



PSI

Center for Scientific Computing,
Theory and Data

Koopmans functionals

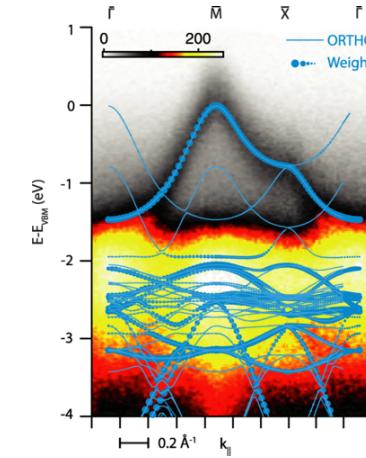
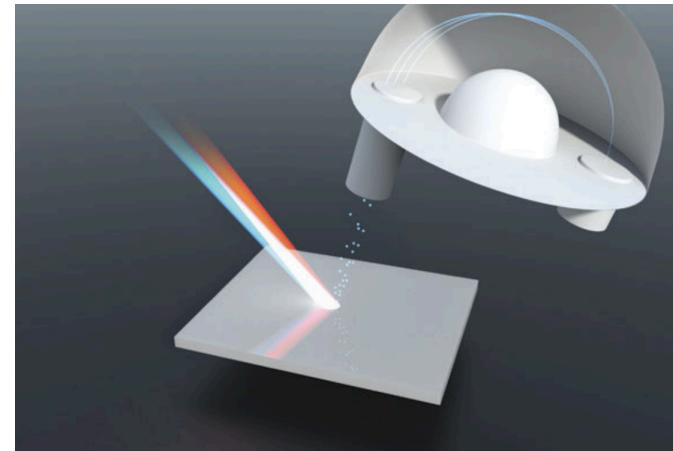
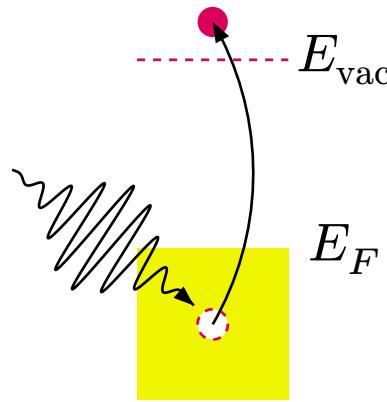
How satisfying piecewise linearity can yield reliable band structures

Edward Linscott

Psi-k, 27 August 2025

Predicting spectral properties

Spectral properties are fundamental to understanding materials...

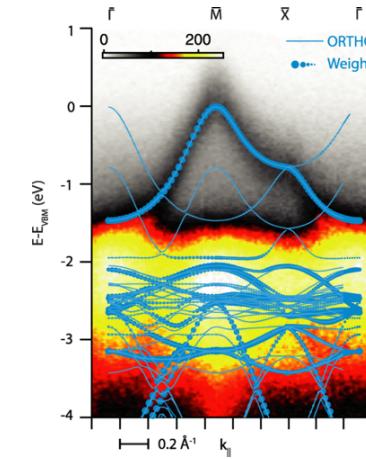
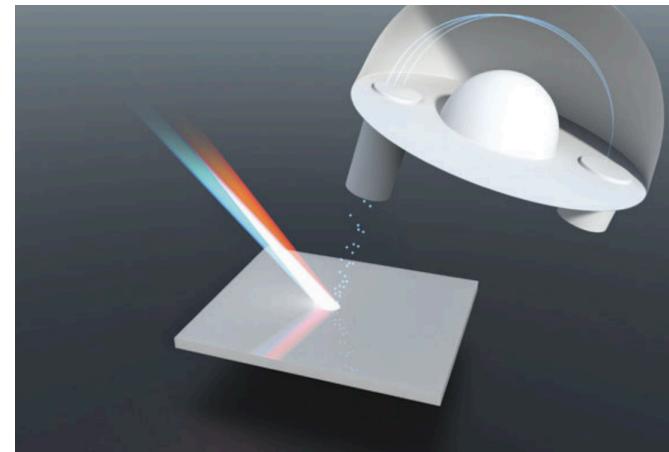
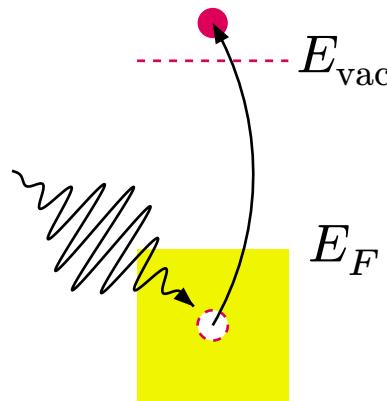


¹M. Puppin et al. *Phys. Rev. Lett.* **124**, 206402 (2020)

Predicting spectral properties

Predicting spectral properties

Spectral properties are fundamental to understanding materials...



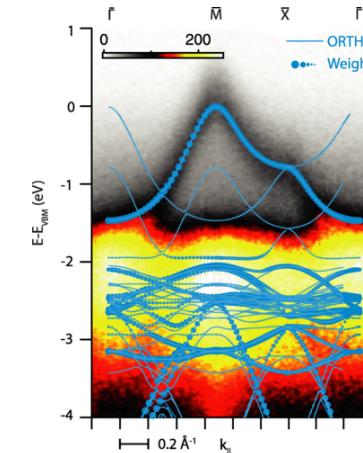
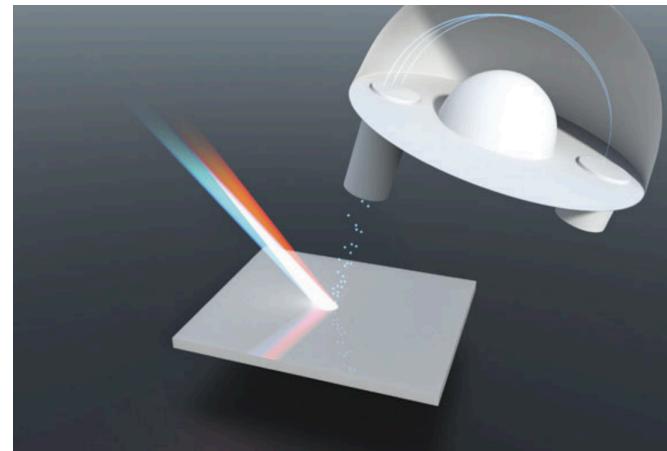
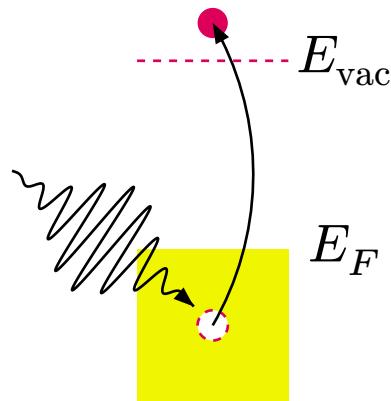
... but how can we routinely compute them?

¹M. Puppin et al. *Phys. Rev. Lett.* **124**, 206402 (2020)

Predicting spectral properties

Predicting spectral properties

Spectral properties are fundamental to understanding materials...



... but how can we routinely compute them?

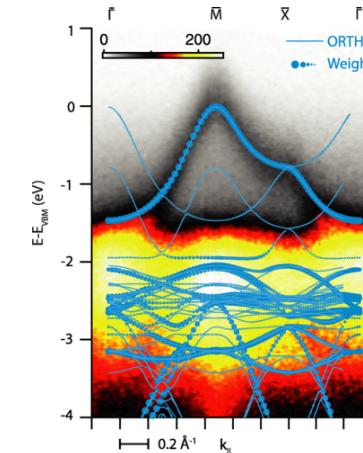
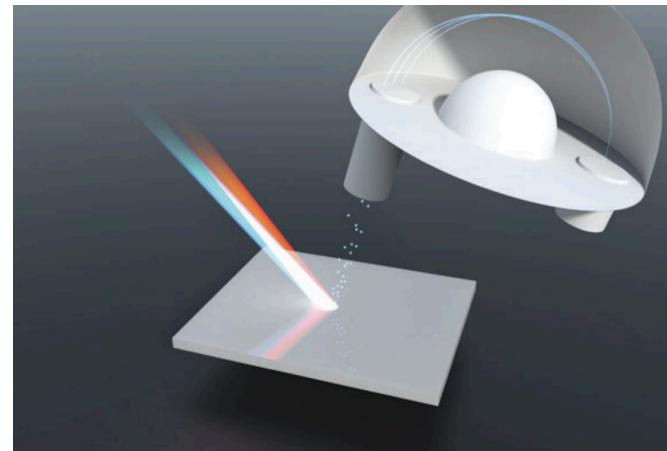
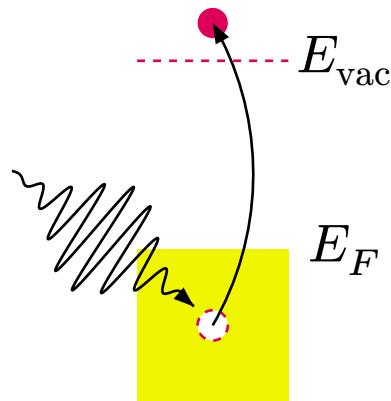
- GW: accurate, expensive, often ill-behaved, diagrammatic
- DFT: plagued by systematic errors

¹M. Puppin *et al.* *Phys. Rev. Lett.* **124**, 206402 (2020)

Predicting spectral properties

Predicting spectral properties

Spectral properties are fundamental to understanding materials...



... but how can we routinely compute them?

- GW: accurate, expensive, often ill-behaved, diagrammatic
- DFT: plagued by systematic errors

¹M. Puppin *et al.* *Phys. Rev. Lett.* **124**, 206402 (2020)

Predicting spectral properties

 Koopmans functionals: cure systematic errors in DFT → a functional that can accurately predict single-particle excitations

The failures of DFT

Total energy differences vs. eigenvalues

We all know that DFT underestimates the band gap. But why?

Total energy differences vs. eigenvalues

We all know that DFT underestimates the band gap. But why?

The exact Green's function has poles that correspond to total energy differences

$$\varepsilon_i = \begin{cases} E(N) - E_i(N-1) & \text{if } i \in \text{occ} \\ E_i(N+1) - E(N) & \text{if } i \in \text{emp} \end{cases}$$

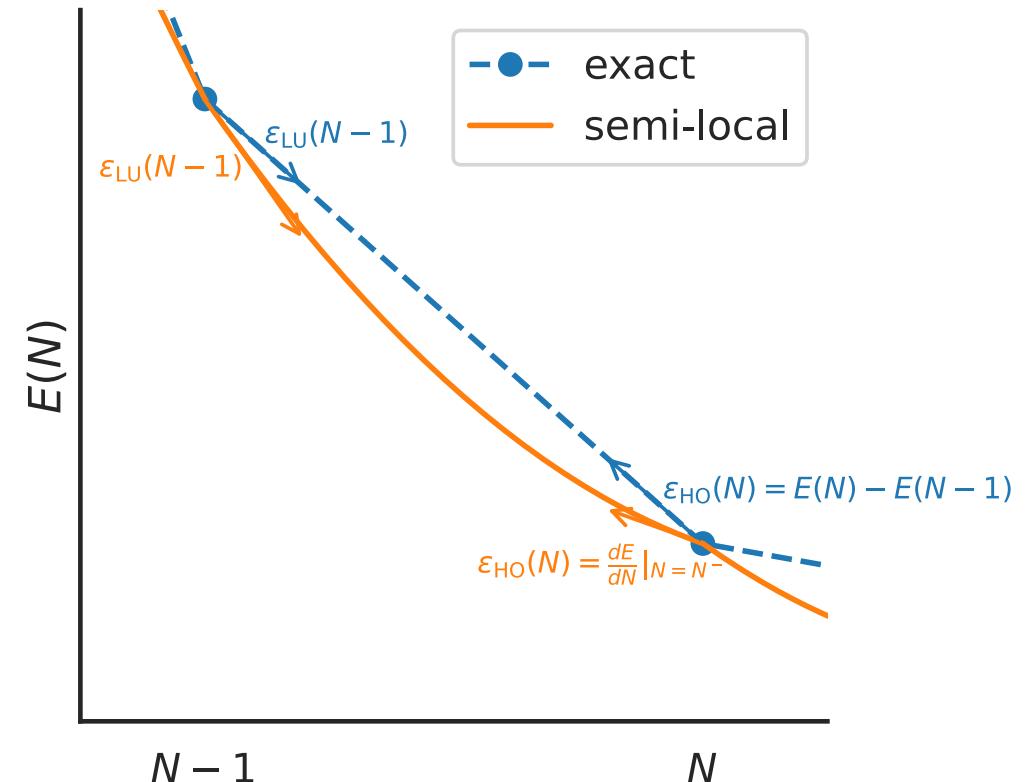
Total energy differences vs. eigenvalues

We all know that DFT underestimates the band gap. But why?

The exact Green's function has poles that correspond to total energy differences

$$\varepsilon_i = \begin{cases} E(N) - E_i(N-1) & \text{if } i \in \text{occ} \\ E_i(N+1) - E(N) & \text{if } i \in \text{emp} \end{cases}$$

but DFT does *not*



**Core idea: impose this condition on
DFT**

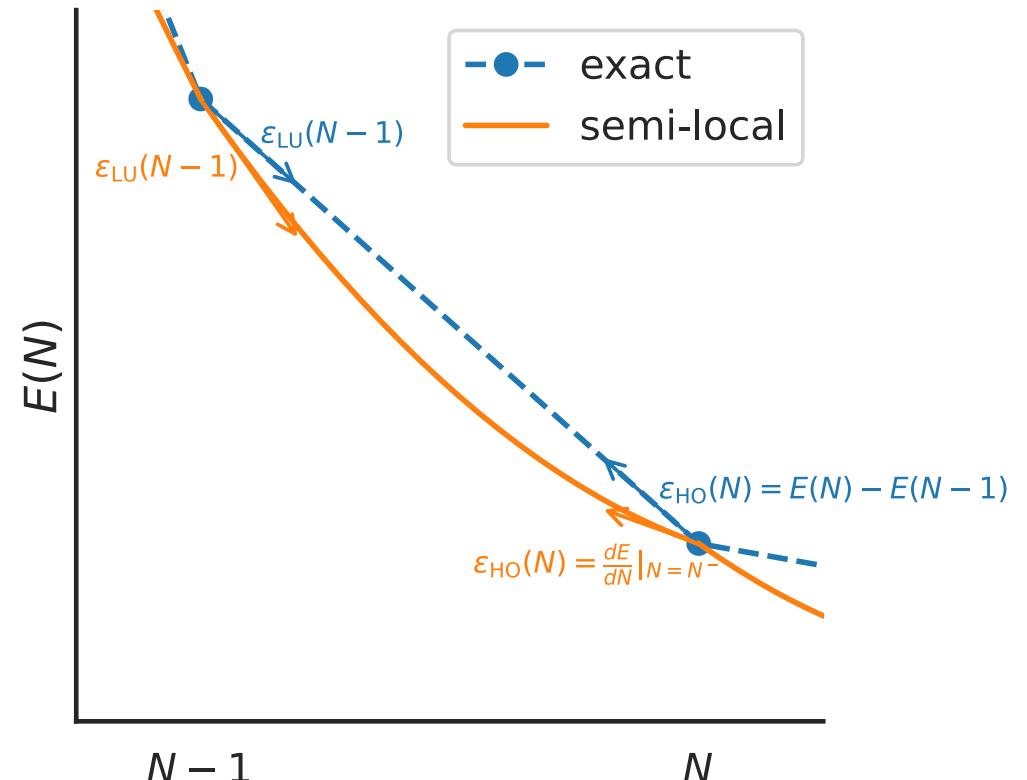
Imposing generalised piecewise linearity

Formally, every orbital i should have an eigenenergy

$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | \hat{H} | \varphi_i \rangle = \frac{dE}{df_i}$$

