



PSI

Center for Scientific Computing,
Theory and Data

Koopmans functionals

How satisfying piecewise linearity can yield reliable band structures

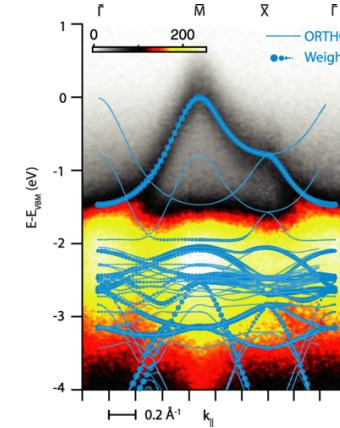
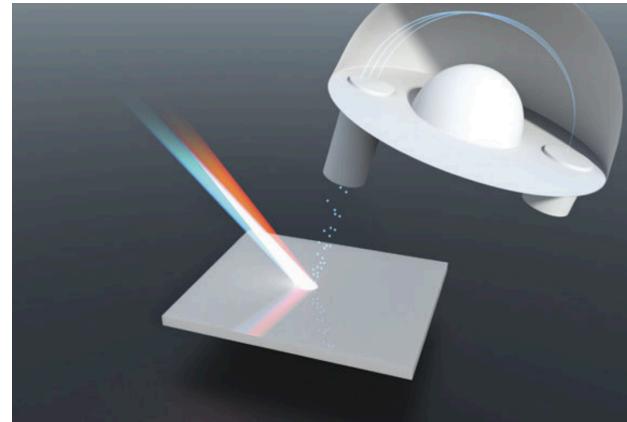
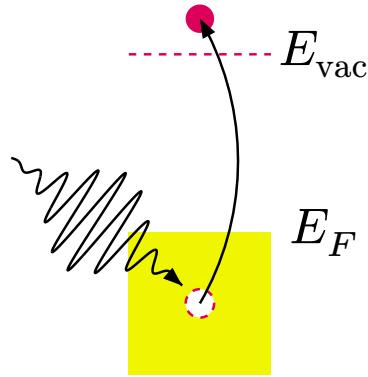
Edward Linscott

Psi-k, 27 August 2025

REMEMBER
THAT BOTH THE AND
Koopmans WILL HAVE
STRESSED SIZES OF
THIS IMPOSSIBLE

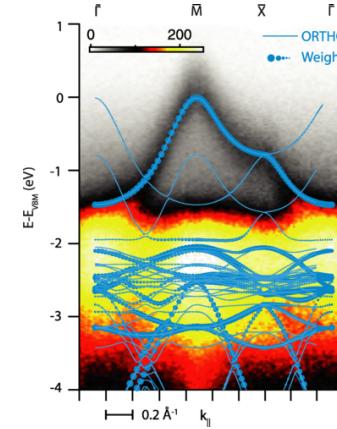
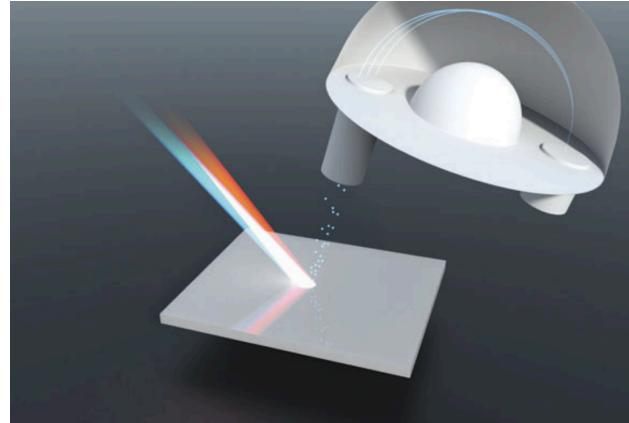
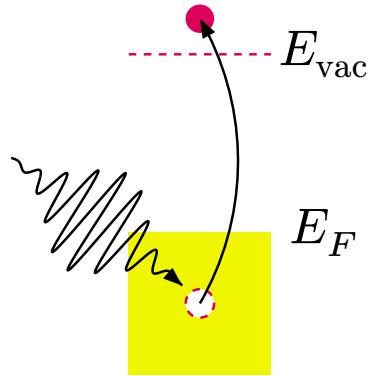
Predicting spectral properties

Spectral properties are fundamental to understanding materials...



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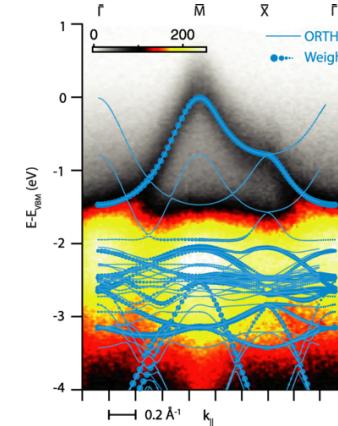
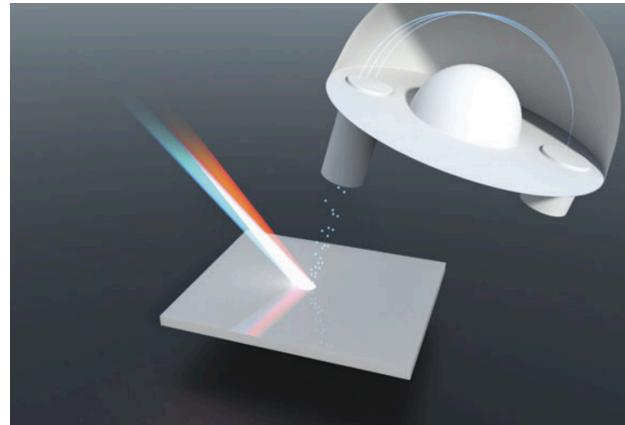
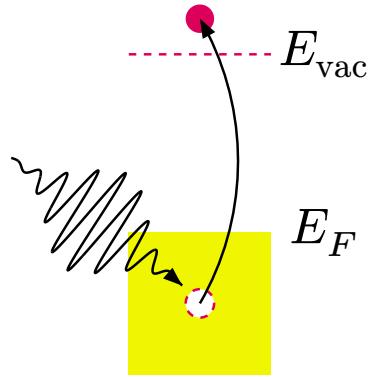


... but how can we routinely compute them?

SOMETIMES IT'S GOOD
TO ACK AUTHORS OF
FIGURES IF YOU DON'T
MAKE THEM!

Predicting spectral properties

Spectral properties are fundamental to understanding materials...



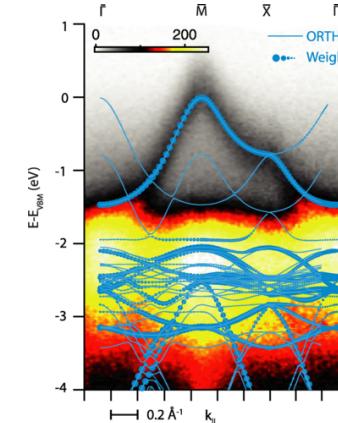
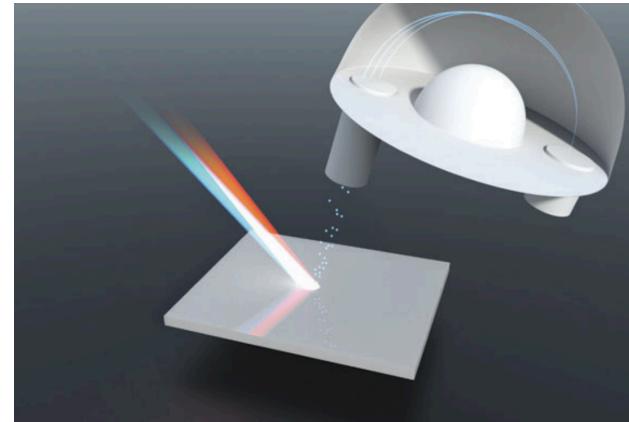
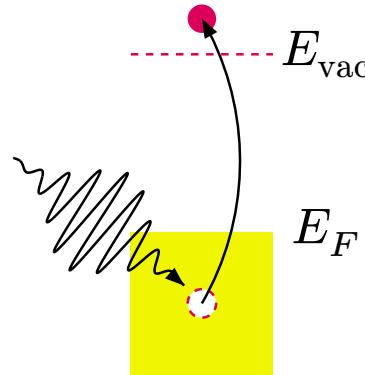
... but how can we routinely compute them?

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

INTRINSIC ?

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

overcomes intrinsic limitation of

 Koopmans functionals: ~~overcomes 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

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

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

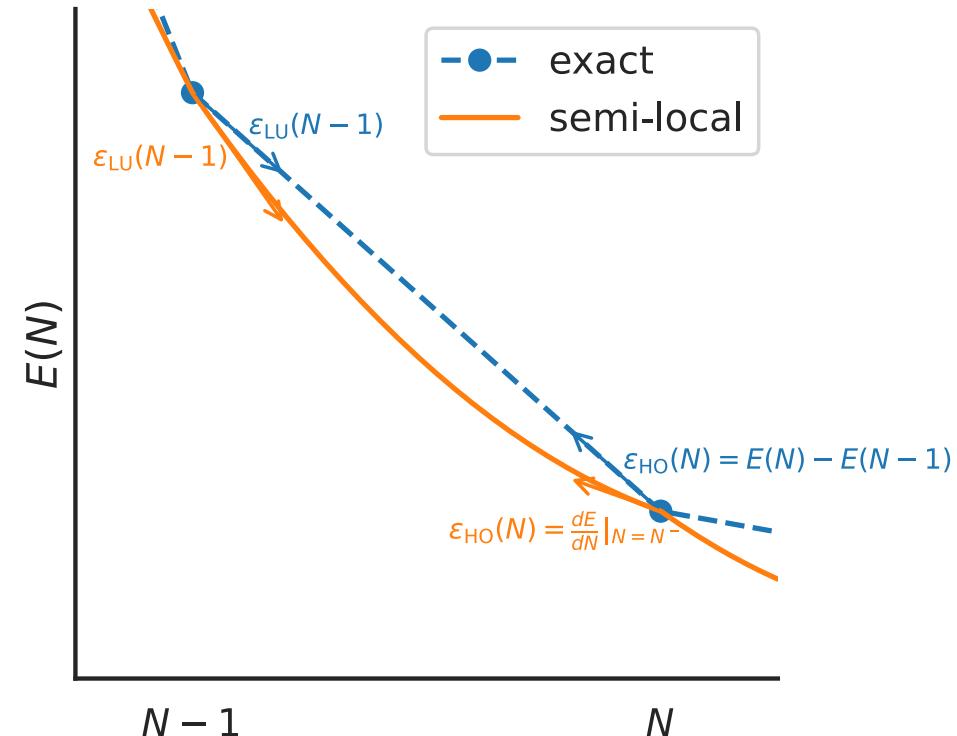
Total energy differences vs. eigenvalues

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but DFT does *not*



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

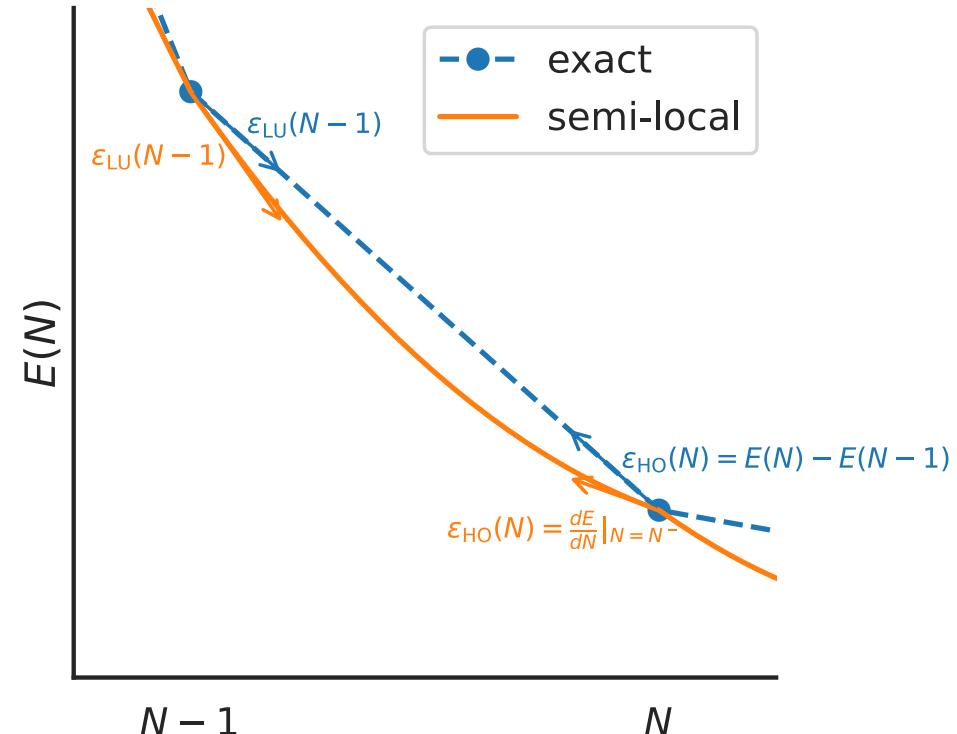
Imposing generalised piecewise linearity

