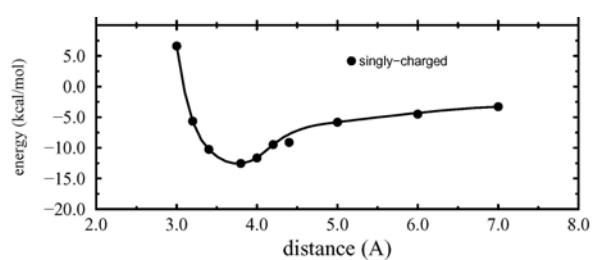
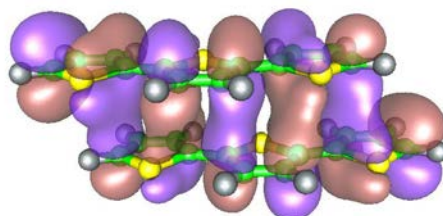
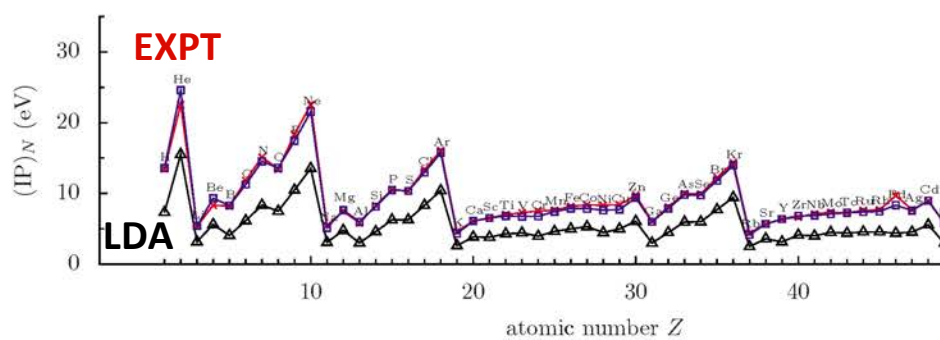


Notable failures II: Delocalization of electrons/holes



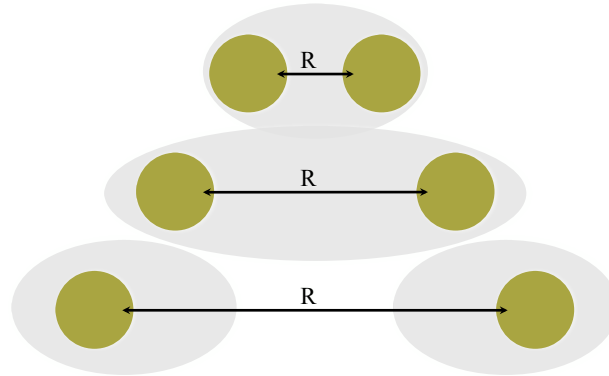
D. A. Scherlis and N. Marzari, JPCB (2004), JACS (2005)

Notable failures III: Photoemission spectra (HOMO from IP)



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

Notable failures IV: H_2^+ dissociation limit

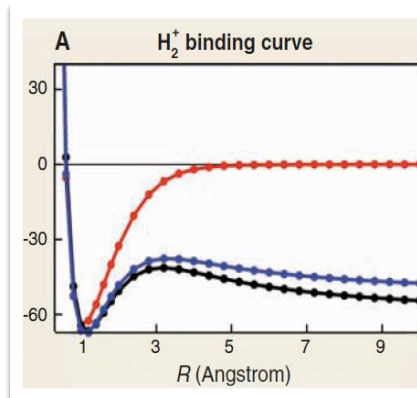


$$\hat{H} = -\frac{1}{2}\vec{\nabla}^2 + V_{\text{ext}}(\vec{r}) \quad \text{Schrödinger}$$

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

It doesn't work even for one electron!

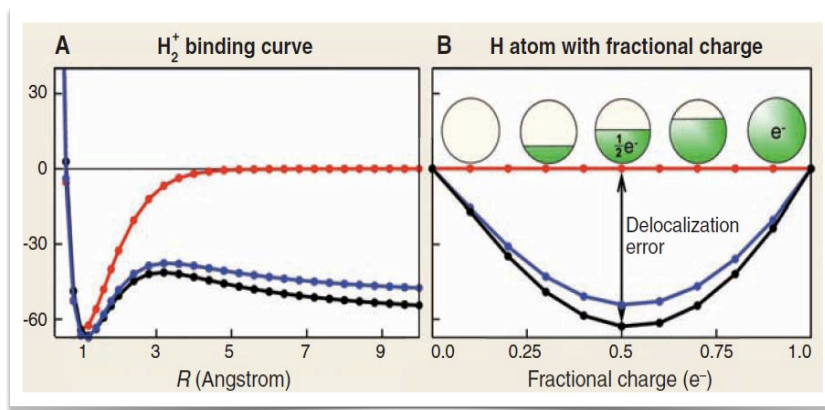
HF B3LYP LDA



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

It doesn't work even for one electron!