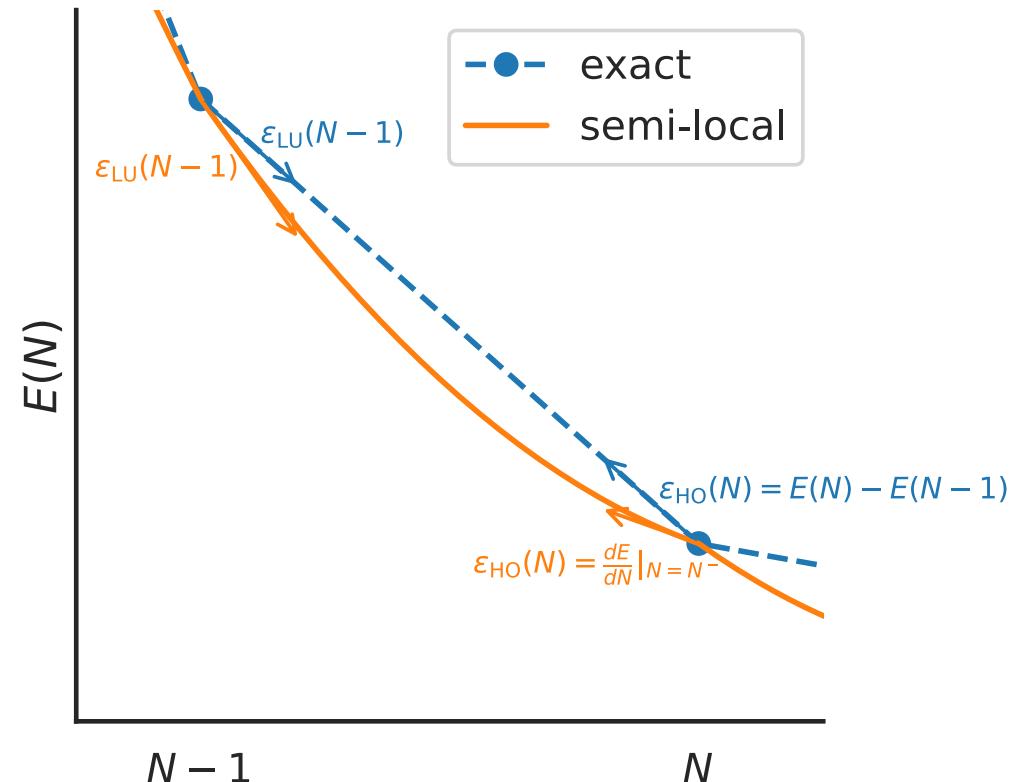
that is

- independent of f_i
- equal to ΔE of explicit electron addition/
removal



Imposing generalised piecewise linearity

$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

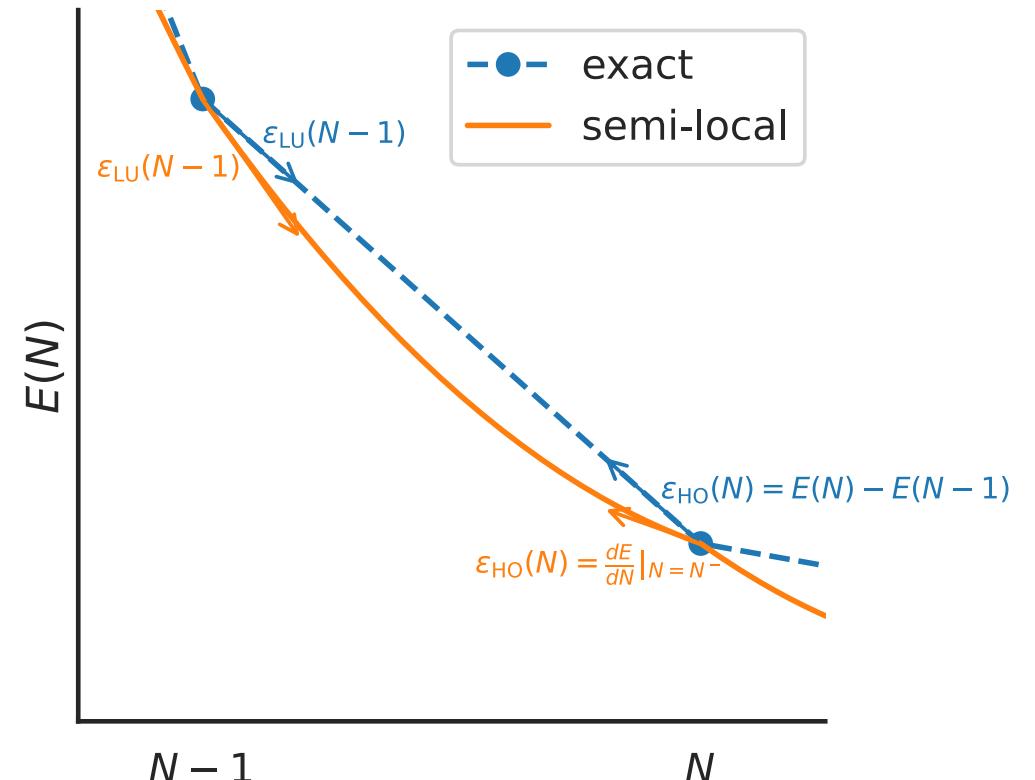


Imposing generalised piecewise linearity

$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

$$+ \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

removes dependence on f_i



Imposing generalised piecewise linearity

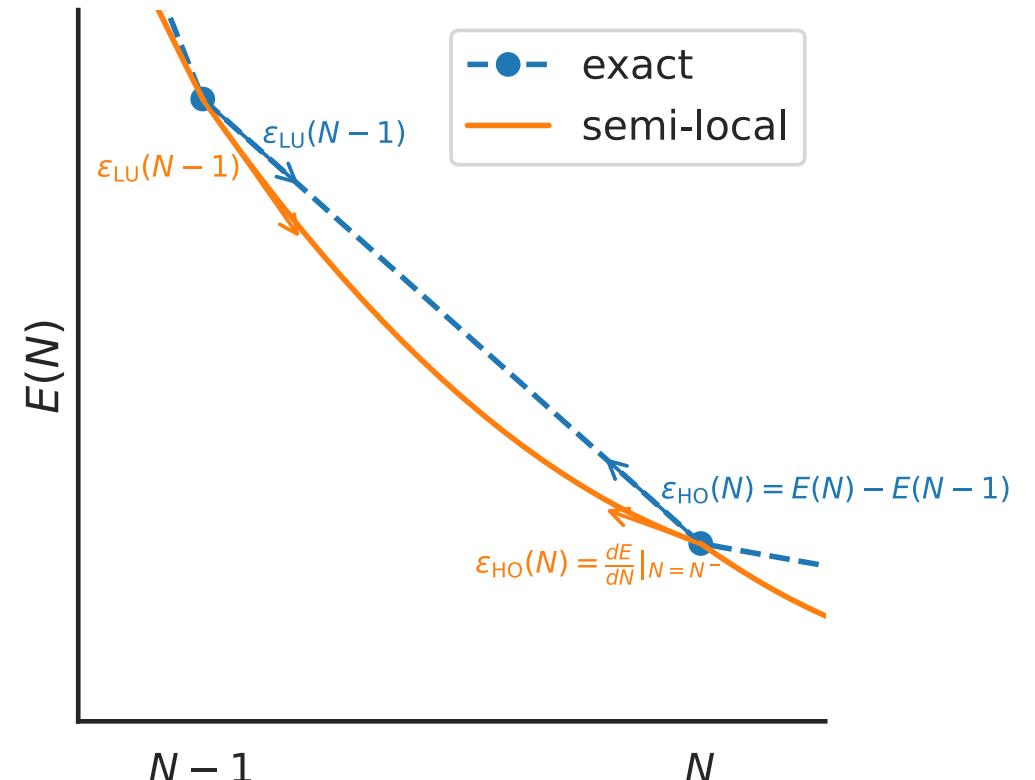
$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

$$+ \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right.$$

removes dependence on f_i

$$\left. + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

restores linear dependence on f_i



Comparison with DFT+*U* (and BLOR)

DFT+*U*

*seeks to
correct...*

in practice...

*correction
applied to...*

*orbitals defined
by...*

*parametrised
by...*

Koopmans

Comparison with DFT+*U* (and BLOR)

DFT+ <i>U</i>	Koopmans
<i>seeks to correct...</i>	erroneous curvature in total energies w.r.t. N
<i>in practice...</i>	
<i>correction applied to...</i>	
<i>orbitals defined by...</i>	
<i>parametrised by...</i>	

Comparison with DFT+*U* (and BLOR)

DFT+ <i>U</i>	Koopmans
<i>seeks to correct...</i>	erroneous curvature in total energies w.r.t. N
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)
<i>correction applied to...</i>	
<i>orbitals defined by...</i>	
<i>parametrised by...</i>	

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous curvature in total energies w.r.t. N	erroneous curvature in total energies w.r.t. $f_i \forall i$
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	
<i>correction applied to...</i>		
<i>orbitals defined by...</i>		
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous curvature in total energies w.r.t. N	erroneous curvature in total energies w.r.t. $f_i \forall i$
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on f_i and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>		
<i>orbitals defined by...</i>		
<i>parametrised by...</i>		

Making the functional tractable

$$E^{\text{KI}}[\{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

Making the functional tractable

$$\begin{aligned}
 E^{\text{KI}}[\{\rho_i\}] &= E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right) \\
 &= E^{\text{DFT}}[\rho] + \sum_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}
 \end{aligned}$$

Making the functional tractable

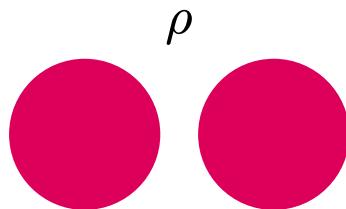
$$\begin{aligned}
 E^{\text{KI}}[\{\rho_i\}] &= E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right) \\
 &= E^{\text{DFT}}[\rho] + \sum_i \left\{ - \left(E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right) + f_i \left(E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right) \right\}
 \end{aligned}$$

cannot evaluate directly cannot evaluate directly cannot evaluate directly

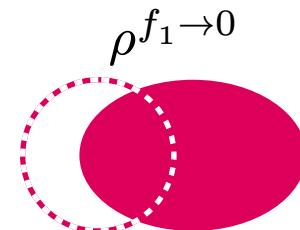
Making the functional tractable

$$\begin{aligned}
 E^{\text{KI}}[\{\rho_i\}] &= E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right) \\
 &= E^{\text{DFT}}[\rho] + \sum_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}
 \end{aligned}$$

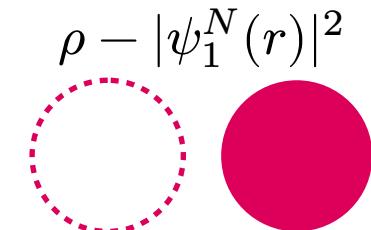
cannot evaluate directly cannot evaluate directly cannot evaluate directly



2-electron solution

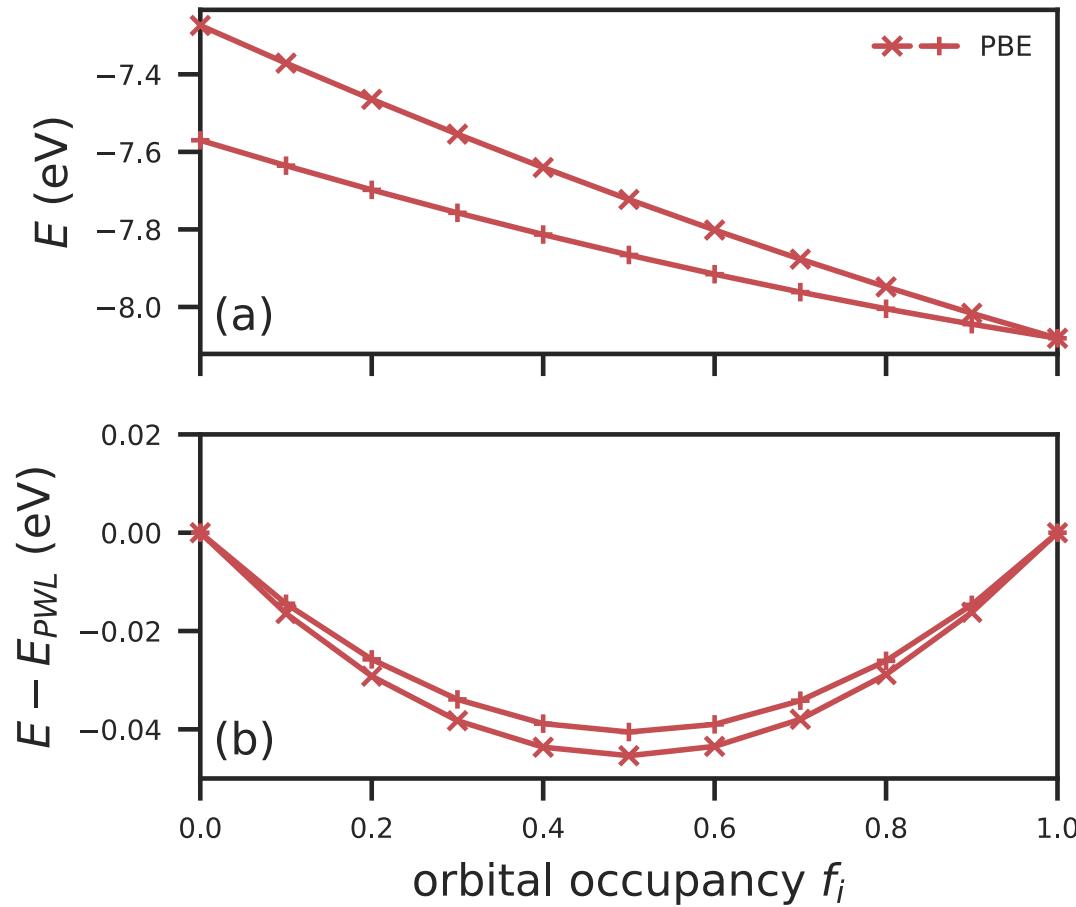


what we'd like to evaluate

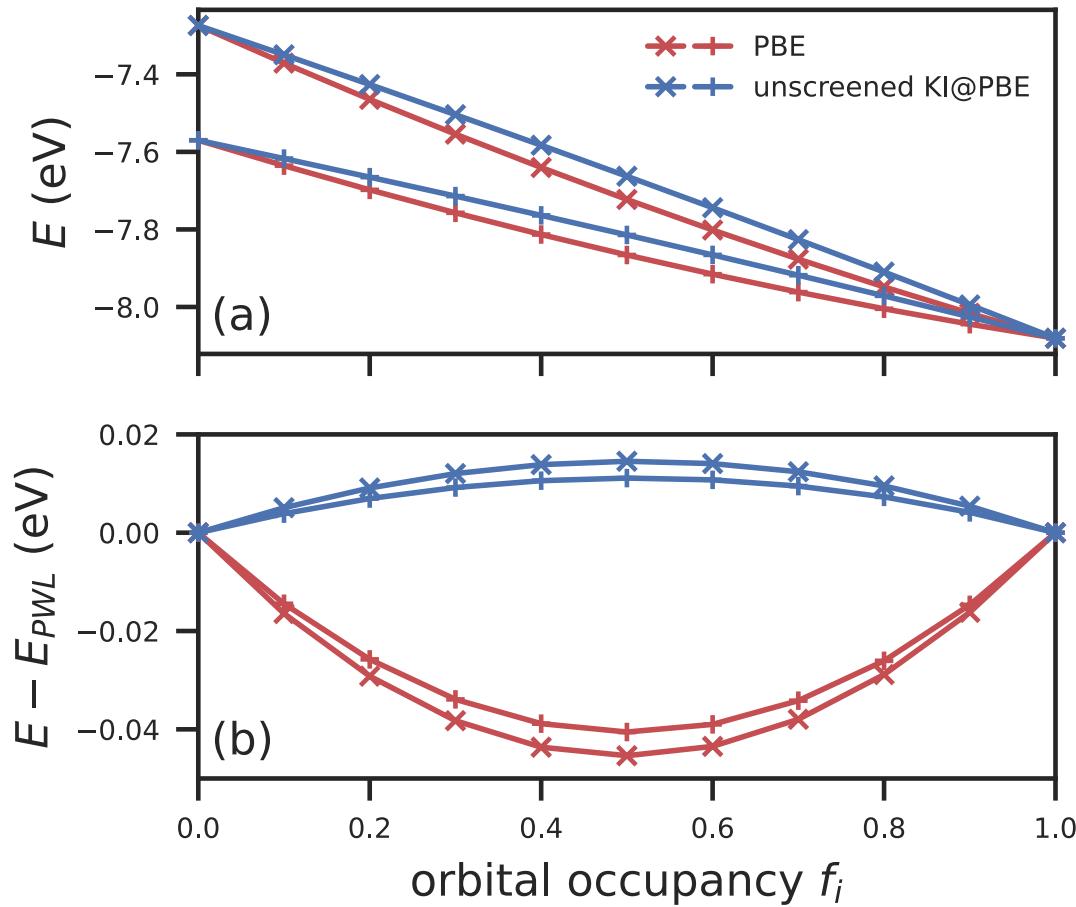


what we can quickly evaluate

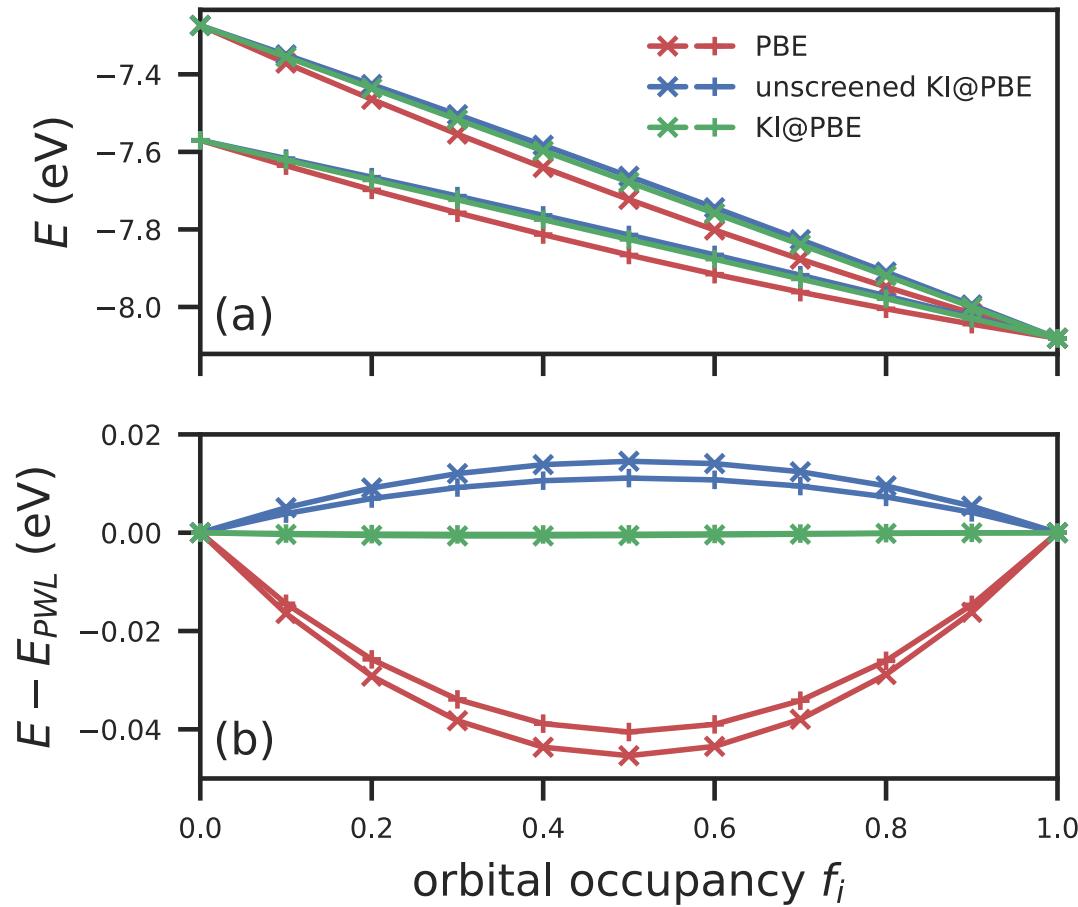
Making the functional tractable



Making the functional tractable



Making the functional tractable



Making the functional tractable

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

$$+ \sum_i \alpha_i \{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \}$$

Making the functional tractable

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

$$+ \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

uses frozen orbitals uses frozen orbitals uses frozen orbitals

Making the functional tractable

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

$$+ \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

screening parameter
uses frozen orbitals
uses frozen orbitals
uses frozen orbitals

Making the functional tractable

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

$$+ \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

which is easy to evaluate e.g.

$$H_{ij}^{\text{KI}} = \langle \varphi_j | \hat{h}^{\text{DFT}} + \alpha_i \hat{v}_i^{\text{KI}} | \varphi_i \rangle \quad \hat{v}_i^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$

Making the functional tractable

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

$$+ \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

which is easy to evaluate e.g.

$$H_{ij}^{\text{KI}} = \langle \varphi_j | \hat{h}^{\text{DFT}} + \alpha_i \hat{v}_i^{\text{KI}} | \varphi_i \rangle \quad \hat{v}_i^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$

Screening parameters *not* a fitting parameter!