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

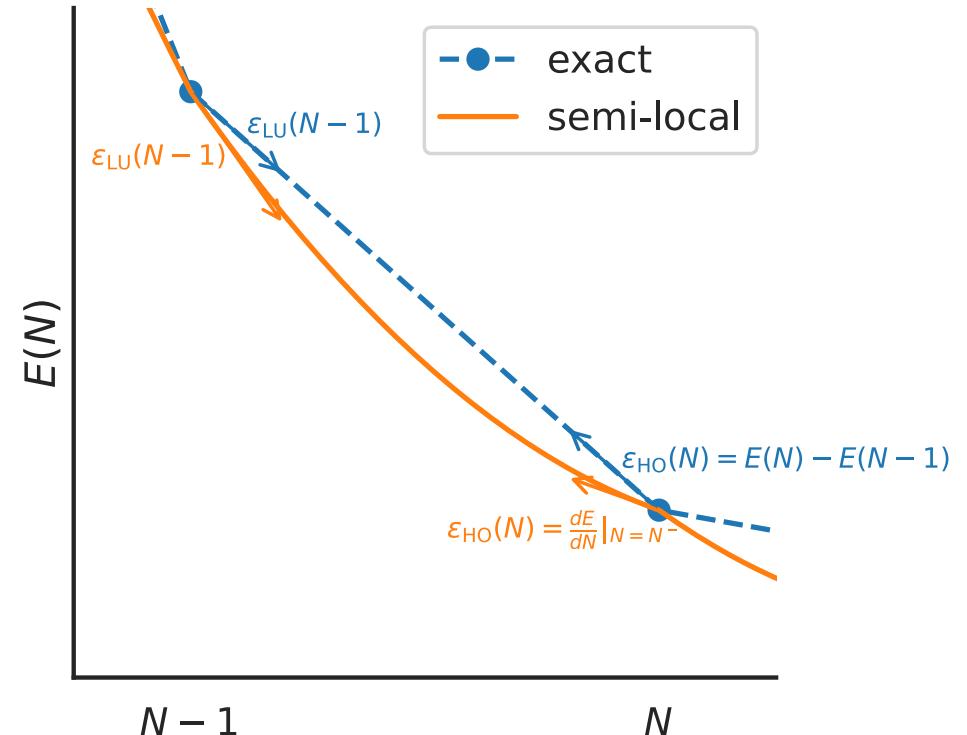
- independent of f_i
- equal to ΔE of explicit electron addition/
removal



Imposing generalised piecewise linearity

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

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

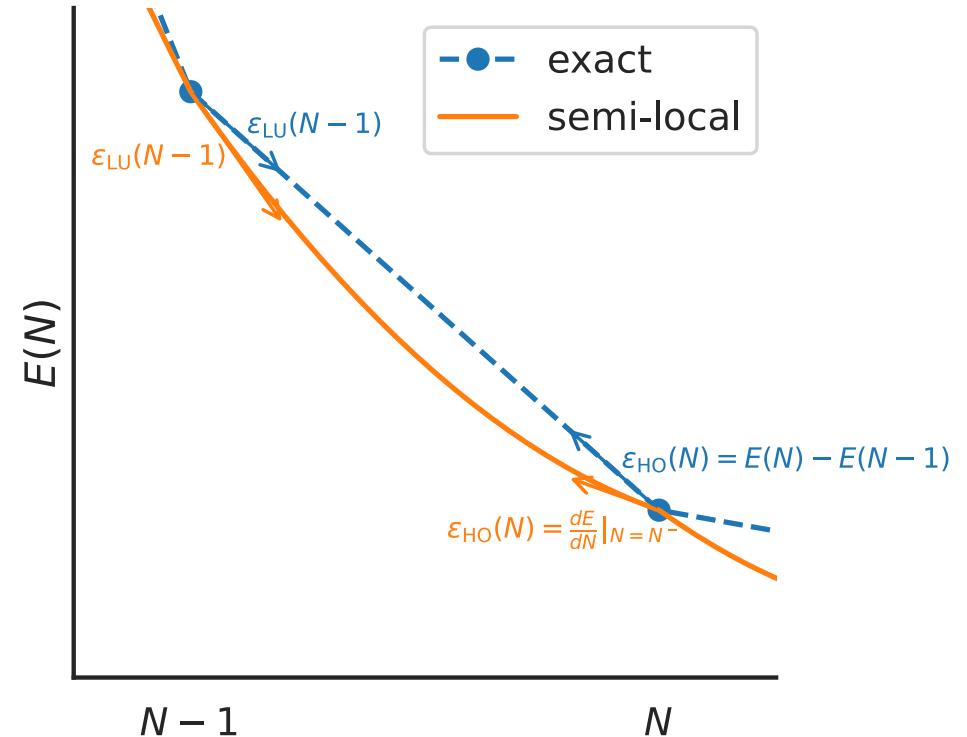


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removes dependence on f_i



Imposing generalised piecewise linearity

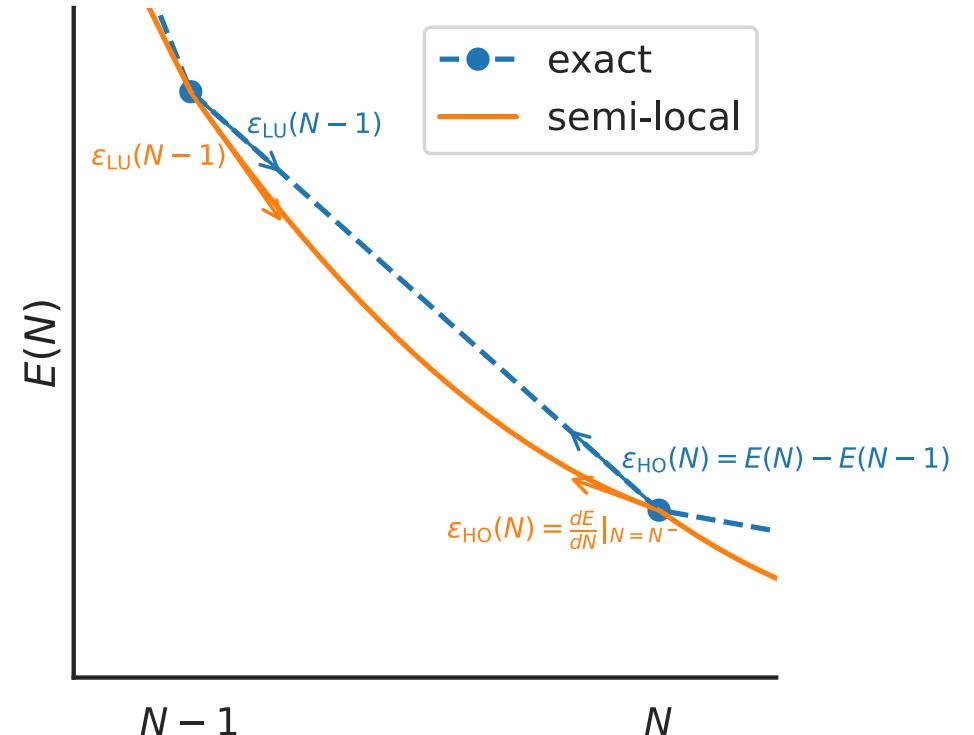
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$$+ f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

removes dependence on f_i

restores linear dependence on f_i



Comparison with DFT+U (and BLOR)

DFT+U	Koopmans
seeks to correct...	
by construction...	NOT SUPPOSE THIS "GLOBAL" VS "LOCAL"
correction applied to...	OF HJ _{KS} IS GOOD?
orbitals defined by...	
parametrised by...	

Comparison with DFT+U (and BLOR)

	DFT+U	Koopmans
seeks to correct...	erroneous global curvature in total energies w.r.t. N	
by construction...		<p>AT THIS ENN DFT + U</p> <p>SEEKS TO CORRECT CURVATURE</p> <p>OF f ON A LOCAL MANIFOLD.</p>
correction applied to...		
orbitals defined by...		
parametrised by...		

Comparison with DFT+ U (and BLOR)

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

Making the functional tractable

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

↓

IT SEEMS VERY DRAMATIC
CALLING IT
UNTRACTABLE?

WARS BE GONE TO FIND A
BOTTLENECK?

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

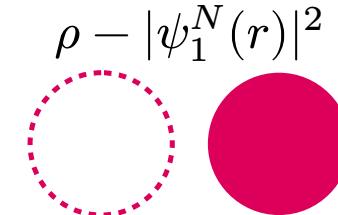
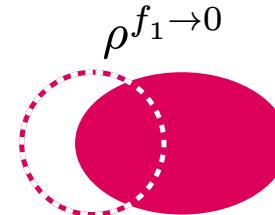
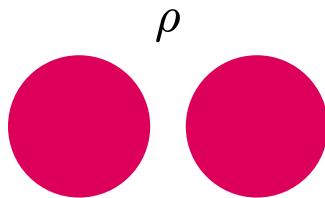
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cannot evaluate directly cannot evaluate directly cannot evaluate directly

Making the functional tractable

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cannot evaluate directly cannot evaluate directly cannot evaluate directly

