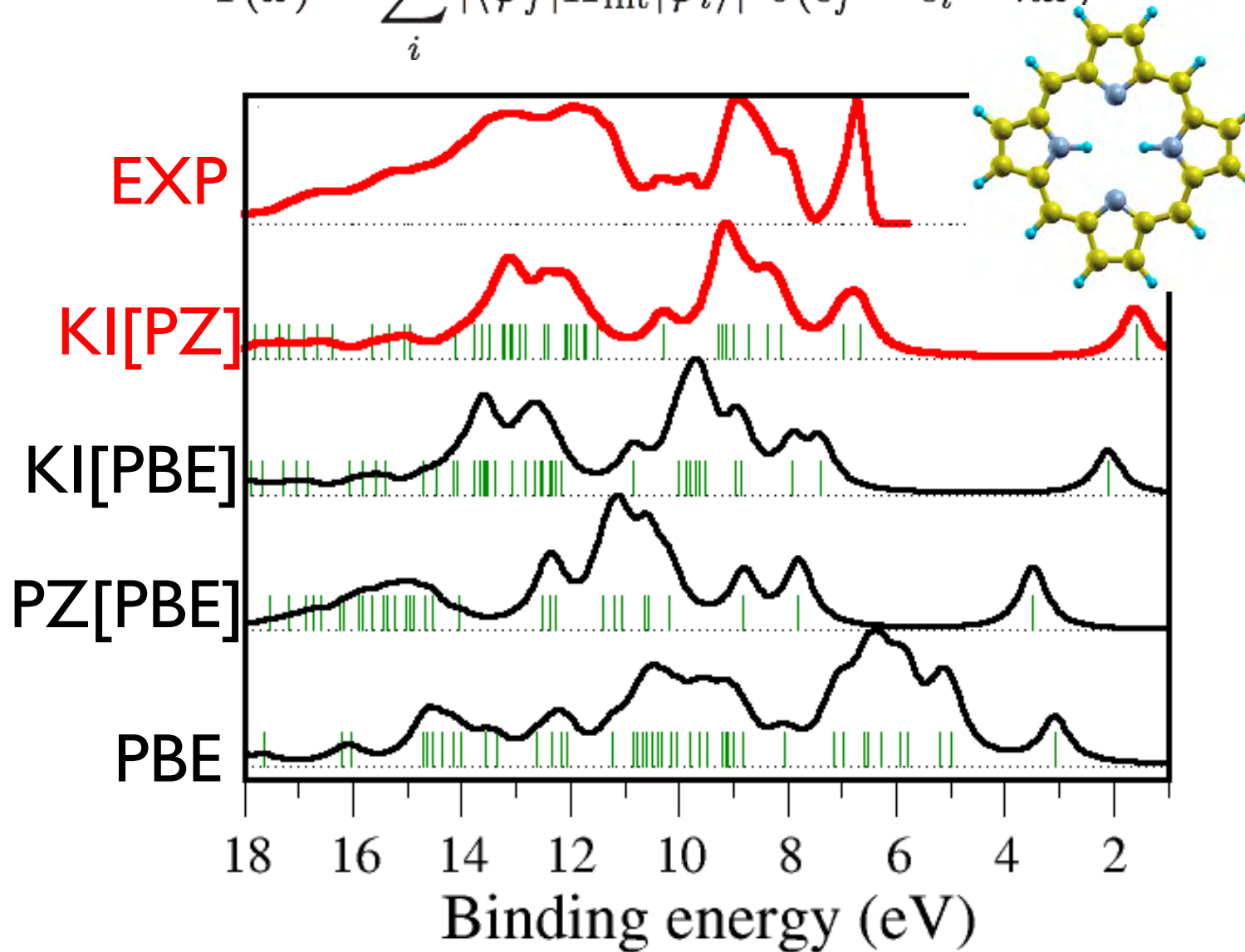
IP, EA from opposite of HOMO, LUMO

GW: Blase et al., Phys. Rev. B 83, 115103 (2011)
Koopmans: Nguyen et al., PRL 114, 166405 (2015)

GW: Korbel et al., JCTC 10, 3934 (2014)
Koopmans: Colonna et al., JCTC 14, 2549 (2018)