HF B3LYP LDA



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

Beautiful, but perverse

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

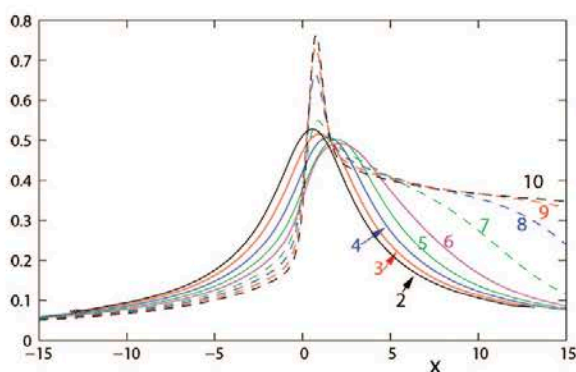
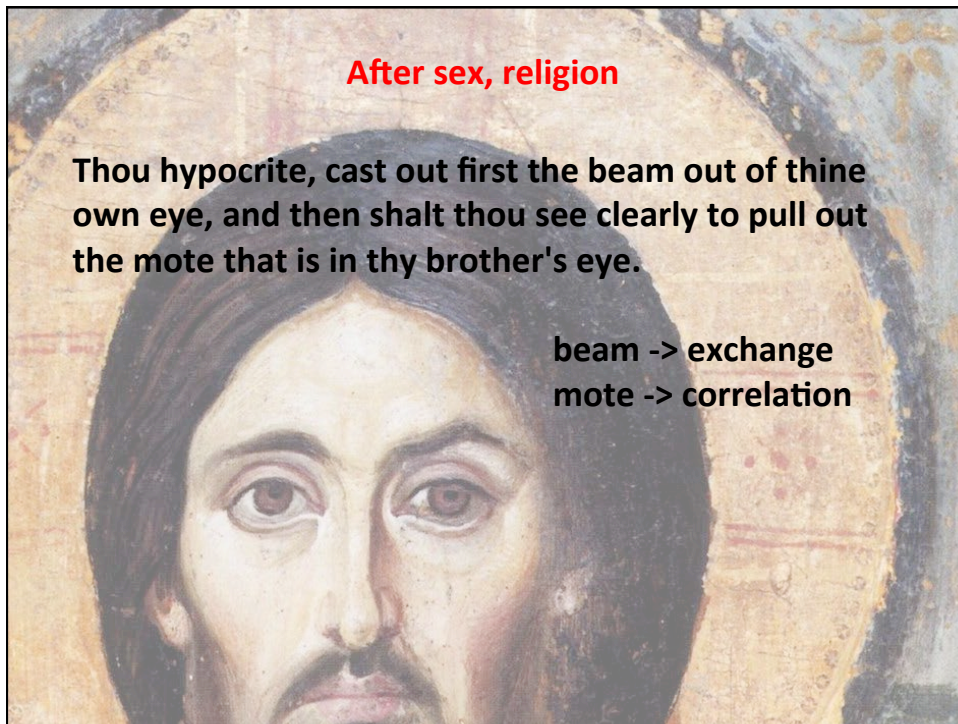


Figure 7. Hartree-exchange-correlation potential, $v_{Hxc}(x)$ for our LiH model ($c = 2.8$); the values of interatomic separation R are indicated.

Neepa Maitra JCTC 2009, Helbig and Rubio JCP 2009



What is self-interaction?

$$\text{Hess}(E_{N,v}) = \begin{pmatrix} 2\eta & f(\mathbf{r}) \\ f(\mathbf{r}) & \chi(\mathbf{r}, \mathbf{r}') \end{pmatrix}$$

What is self-interaction?

$$\text{Hess}(E_{N,v}) = \begin{pmatrix} 2\eta & f(\mathbf{r}) \\ f(\mathbf{r}) & \chi(\mathbf{r}, \mathbf{r}') \end{pmatrix}$$