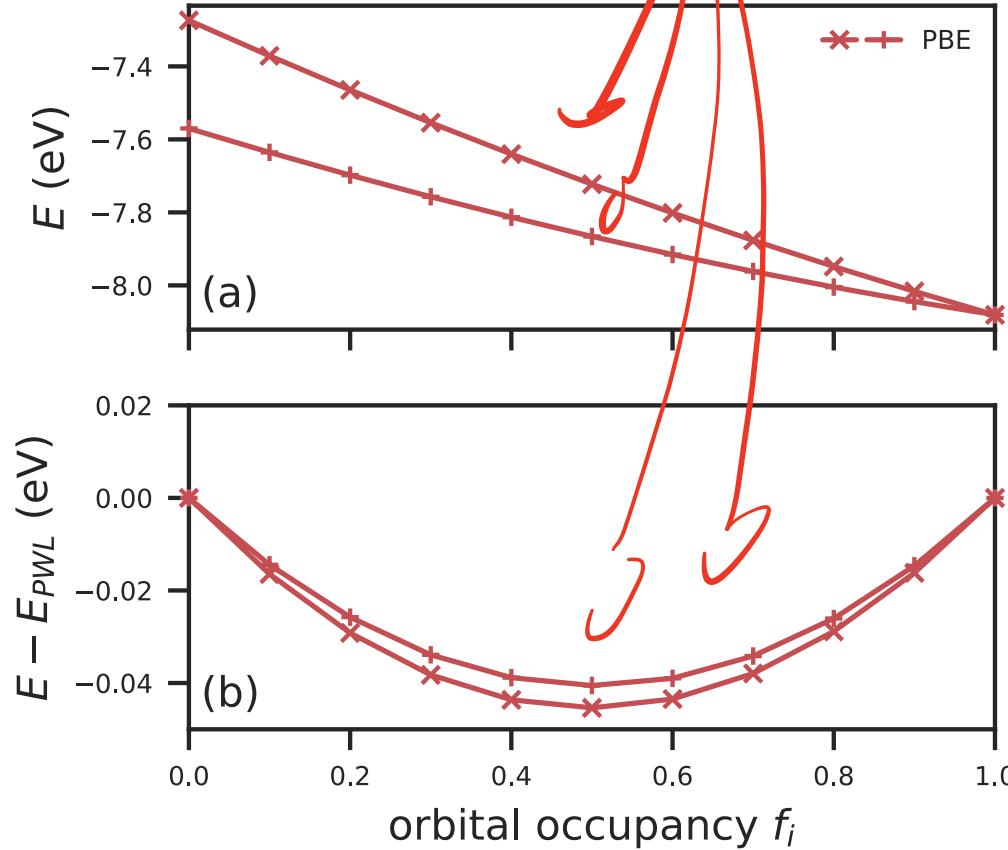


2-electron solution

what we'd like to evaluate

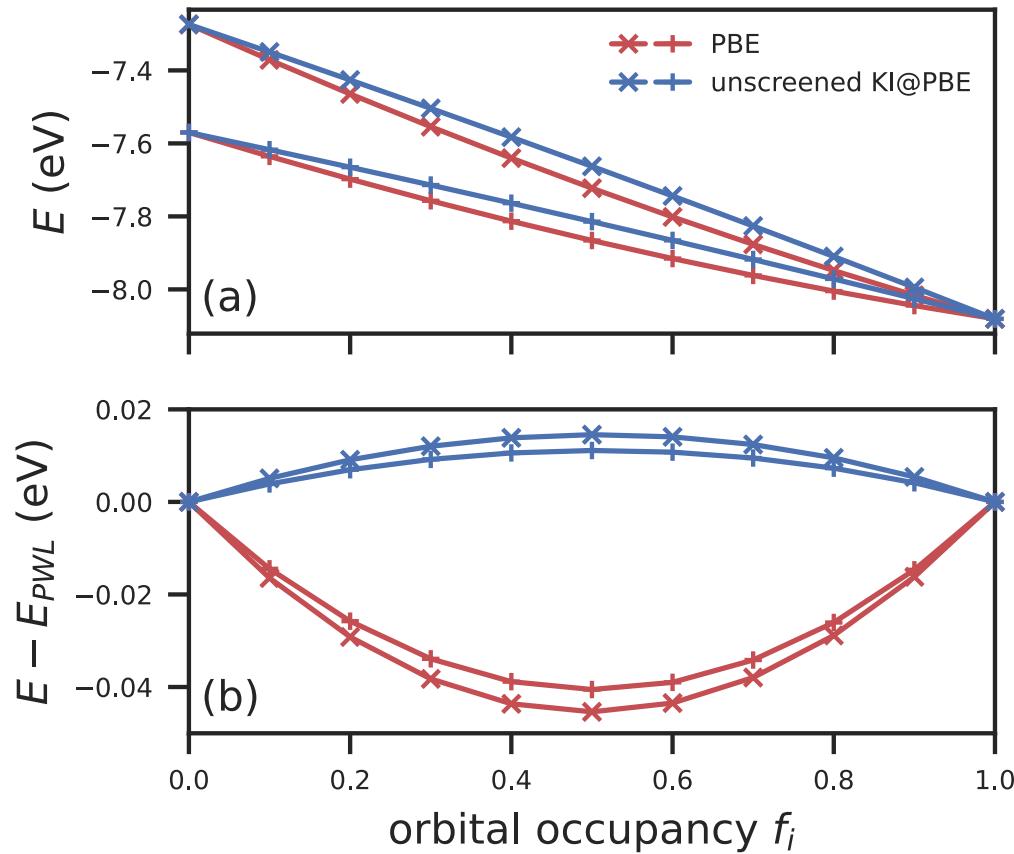
what we can quickly evaluate

Making the functional tractable

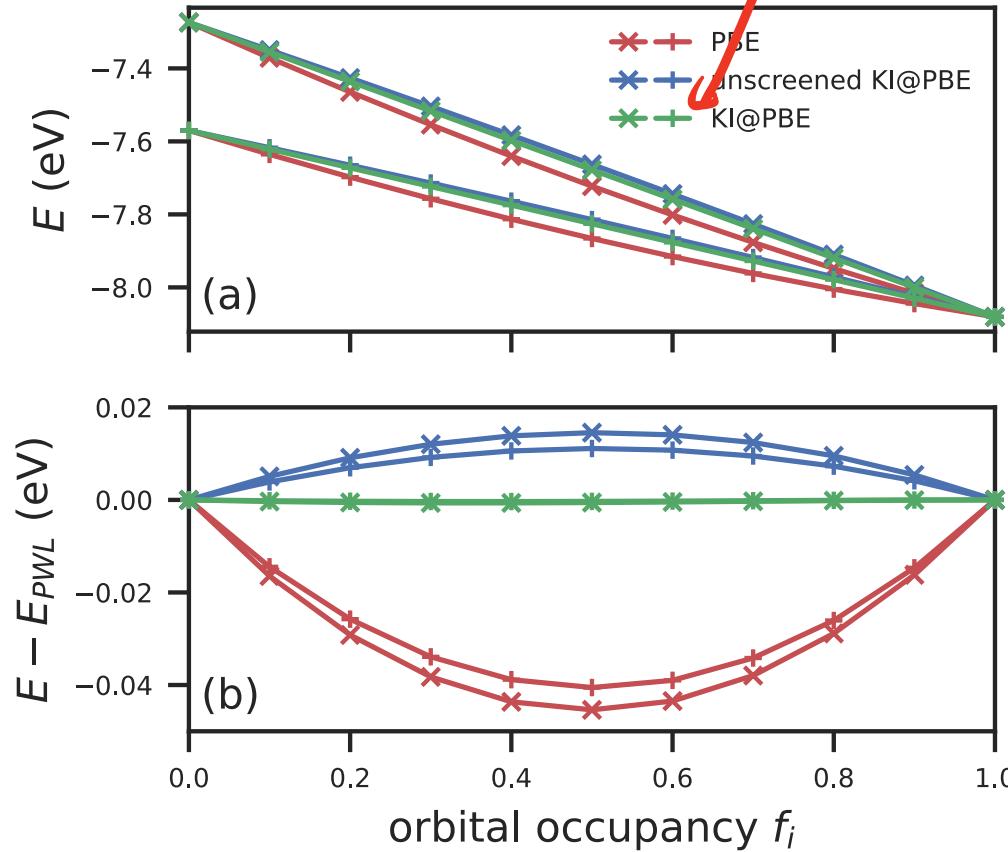


SPECIFY IT'S
TWO ORBITALS
IN HFRHAN

Making the functional tractable



Making the functional tractable



Making the functional tractable

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

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

Making the functional tractable

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uses frozen orbitals uses frozen orbitals uses frozen orbitals

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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

which is easy to evaluate e.g.

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

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Screening parameters *not* a fitting parameter!

Orbital-density dependence

The potential is orbital-density-dependent!

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

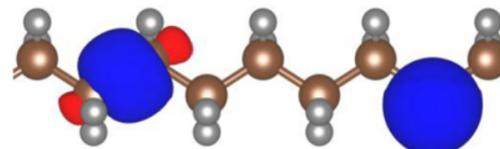
¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

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

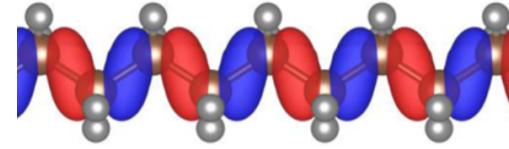
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two variational orbitals



a canonical orbital

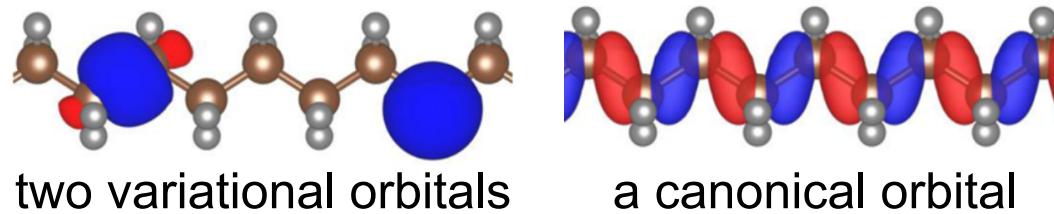
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- minimisation gives localised orbitals, so we can use MLWFs¹

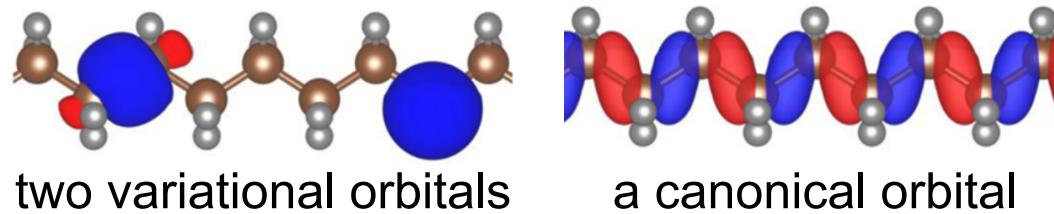
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- minimisation gives localised orbitals, so we can use MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}

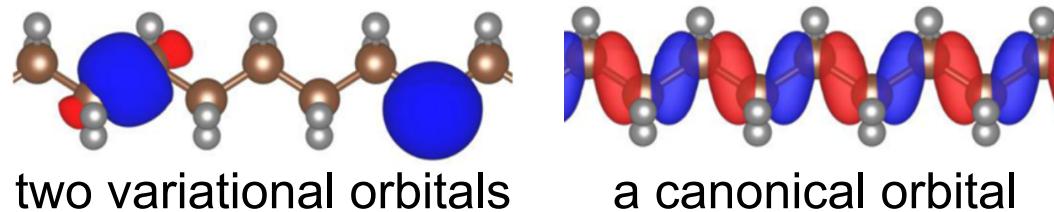
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- minimisation gives localised orbitals, so we can use MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}
- we have a natural generalisation of DFT towards spectral functional theory²

I WOULD IF ONE SHOULD
USE / DISCUSS HOW THE
POLYETHYLENE CHAIN.

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

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

To summarise...

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

ADDITION

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

*AT INTEGRAL
occupation*

Comparison with DFT+U (and BLOR)

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

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
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<i>correction applied to...</i>	selected subspaces (e.g. $3d$ orbitals)	
<i>orbitals defined by...</i>		
<i>parametrised by...</i>		

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	DFT+U	Koopmans
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<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>		

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<i>by construction...</i>	corrects local curvature in total energies (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>		

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	DFT+U	Koopmans
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<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
<i>seeks to correct...</i>	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. canonical orbital occupancies
<i>by construction...</i>	corrects local curvature in total energies (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
<i>seeks to correct...</i>	erroneous global curvature in total energies w.r.t. N	erroneous global curvature in total energies w.r.t. canonical orbital occupancies
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<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>	$\{U_I\}$	

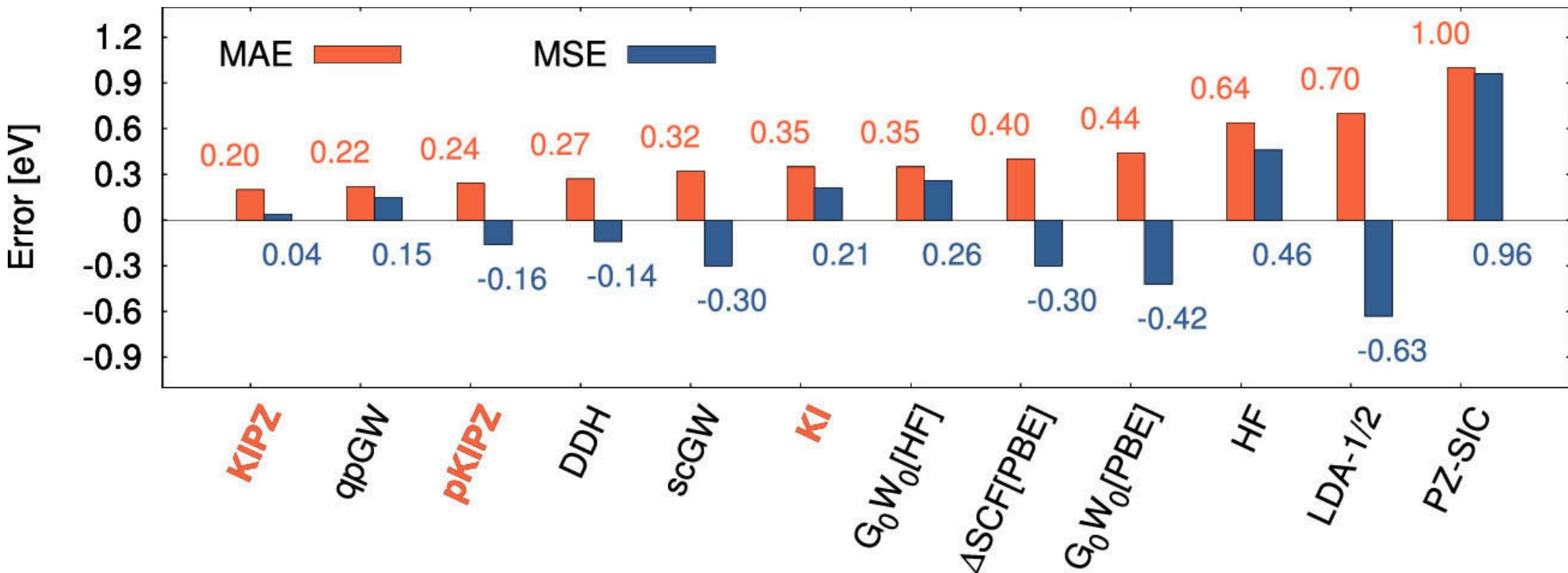
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<i>orbitals defined by...</i>	Hubbard projectors (atom-centred, frozen, incomplete)	variational (localised) orbitals
<i>parametrised by...</i>	$\{U_I\}$	$\{\alpha_i\}$

Results

Molecular systems

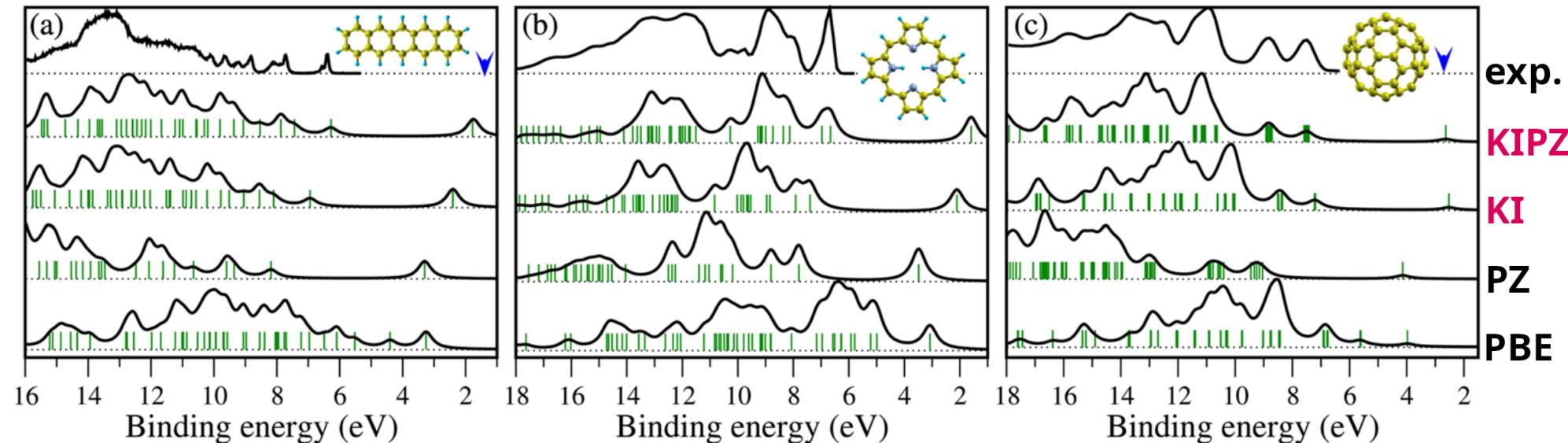
Ionisation potentials¹



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

Molecular systems

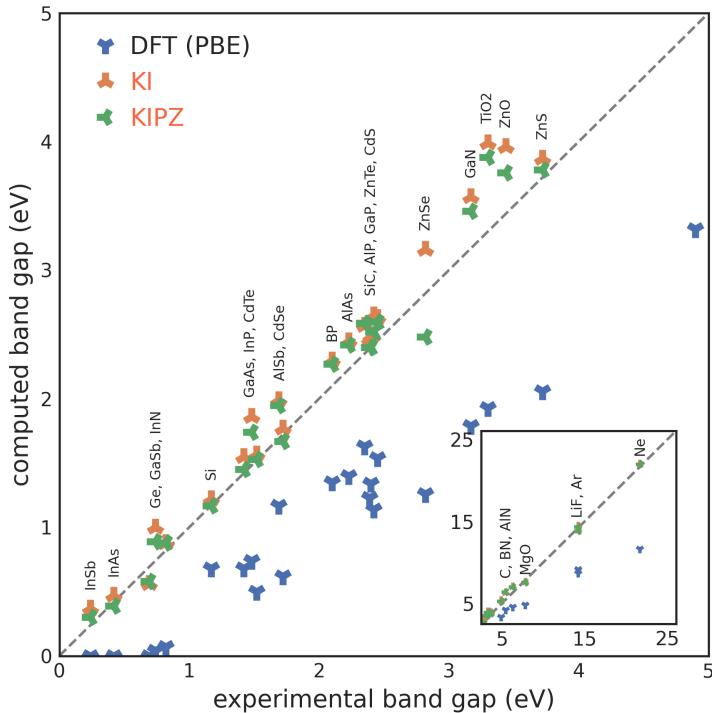
UV photoemission spectra¹



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

Extended systems

Prototypical semiconductors and insulators¹

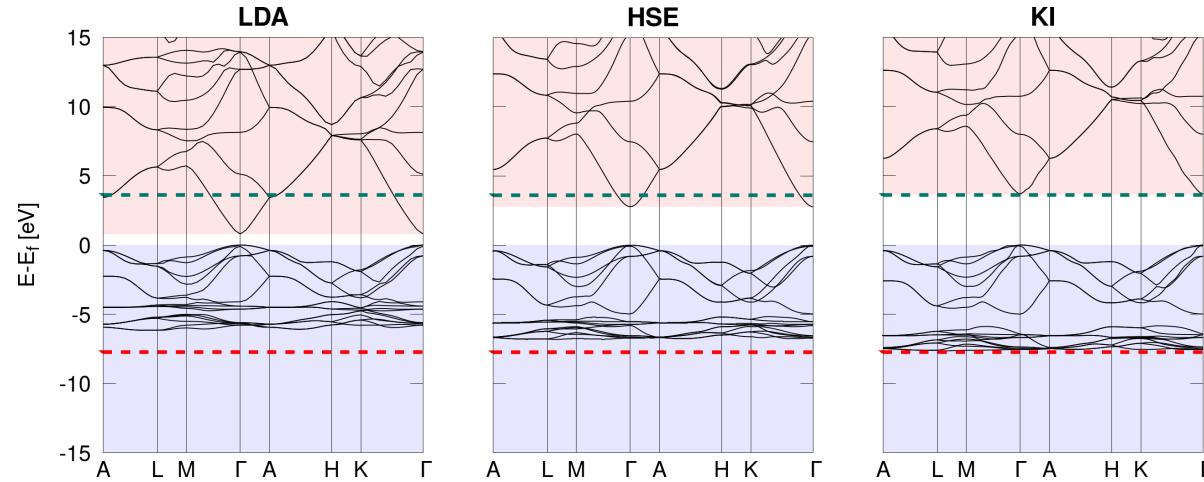


	PBE	G_0W_0	KI	KIPZ	$QSG\tilde{W}$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

