Koopmans-compliant functionals: A reliable and efficient tool for the prediction of spectroscopic quantities

> N. Colonna, N. L. Nguyen, G. Borghi, A. Ferretti, and N. Marzari "What about U?" Trieste 20/10/2016

THEOS

THEORY AND SIMULATION Of materials



NATIONAL CENTRE OF COMPETENCE IN RESEARCH



# Outline

- Introduction
- Koopmans-compliant functionals
  - Theory and method
- Benchmarks on molecular systems
  - Spectral properties of organic molecules and small transition metal complexes
- Application to extended system
  - The band gap of semiconductors

## Kohn-Sham Density Functional Theory

$$\begin{bmatrix} -\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}[n](\mathbf{r}) \end{bmatrix} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \qquad \qquad n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$
$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d\mathbf{r} \ V_{ext}(\mathbf{r}) n(\mathbf{r})$$

Exact in principle but within approximate xc functionals



#### **Self-interaction error**

For one electron systems the interaction term should be zero:

 $E_H[\rho_1] + E_{xc}[\rho_1] = 0$ 

First SIC scheme:

$$E_{xc}^{PZ} = E_{xc}^{DFA}[n_{\uparrow}, n_{\downarrow}] + -\sum_{\alpha, \sigma} \left\{ E_{H}[n_{\alpha\sigma}] + E_{xc}^{DFA}[n_{\alpha\sigma}, 0] \right\}$$
  
Perdew and Zunger PRB **23**, 5048 (1981)

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What about U?

# Kohn-Sham Density Functional Theory

$$n(\mathbf{r}) \stackrel{|\mathbf{r}| \to \infty}{\sim} exp[-2\sqrt{2IP}|\mathbf{r}|] \qquad n(\mathbf{r}) \stackrel{|\mathbf{r}| \to \infty}{\sim} exp[-2\sqrt{2[-\varepsilon_{ho}]}|\mathbf{r}|]$$
$$IP = E(N-1) - E(N) = -\varepsilon_{ho}$$

Exact in principle but within approximate xc functionals



#### **Self-interaction error**

Self-interaction error leads to incorrect asymptotic behavior of KS potential and ultimately to the underestimation of the Ionization Potential.

! SELF-INTERACTION ERROR WELL DEFINED ONLY FOR ONE-ELECTRON SYSTEMS !

# Piece-wise linearity (PWL)

The true functional is **piecewise linear** as a function of the number of particles



Perdew et al. Phys.Rev. Lett 49, 1691 (1982)

# Piece-wise linearity (PWL)



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## Restoring the Piece-wise linearity



$$E_U = \frac{U}{2} \sum_{I,\sigma} \operatorname{Tr}[\mathbf{n}^{I\sigma} (\mathbf{1} - \mathbf{n}^{I\sigma})]$$

- <u>The energy functional</u> has an unphysical curvature
- •<u>the exact solution</u> is piecewise linear
- <u>a +U correction</u> reproduces the exact solution

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

LDA+U: The Hubbard U term is meant to correct the missing piece-wise linear behavior Cococcioni and de Gironcoli PRB **71**, 035105 (2005)

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# Imposing a generalized PWL condition

#### Can we make DFT+U idea more general?



- Our goal is to linearize the total energy when changing the occupation *f<sub>i</sub>* of **any orbital** 
  - We construct a self-interaction free mean-field theory by imposing for **every orbital** the expectation value

$$\varepsilon_i = \frac{dE}{df_i} = \langle \phi_i | \hat{H} | \phi_i \rangle$$

to be independent on its own occupation

I. Dabo, M. Cococcioni, and N. Marzari arXiv0910.2637 (2009); I. Dabo, et al. PRB 82, 115121 (2010)

### Koopmans-compliant functionals

### How do we enforce this?

What we have (Slater)

$$\Delta E_i|_S = \int_0^{f_i} \varepsilon_i^{DFA}(f) \, df = E[f_i] - E[0]$$

**What we want** (Koopmans)  $\Delta E_i|_K = f_i \varepsilon_i^{\text{ref}}$  ( $\varepsilon_i^{\text{ref}}$  to be defined)

**Koopmans-compliant**  
functional 
$$E^{KC} = E^{DFA} + \sum_{i} \left[ f_i \varepsilon_i^{\text{ref}} - \Delta E_i |_S \right]$$