Chemical hardness



Fractional-charge error

Fukui function



Charge-localization error

Response function



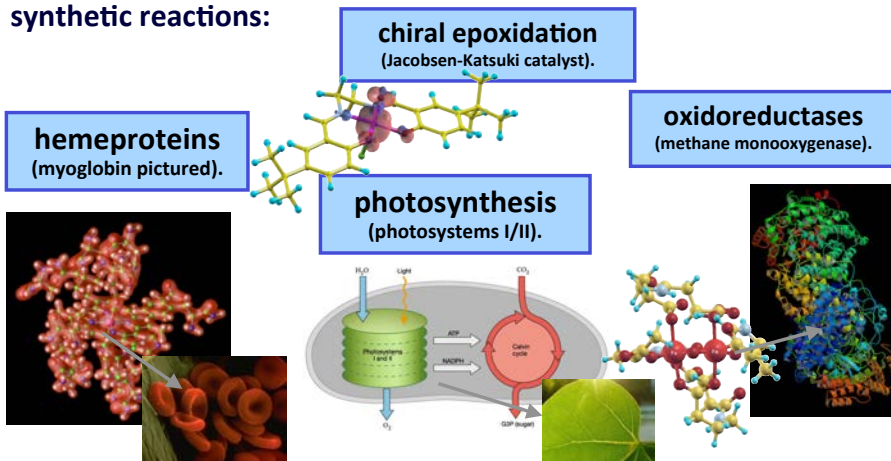
Charge-polarization error

Self-interaction challenges (all key to energy applications)

- Transition-metal catalysis (localized d, f orbitals, short-range self-interaction): **DFT+Hubbard**
- Energy levels and direct/inverse photoemission spectra (total and partial electron removal energies): **Koopmans' compliant functionals**
- Moving towards **frequency-dependent functionals**

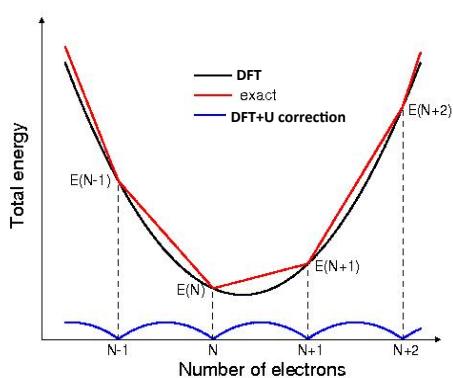
Transition-metal chemistry

Transition metals are reactive centers of fundamental natural and synthetic reactions:



But most electronic-structure approaches fail to describe transition metal chemistry accurately!

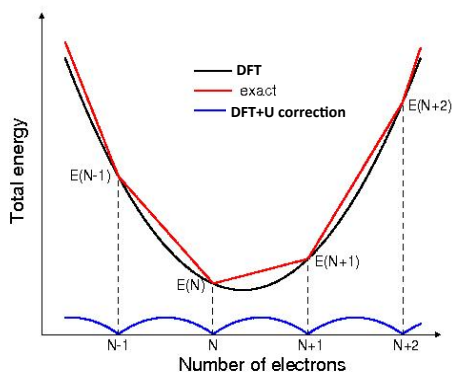
A DFT + Hubbard U approach



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

A DFT + Hubbard U approach

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



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

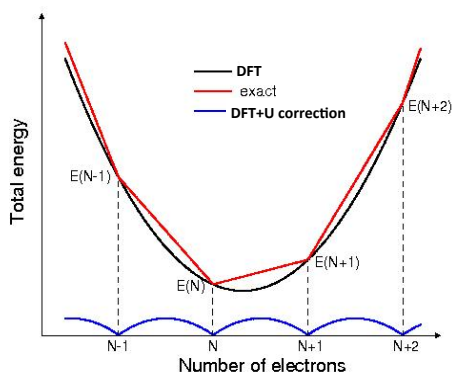
LRT U: M. Cococcioni (PhD 2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

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

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

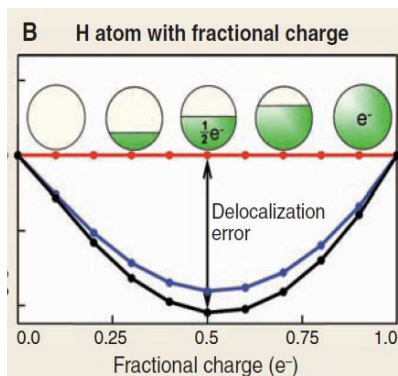
A DFT + Hubbard U approach

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



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	⁶ FeO ⁺			⁴ FeO ⁺		
	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⁺

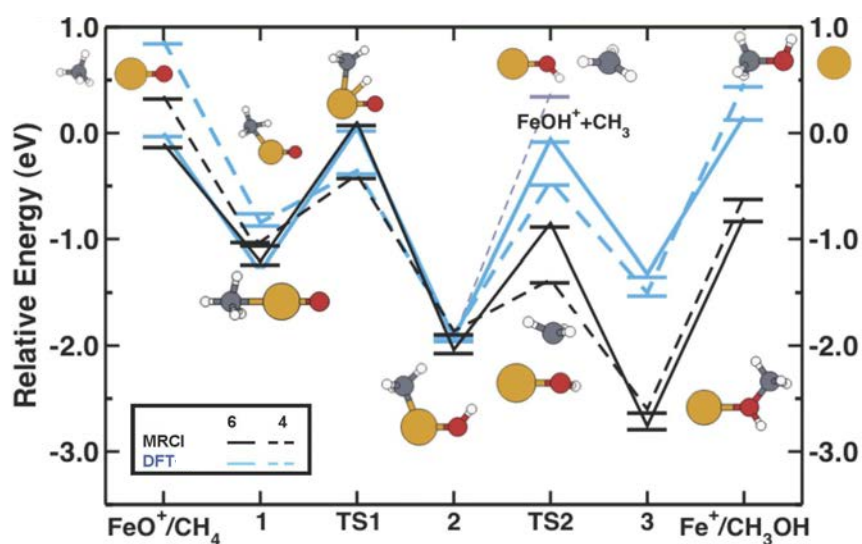
H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, *Phys. Rev. Lett.* (2006)