Orbital-density dependence

The potential is orbital-density-dependent!

$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$

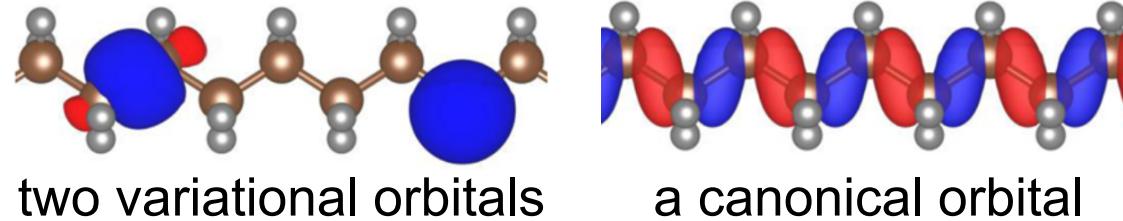
¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Orbital-density dependence

The potential is orbital-density-dependent!

$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$



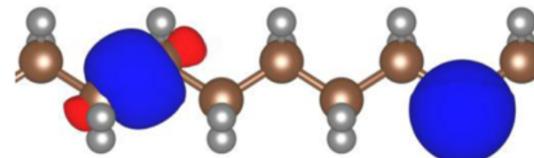
¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

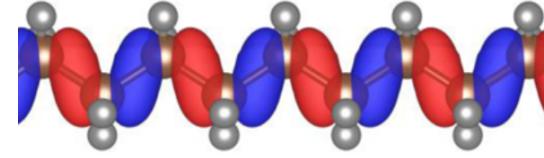
Orbital-density dependence

The potential is orbital-density-dependent!

$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$



two variational orbitals



a canonical orbital

- minimisation gives localised orbitals, so we can use MLWFs¹

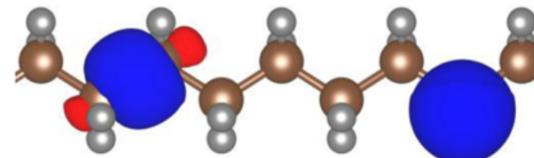
¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

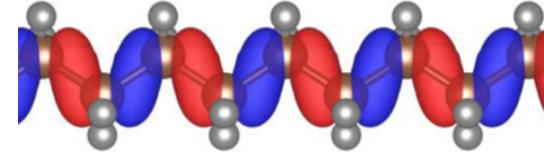
Orbital-density dependence

The potential is orbital-density-dependent!

$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$



two variational orbitals



a canonical orbital

- minimisation gives localised orbitals, so we can use MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}

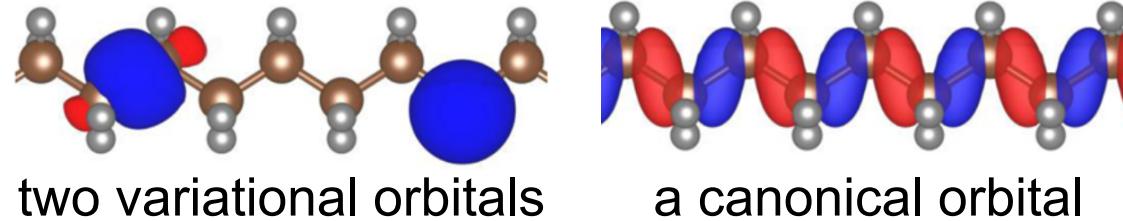
¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Orbital-density dependence

The potential is orbital-density-dependent!

$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$



- minimisation gives localised orbitals, so we can use MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}
- we have a natural generalisation of DFT towards spectral functional theory²

¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

To summarise...

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

- an orbital-by-orbital correction to DFT
- screening parameters
- orbital-density-dependence
- total energy unchanged!

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
<i>seeks to correct...</i>	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>		
<i>orbitals defined by...</i>		
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	
<i>orbitals defined by...</i>		
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	the entire system
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	the entire system
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. canonical orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	the entire system
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. canonical orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on variational orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	the entire system
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>		

Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. canonical orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on variational orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	the entire system
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>	$\{U_I\}$	

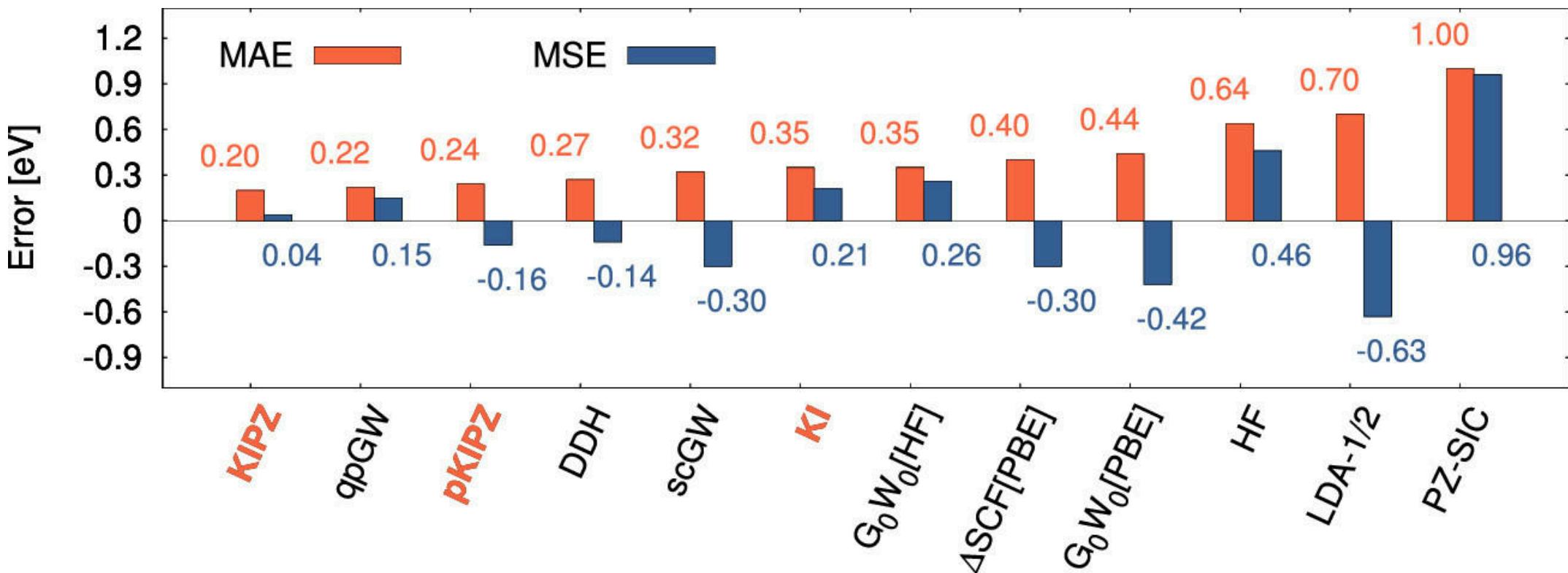
Comparison with DFT+ U (and BLOR)

	DFT+ U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. canonical orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local populations (BLOR does so more faithfully)	removes dependence of ε_i on variational orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>	selected subspaces (e.g. 3d orbitals)	the entire system
<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>	$\{U_I\}$	$\{\alpha_i\}$

Results

Molecular systems

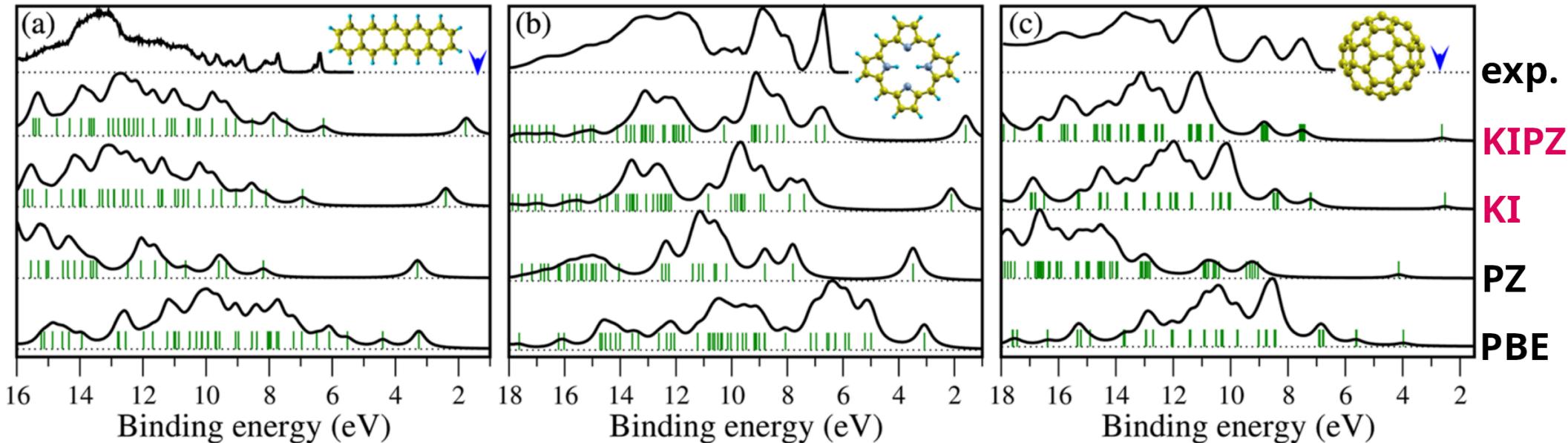
Ionisation potentials¹



¹N. Colonna et al. J. Chem. Theory Comput. **15**, 1905 (2019)

Molecular systems

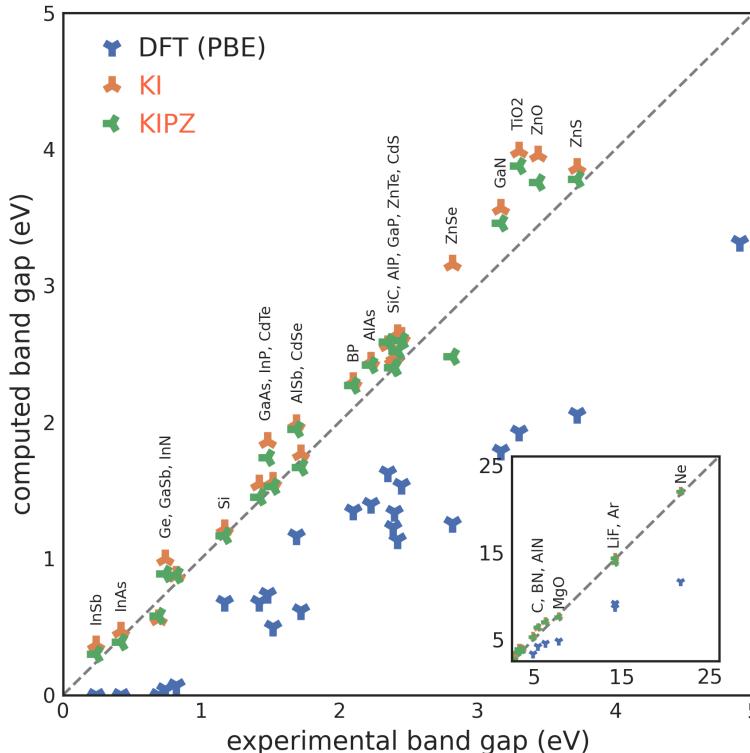
UV photoemission spectra¹



¹N. L. Nguyen *et al.* *Phys. Rev. Lett.* **114**, 166405 (2015)

Extended systems

Prototypical semiconductors and insulators¹

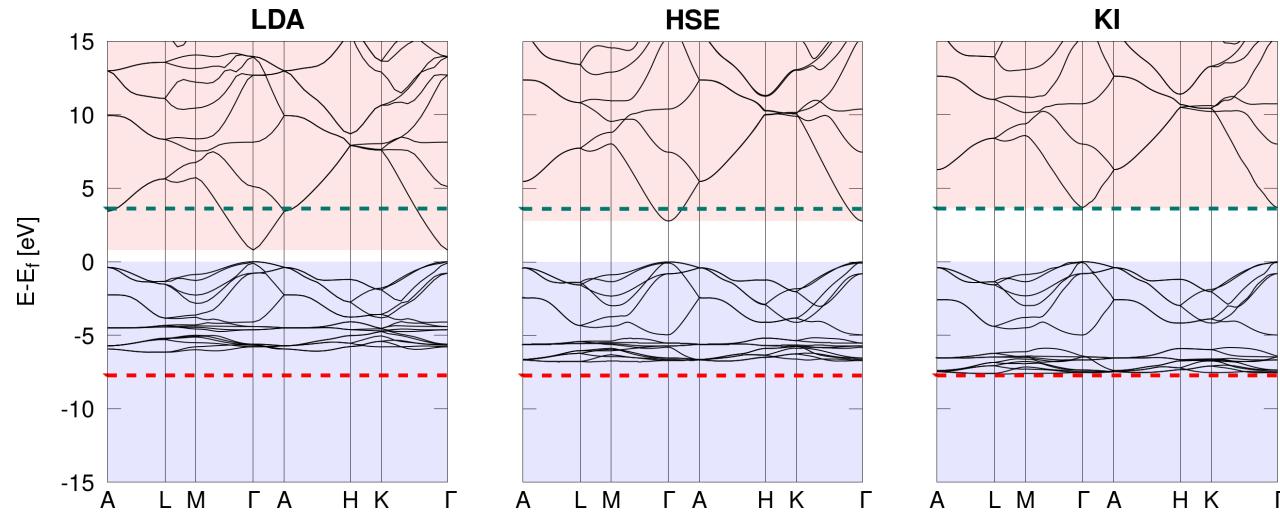


	PBE	G_0W_0	KI	KIPZ	$QSG\tilde{W}$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

Extended systems

ZnO¹

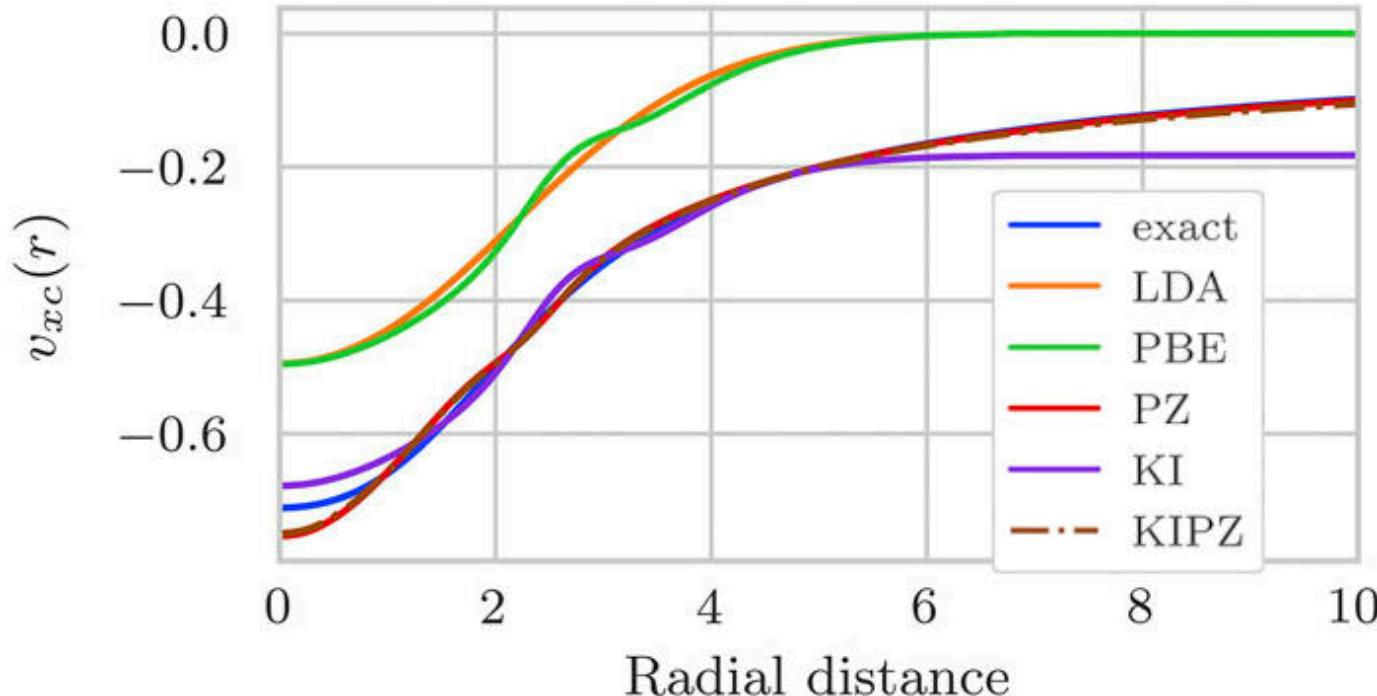


	LDA	HSE	GW_0	$scG\tilde{W}$	KI	exp
E_{gap}	0.79	2.79	3.0	3.2	3.68	3.60
$\langle \varepsilon_d \rangle$	-5.1	-6.1	-6.4	-6.7	-6.93	-7.5 to -8.81
Δ	4.15				4.99	5.3

¹N. Colonna et al. *J. Chem. Theory Comput.* **18**, 5435 (2022)

Model systems

Hooke's atom¹



¹Y. Schubert *et al.* *J. Chem. Phys.* **158**, 144113 (2023)