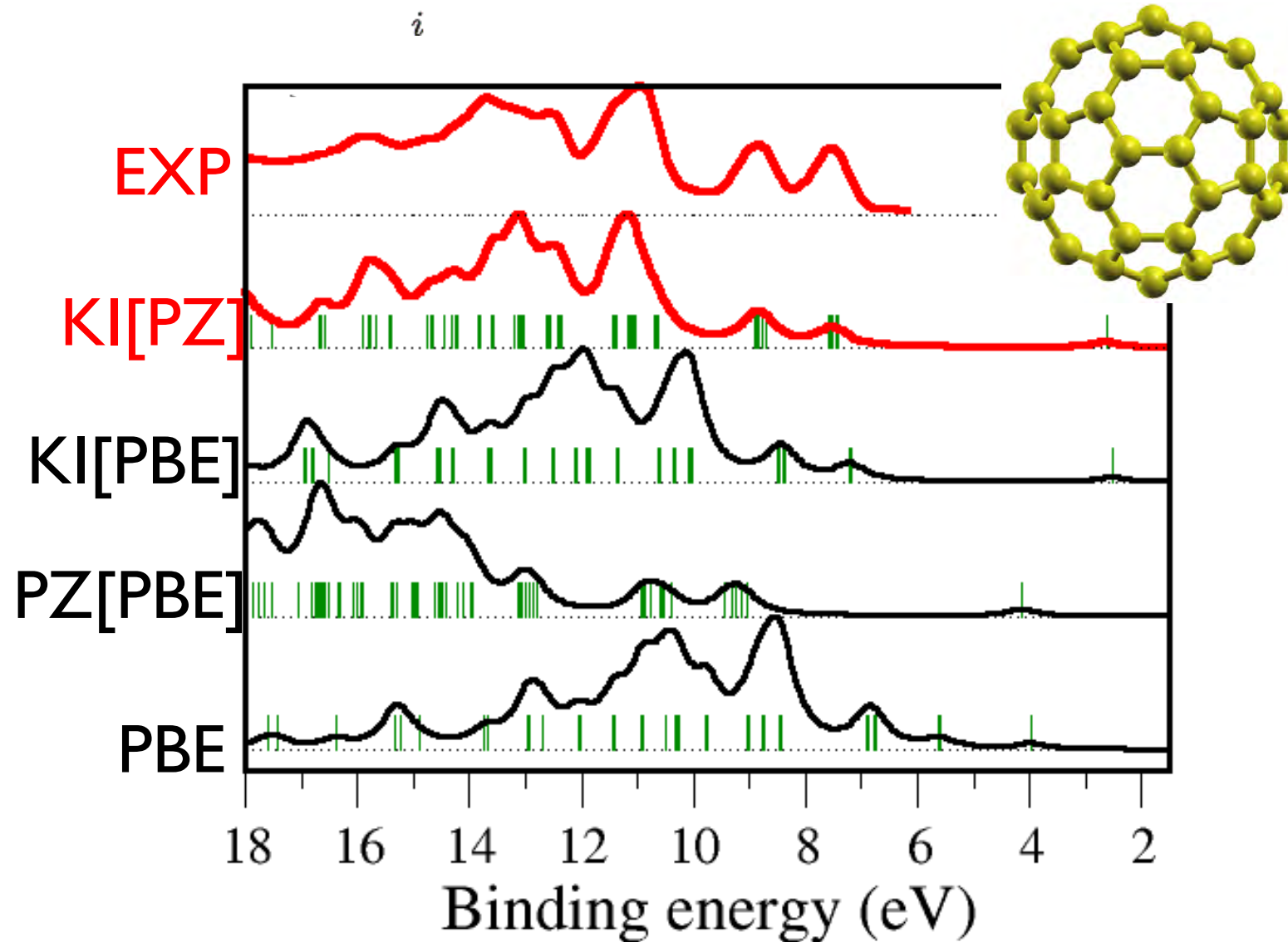
Ultraviolet photoemission spectroscopy

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

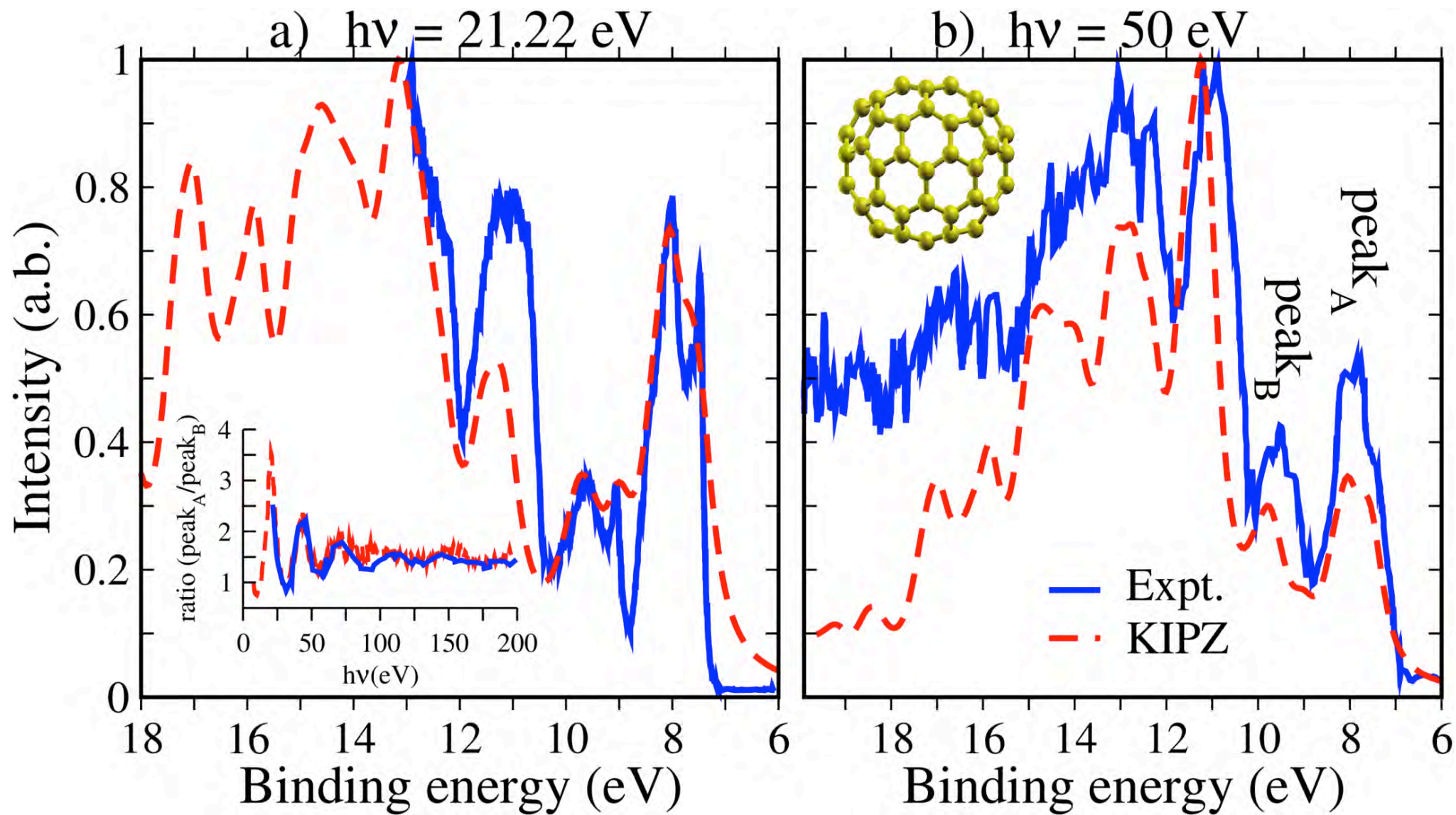


Fullerene UPS

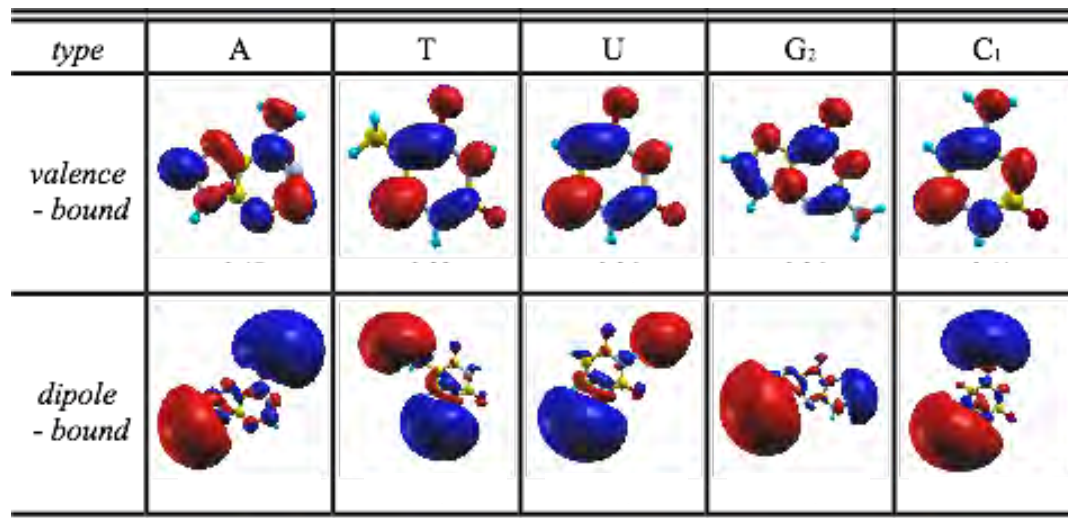
$$I(\omega) = \sum_i |\langle \varphi_f | \hat{H}_{\text{int}} | \varphi_i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \hbar\omega)$$