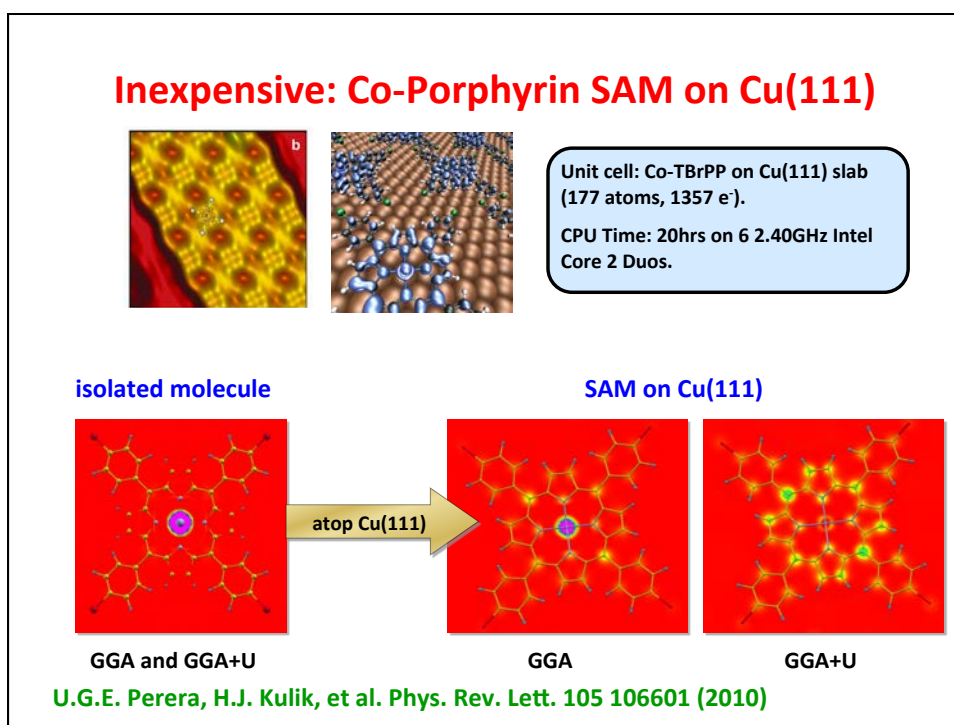
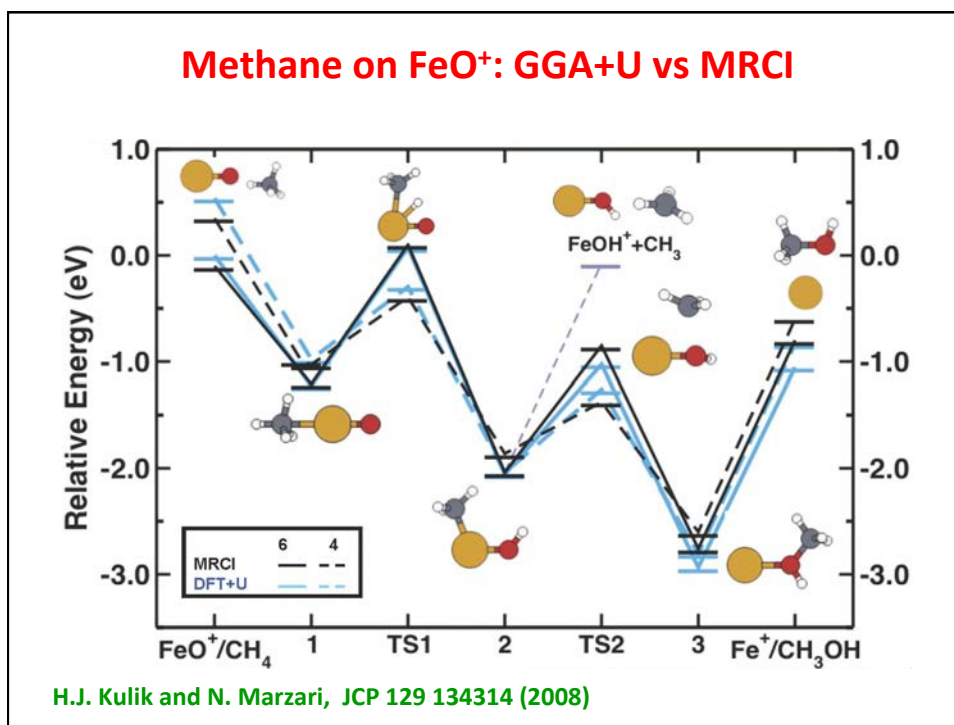
Fe₂⁻**Multiplet Splittings (eV)**