Caveats

Limitations

- only valid for systems with $E_{\text{gap}} > 0$

Limitations

- only valid for systems with $E_{\text{gap}} > 0$
- empty state localisation in the bulk limit

Limitations

- only valid for systems with $E_{\text{gap}} > 0$
- empty state localisation in the bulk limit
- can break crystal point group symmetry

Resonance with other efforts

- Wannier transition state method of Anisimov and Kozhevnikov¹
- Optimally-tuned range-separated hybrid functionals of Kronik, Pasquarello, and others²
- Ensemble DFT of Kraisler and Kronik³
- Koopmans-Wannier method of Wang and co-workers⁴
- Dielectric-dependent hybrid functionals of Galli and co-workers⁵
- Scaling corrections of Yang and co-workers⁶

¹V. I. Anisimov *et al.* *Phys. Rev. B* **72**, 75125 (2005)

²L. Kronik *et al.* *J. Chem. Theory Comput.* **8**, 1515–1531 (2012), D. Wing *et al.* *Proc. Natl. Acad. Sci.* **118**, e2104556118 (2021)

³E. Kraisler *et al.* *Phys. Rev. Lett.* **110**, 126403 (2013)

⁴J. Ma *et al.* *Sci. Rep.* **6**, 24924 (2016)

⁵J. H. Skone *et al.* *Phys. Rev. B* **93**, 235106 (2016)

⁶C. Li *et al.* *Natl. Sci. Rev.* **5**, 203–215 (2018)

Extensions

Non-collinear spin

Non-collinear spin

$$\rho_i(\mathbf{r})$$

¹A. Marrazzo *et al.* *Phys. Rev. Res.* **6**, 33085 (2024)

Non-collinear spin

$$\rho_i(\mathbf{r}) \rightarrow \boldsymbol{\rho}_i(\mathbf{r}) = (\rho_i(\mathbf{r}), m_i^x(\mathbf{r}), m_i^y(\mathbf{r}), m_i^z(\mathbf{r}))$$

¹A. Marrazzo *et al.* *Phys. Rev. Res.* **6**, 33085 (2024)

Non-collinear spin

$$\rho_i(\mathbf{r}) \rightarrow \rho_i(\mathbf{r}) = (\rho_i(\mathbf{r}), m_i^x(\mathbf{r}), m_i^y(\mathbf{r}), m_i^z(\mathbf{r}))$$

e.g. for the corrective potential

$$v_i^{\text{qKI}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_i(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \rho_i(\mathbf{r}') + (1 - f_i) \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \rho_i(\mathbf{r}')$$

¹A. Marrazzo *et al.* *Phys. Rev. Res.* **6**, 33085 (2024)

Non-collinear spin

$$\rho_i(\mathbf{r}) \rightarrow \boldsymbol{\rho}_i(\mathbf{r}) = (\rho_i(\mathbf{r}), m_i^x(\mathbf{r}), m_i^y(\mathbf{r}), m_i^z(\mathbf{r}))$$

e.g. for the corrective potential

$$v_i^{\text{qKI}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_i(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \rho_i(\mathbf{r}') + (1 - f_i) \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \rho_i(\mathbf{r}')$$

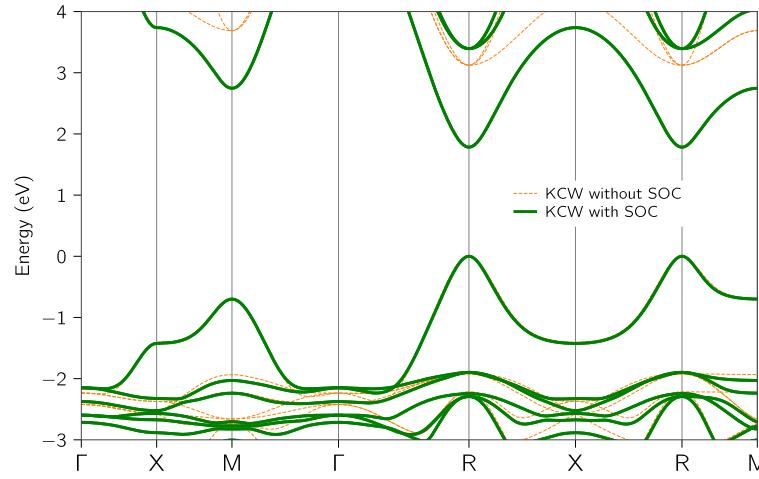
↓

$$v_i^{\text{qKI}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \boldsymbol{\rho}_i(\mathbf{r}) \mathbb{F}_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\rho}_i(\mathbf{r}') \sigma_0 + (1 - f_i) \sum_{\alpha} \int d\mathbf{r}' [\mathbb{F}_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\rho}_i(\mathbf{r}')]_{\alpha} \sigma_{\alpha}$$

¹A. Marrazzo *et al.* *Phys. Rev. Res.* **6**, 33085 (2024)

Non-collinear spin

CsPbBr₃



	LDA	HSE	G ₀ W ₀	scG \tilde{W}	KI	exp
with SOC	0.18	0.78	0.94	1.53	1.78	1.85
without SOC	1.40	2.09	2.56	3.15	3.12	

¹A. Marrazzo *et al.* Phys. Rev. Res. **6**, 33085 (2024)

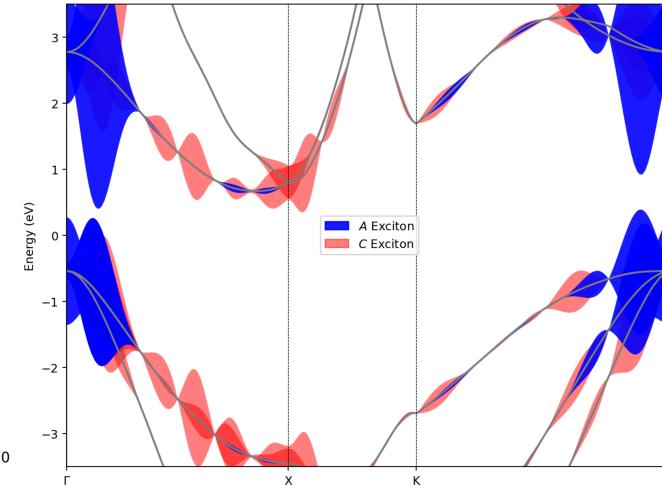
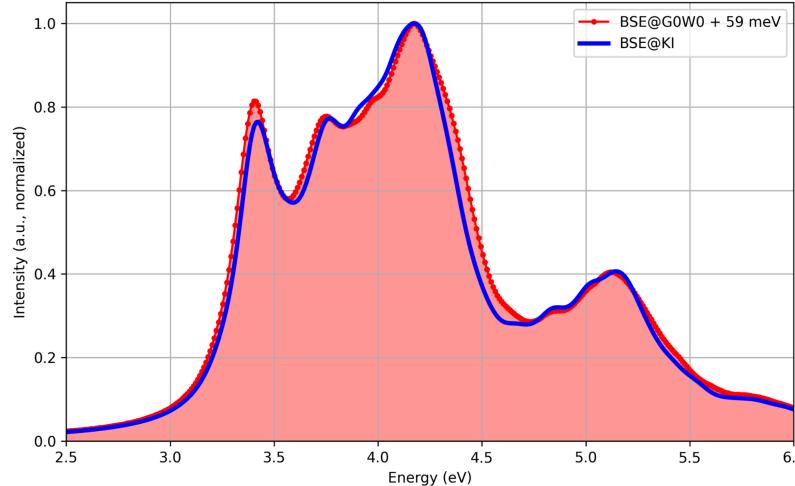
Optical spectra

Optical spectra

Solve the BSE, using Koopmans eigenvalues in lieu of GW

Optical spectra

Solve the BSE, using Koopmans eigenvalues in lieu of GW



silicon

indirect gap

direct gap

first excitonic peak

excitonic binding
energy

qKI+BSE

1.12

3.31

3.42

0.09

G_0W_0 +BSE

1.17

3.25

3.34

0.09

Scaling

Scaling

The vast majority of the computational cost: determining screening parameters

$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

Scaling

The vast majority of the computational cost: determining screening parameters

$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of screening of electronic interactions

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

Scaling

The vast majority of the computational cost: determining screening parameters

$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of screening of electronic interactions
- one screening parameter per orbital

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

Scaling

The vast majority of the computational cost: determining screening parameters

$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of screening of electronic interactions
- one screening parameter per orbital
- must be computed *ab initio* via...

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

Scaling

The vast majority of the computational cost: determining screening parameters

$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of screening of electronic interactions
- one screening parameter per orbital
- must be computed *ab initio* via...
 - ΔSCF¹: embarrassingly parallel steps which each cost $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

Scaling

The vast majority of the computational cost: determining screening parameters

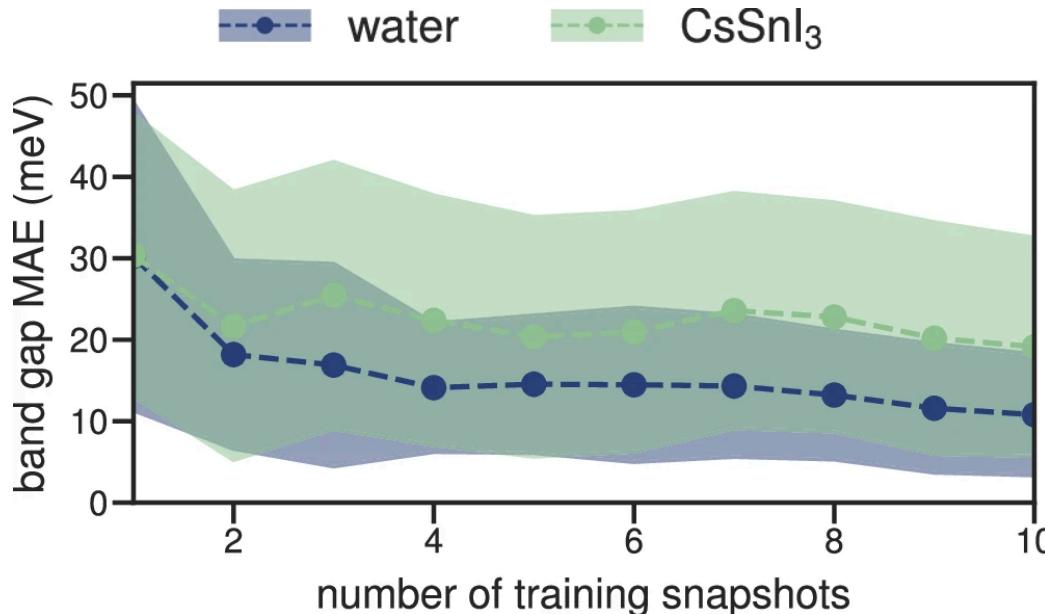
$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of screening of electronic interactions
 - one screening parameter per orbital
 - must be computed *ab initio* via...
 - ΔSCF¹: embarrassingly parallel steps which each cost $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$
 - DFPT²: $\mathcal{O}(N_{\mathbf{k}}^2 N^3)$
- ... can we go even faster?

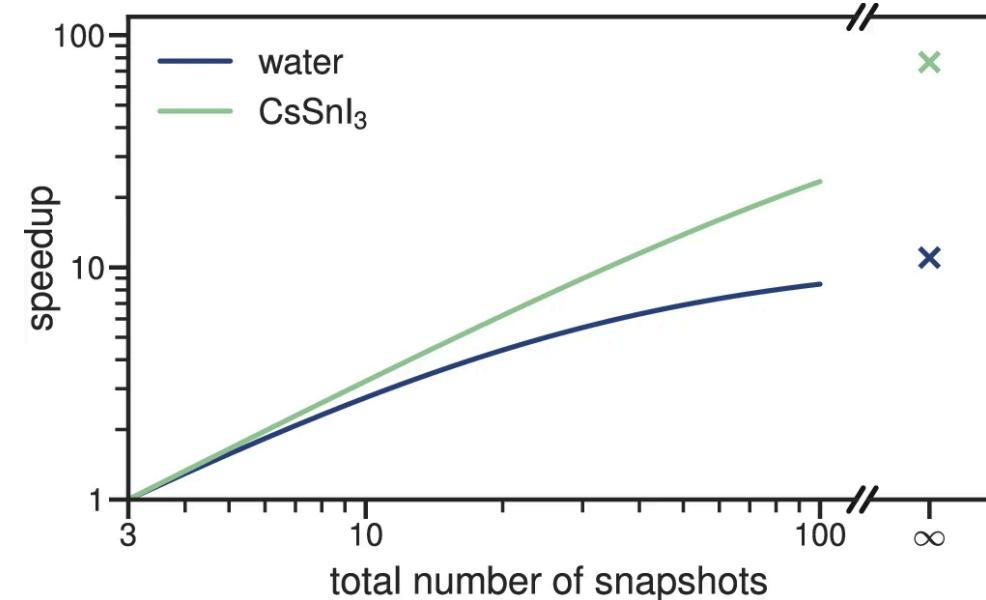
¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

Machine-learned electronic screening



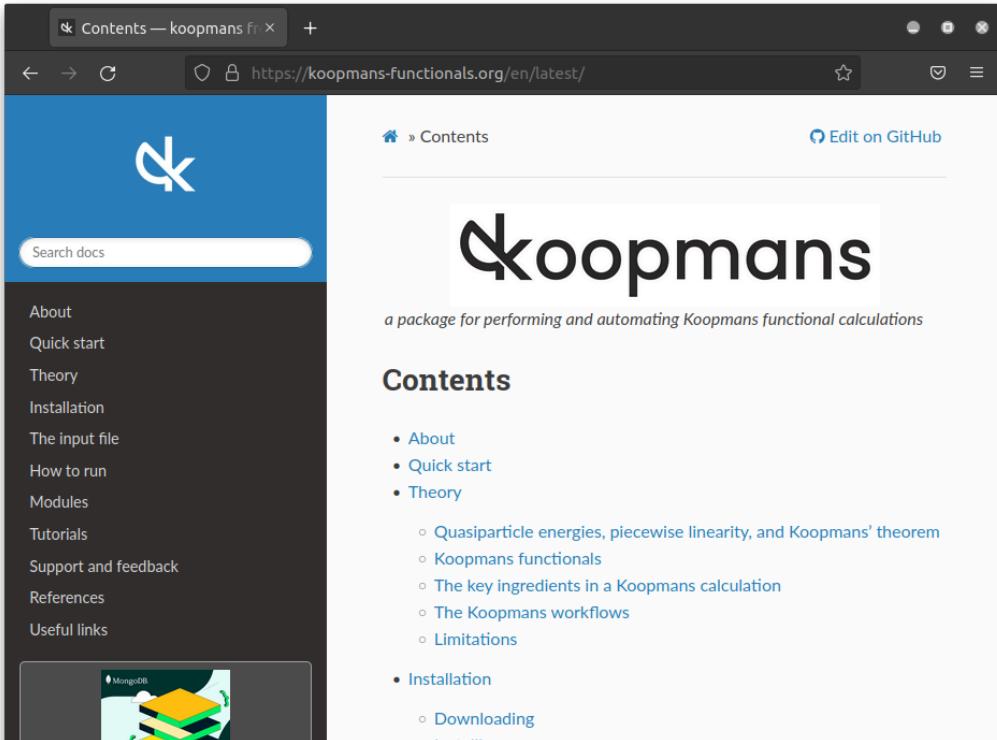
accurate to within $\mathcal{O}(10 \text{ meV})$ cf. typical
band gap accuracy of $\mathcal{O}(100 \text{ meV})$



speedup of $\mathcal{O}(10)$ to $\mathcal{O}(100)$

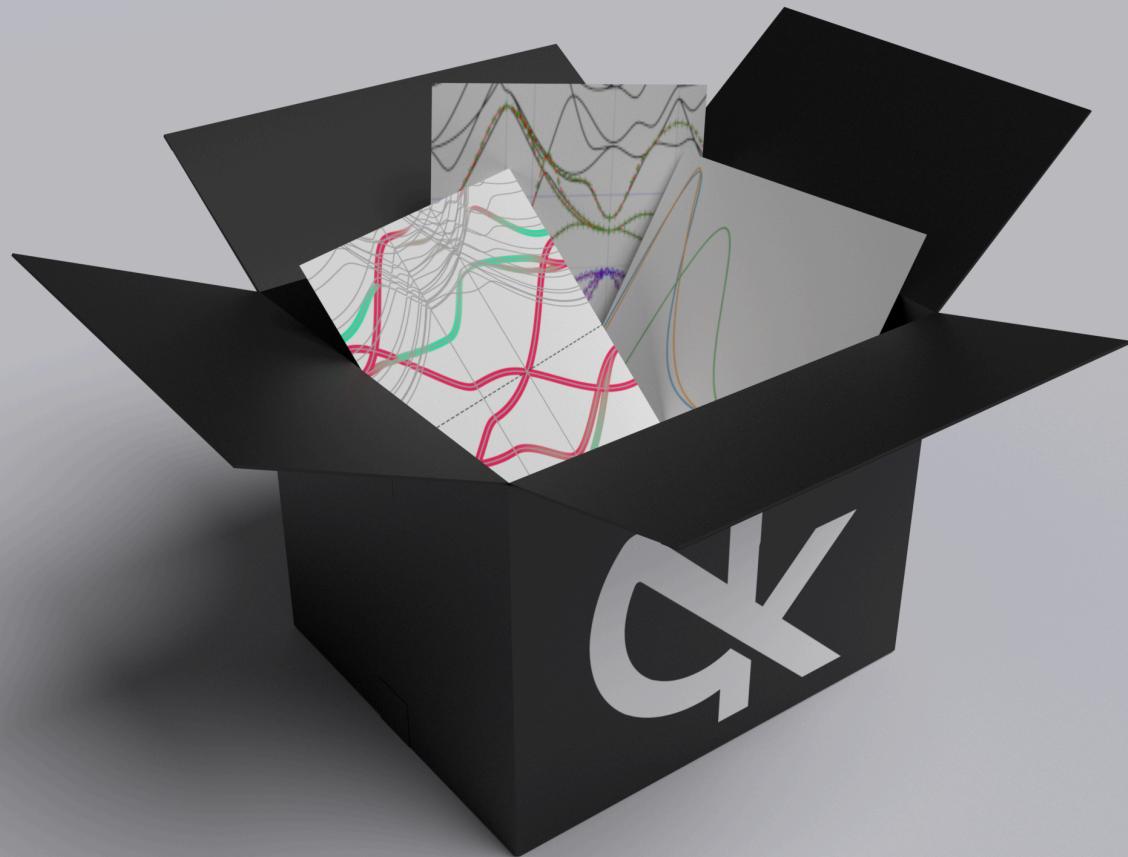
¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

koopmans



- automated workflows
- Quantum ESPRESSO backend
- easy installation
- python API