Fullerene (C₇₀) UPS (HeI, HeII)



DIFFICULT AFFINITIES: DNA/RNA bases



Mean absolute deviations

Valence bound EA

PBE 2.51 eV

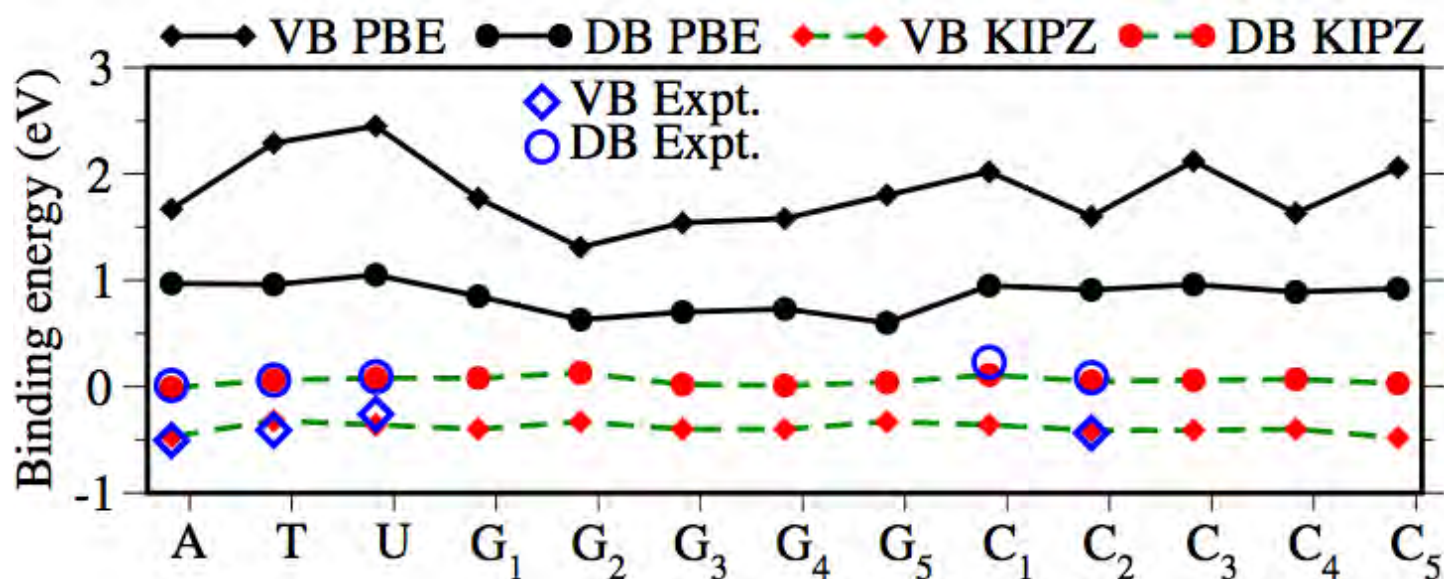
CCSD(T) 0.32 eV

KI[PZ] 0.06 eV

Dipole bound EA

PBE 0.59 eV

KI[PZ] 0.09 eV



CCSD(T) ref: D. Roca-Sanjuan et al., JCP 129, 095104 (2008)