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

Extended systems

ZnO¹

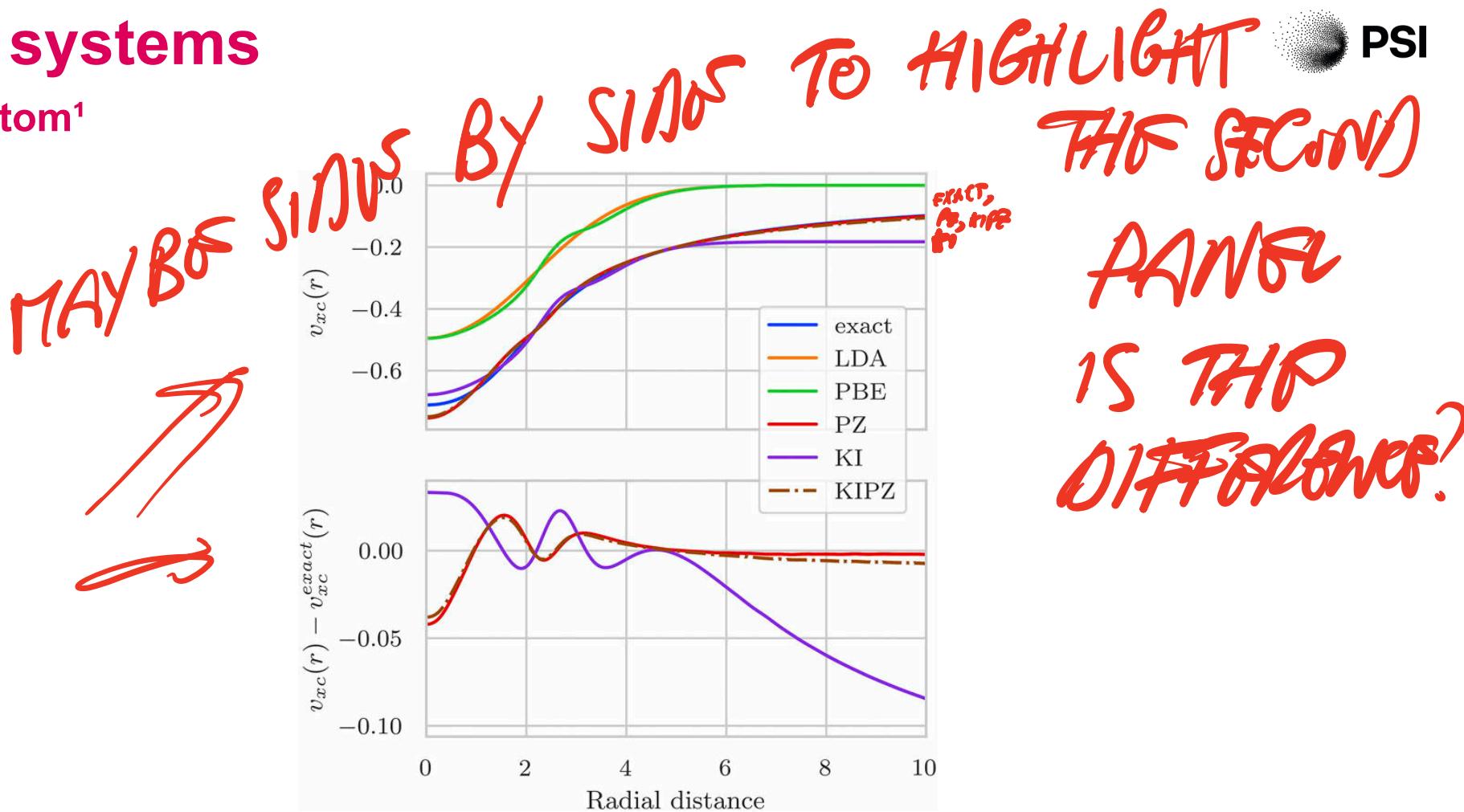


	LDA	HSE	GW_0	$scG\tilde{W}$	KI	exp
E_{gap}	0.79	2.79	3.0	3.2	3.68	3.60
$\langle \varepsilon_d \rangle$	-5.1	-6.1	-6.4	-6.7	-6.93	-7.5 to -8.81
Δ	4.15				4.99	5.3

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 $E_{\text{gap}} > 0$

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- empty state localisation in the bulk limit

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- 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)

On the nice coloring
(you do not use ET AL
for two authors).

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)

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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)

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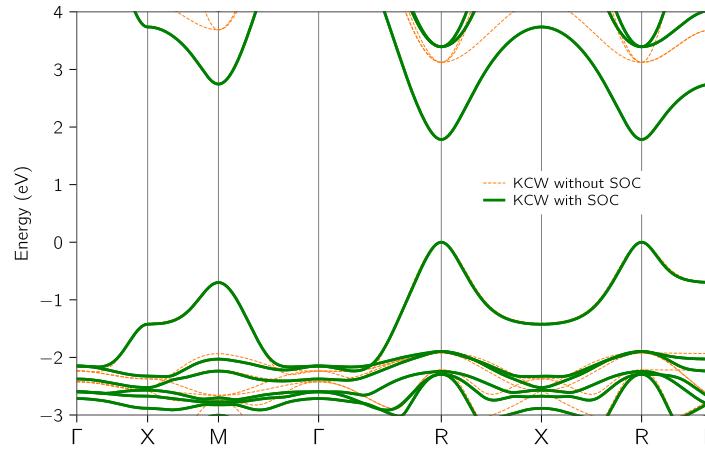
↓

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

¹A. Marrazzo  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)

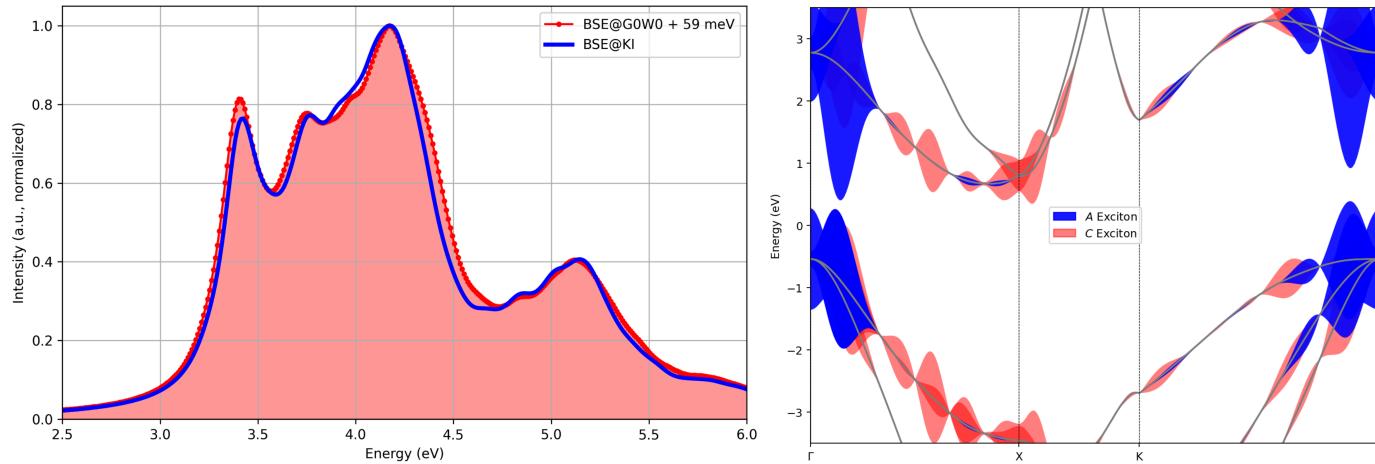
Optical spectra

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)

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- a local measure of screening of electronic interactions

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 - ▶ ΔSCF^1 : embarrassingly parallel steps which each cost $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$

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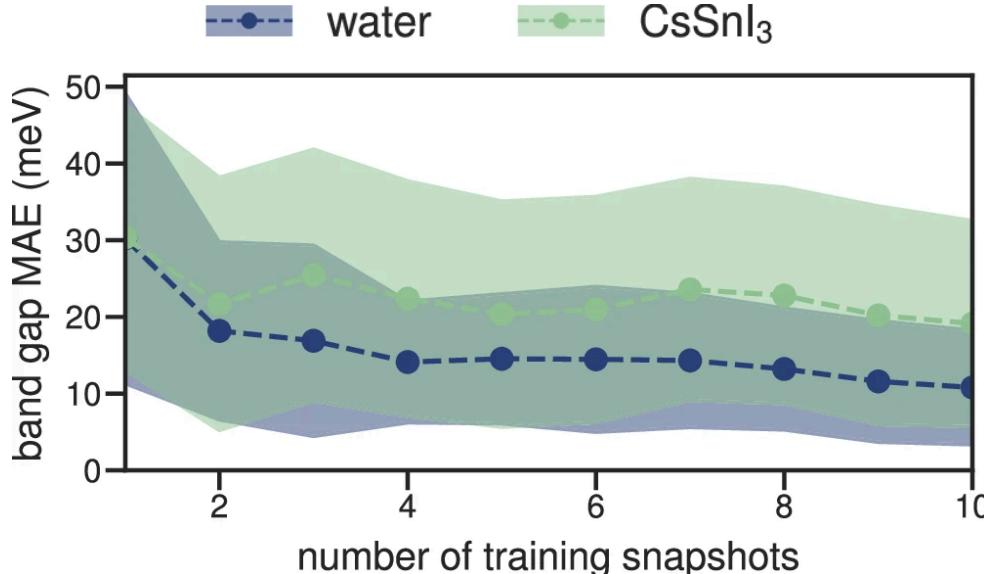
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- a local measure of screening of electronic interactions
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 - ΔSCF¹: embarrassingly parallel steps which each cost $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$
 - DFPT²: $\mathcal{O}(N_{\mathbf{k}}^2 N^3)$
- ... can we go even faster?

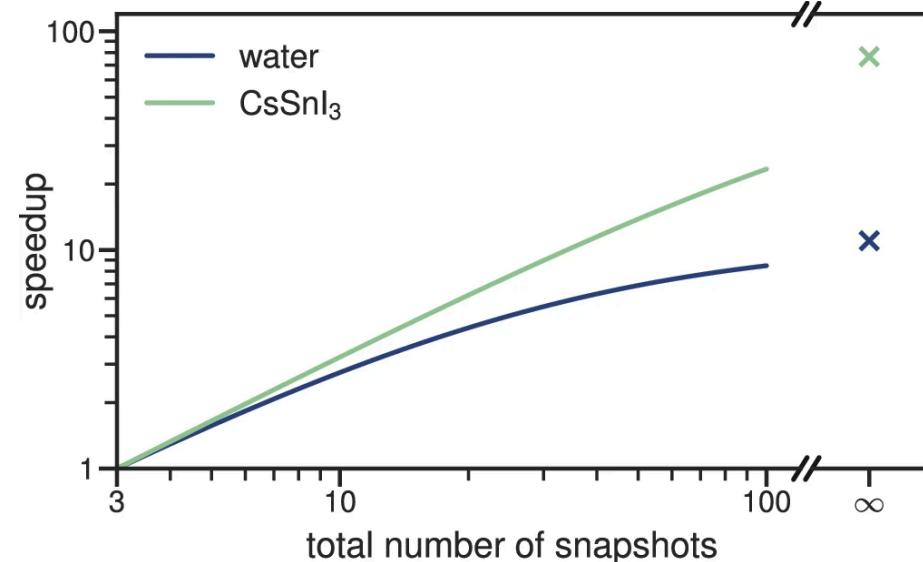
¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

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



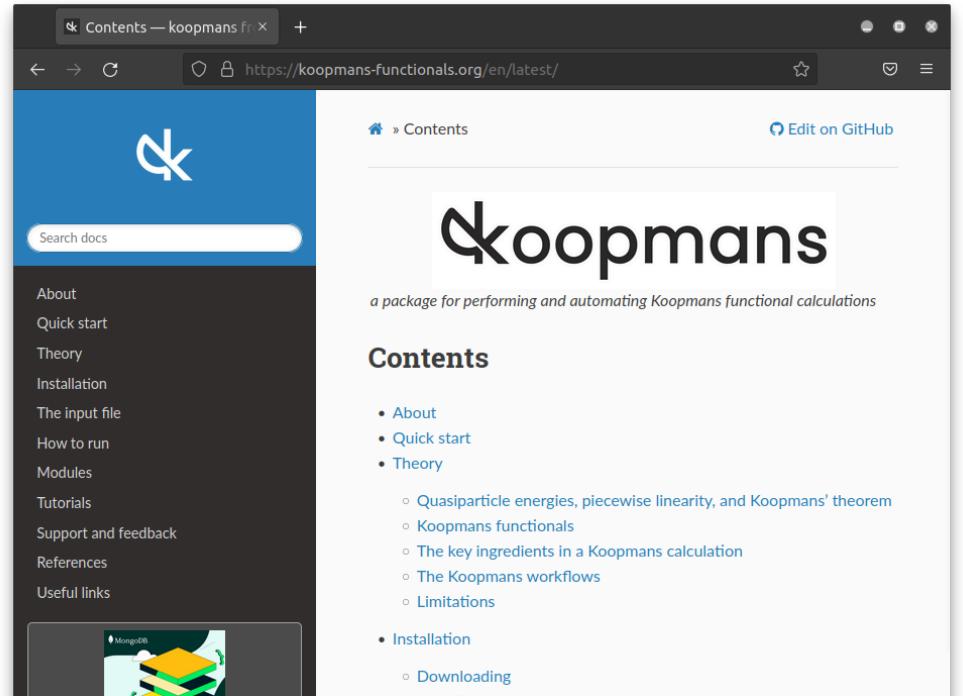
accurate to within $\mathcal{O}(10 \text{ meV})$ cf. typical
band gap accuracy of $\mathcal{O}(100 \text{ meV})$