State	B3LYP	GGA	+U ₀ (2eV)	+U _{scf} (3eV)	CCSD(T)	MRCI ^a
⁸ Σ _g ⁻	0.00	0.00	0.00	0.00	0.00	0.00
⁸ Δ _g	0.14	-0.52	0.04	0.38	0.40	0.45

Fe₂

⁹ Σ _g ⁻	0.00	0.00	0.00	0.00	0.00	0.00
⁷ Σ _g ⁻	0.34	0.65	0.66	0.60	0.55	0.62
⁷ Δ _u	0.18	-0.12	0.48	0.72	0.86	0.69
⁹ Δ _g	0.36	0.28	0.36	0.41	0.38	0.45

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)



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

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

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

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

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

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

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

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

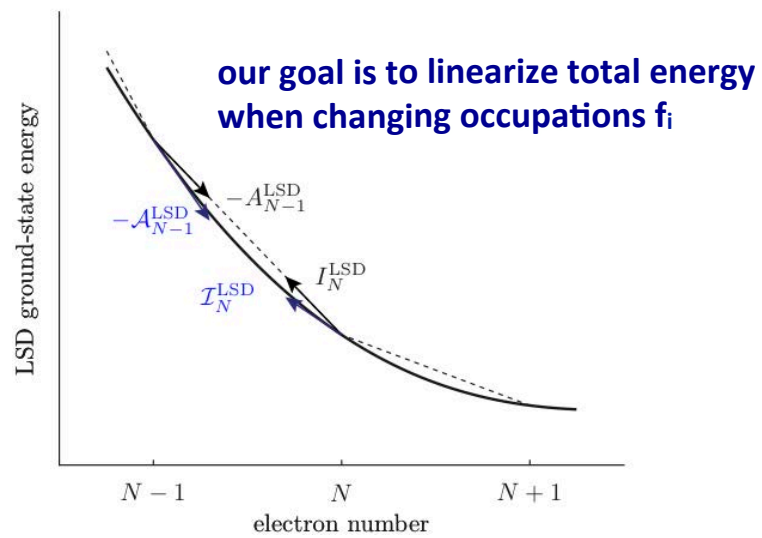
Seesawing TM dioxides: Mn, Fe, Co

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)

Self-interaction as a breakdown of linearity



Imposing Koopmans' condition to DFT

what we have
(Slater)

$$\Delta E_i|_{\mathcal{S}} = \int_0^{f_i} \epsilon_i|_{\text{unrel}}(f) df = E[f_i] - E[0]$$

Imposing Koopmans' condition to DFT

what we have
(Slater)

$$\Delta E_i|_{\mathcal{S}} = \int_0^{f_i} \epsilon_i|_{\text{unrel}}(f) df = E[f_i] - E[0]$$

what we want
(Koopmans)

$$\Delta E_i|_{\mathcal{K}} = f_i \epsilon_i^{\text{ref}}$$

Imposing Koopmans' condition to DFT

what we have
(Slater)

$$\Delta E_i|_{\mathcal{S}} = \int_0^{f_i} \epsilon_i|_{\text{unrel}}(f) df = E[f_i] - E[0]$$

what we want
(Koopmans)

$$\Delta E_i|_{\mathcal{K}} = f_i \epsilon_i^{\text{ref}}$$

$$\epsilon_i^{\text{ref}} = \epsilon_i(f=1/2)$$

Koopmans'
compliant
functionals

$$E^{\text{NK}} = E^{\text{LSD}} + \sum_i \left[f_i \epsilon_i^{\text{ref}} - \Delta E_i|_{\mathcal{S}} \right]$$

I. Dabo, M. Cococcioni, and N. Marzari, arXiv:0910.2637
I. Dabo et al. Phys. Rev. B 82 115121 (2010)

Hamiltonian: orbital-density dependent, non-unitary invariant

$$\frac{\delta E^{\text{NK}}}{\delta \rho_i(\mathbf{r})} = h_i^{\text{NK}}(\mathbf{r})$$



$$h_i^{\text{NK}} = h^{\text{LSD}}[\rho_i^{\text{ref}}] + w_{\text{ref},i}^{\text{LSD}} + w_{\text{xd},i}^{\text{LSD}}$$

A functional form
for Slater ("NK₀")

$$\rho_i^{\text{ref}}(\mathbf{r}) = \sum_{j \neq i} \rho_j(\mathbf{r}) + f_{\text{ref}} n_i(\mathbf{r})$$