UPS and geometries

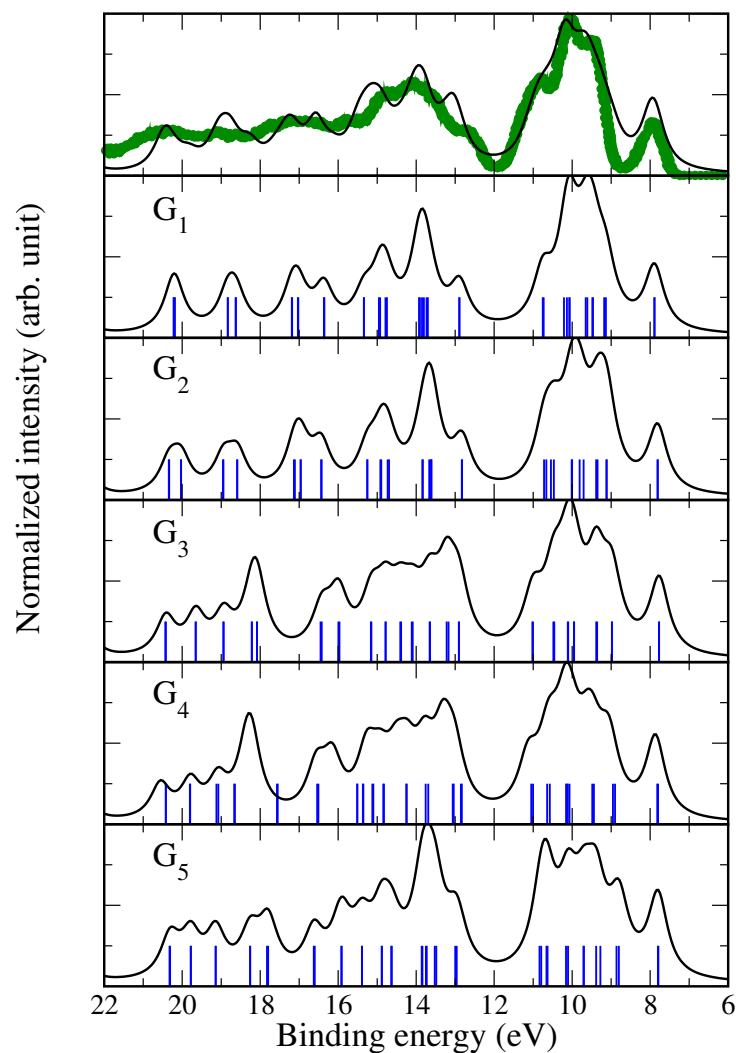
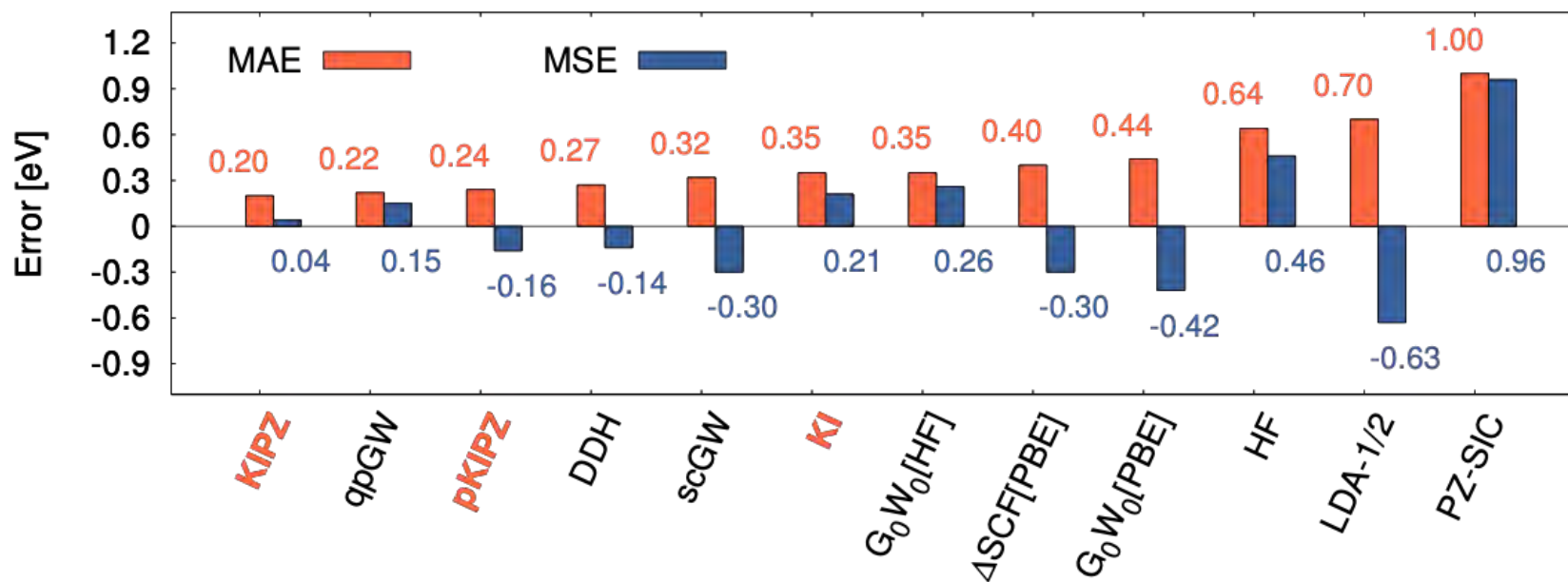