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

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

skoopmans



A screenshot of a web browser displaying the Koopmans documentation at <https://koopmans-functionals.org/en/latest/>. The page has a blue header with a logo and a search bar. The main content area features the Koopmans logo and a brief description: "a package for performing and automating Koopmans functional calculations". Below this is a "Contents" section with a table of contents:

- About
- Quick start
- Theory
- Installation
- The input file
- How to run
- Modules
- Tutorials
- Support and feedback
- References
- Useful links

Under the "Theory" section, there is a list:

- Quasiparticle energies, piecewise linearity, and Koopmans' theorem
- Koopmans functionals
- The key ingredients in a Koopmans calculation
- The Koopmans workflows
- Limitations

Under the "Installation" section, there is a list:

- Installation
 - Downloading
 - Installation

- I WOULD RECOMMEND
MOMS SPACES TO
THIS - IT IS BORN
A LOT OF
WORK -
- automated workflows
 - Quantum ESPRESSO backend
 - easy installation
 - python API

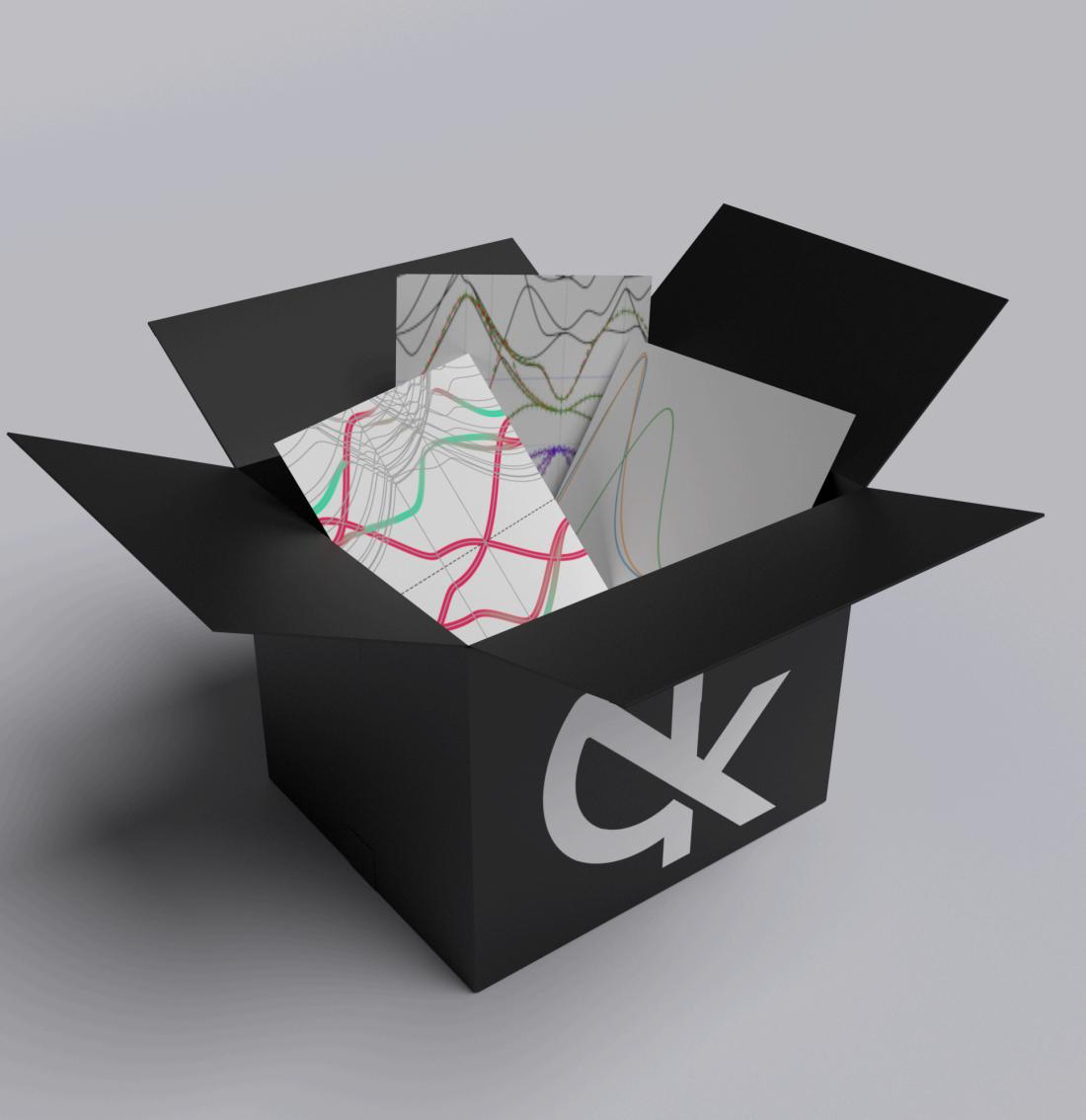
See koopmans-functionals.org

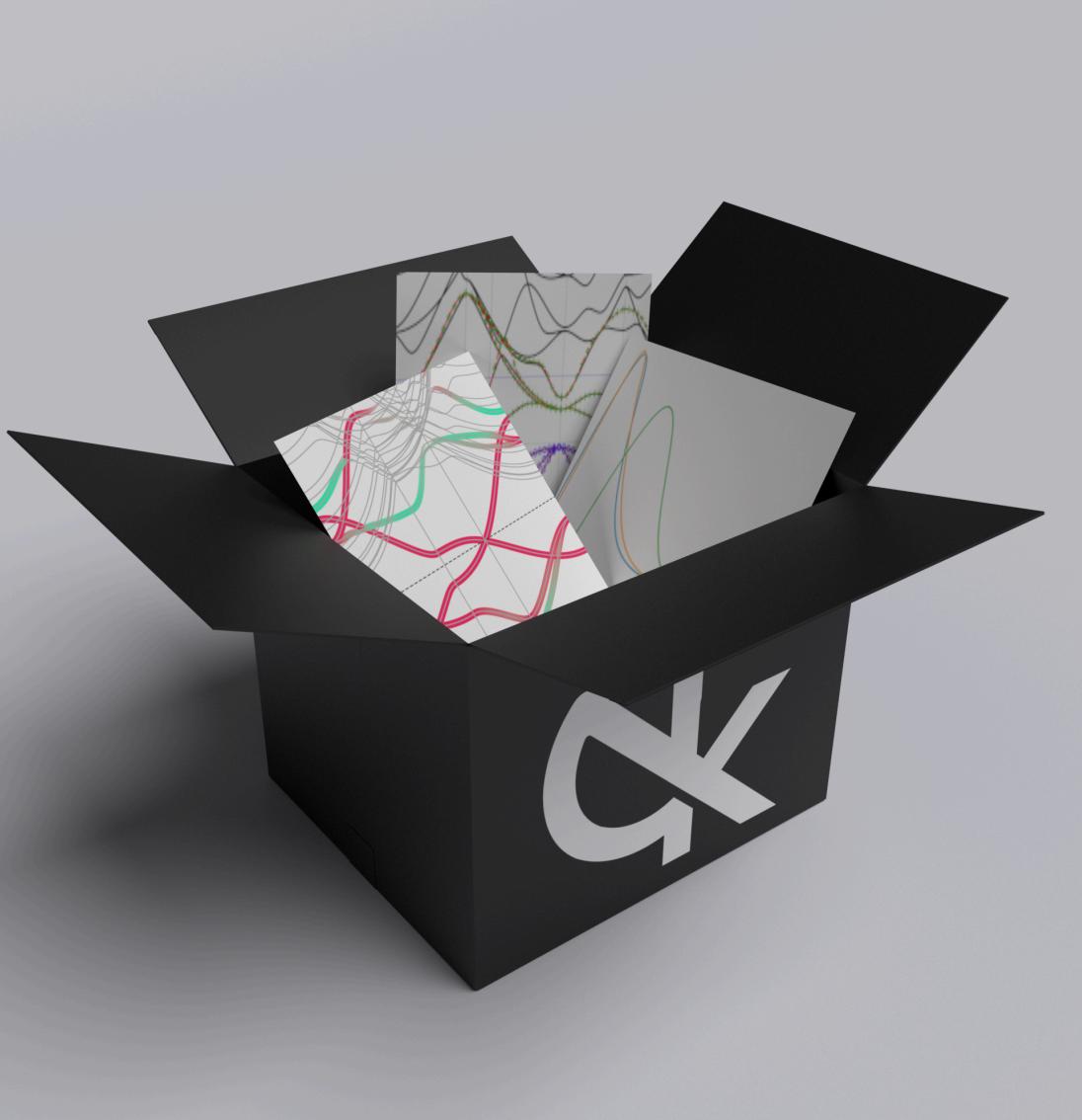
AND SUMMARIZING THE
STEPS MOMS IN DETAIL

DFT → MLWF (PANF) →
(SOMS) VALENCE CONDUCTION + ---
KINN OF WORKER)

Our goal:

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

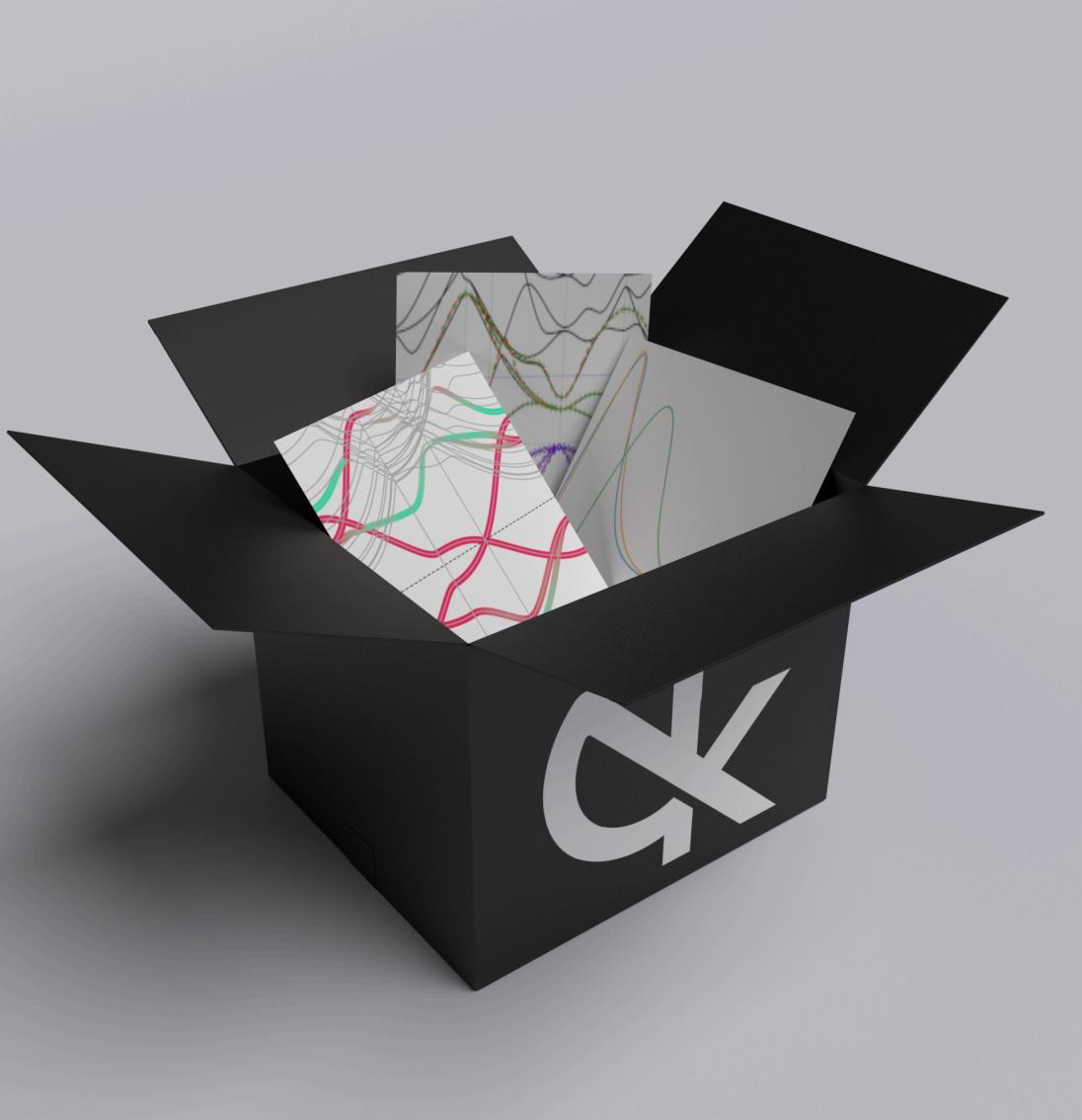




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To this end...