+ small variational terms ("full NK")

$$w_{\text{xd},i}^{\text{LSD}}(\mathbf{r}) = \sum_{j \neq i} \frac{\delta \Pi_j^{u,\text{LSD}}}{\delta \rho_i(\mathbf{r})}$$

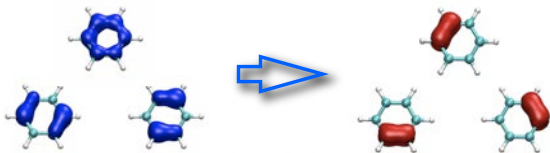
$$w_{\text{ref},i}^{\text{LSD}}(\mathbf{r}) = f_{\text{ref}} \left[\int d\mathbf{r}_1 f_{\text{Hxc}}^{\text{LSD}}(\mathbf{r}\mathbf{r}_1; [\rho_i^{\text{ref}}]) n_i(\mathbf{r}_1) - \int d\mathbf{r}_1 d\mathbf{r}_2 f_{\text{Hxc}}^{\text{LSD}}(\mathbf{r}_1\mathbf{r}_2; [\rho_i^{\text{ref}}]) n_i(\mathbf{r}_1) n_i(\mathbf{r}_2) \right]$$

Minimization: Ensemble DFT

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

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

$$G_{\sigma ij} \equiv \frac{\partial E_{\text{SIC}}}{\partial A_{\sigma ij}}$$

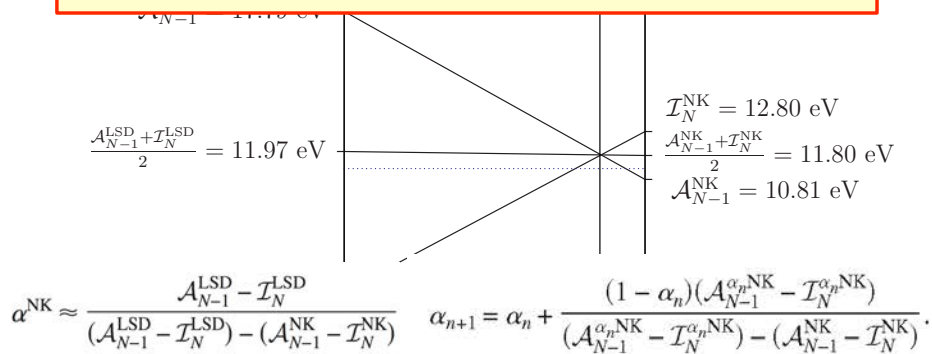


$$= 2 \int \psi_{\sigma i}(\mathbf{r}) [v_{\sigma j}^{\text{SIC}}(\mathbf{r}) - v_{\sigma i}^{\text{SIC}}(\mathbf{r})] \psi_{\sigma j}(\mathbf{r}) d\mathbf{r},$$

C.-H. Park, A. Ferretti, I. Dabo, N. Poilvert, and N. Marzari, arXiv

Orbital relaxation: α screening

$$E^{\alpha\text{NK}} = E^{\text{LSD}} + \alpha^{\text{NK}}(E^{\text{NK}} - E^{\text{LSD}})$$



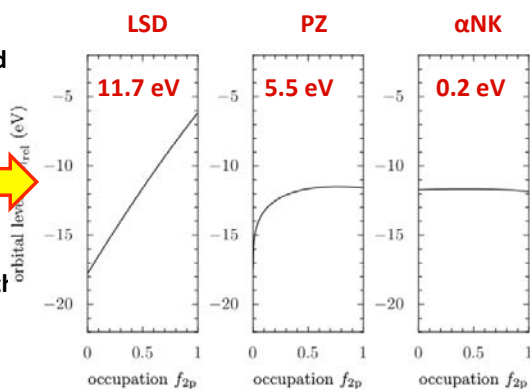
How does it work?

Spread of the expectation value (C 2p)

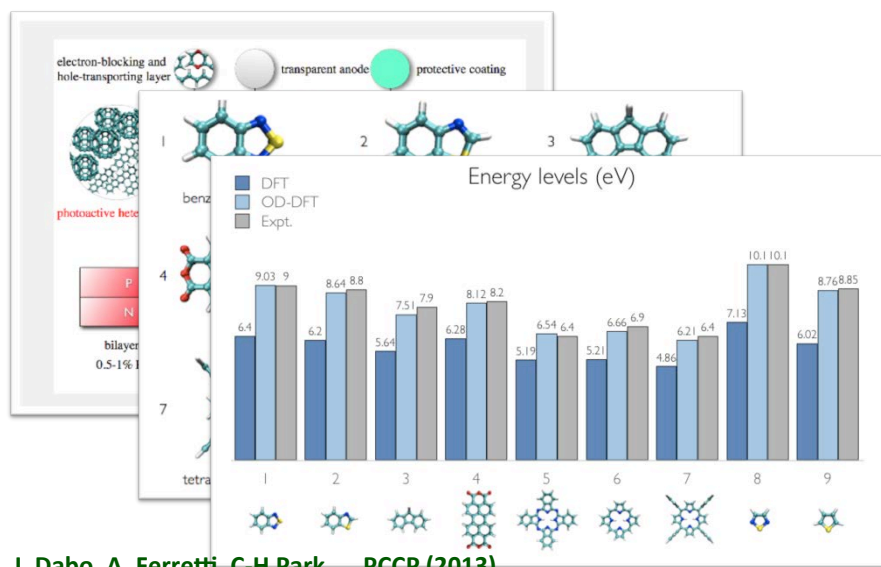
In a **self-interaction free** mean-field theory the expectation value is