Table IV. Absolute dihedral angles (β_1 and β_2) of the nucleobases with amino group. For A $\beta_1 = \angle \text{H}_2\text{N}_{10}\text{C}_4\text{N}_3$ and $\beta_2 = \angle \text{H}_1\text{N}_{10}\text{C}_4\text{C}_5$; for G_{1..5} $\beta_1 = \angle \text{H}_2\text{N}_{10}\text{C}_2\text{N}_1$ and $\beta_2 = \angle \text{H}_1\text{N}_{10}\text{C}_2\text{N}_3$, and for C_{1,2,4} $\beta_1 = \angle \text{H}_1\text{N}_7\text{C}_4\text{C}_5$ and $\beta_2 = \angle \text{H}_2\text{N}_7\text{C}_4\text{N}_3$, where the index of the atoms can be seen in SM³⁹.

	β_1			β_2		
	PBE	KIPZ	MP2 ⁴⁰	PBE	KIPZ	MP2 ⁴⁰
A	0.05	23.16	18.70	0.05	23.15	21.10
G ₁	2.00	10.80	-	2.03	46.12	-
G ₂	2.05	17.60	11.80	2.03	35.364	43.20
G ₃	1.82	23.69	-	1.92	24.44	-
G ₄	1.81	25.35	-	1.88	22.51	-
G ₅	1.82	21.97	-	1.88	27.69	-
C ₁	8.25	30.64	26.20	7.20	17.27	14.10
C ₂	8.68	27.97	-	8.01	21.01	-
C ₄	8.90	28.57	-	8.02	20.53	-