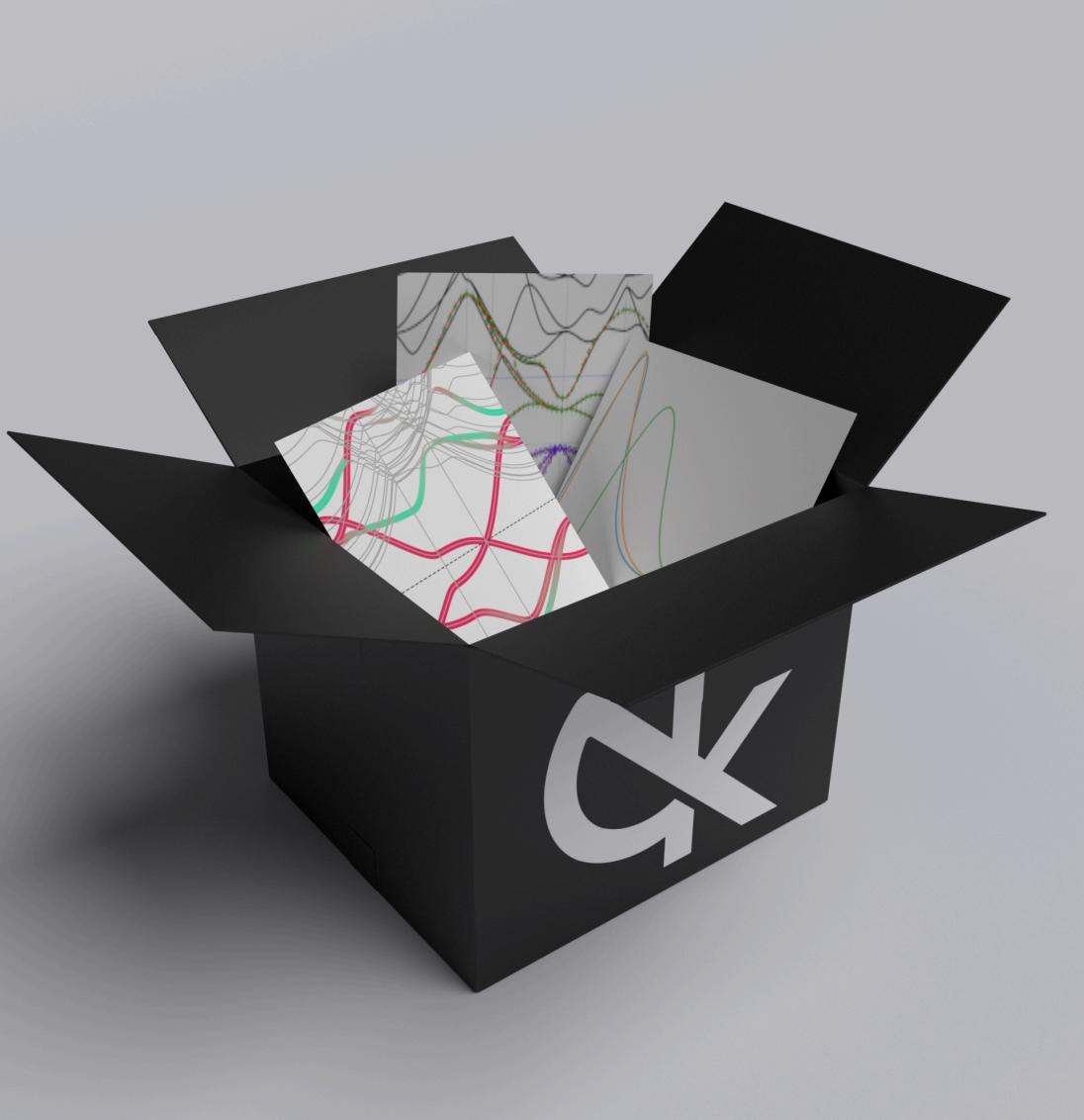


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To this end...

- symmetries

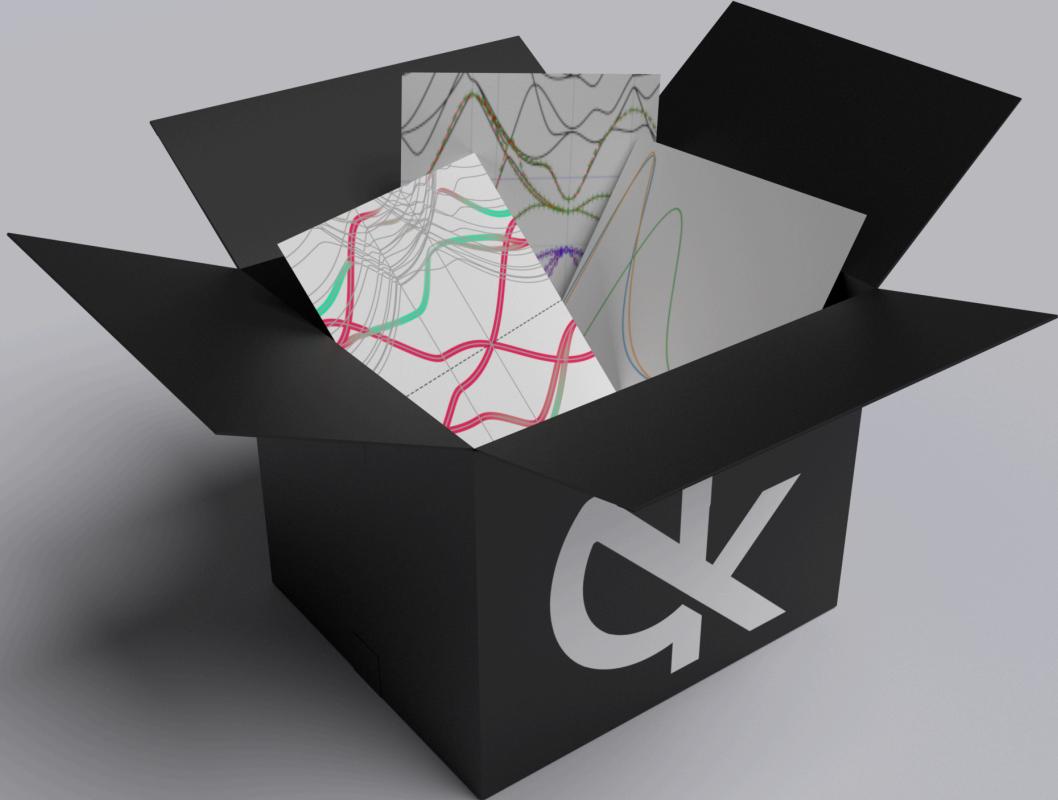


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To this end...

- symmetries
- automated Wannierisation



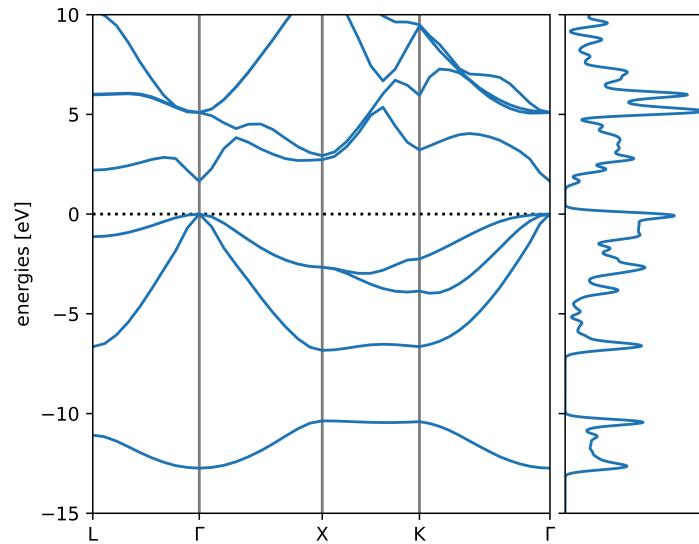
Our goal:

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To this end...