See koopmans-functionals.org



Our goal:

1. accurate
2. robust
3. minimal input
4. fast

Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

- to initialise the minimising orbitals, or
- in place of the minimising orbitals entirely

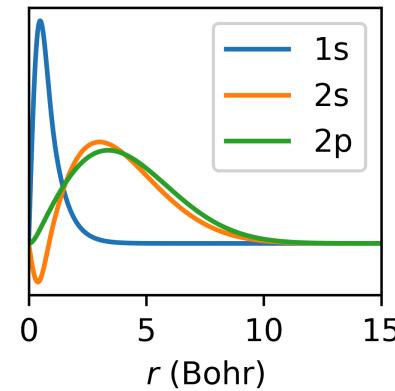
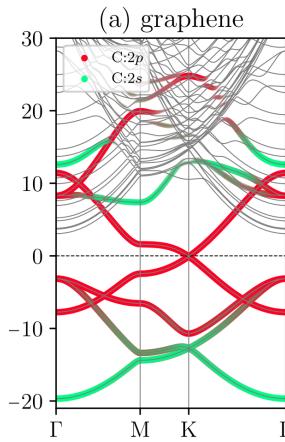
¹J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

²J. Qiao *et al.* *npj Comput Mater* **9**, 206 (2023)

Automated Wannierisation

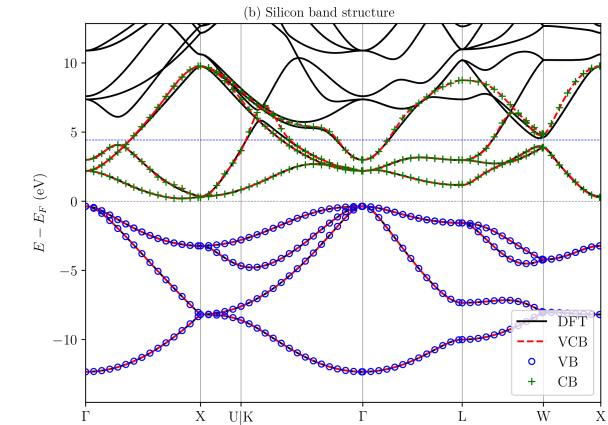
Koopmans functionals rely heavily on Wannier functions...

- to initialise the minimising orbitals, or
- in place of the minimising orbitals entirely



projectability-based
disentanglement¹

use PAOs found in
pseudopotentials



parallel transport to separate
manifolds²

¹J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

²J. Qiao *et al.* *npj Comput Mater* **9**, 206 (2023)



```
$ koopmans run tio2.json
```

¹S. P. Huber *et al.* *Sci Data* **7**, 300 (2020)



```
$ koopmans run tio2.json → $ koopmans run --engine=aiida tio2.json
```

remote compute, parallel step execution, provenance-tracking, (requires configuration,
WIP...)

¹S. P. Huber *et al.* *Sci Data* **7**, 300 (2020)

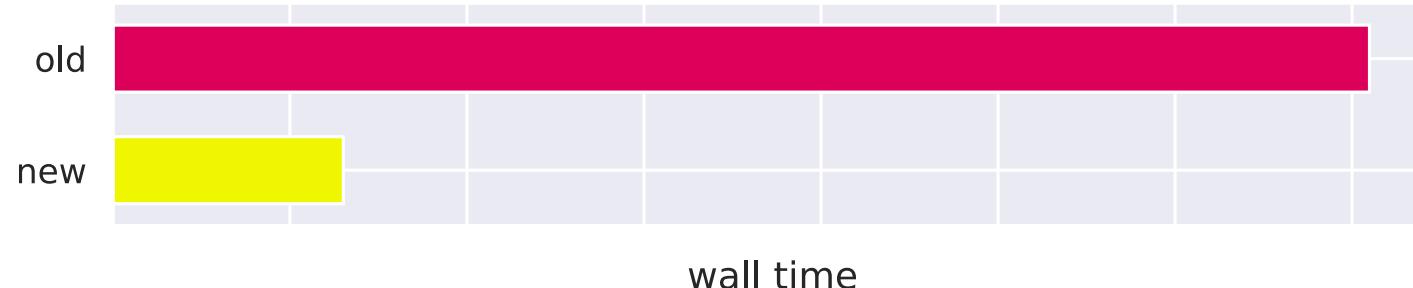
koopmans

AiiDA

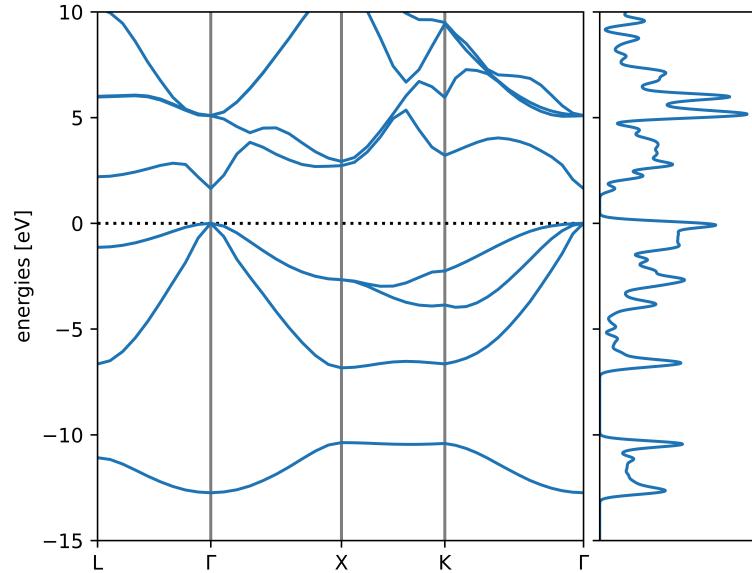
```
$ koopmans run tio2.json → $ koopmans run --engine=aiida tio2.json
```

remote compute, parallel step execution, provenance-tracking, (requires configuration,
WIP...)



¹S. P. Huber *et al.* *Sci Data* **7**, 300 (2020)

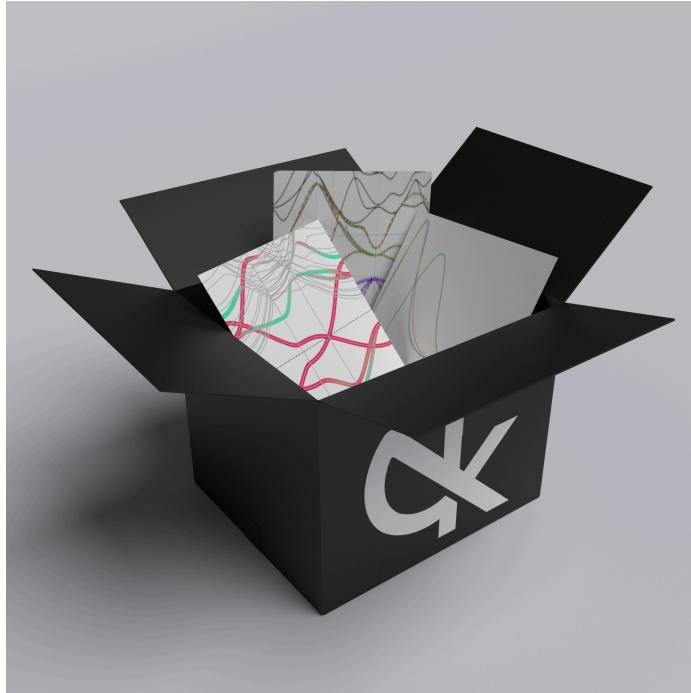
```
{
  "workflow": {
    "functional": "ki",
    "method": "dfpt",
    "init_orbitals": "mlwfs",
    "pseudo_library": "PseudoDojo/0.4/LDA/SR/standard/upf",
    "block_wannierization_threshold": 5.0,
    "orbital_groups_spread_tol": 0.05
  },
  "atoms": {
    "cell_parameters": {
      "periodic": true,
      "ibrav": 2,
      "celldms": {"l": 10.68374}
    },
    "atomic_positions": {
      "units": "crystal",
      "positions": [[{"Ga": 0.0, 0.0, 0.0}, {"As": 0.25, 0.25, 0.25}]]
    }
  },
  "kpoints": {
    "grid": [6, 6, 6]
  },
  "calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
      "dis_proj_max": 0.8,
      "auto_projections": true
    },
    "ui": {
      "smooth_int_factor": 2
    }
  }
}
```



	LDA	HSE	GW_0	scG \tilde{W}	KI	exp
E_{gap}	0.26	1.28	1.55	1.62	1.54	1.55
$\langle \varepsilon_d \rangle$	-14.9	-15.6	-17.3	-17.6	-17.9	-18.9
Δ	12.8	13.9			12.7	13.1

Summary

Summary



Koopmans functionals...

- impose generalised piecewise linearity condition to DFT
- give band structures with comparable accuracy to state-of-the-art GW
- can be used in place of GW in BSE calculation of excitons, for systems with strong SOC, ...
- are increasingly black-box

Open questions

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they take?

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they take?
- how to extend to metallic systems?

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they take?
- how to extend to metallic systems?
- can we provide a formal basis for the Koopmans correction?

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they take?
- how to extend to metallic systems?
- can we provide a formal basis for the Koopmans correction?
 - GKS
 - spectral functional theory¹
 - ensemble DFT
 - RDMFT

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Want to find out more?



Nicola Marzari

Monday

spectral theories



Marija Stojkovic

Monday

band alignment for
photocatalysis



Nicola Colonna

Tuesday

non-collinear spin



Junfeng Qiao

Poster B4.16
today!

automated
Wannierisation



Aleksandr Poliukhin

Thu 1000 Room C

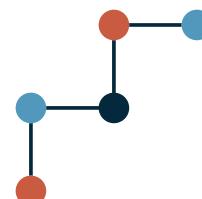
phonons

... or go to koopmans-functionals.org

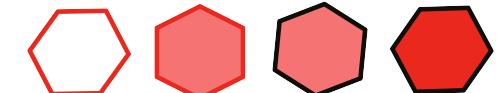
Acknowledgements



Nicola Colonna Miki Bonacci Aleksandr Poliukhin Marija Stojkovic Giovanni Cistaro Julian Geiger Junfeng Qiao Yannick Schubert Nicola Marzari



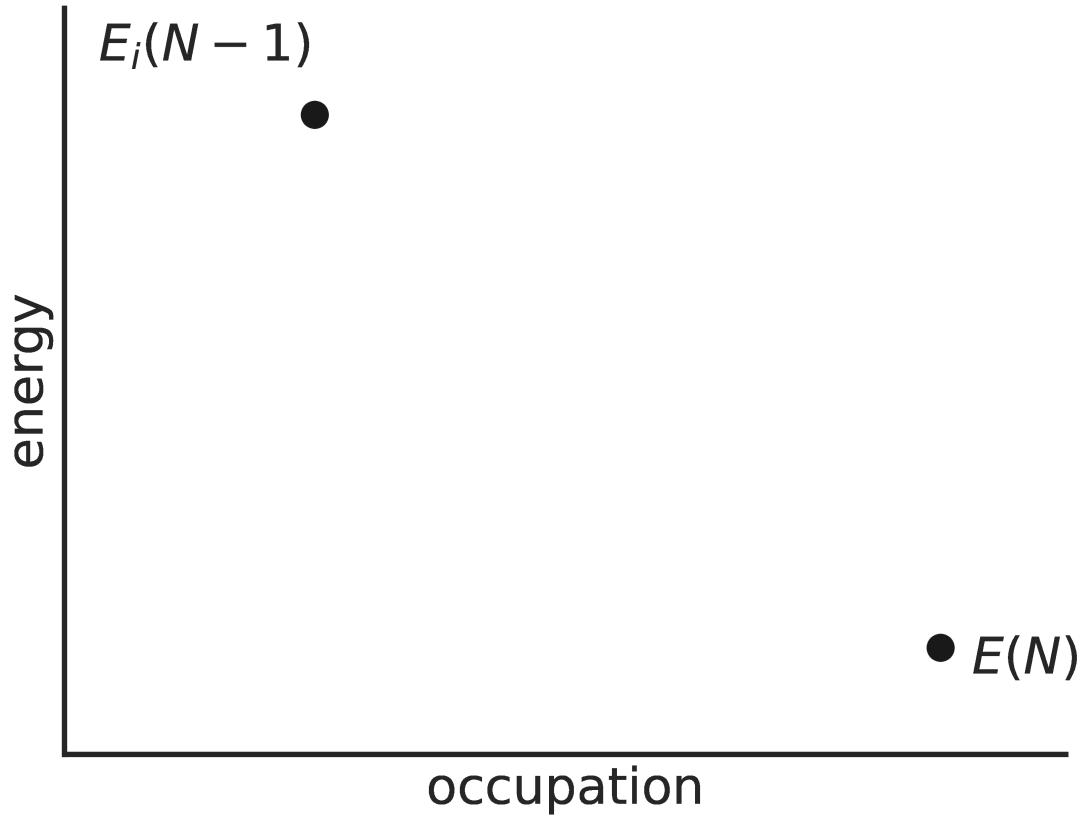
**Swiss National
Science Foundation**

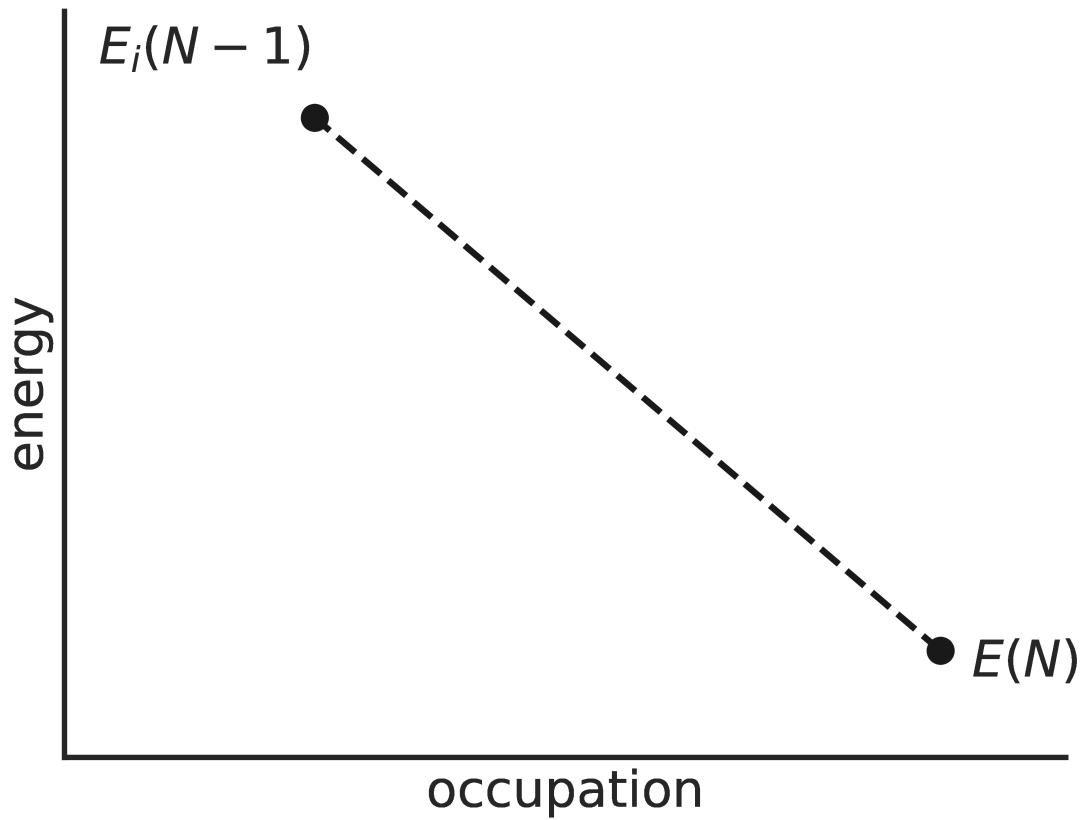
MARVEL


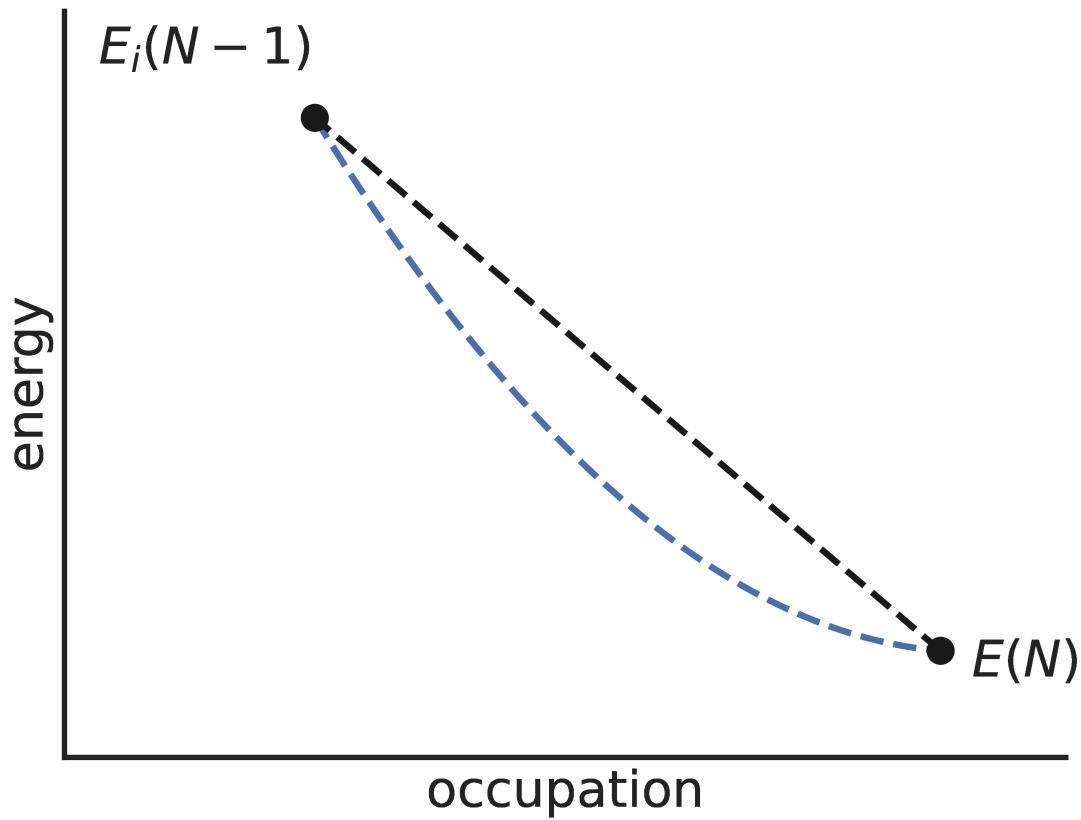
Thank you!