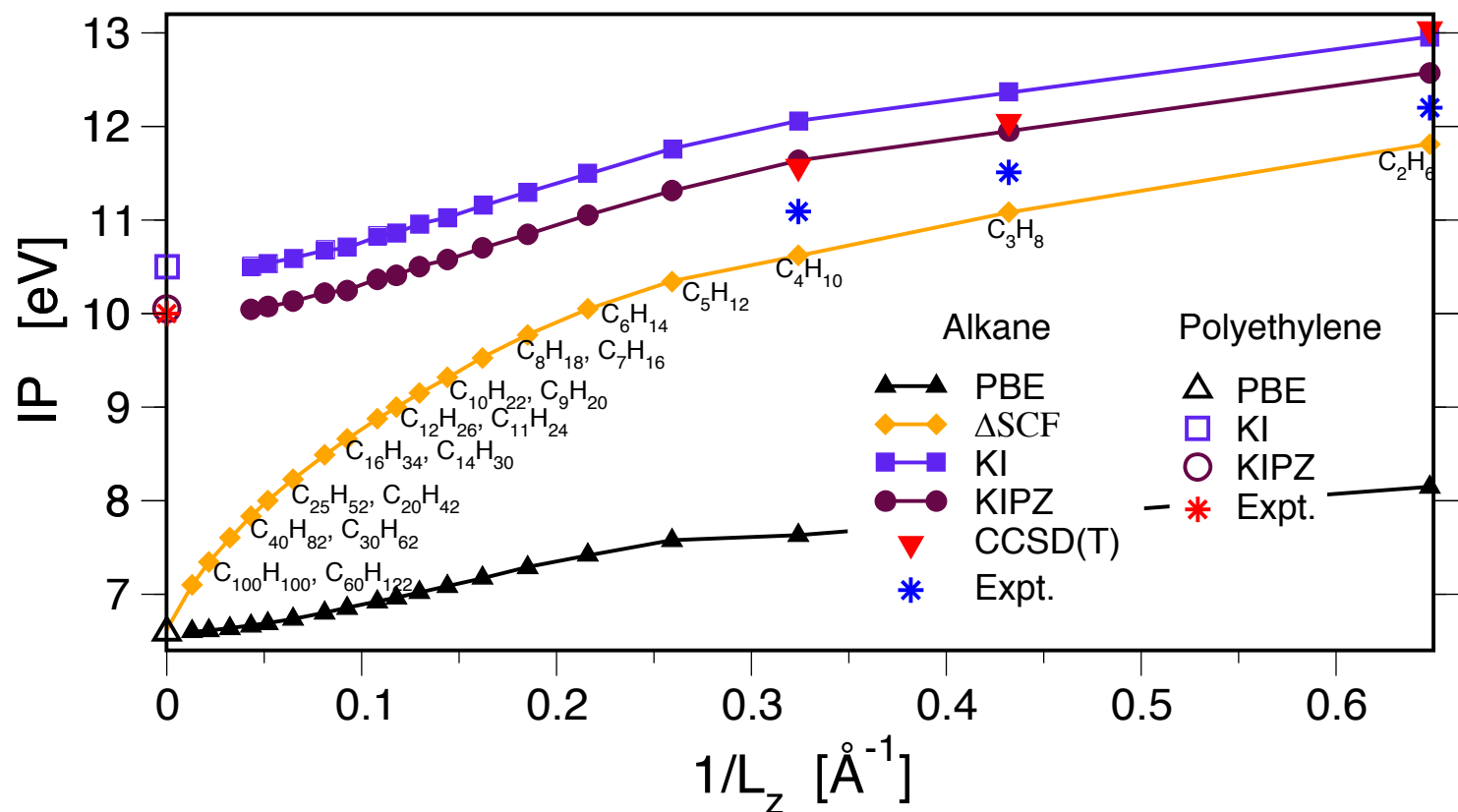
KOOPMANS SPECTRAL FUNCTIONALS

GW100 TEST SET

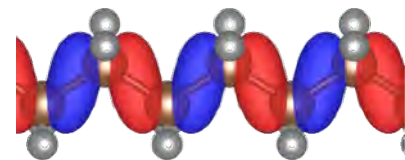


N. Colonna, L. Nguyen, A. Ferretti, and N. Marzari, JCTC (2018)

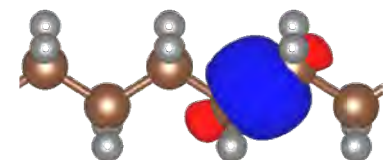
SOLID-STATE LIMIT



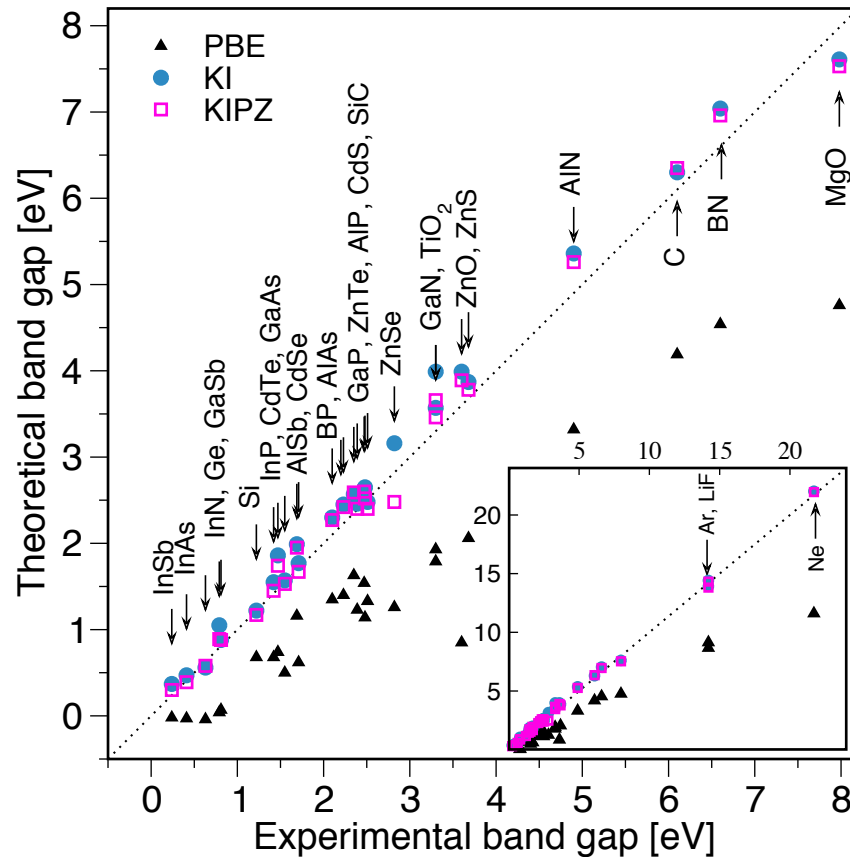
Canonical orbital



Variational (minimizing) orbital



BAND GAPS AND IPs (30 SOLIDS)



MAE (eV)	Gap	IP
PBE	2.54	1.09
G₀W₀	0.56	0.39
QSGW	0.18	0.49
KI	0.27	0.19
KIPZ	0.22	0.21

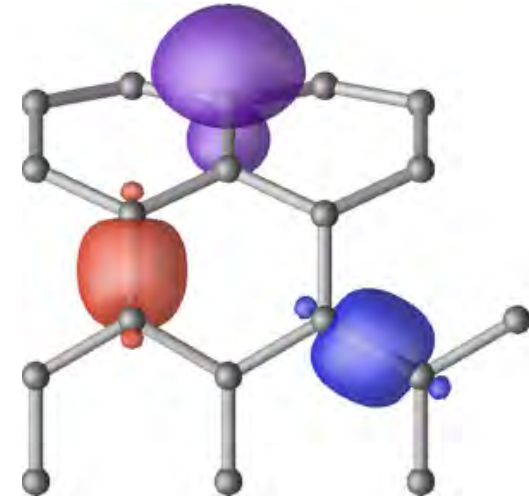
GW: W. Chen and A. Pasquarello PRB 92 041115 (2015)

Koopmans: L. Nguyen, N. Colonna, A. Ferretti, and N. Marzari, PRX (2018)