- symmetries
- automated Wannierisation
- AiiDA integration

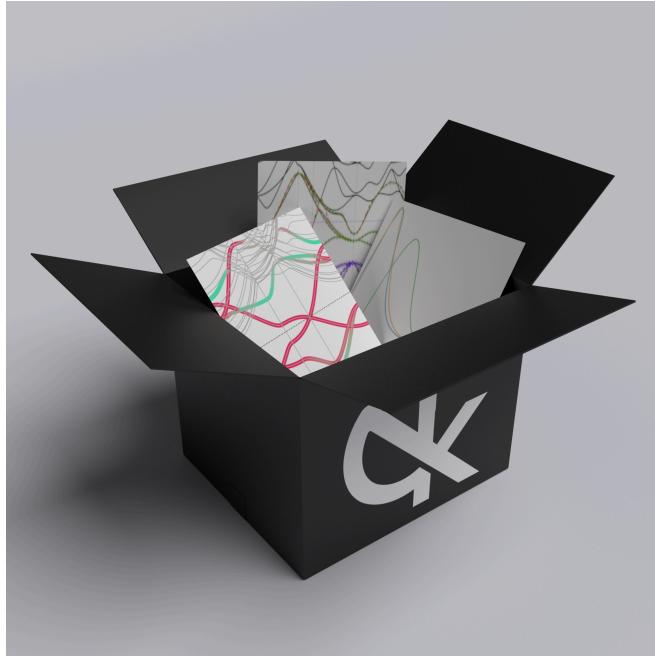
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}
```



	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, 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)

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 - ▶ 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

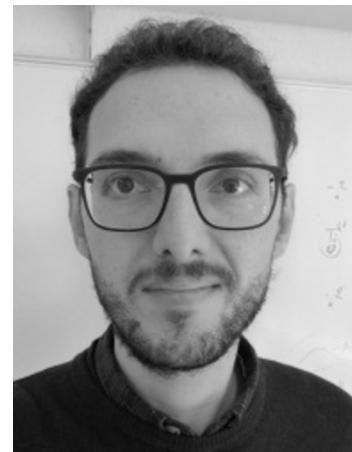
spectral theories



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



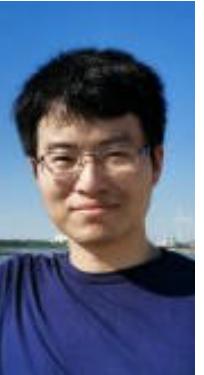
Marija
Stojkovic



Giovanni
Cistaro



Julian
Geiger



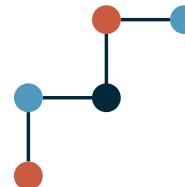
Junfeng
Qiao



Yannick
Schubert



Nicola
Marzari



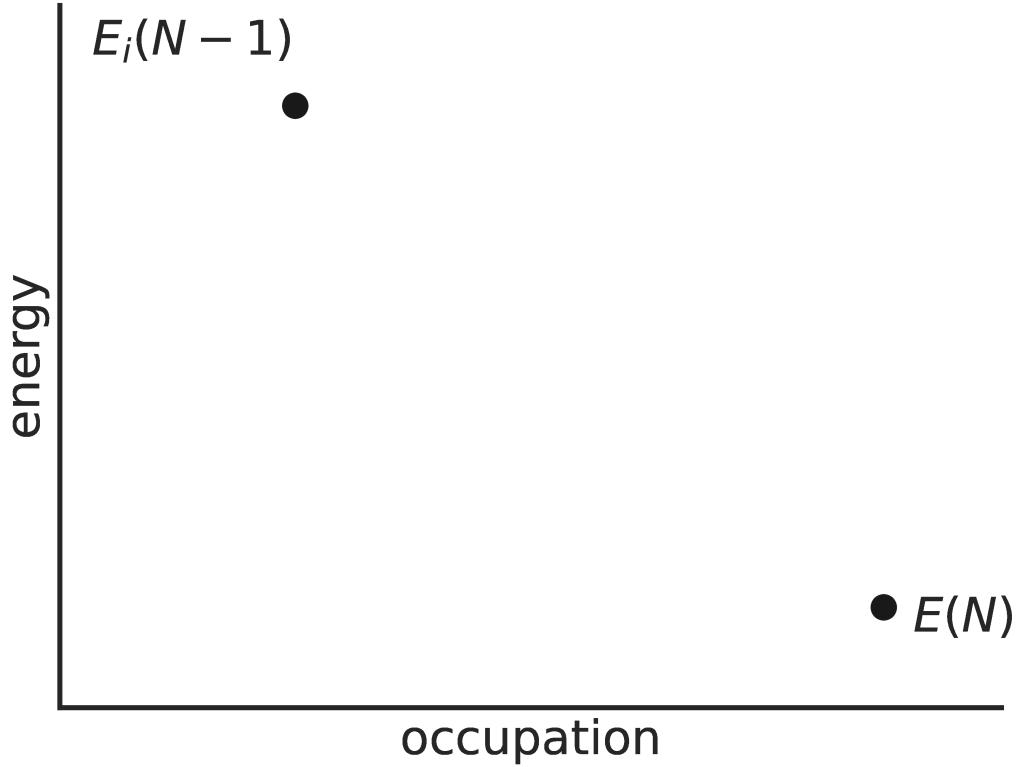
**Swiss National
Science Foundation**

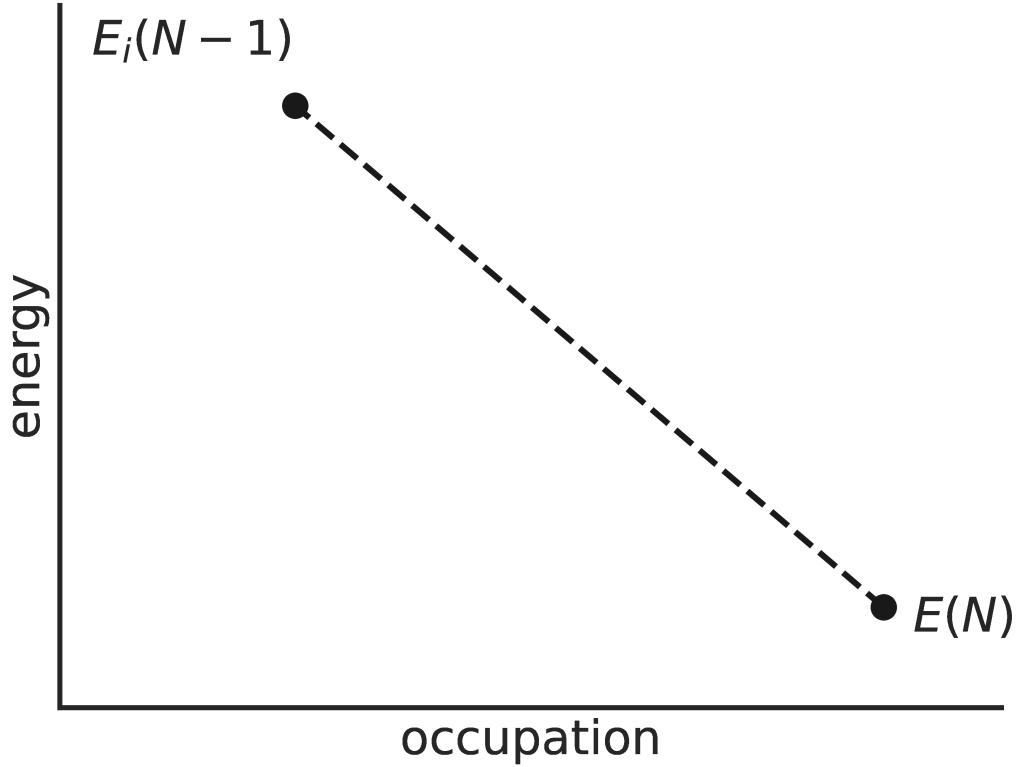
MARVEL

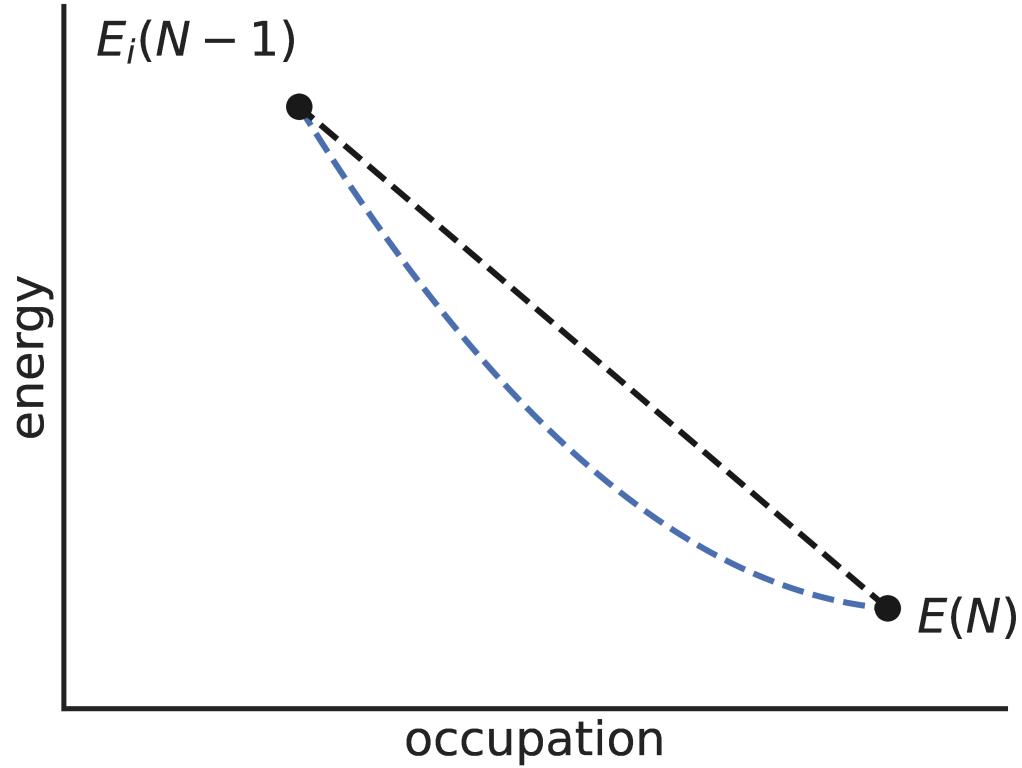

Thank you!

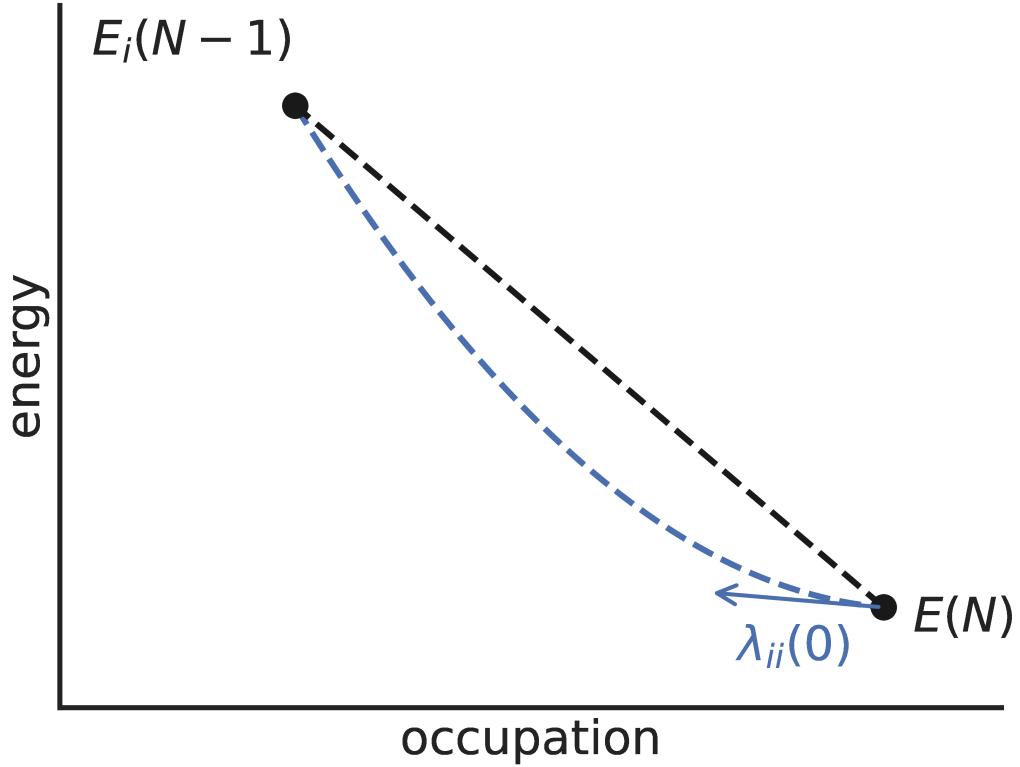
these slides are available at  [elinscott-talks](https://github.com/elinscott-talks)

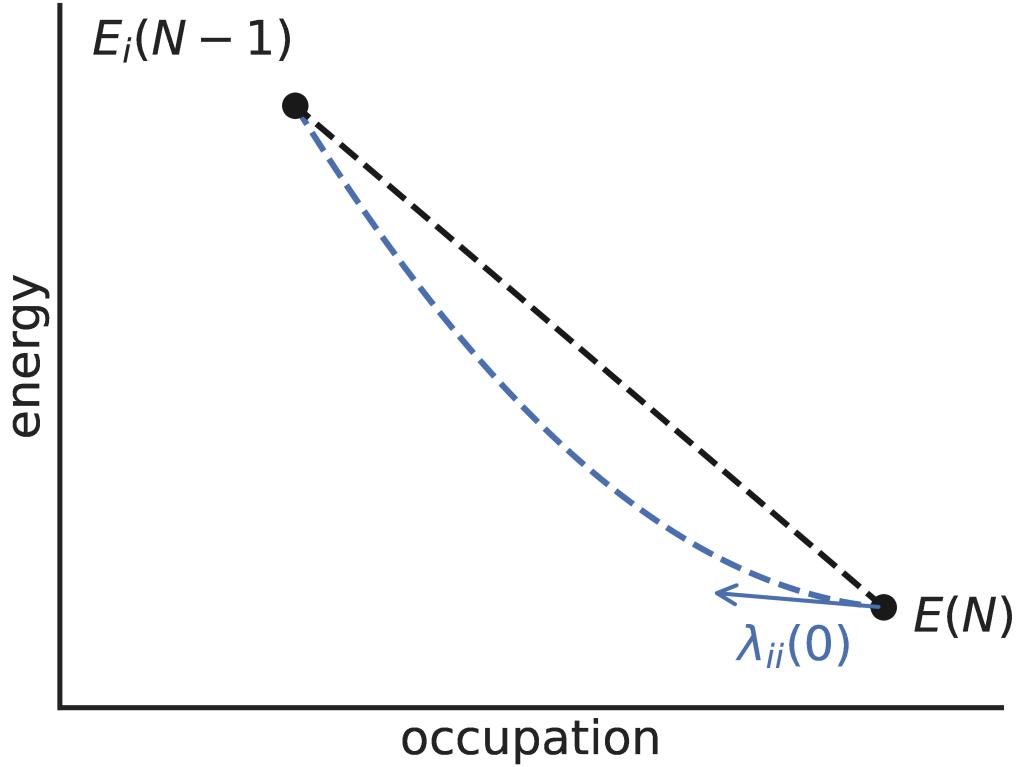
spare slides

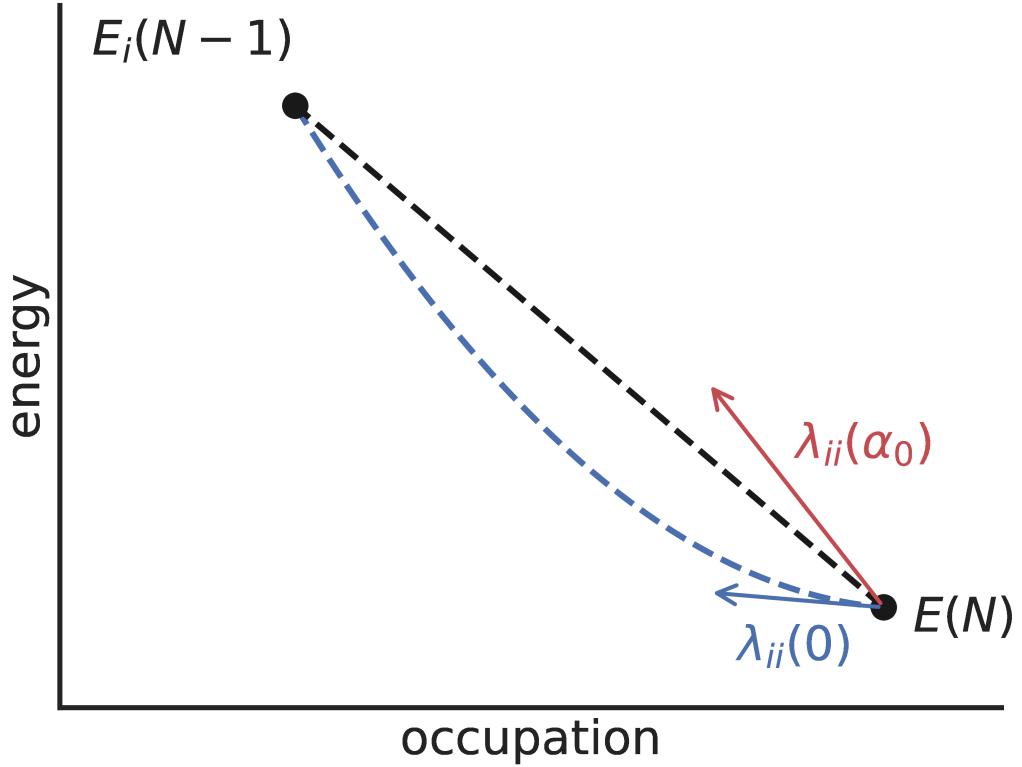


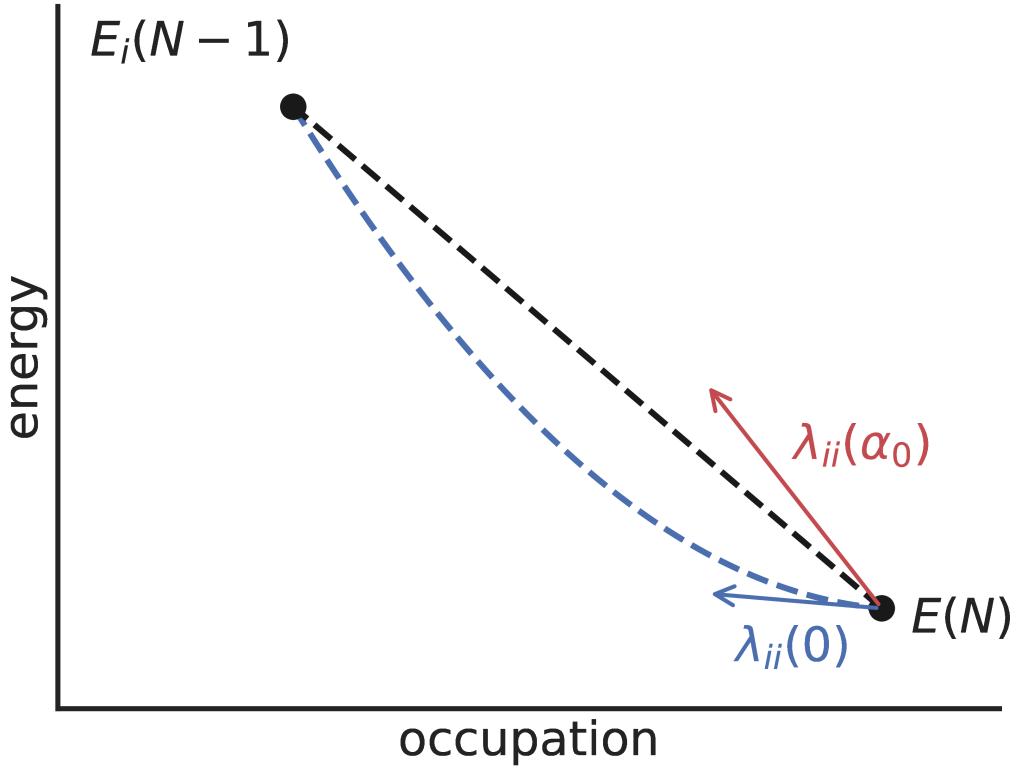








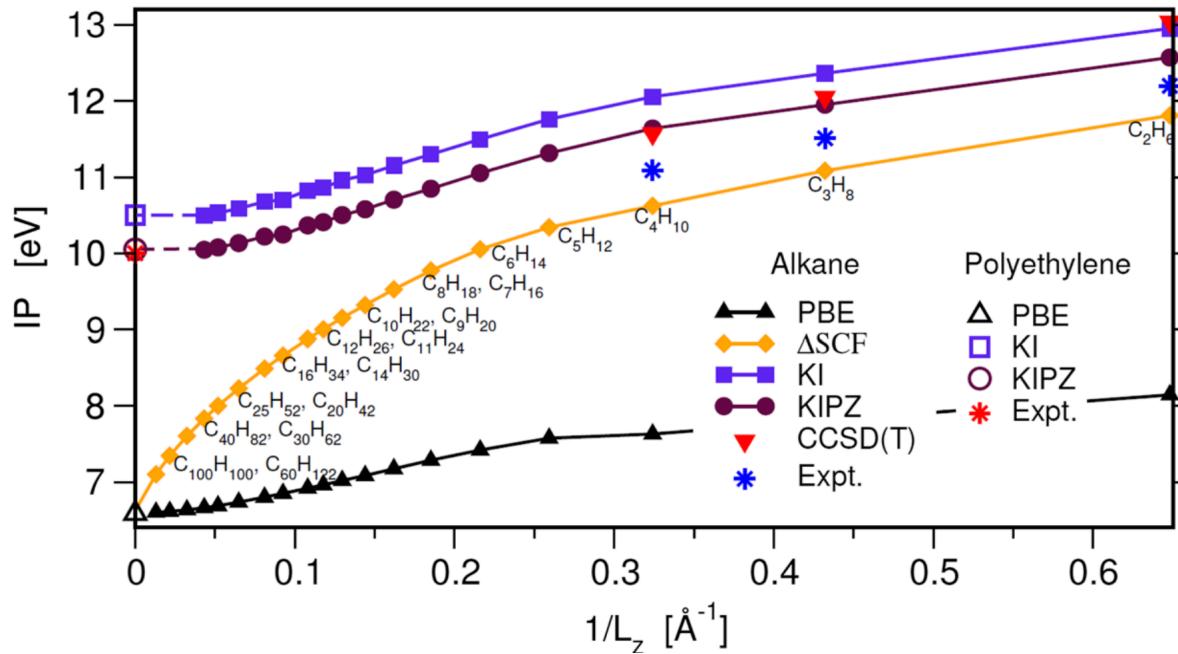




$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

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

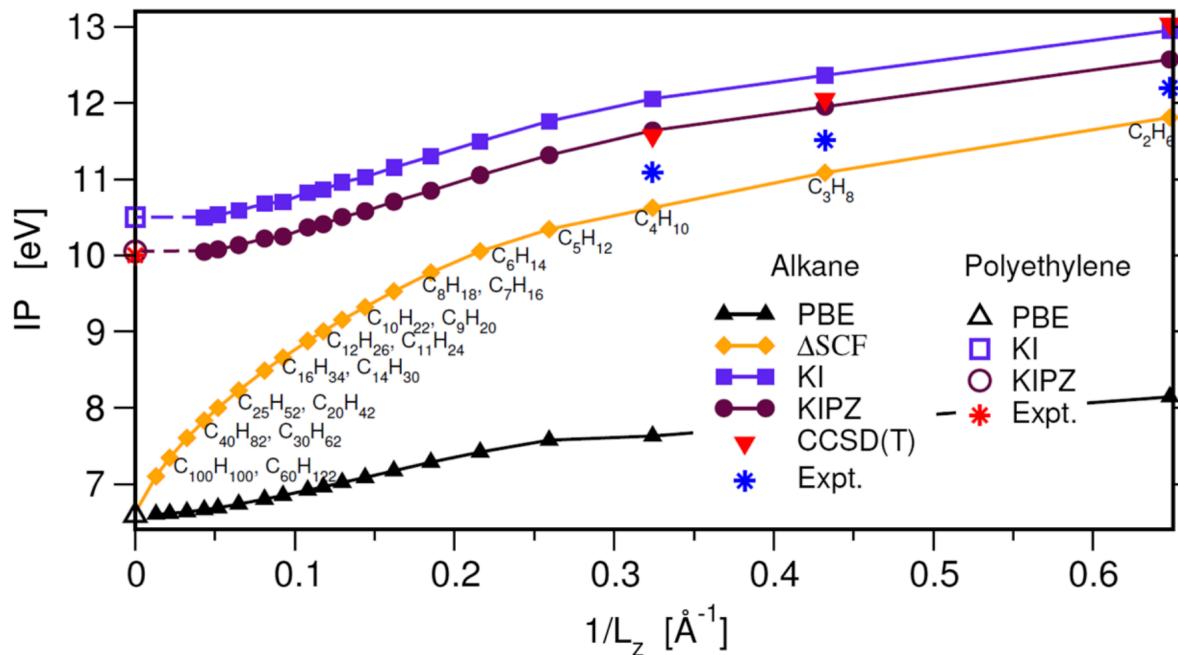
Issues with extended systems



Two options:

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

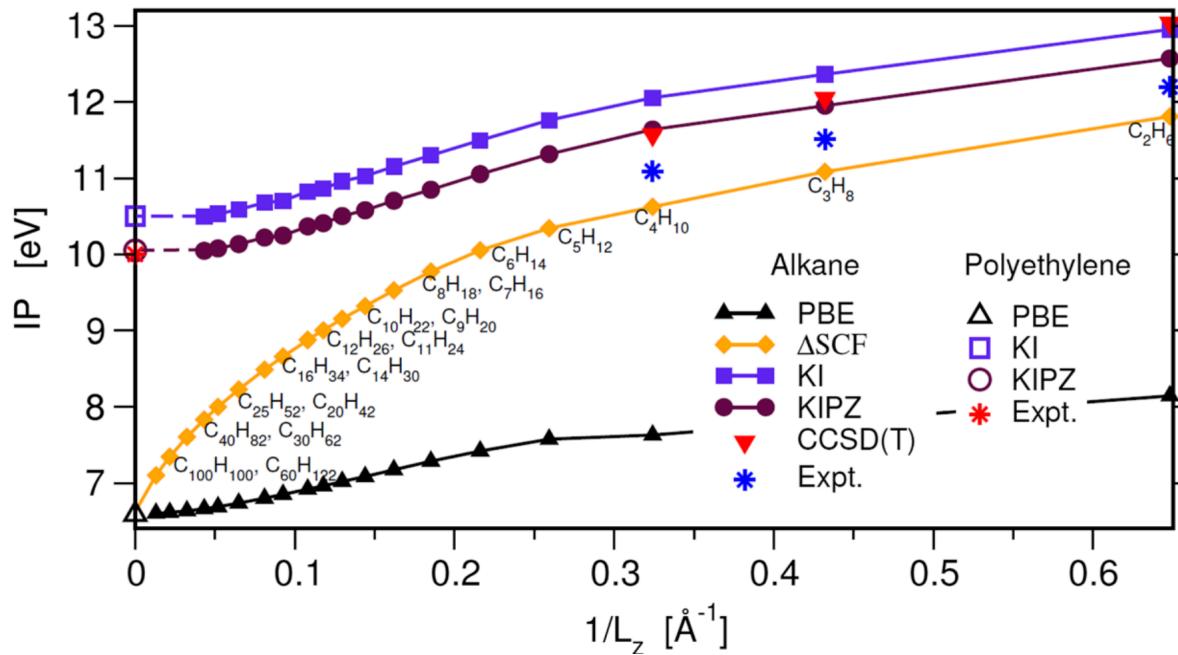
Issues with extended systems



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
        }
    }
}