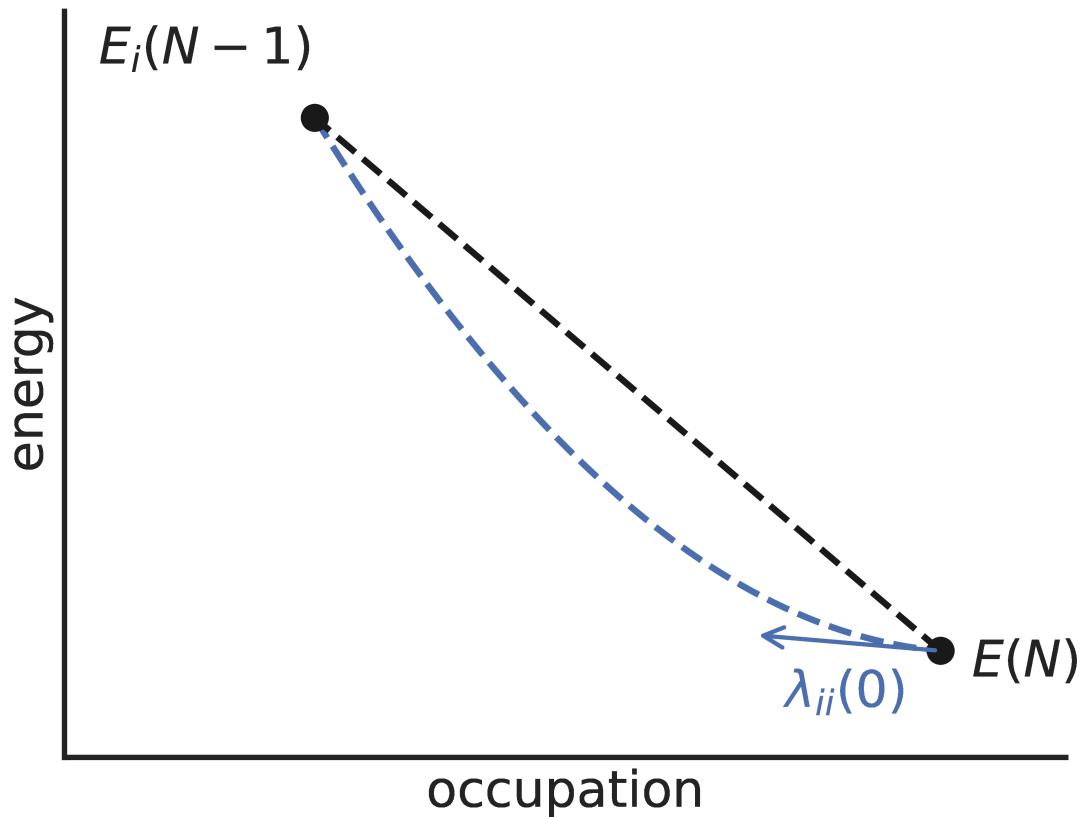
these slides are available at  [*elinscott-talks*](https://github.com/elinscott-talks)

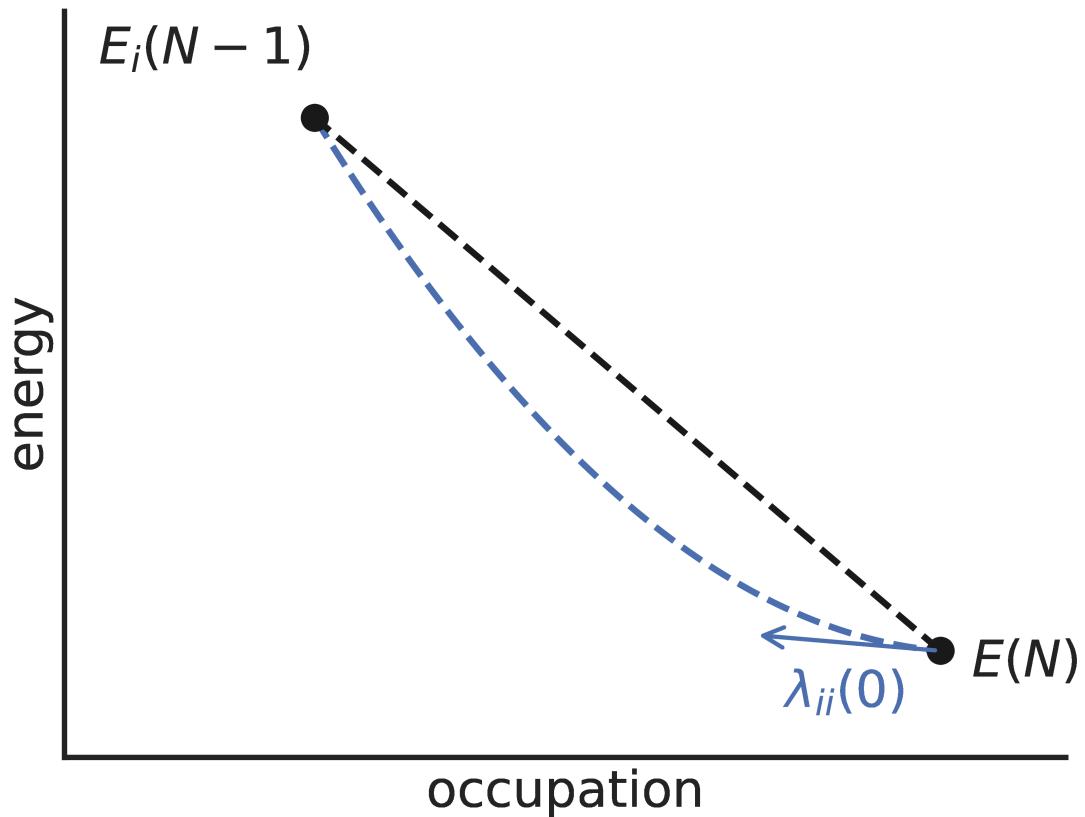
spare slides

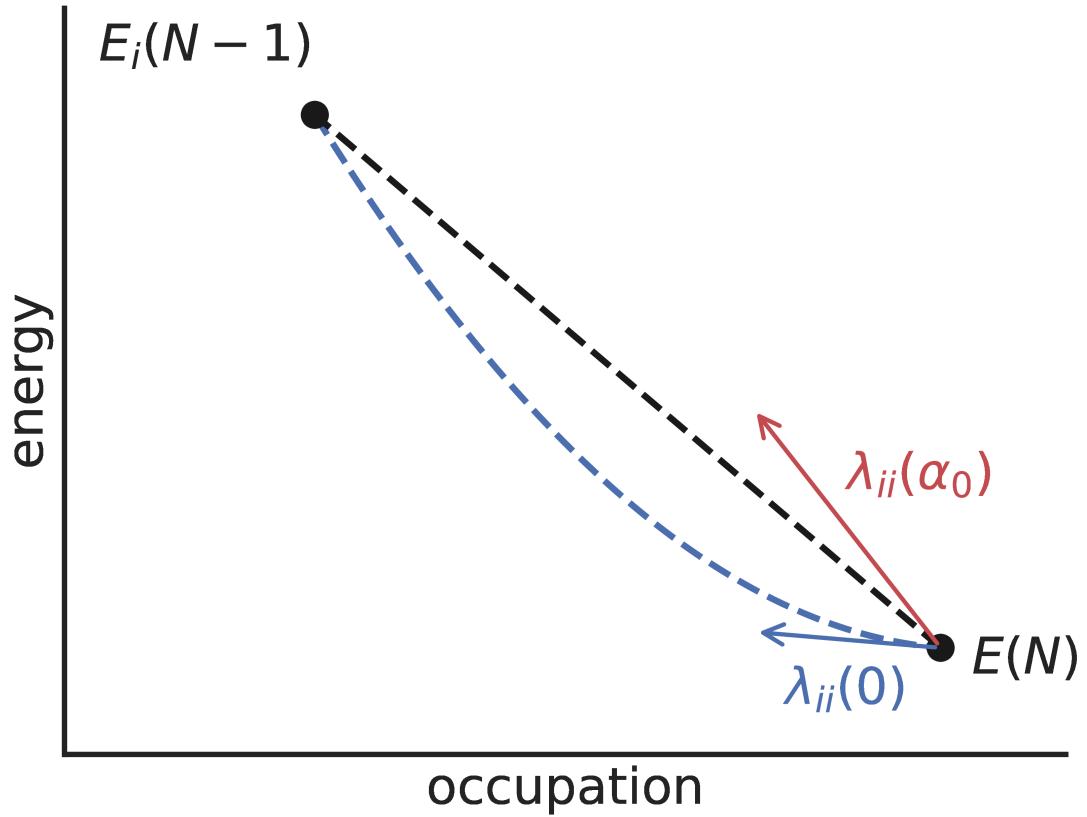


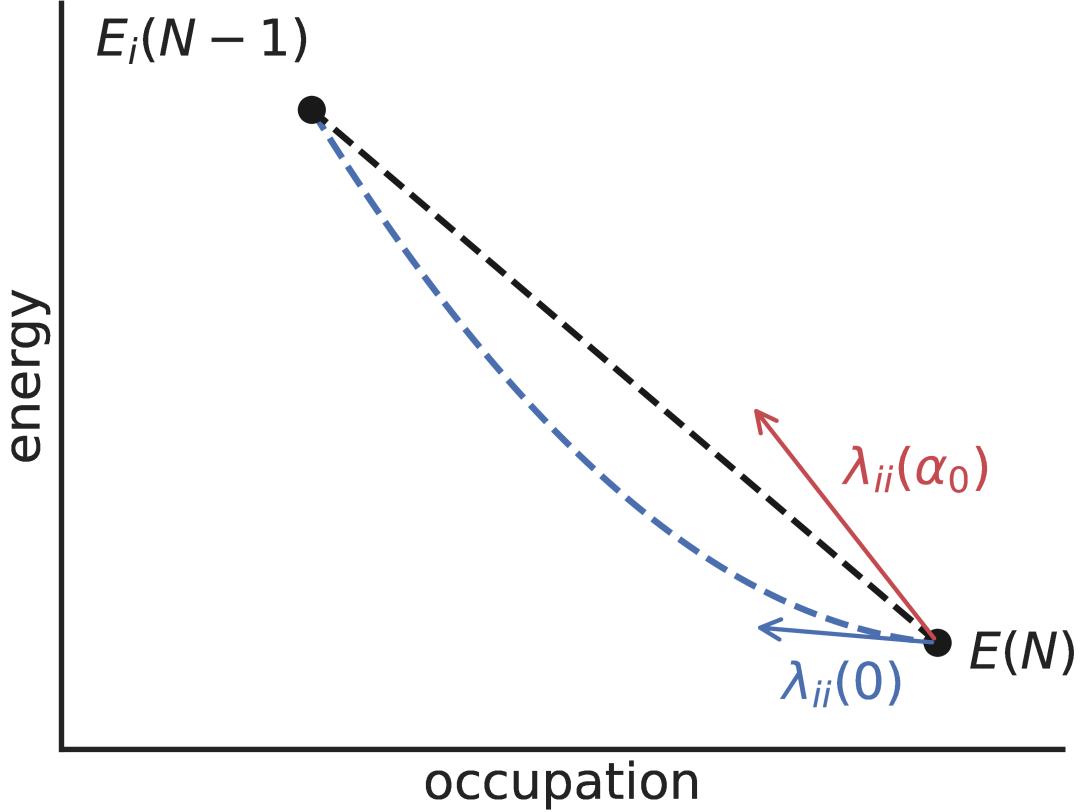








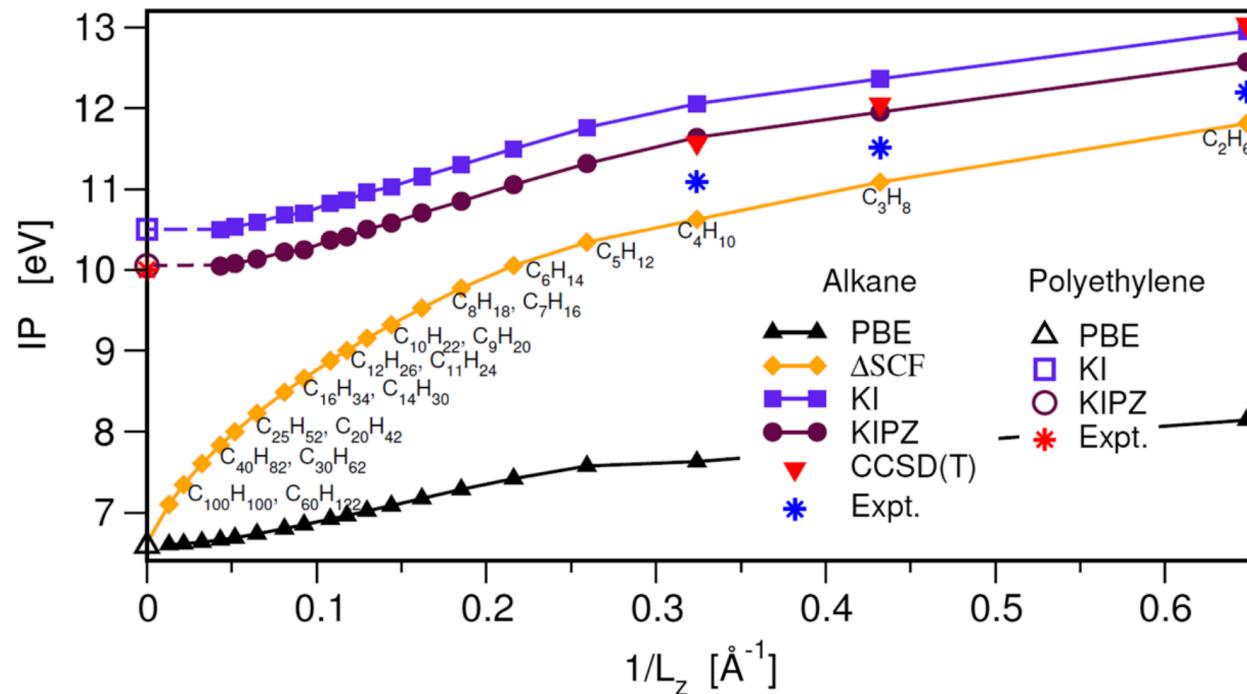




$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

$$\lambda_{ii}(\alpha) = \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}_i^{\text{KI}} | \varphi_i \rangle$$

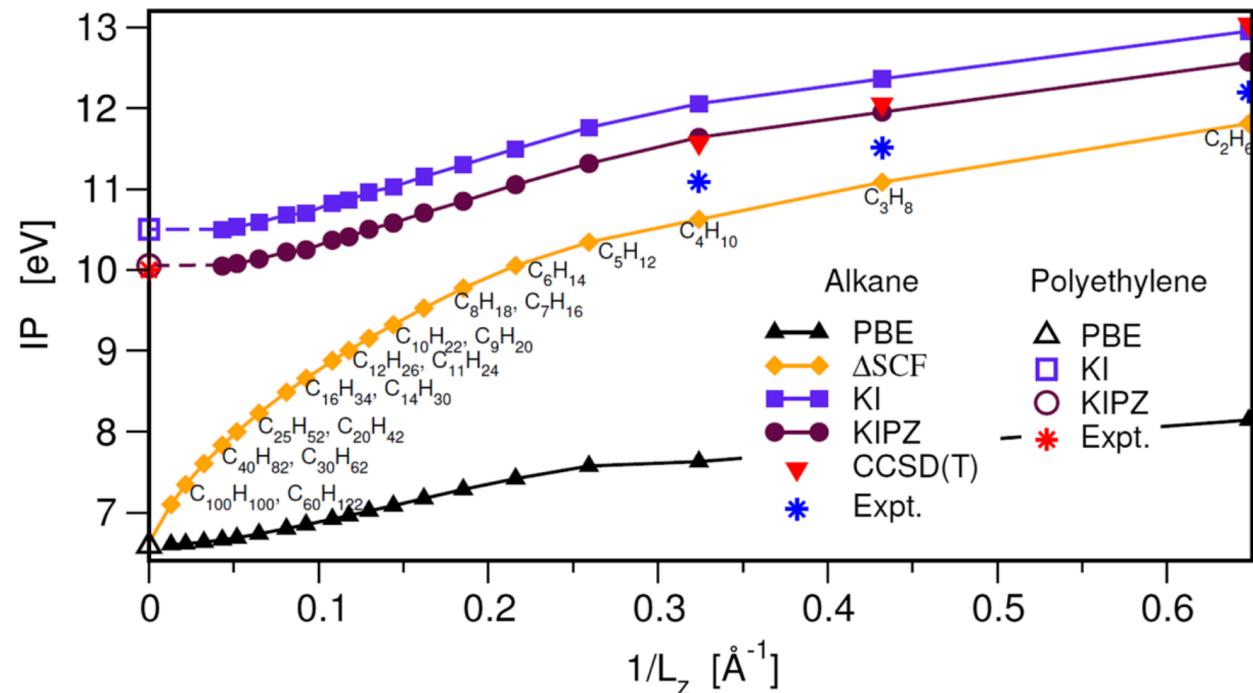
Issues with extended systems



Two options:

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

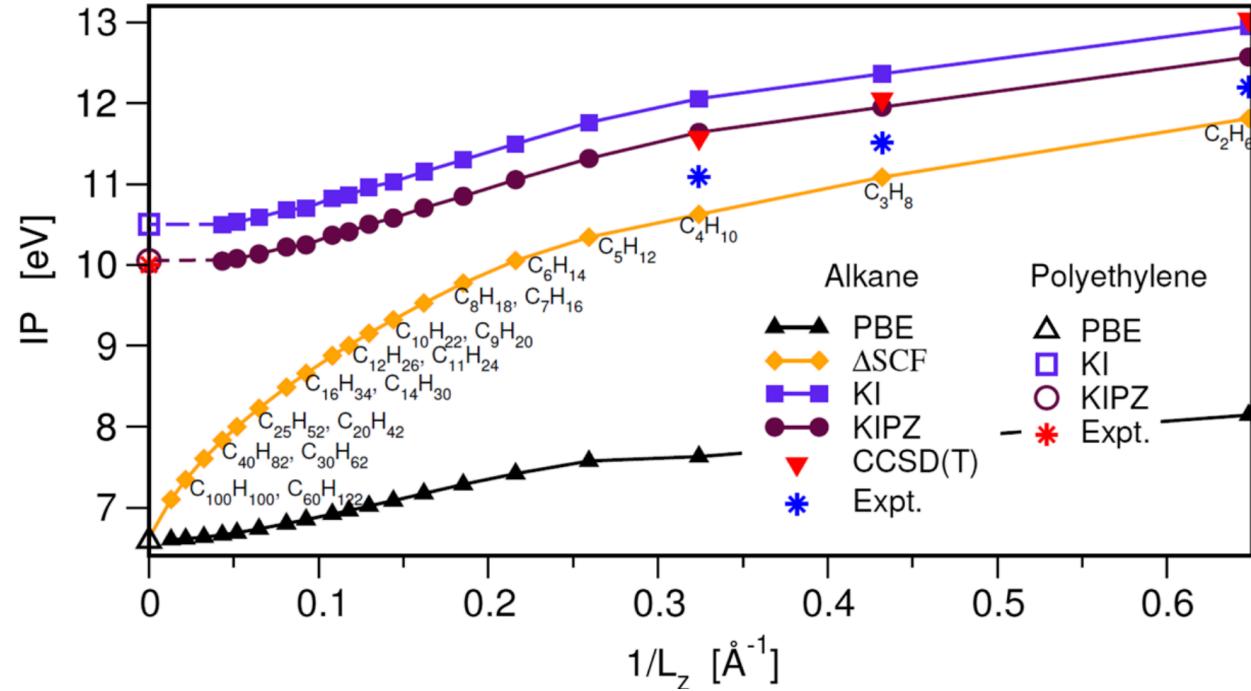
Issues with extended systems



Two options: 1. use a more advanced functional

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

Issues with extended systems



Two options: 1. use a more advanced functional, or 2. stay in the “safe” region

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

Issues with extended systems

```
{  
    "workflow": {  
        "functional": "ki",  
        "method": "dfpt",  
        "init_orbitals": "mlwfs",  
        "pseudo_library": "PseudoDojo/0.4/LDA/SR/standard/upf",  
        "block_wannierization_threshold": 5.0,  
        "orbital_groups_spread_tol": 0.05  
    },  
    "atoms": {  
        "cell_parameters": {  
            "periodic": true,  
            "ibrav": 2,  
            "celldms": {"1": 10.68374}  
        },  
        "atomic_positions": {  
            "units": "crystal",  
            "positions": [[{"Ga": 0.00, 0.00, 0.00},  
                          {"As": 0.25, 0.25, 0.25}]]  
        }  
    },  
}
```

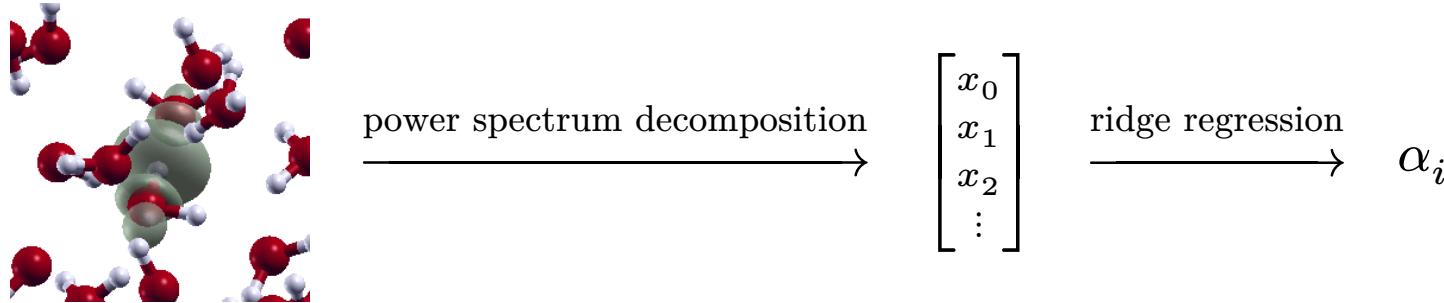
Issues with extended systems

```

"kpoints": {
    "grid": [6, 6, 6]
},
"calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
        "projections": [
            [{"site": "As", "ang_mtm": "d"}, {"site": "Ga", "ang_mtm": "d"}, {"site": "As", "ang_mtm": "sp3"}], [{"site": "Ga", "ang_mtm": "sp3"}]
        ],
        "dis_froz_max": 14.6,
        "dis_win_max": 18.6
    },
    "ui": {
        "smooth_int_factor": 2
    }
}
}

```

Machine-learned electronic screening

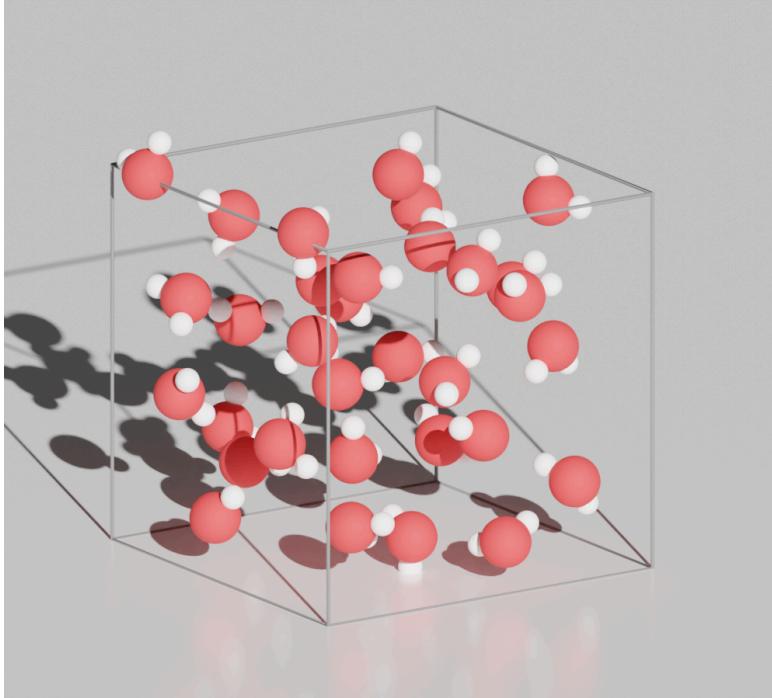


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

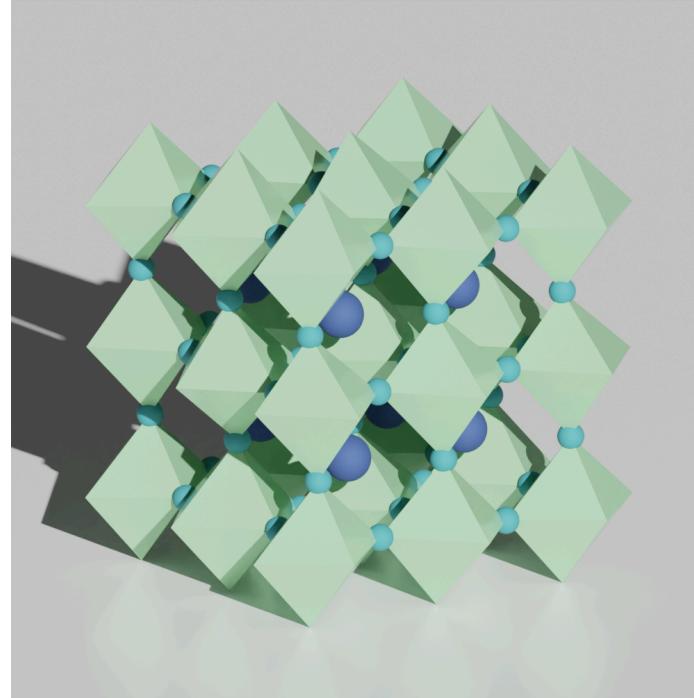
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

Machine-learned electronic screening



water

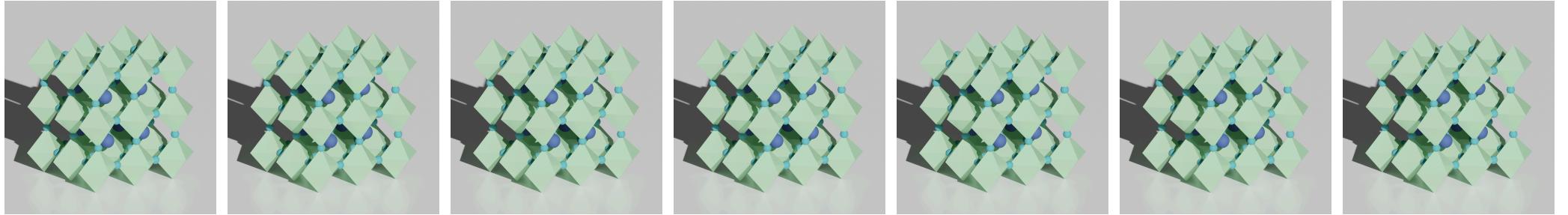


CsSnI₃

¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

Machine-learned electronic screening

The use-case

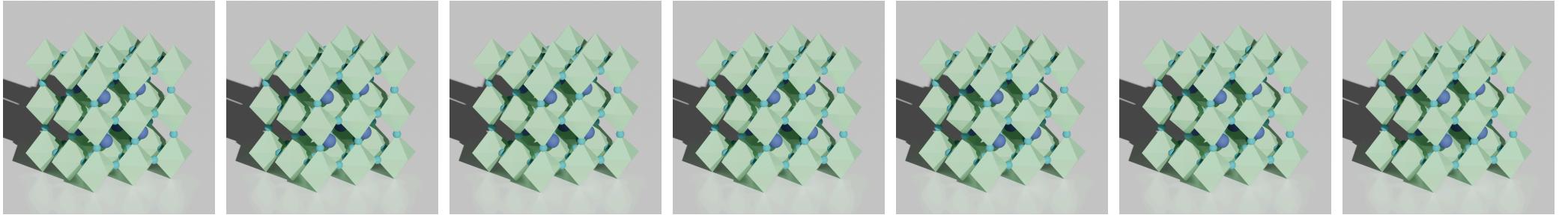


train

predict

Machine-learned electronic screening

The use-case

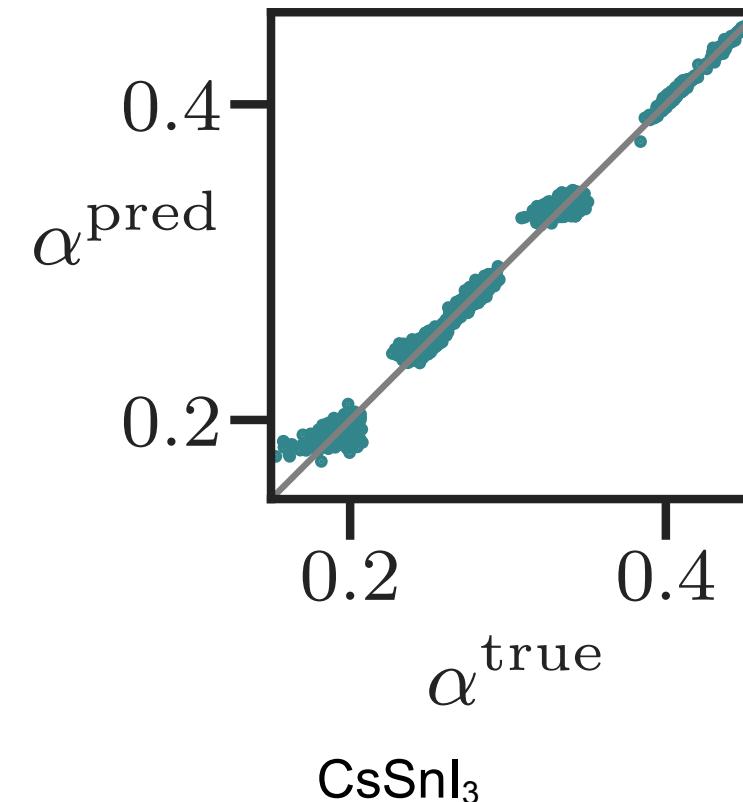
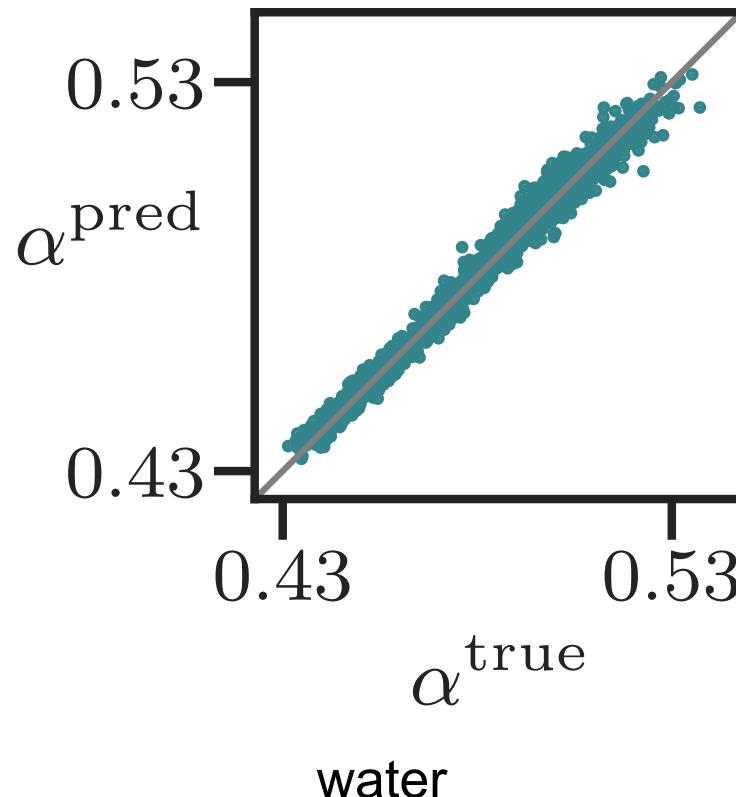


train

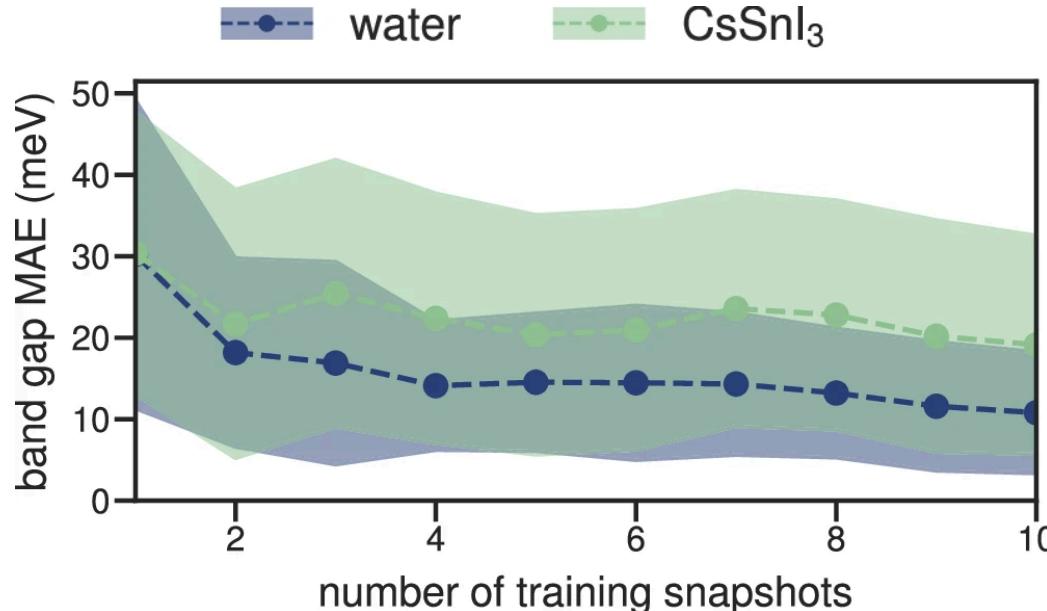
predict

N.B. not a general model

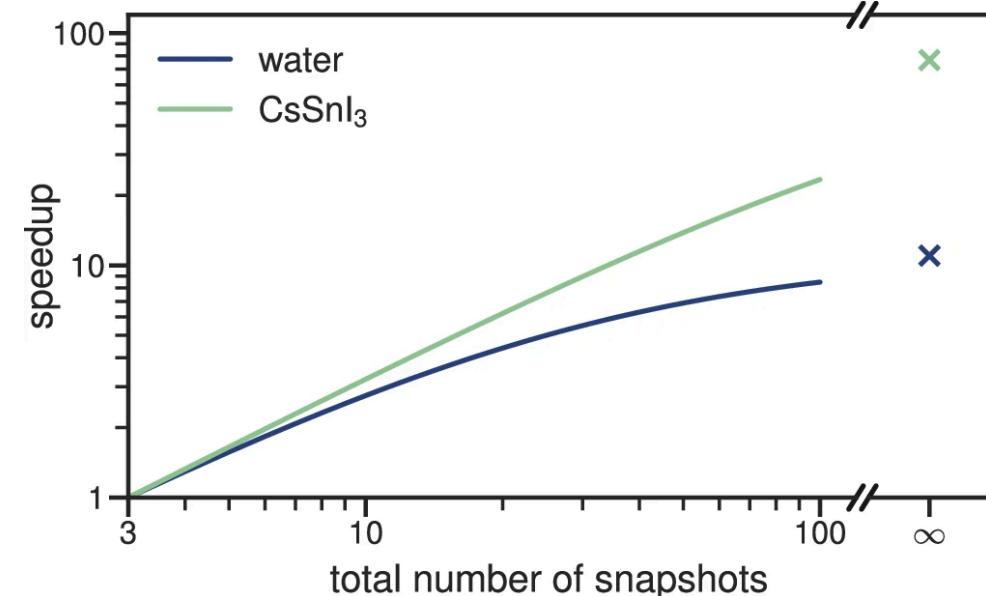
Machine-learned electronic screening



Machine-learned electronic screening



accurate to within $\mathcal{O}(10 \text{ meV})$ cf. typical
band gap accuracy of $\mathcal{O}(100 \text{ meV})$