For the moment we work in a **frozen orbital** picture

I. Dabo, M. Cococcioni, and N. Marzari arXiv0910.2637 (2009); I. Dabo, et al. PRB 82, 115121 (2010)



**N.B.** KC can correct also PZ  $\Rightarrow$  KPZ and KIPZ

I. Dabo, et al. PRB 82, 115121 (2010); G. Borghi et al. PRB 90, 075135 (2014)

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# Orbital relaxation: screening parameter $\alpha$ $E^{KC}[\rho, \{\rho_i\}] = E^{DFA}[\rho] + \sum_i \alpha_i \prod_i^{KC}[\rho_i]$

 $\alpha_i$  is computed imposing Koopmans' condition on the frontier orbitals



For occupied orbitals  $\alpha_i$  is computed from:

$$f_v(\alpha) = \varepsilon_{lu}^{N-1}(\alpha) - \varepsilon_{ho}^N(\alpha) = 0$$

For empty orbitals  $\alpha_i$  is computed from:

$$f_c(\alpha) = \varepsilon_{lu}^N(\alpha) - \varepsilon_{ho}^{N+1}(\alpha) = 0$$

I. Dabo, et al. PRB 82, 115121 (2010); G. Borghi et al. PRB 90, 075135 (2014)

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### IPs: G2-1(R) set: 34 molecules



G. Borghi et al. PBE 90, 075135

GW ref: C. Rostgaard et al. PRB 81, 085103 (2010)

### IPs: G2-1(R) set: 34 molecules



G. Borghi et al. PBE 90, 075135

GW ref: C. Rostgaard et al. PRB 81, 085103 (2010)

## IPs and EAs: organic molecules for photovoltaics

#### 23 molecules

![](_page_15_Figure_2.jpeg)

N.L. Nguyen et al. PRL 114, 166405 (2015)

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# IPs and EAs: organic molecules for photovoltaics

#### 23 molecules

Mean absolute Error			
	IP (eV)	EA (eV)	H-L GAP(eV)
PBE	2.28	1.57	2.20
PZ[PBE]	1.23	1.72	1.35
KI[PBE]	0.45	0.22	0.32
scfGW	0.31	0.27	0.28
KI[PZ]	0.24	0.17	0.20

N.L. Nguyen *et al.* PRL **114**, 166405 (2015)

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![](_page_17_Figure_0.jpeg)

![](_page_18_Figure_0.jpeg)

![](_page_19_Figure_0.jpeg)

## Difficult affinities: DNA/RNA basis

![](_page_20_Figure_1.jpeg)

The extra electron added to a DNA base can either occupy a stable, but very weakly bound, "dipole-bound" (DB) anionic state or a valence anti-bounding (VB) state. KIPZ correctly predicts the order and the energies for these states.

#### **VB-MAE (eV)**

![](_page_20_Figure_4.jpeg)

N.L. Nguyen *et al.* JCTC **12**, 3948 (2016); CCSD(T): Roca-Sanjuan *et al.* J. Chem. Phys **125**, 084302 (2008)

Toward complex systems: orbital dependent screening

$$E^{KC}[\rho, \{\rho_i\}] = E^{DFA}[\rho] + \sum_i \frac{\alpha_i}{\alpha_i} \prod_i^{KC}[\rho_i]$$

 $\alpha_i$  is computed imposing Koopmans' condition on the frontier orbitals

$$f_v(\alpha) = \varepsilon_{lu}^{N-1}(\alpha) - \varepsilon_{ho}^N(\alpha) = 0$$
 valence manifold

$$f_c(\alpha) = \varepsilon_{lu}^N(\alpha) - \varepsilon_{ho}^{N+1}(\alpha) = 0$$

conduction manifold

Only two values of *α*. One for valence and one for conduction states Requires calculations at N, N-1 and N+1 electrons

# We would like to have a general and efficient orbital dependent scheme!

Orbital relaxation: linear response (I)  $\Pi_{i}^{rKI} = f_{i} \left\{ E_{DFA}[\rho^{f_{i}=1}] - E_{DFA}[\rho^{f_{i}=0}] \right\} - E_{DFA}[\rho] + E_{DFA}[\rho^{f_{i}=0}]$ 

Expanding the DFA energy wrt  $f_i$  around some reference occupation  $f_{ref}$  ...