BAND STRUCTURES FROM LOCALIZED ORBITALS

Compact mapping of Bloch states into local orbitals

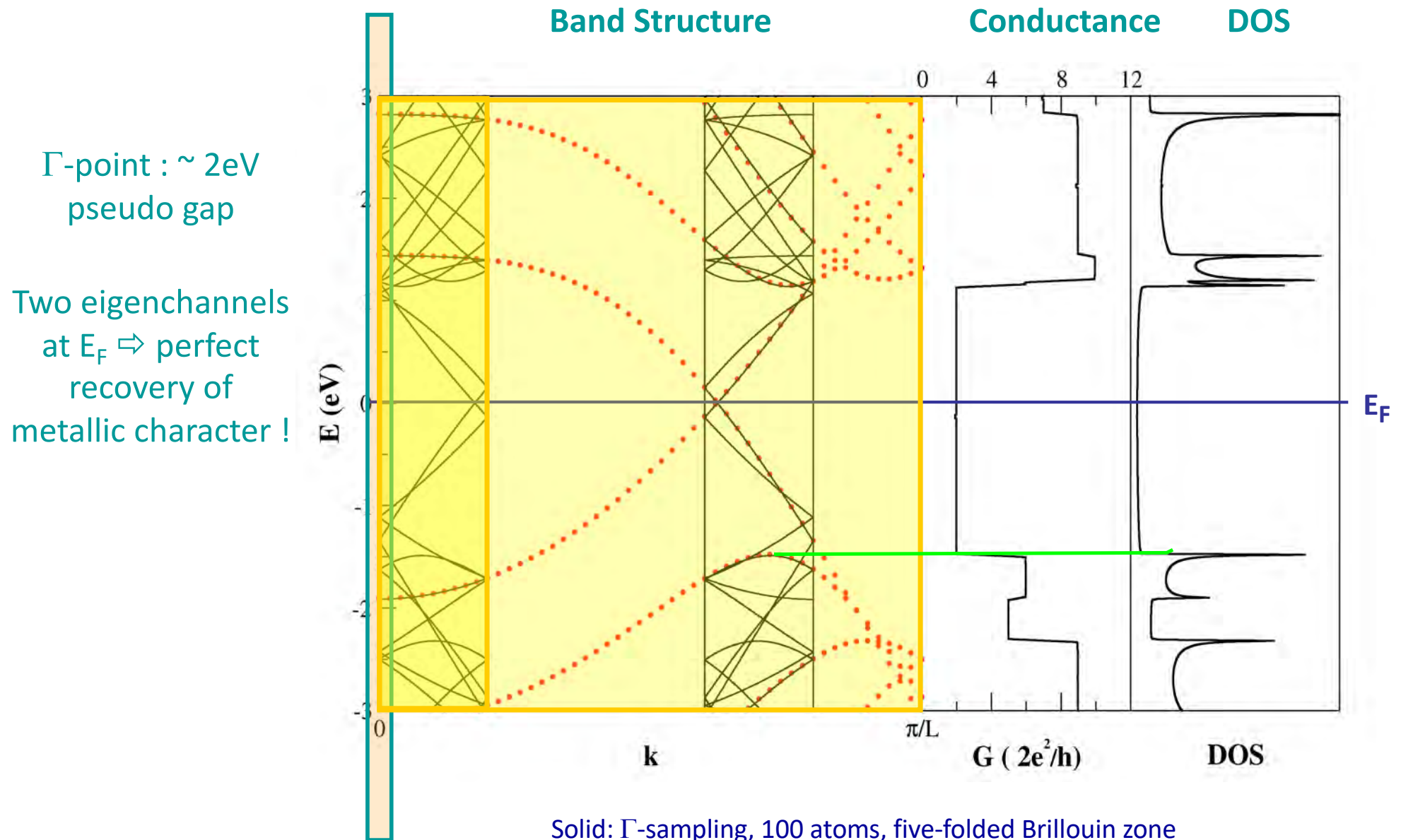
$$\omega_n(\mathbf{r} - \mathbf{R}) = \frac{V}{8\pi^3} \int_{BZ} e^{-i\mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) d\mathbf{k}$$
$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_R}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \omega_n(\mathbf{r} - \mathbf{R})$$



$$\left\langle \psi_{i\mathbf{k}} \left| \hat{H} \right| \psi_{j\mathbf{k}} \right\rangle = H_{ij}^{00} + e^{i\mathbf{k} \cdot \mathbf{R}} H_{ij}^{01} + e^{-i\mathbf{k} \cdot \mathbf{R}} H_{ij}^{0\bar{1}}$$

⇒ Diagonalize H Matrix

BAND STRUCTURES FROM LOCALIZED ORBITALS



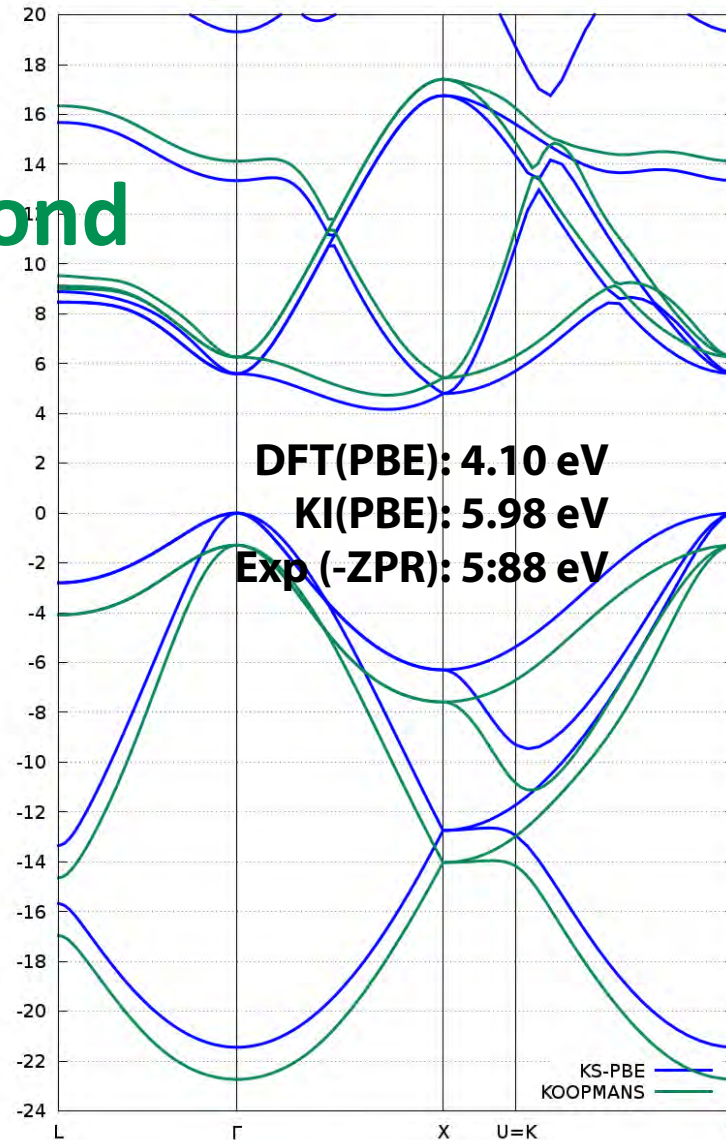
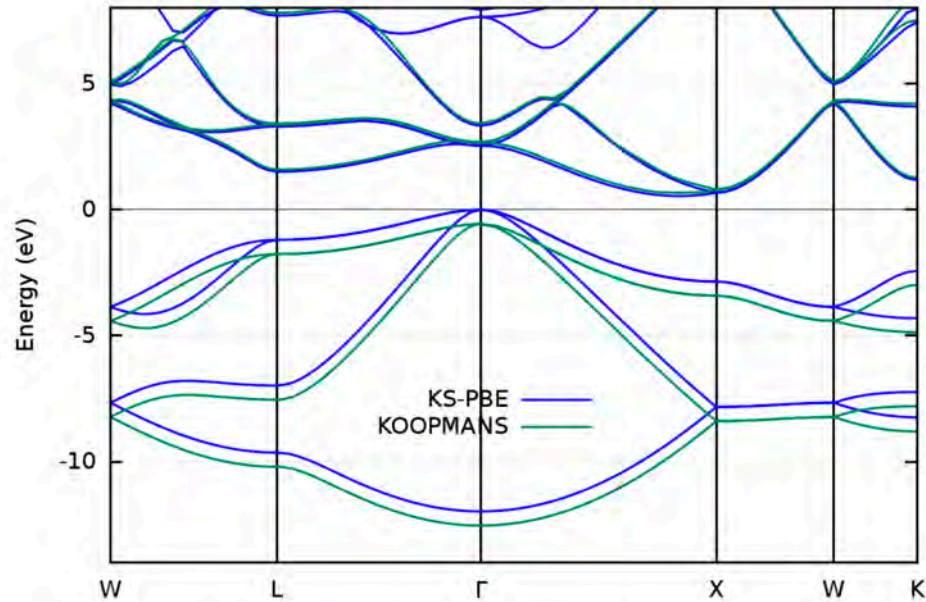
Solid: Γ -sampling, 100 atoms, five-folded Brillouin zone
 Dotted: Full SCF calculation (5 k-points, 20 atoms supercell)