$$\epsilon_i = \langle \phi_i | \hat{H} | \phi_i \rangle$$

independent of the occupation of the orbital i for a **frozen** configuration

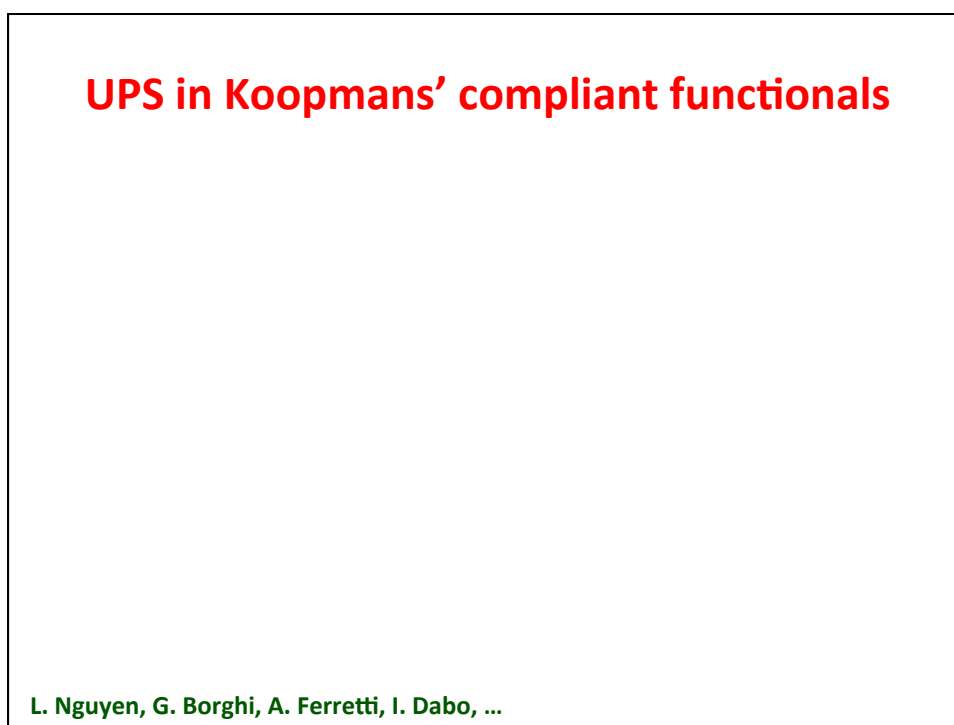
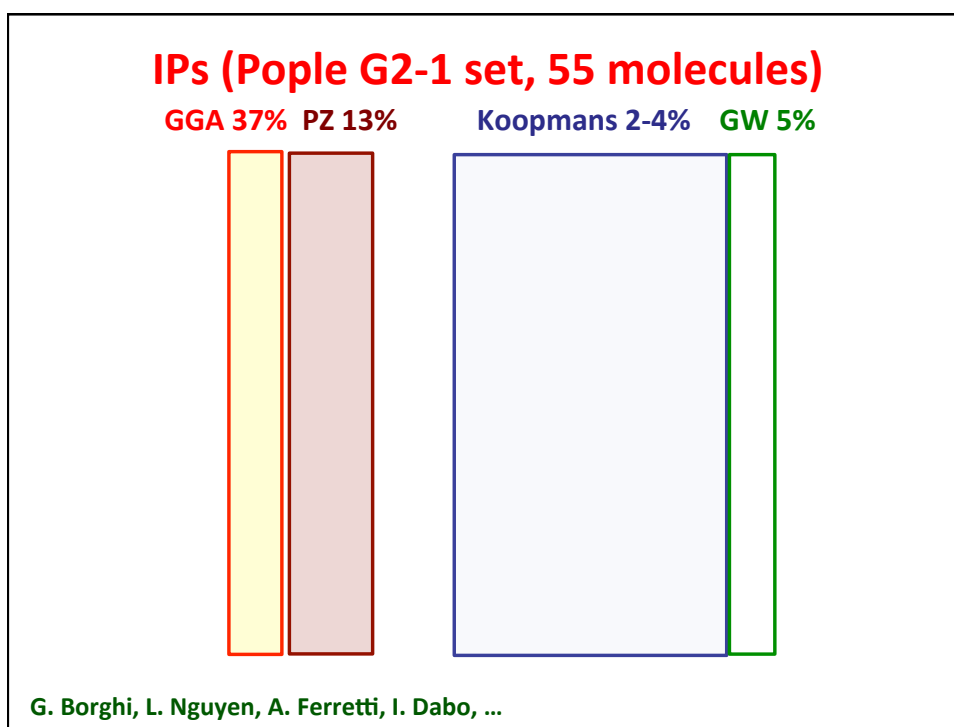