## Orbital relaxation: linear response (I)

$$\Pi_{i}^{rKI} = f_{i} \left\{ E_{DFA}[\rho^{f_{i}=1}] - E_{DFA}[\rho^{f_{i}=0}] \right\} - E_{DFA}[\rho] + E_{DFA}[\rho^{f_{i}=0}] = \frac{1}{2} f_{i}(1 - f_{i}) \frac{d^{2}E_{DFA}}{df_{i}^{2}} \Big|_{f_{ref}} + o(f_{i}^{3})$$
 KI correction to second in the occupation, in

ond order in the occupation, **including** orbitals relaxation

## Orbital relaxation: linear response (I)

$$\Pi_{i}^{rKI} = f_{i} \left\{ E_{DFA}[\rho^{f_{i}=1}] - E_{DFA}[\rho^{f_{i}=0}] \right\} - E_{DFA}[\rho] + E_{DFA}[\rho^{f_{i}=0}]$$

$$= \frac{1}{2} f_{i}(1 - f_{i}) \left. \frac{d^{2}E_{DFA}}{df_{i}^{2}} \right|_{f_{ref}} + o(f_{i}^{3}) \qquad \text{KI correction to second order in the occupation, including orbitals relaxation}$$

 $\frac{d^2 E_{DFA}}{df_i^2} = \frac{d\varepsilon_i}{df_i} = \langle \varphi_i | \frac{dv_{Hxc}}{df_i} | \varphi_i \rangle = \int d\mathbf{r} \, d\mathbf{r}' \, n_i(\mathbf{r}) f_{Hxc}[\rho](\mathbf{r}, \mathbf{r}') \frac{d\rho(\mathbf{r}')}{df_i}$ 

## Orbital relaxation: linear response (I)

$$\Pi_{i}^{rKI} = f_{i} \left\{ E_{DFA}[\rho^{f_{i}=1}] - E_{DFA}[\rho^{f_{i}=0}] \right\} - E_{DFA}[\rho] + E_{DFA}[\rho^{f_{i}=0}]$$

$$= \frac{1}{2} f_{i}(1 - f_{i}) \left. \frac{d^{2}E_{DFA}}{df_{i}^{2}} \right|_{f_{ref}} + o(f_{i}^{3}) \qquad \text{KI correction to second in the occupation, inclusion}$$

ond order ncluding orditals relaxation

$$\frac{d^2 E_{DFA}}{df_i^2} = \frac{d\varepsilon_i}{df_i} = \langle \varphi_i | \frac{dv_{Hxc}}{df_i} | \varphi_i \rangle = \int d\mathbf{r} \, d\mathbf{r}' \, n_i(\mathbf{r}) f_{Hxc}[\rho](\mathbf{r}, \mathbf{r}') \frac{d\rho(\mathbf{r}')}{df_i}$$

$$\frac{d\rho(\mathbf{r})}{df_{i}} = n_{i}(\mathbf{r}) + \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r})}{\delta v_{KS}(\mathbf{r}')} \frac{dv_{KS}(\mathbf{r}')}{df_{i}} \qquad \text{Two contributions in the derivative:} 
= n_{i}(\mathbf{r}) + \int d\mathbf{r}' \chi_{0}(\mathbf{r}, \mathbf{r}') \frac{dv_{Hxc}(\mathbf{r}')}{df_{i}} \qquad \text{Explicit dependence on } f_{i} 
= n_{i}(\mathbf{r}) + \int d\mathbf{r}' \left[\chi_{0} f_{Hxc}\right]_{(\mathbf{r},\mathbf{r}')} \frac{d\rho(\mathbf{r}')}{df_{i}} = n_{i}(\mathbf{r}) + \int d\mathbf{r}' \left[\chi_{f_{Hxc}}\right]_{(\mathbf{r},\mathbf{r}')} n_{i}(\mathbf{r}')$$

**Dyson-like equation** for the derivative of the orbital density

# Orbital relaxation: linear response (II)

#### **Relaxed** and **Unrelaxed** Koopmans corrections

$$\Pi_{i}^{(2),rKI} = \frac{1}{2} f_{i}(1-f_{i}) \int d\mathbf{r} d\mathbf{r}' n_{i}(\mathbf{r}) \left[\tilde{\epsilon}^{-1} f_{Hxc}\right]_{(\mathbf{r},\mathbf{r}')} n_{i}(\mathbf{r}') \qquad \tilde{\epsilon}^{-1} = \mathbf{I} + f_{Hxc}\chi$$
$$\Pi_{i}^{(2),uKI} = \frac{1}{2} f_{i}(1-f_{i}) \int d\mathbf{r} d\mathbf{r}' n_{i}(\mathbf{r}) \left[f_{Hxc}\right]_{(\mathbf{r},\mathbf{r}')} n_{i}(\mathbf{r}')$$