speedup of $\mathcal{O}(10)$ to $\mathcal{O}(100)$

¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

Taking advantage of symmetries

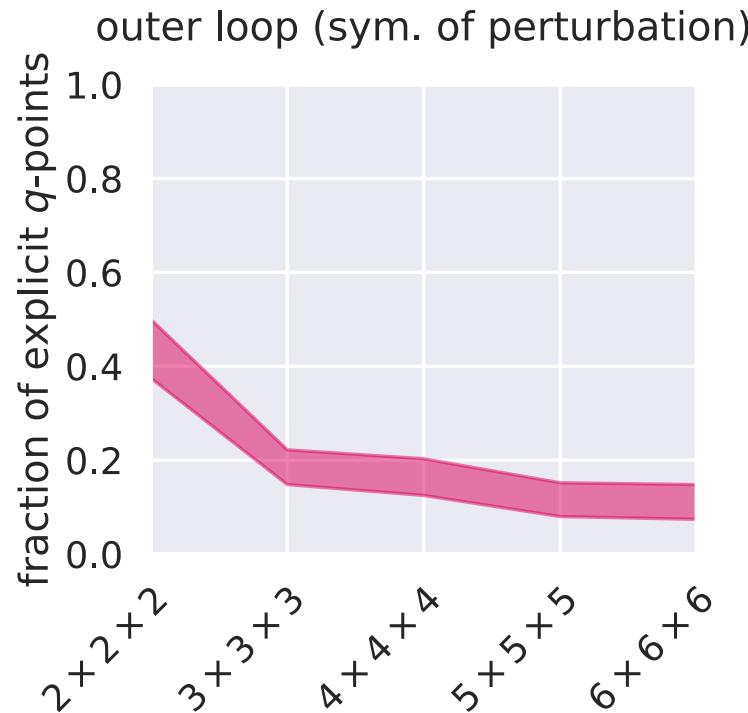
To compute screening parameters via DFPT...

```

1:function CalculateAlpha( $n$ )
2:   for  $q \in \text{BZ}$  do
3:     for  $k \in \text{BZ}$  do
4:       ▷ Linear system  $Ax = b$  to obtain  $\Delta\psi_{\mathbf{k}+\mathbf{q},v}(\mathbf{r})$ 
5:     end
6:      $\Delta\rho_q^{0n} \leftarrow \sum_{\mathbf{k}\mathbf{v}} \psi_{\mathbf{k}\mathbf{v}}^*(\mathbf{r}) \Delta\psi_{\mathbf{k}+\mathbf{q},v}(\mathbf{r}) + c.c.$ 
7:      $\Pi_{0n,\mathbf{q}}^{(r)} \leftarrow \langle \Delta\rho_q^{0n} | f_{\text{Hxc}} | \rho_{\mathbf{q}}^{0n} \rangle$ 
8:      $\Pi_{0n,\mathbf{q}}^{(u)} \leftarrow \langle \rho_{\mathbf{q}}^{0n} | f_{\text{Hxc}} | \rho_{\mathbf{q}}^{0n} \rangle$ 
9:   end
10:  return  $1 + \sum_{\mathbf{q}} \Pi_{0n,\mathbf{q}}^{(r)} / \sum_{\mathbf{q}} \Pi_{0n,\mathbf{q}}^{(u)}$ 
11end

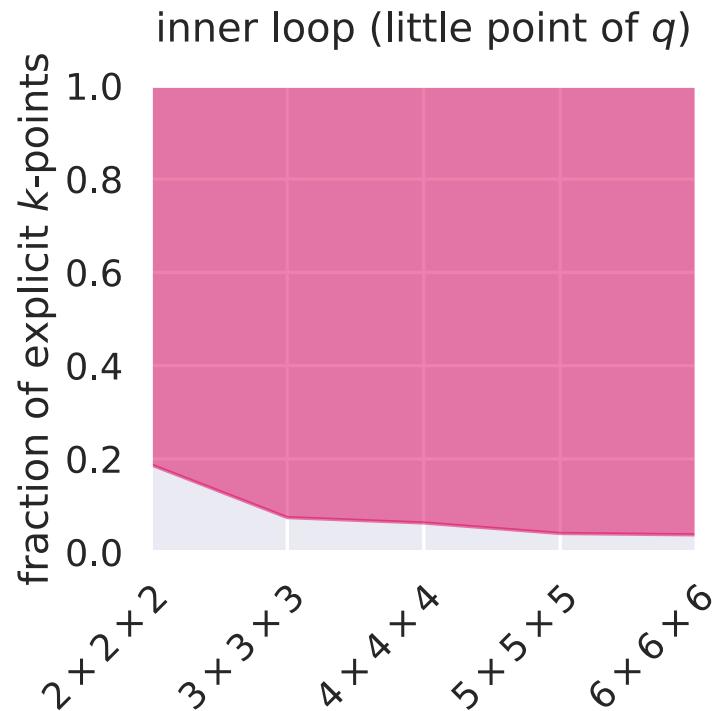
```

Taking advantage of symmetries



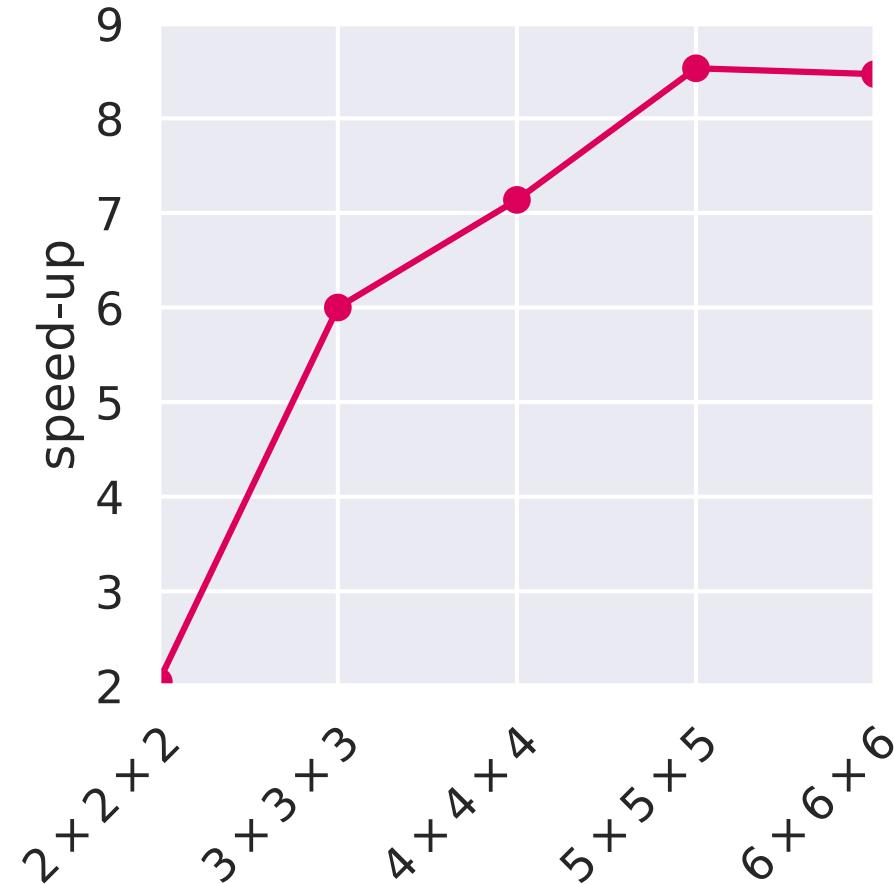
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$ (the symmetry of the perturbation; lower than that of the primitive cell)

Taking advantage of symmetries



$k \in \text{BZ} \rightarrow k \in \text{IBZ}(q)$ (can only use symmetries that leave q invariant)

Taking advantage of symmetries



Connections with approx. self-energies

Orbital-density functional theory:

$$(h + \alpha_i v_i^{KI}) |\psi_i\rangle = \lambda_i |\psi_i\rangle$$

$v_i^{KI}(\mathbf{r})$ is real, local, and state-dependent

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014), N. Colonna *et al.* *J. Chem. Theory Comput.* **15**, 1905 (2019)

Connections with approx. self-energies

Orbital-density functional theory:

$$(h + \alpha_i v_i^{KI}) |\psi_i\rangle = \lambda_i |\psi_i\rangle$$

$v_i^{KI}(\mathbf{r})$ is real, local, and state-dependent

cf. Green's function theory:

$$(h + \Sigma_i) |\psi_i\rangle = z_i |\psi_i\rangle$$

$\Sigma_i(\mathbf{r}, \mathbf{r}')$ is complex, non-local, and state-dependent

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014), N. Colonna *et al.* *J. Chem. Theory Comput.* **15**, 1905 (2019)

Connections with approx. self-energies

Hartree-Fock self-energy in localized representation

$$\begin{aligned}\Sigma_x(\mathbf{r}, \mathbf{r}') &= -\sum_{k\sigma}^{\text{occ}} \psi_{k\sigma}(\mathbf{r}) f_H(\mathbf{r}, \mathbf{r}') \psi_{k\sigma}^*(\mathbf{r}') \\ &\implies \langle \varphi_{i\sigma} | \Sigma_x | \varphi_{j\sigma'} \rangle \approx -\langle \varphi_{i\sigma} | v_H[n_{i\sigma}] | \varphi_{i\sigma} \rangle \delta_{ij} \delta_{\sigma\sigma'}\end{aligned}$$

Unscreened KIPZ@ Hartree ($v_{\text{xc}} \rightarrow 0$; $f_{\text{Hxc}} \rightarrow f_H$; $\varepsilon^{-1} \rightarrow 1$)

$$\langle \varphi_{i\sigma} | v_{j\sigma', \text{xc}}^{\text{KIPZ}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | f_H | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \approx -\langle \varphi_{i\sigma} | v_H[n_{i\sigma}] | \varphi_{i\sigma} \rangle \delta_{ij} \delta_{\sigma\sigma'}$$

Connections with approx. self-energies

Screened exchange plus Coulomb hole (COHSEX)

$$\Sigma_{\text{xc}}^{\text{SEX}}(s, s') = - \sum_{k\sigma}^{\text{occ}} \psi_{k\sigma}(\mathbf{r}) \psi_{k\sigma}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}')$$

$$\Sigma_{\text{xc}}^{\text{COH}}(s, s') = \frac{1}{2} \delta(s, s') \{W(\mathbf{r}, \mathbf{r}') - f_H(\mathbf{r}, \mathbf{r}')\}$$

$$\Rightarrow \langle \varphi_{i\sigma} | \Sigma_{\text{xc}}^{\text{COHSEX}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | W | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

KIPZ@ Hartree with RPA screening ($v_{\text{xc}} \rightarrow 0$; $f_{\text{Hxc}} \rightarrow f_H$; $\varepsilon^{-1} \rightarrow \text{RPA}$)

$$\langle \varphi_{i\sigma} | v_{j\sigma', \text{xc}}^{\text{KIPZ}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | W | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

Connections with approx. self-energies

Static $\text{GW}\Gamma_{\text{xc}}$ — local (DFT-based) vertex corrections¹

$$\Sigma_{\text{xc}(1,2)}^{G\text{W}\Gamma_{\text{xc}}} = iG(1,2)W_{t-e}(1,2)$$

$$W_{t-e} = (1 - f_{\text{Hxc}}\chi_0)^{-1}f_H$$

$$\Rightarrow \langle \varphi_{i\sigma} | \Sigma_{\text{xc}}^{G\text{W}\Gamma_{\text{xc}}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | W_{t-e} | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

KIPZ@ DFT ($v_{\text{xc}} \rightarrow \text{DFT}$; $f_{\text{Hxc}} \rightarrow \text{DFT}$; $\varepsilon^{-1} \rightarrow \text{DFT}$)

$$\langle \varphi_{i\sigma} | v_{j\sigma',\text{xc}}^{\text{KIPZ}} | \varphi_{j\sigma'} \rangle \approx \left\{ \langle \varphi_{i\sigma} | v_{\sigma,\text{xc}}^{\text{DFT}} | \varphi_{i\sigma} \rangle + \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | \varepsilon_{t-e}^{-1} f_{\text{Hxc}} | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

¹M. S. Hybertsen *et al.* *Phys. Rev. B* **35**, 5585–5601 (1987), R. Del Sole *et al.* *Phys. Rev. B* **49**, 8024–8028 (1994)

References

References



- M. Puppin *et al.* Evidence of Large Polarons in Photoemission Band Mapping of the Perovskite Semiconductor CsPbBr₃. *Phys. Rev. Lett.* **124**, 206402 (2020).
- N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza & D. Vanderbilt. Maximally localized Wannier functions: Theory and applications. *Rev. Mod. Phys.* **84**, 1419–1475 (2012).
- A. Ferretti, I. Dabo, M. Cococcioni & N. Marzari. Bridging density-functional and many-body perturbation theory: orbital-density dependence in electronic-structure functionals. *Phys. Rev. B* **89**, 195134 (2014).
- N. Colonna, N. L. Nguyen, A. Ferretti & N. Marzari. Koopmans-compliant functionals and potentials and their application to the GW100 test set. *J. Chem. Theory Comput.* **15**, 1905 (2019).
- N. L. Nguyen, G. Borghi, A. Ferretti, I. Dabo & N. Marzari. First-Principles Photoemission Spectroscopy and Orbital Tomography in Molecules from Koopmans-Compliant Functionals. *Phys. Rev. Lett.* **114**, 166405 (2015).
- N. L. Nguyen, N. Colonna, A. Ferretti & N. Marzari. Koopmans-compliant spectral functionals for extended systems. *Phys. Rev. X* **8**, 21051 (2018).
- N. Colonna, R. De Gennaro, E. Linscott & N. Marzari. Koopmans spectral functionals in periodic boundary conditions. *J. Chem. Theory Comput.* **18**, 5435 (2022).
- Y. Schubert, N. Marzari & E. Linscott. Testing Koopmans spectral functionals on the analytically solvable Hooke's atom. *J. Chem. Phys.* **158**, 144113 (2023).
- V. I. Anisimov & A. V. Kozhevnikov. Transition state method and Wannier functions. *Phys. Rev. B* **72**, 75125 (2005).
- L. Kronik, T. Stein, S. Refaelly-Abramson & R. Baer. Excitation Gaps of Finite-Sized Systems from Optimally Tuned Range-Separated Hybrid Functionals. *J. Chem. Theory Comput.* **8**, 1515–1531 (2012).
- D. Wing *et al.* Band gaps of crystalline solids from Wannier-localization-based optimal tuning of a screened range-separated hybrid functional. *Proc. Natl. Acad. Sci.* **118**, e2104556118 (2021).

References



- E. Kraisler & L. Kronik. Piecewise Linearity of Approximate Density Functionals Revisited: Implications for Frontier Orbital Energies. *Phys. Rev. Lett.* **110**, 126403 (2013).
- J. Ma & L.-W. Wang. Using Wannier functions to improve solid band gap predictions in density functional theory. *Sci. Rep.* **6**, 24924 (2016).
- J. H. Skone, M. Govoni & G. Galli. Nonempirical range-separated hybrid functionals for solids and molecules. *Phys. Rev. B* **93**, 235106 (2016).
- C. Li, X. Zheng, N. Q. Su & W. Yang. Localized orbital scaling correction for systematic elimination of delocalization error in density functional approximations. *Natl. Sci. Rev.* **5**, 203–215 (2018).
- A. Marrazzo & N. Colonna. Spin-dependent interactions in orbital-density-dependent functionals: Noncollinear Koopmans spectral functionals. *Phys. Rev. Res.* **6**, 33085 (2024).
- R. De Gennaro, N. Colonna, E. Linscott & N. Marzari. Bloch's theorem in orbital-density-dependent functionals: Band structures from Koopmans spectral functionals. *Phys. Rev. B* **106**, 35106 (2022).
- N. Colonna, N. L. Nguyen, A. Ferretti & N. Marzari. Screening in Orbital-Density-Dependent Functionals. *J. Chem. Theory Comput.* **14**, 2549 (2018).
- Y. Schubert, S. Luber, N. Marzari & E. Linscott. Predicting electronic screening for fast Koopmans spectral functional calculations. *npj Comput Mater* **10**, 1–12 (2024).
- J. Qiao, G. Pizzi & N. Marzari. Projectability disentanglement for accurate and automated electronic-structure Hamiltonians. *npj Comput Mater* **9**, 208 (2023).
- J. Qiao, G. Pizzi & N. Marzari. Automated mixing of maximally localized Wannier functions into target manifolds. *npj Comput Mater* **9**, 206 (2023).
- S. P. Huber *et al.* AiiDA 1.0, a scalable computational infrastructure for automated reproducible workflows and data provenance. *Sci Data* **7**, 300 (2020).
- M. S. Hybertsen & S. G. Louie. Ab initio static dielectric matrices from the density-functional approach. I. Formulation and application to semiconductors and insulators. *Phys. Rev. B* **35**, 5585–5601 (1987).

References

R. Del Sole, L. Reining & R. W. Godby. GW\ensuremath{}\Gamma approximation for electron self-energies in semiconductors and insulators. *Phys. Rev. B* **49**, 8024–8028 (1994).