KOOPMANS BAND STRUCTURES

Diamond

Silicon

DFT(PBE): 0.68 eV
KI(PBE): 1.21 eV
Exp: 1.17 eV

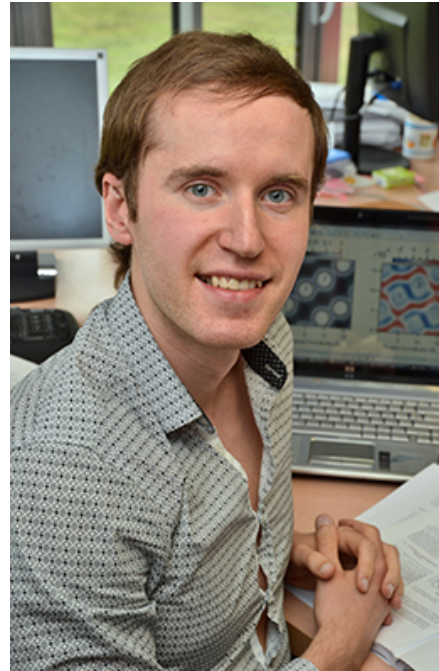
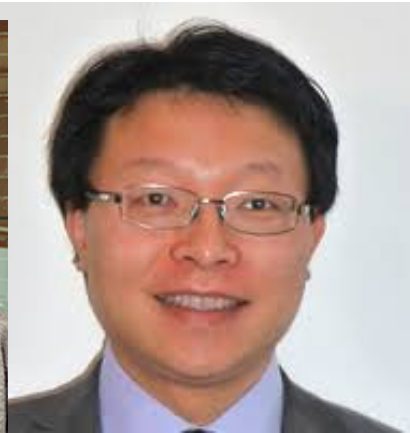


DFT(PBE): 4.10 eV
KI(PBE): 5.98 eV
Exp (-ZPR): 5.88 eV

CONCLUSIONS

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

Hubbard acknowledgments



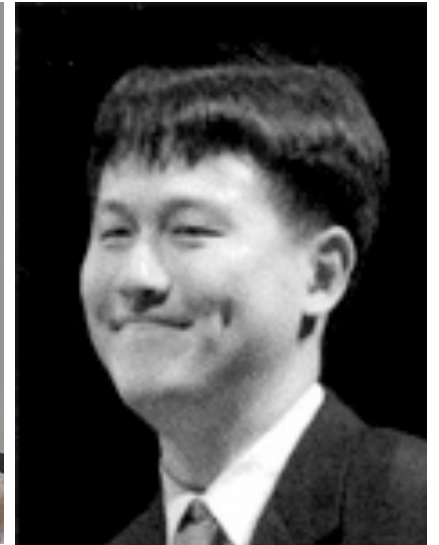
Earlier work: Heather Kulik, Patrick Sit, Damian Scherlis, Matteo Cococcioni (MIT)

DFPT: Iurii Timrov and Matteo Cococcioni (EPFL)

Hubbard parameters from density-functional perturbation theory

Iurii Timrov, Nicola Marzari, and Matteo Cococcioni
Phys. Rev. B **98**, 085127 – Published 16 August 2018

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Giovanni Borghi (Modena), Cheol Hwan Park (SNU)

Koopmans acknowledgments

Ismaila Dabo (U. Penn)

Matteo Cococcioni (EPFL)

Andrea Ferretti
(Modena)



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



THEOS

THEORY AND SIMULATION
OF MATERIALS



ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Thank you!