We can define the screening parameter as the ratio between the two

$$\alpha_{i} = \frac{\prod_{i}^{(2),rKI}}{\prod_{i}^{(2),uKI}} = 1 + \frac{\int d\mathbf{r} d\mathbf{r}' n_{i}(\mathbf{r}) \left[f_{Hxc} \chi f_{Hxc}\right]_{(\mathbf{r},\mathbf{r}')} n_{i}(\mathbf{r}')}{\int d\mathbf{r} d\mathbf{r}' n_{i}(\mathbf{r}) f_{Hxc}(\mathbf{r},\mathbf{r}') n_{i}(\mathbf{r}')} = 1 + \beta_{i}$$

- Relaxation leads to a **screening** of the Koopmans correction
- Dielectric function defined using Hxc kernel instead of the Coulomb kernel only
- Orbital-dependent formulation in a natural way
- The standard screening parameter is recovered considering the dielectric function as a scalar such that  $\tilde{\epsilon}^{-1} = \alpha$
- Efficiently implemented trough DFPT:  $\Delta V_i^{bare}(\mathbf{r}) = \int d\mathbf{r}' f_{Hxc}(\mathbf{r}, \mathbf{r}') n_i(\mathbf{r}')$

Transition metal complexes: Ionization Potentials

![](_page_27_Figure_1.jpeg)

GW ref: Korbel *et al*. JCTC **10**, 3934 (2014)

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### The importance to be localized: extended systems

The KC functionals are minimized by variational, localized orbitals

![](_page_29_Figure_2.jpeg)

![](_page_29_Figure_3.jpeg)

Unitary Transformation

![](_page_29_Picture_5.jpeg)

#### **Ensemble-DFT** minimization

$$E_{gs}^{KC} = \min_{\{\phi_i\}} \left( \min_{U} E^{KC}[\{\phi_i\}, U] \right)$$

**Inner-loop**: minimization over unitary transformation *U* 

**Outern-loop**: minimization over occupied-orbital wavefunctons

Inner-loop enforce **Pederson condition**:  $\int d\mathbf{r} \ \phi_j^*(\mathbf{r}) \left[ v_j^{ODD}(\mathbf{r}) - v_i^{ODD}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = 0$ 

Pederson condition usually leads to a **localization** of the orbitals

Localization is necessary to have non-vanishing Koopmans corrections!

# Fundamental band-gap of semiconductors

![](_page_30_Figure_1.jpeg)

GW refs.: M. Shinshkin, and G. Kresse PRB 75, 235102 (2007) W. Chen, and A. Pasquarello PRB 92, 041115 (2015)

# Conclusions

- Koopmans-compliant functionals are able to deliver accurate spectroscopic properties imposing a generalized constraint of PWL
- Calculated IPs, EAs, and fundamental band gaps of molecules and extended systems agree well with experiment with error comparable or smaller than that of GW.
- Being a functional approach, forces and other derivatives are readily accessible.
- The computational costs are much reduced with respect to many-body technique:

 $\propto N_v \times {
m DFT}$  (small systems, where FFT dominates)  $\propto {
m DFT}$  (large systems, where orthogonalization dominates)

# Acknowledgements

![](_page_32_Picture_1.jpeg)

**Ngoc Linh Nguyen** THEOS EPFL

![](_page_32_Picture_3.jpeg)

Giovanni Borghi

![](_page_32_Picture_5.jpeg)

Andrea Ferretti S3-NANO-CNR, \_\_\_\_\_Modena

![](_page_32_Picture_7.jpeg)

Matteo Cococcioni THEOS EPFL

![](_page_32_Picture_9.jpeg)

Nicola Marzari THEOS EPFL

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![](_page_33_Picture_1.jpeg)

**Ngoc Linh Nguyen** THEOS EPFL

![](_page_33_Picture_3.jpeg)

Giovanni Borghi

![](_page_33_Picture_5.jpeg)

Andrea Ferretti S3-NANO-CNR, \_\_\_\_\_Modena

![](_page_33_Picture_7.jpeg)

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![](_page_33_Picture_8.jpeg)

Nicola Marzari THEOS EPFL

Thank you for the attention

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What about U?