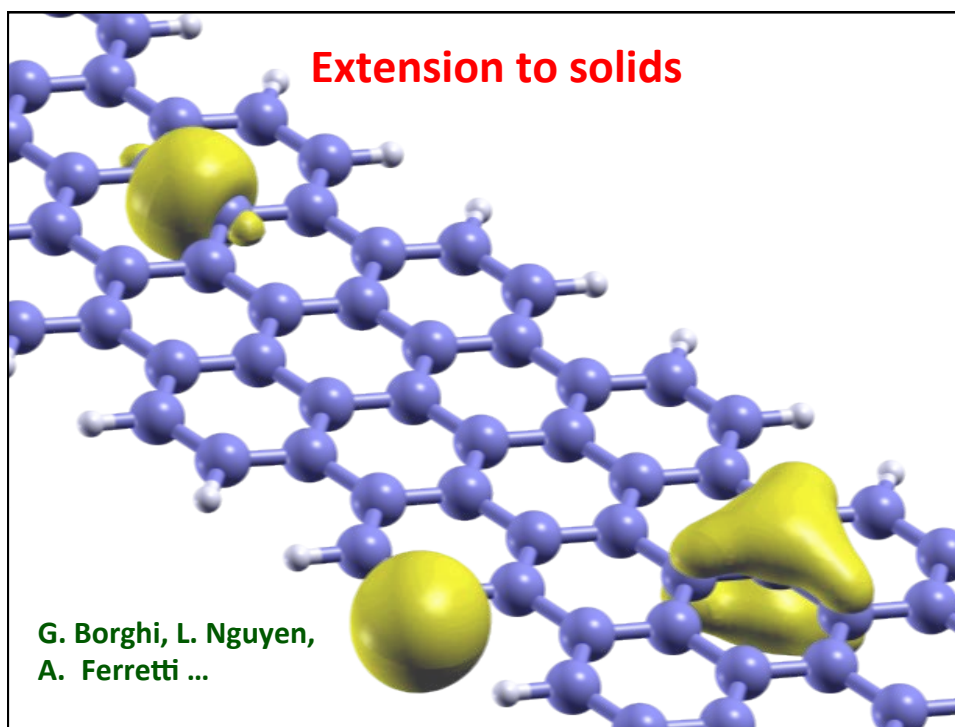
Energy levels in photovoltaics



Electron affinities: Fullerenes (eV)

	LSDA	α NK ₀	QMC	GW ₀	scGW _f	Expt.
C ₂₀	4.24	2.13	1.76(11)	3.55	2.36	2.25
C ₂₄	5.06	2.84	2.57(11)	4.19	2.88	—
C ₅₀	5.20	3.49	3.52(14)	4.75	3.73	<3.10
C ₆₀	4.27	2.64	2.23(19)	3.87	2.98	2.69
C ₇₀	4.10	2.61	2.46(11)	3.98	2.83	2.76
C ₈₀ (D _{5d})	5.00	3.91	3.25(10)	4.62	3.88	3.70
C ₈₀ (I _h)	4.56	2.99	3.90(11)	5.17	4.38	—
MAD	1.66	0.18	0.42	1.25	0.26	
RMS	0.32	0.12	0.06	0.26	0.21	
	LSDA	α NK ₀	QMC	GW ₀	scGW _f	





Moving on from DFT ?

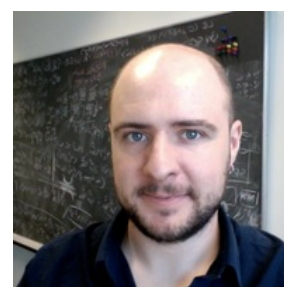
No derivative discontinuity is needed !

Easy to approximate?

Conclusions

- **Self-interaction failures in DFT**
 - constrained DFT (not discussed today)
 - DFT + onsite, intersite Hubbard
 - Koopmans' compliant functionals
- **From functional theories of the density to functional theories of the Green's function**
 - Total energy and spectral density can be independently preserved

Acknowledgments (constrained DFT, DFT+U, DFT+U(ω))



David O' Regan
(EPFL -> Trinity
College Dublin)



THEOS

THEORY AND SIMULATION
OF MATERIALS



ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Thank you!