```

Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

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

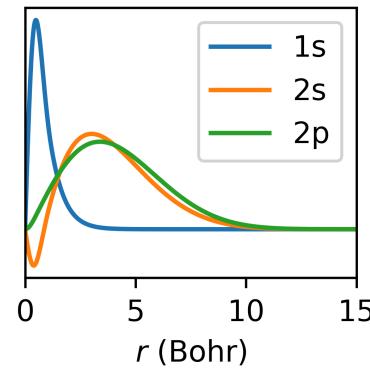
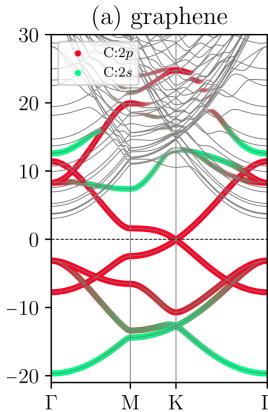
¹J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

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

Automated Wannierisation

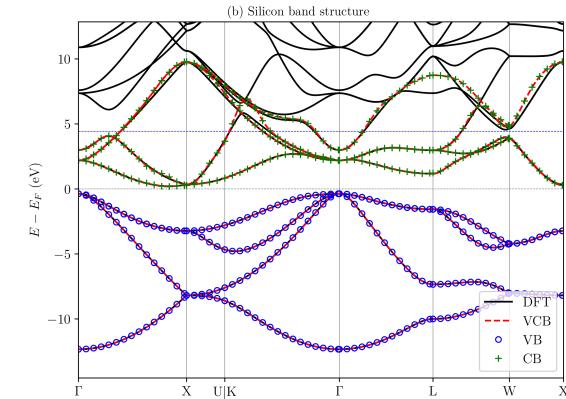
Koopmans functionals rely heavily on Wannier functions...

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



projectability-based
disentanglement¹

use PAOs found in
pseudopotentials

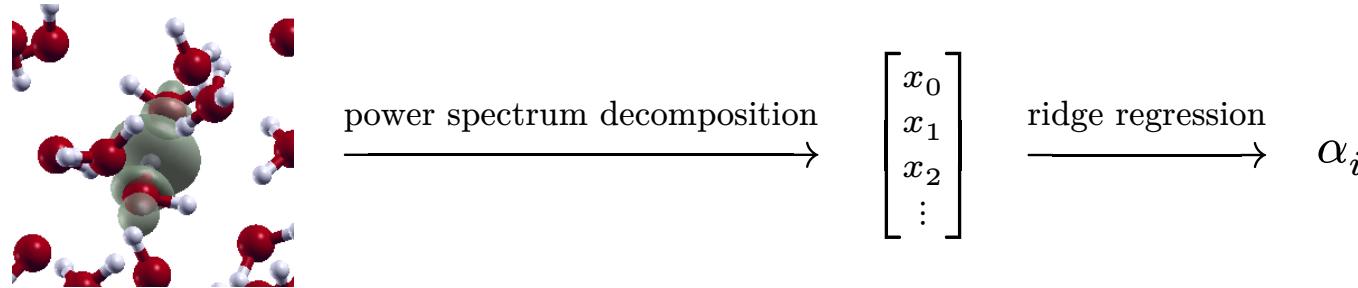


parallel transport to separate
manifolds²

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

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

Machine-learned electronic screening

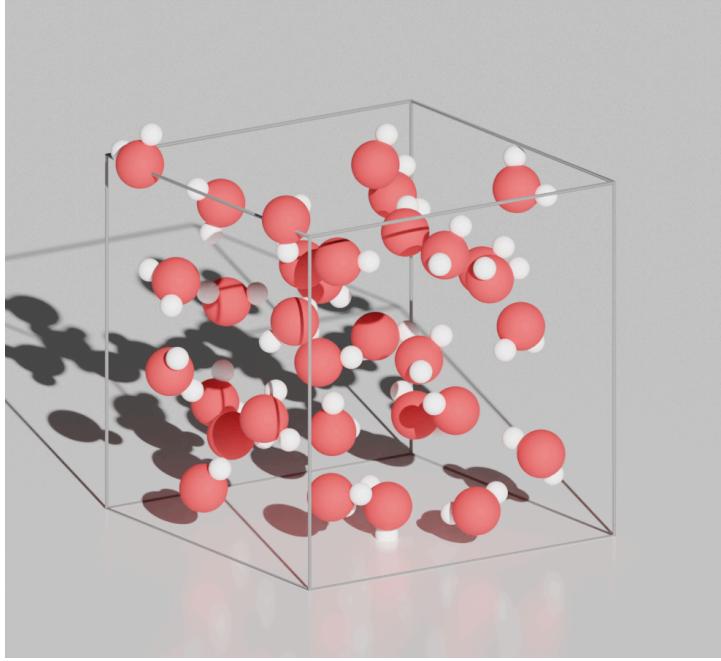


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

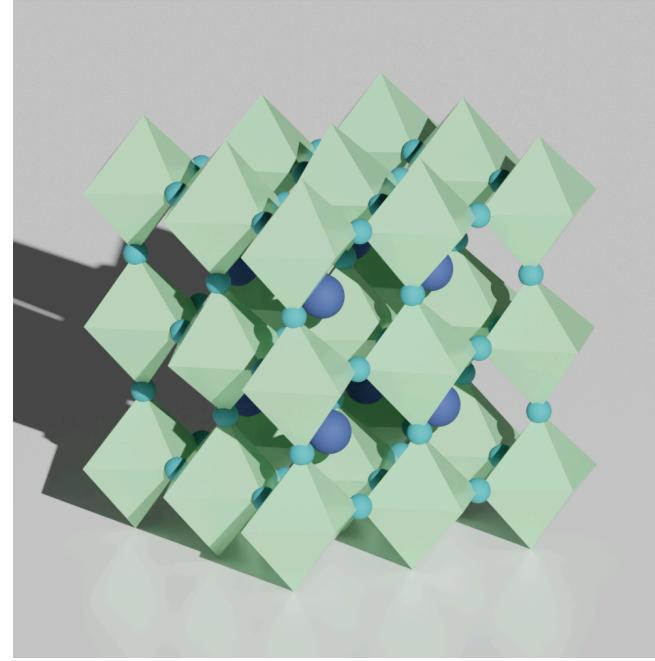
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

Machine-learned electronic screening



water

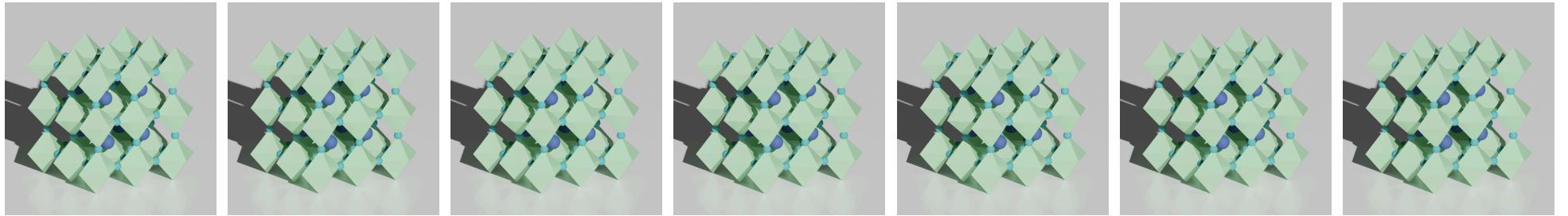


CsSnI₃

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

Machine-learned electronic screening

The use-case

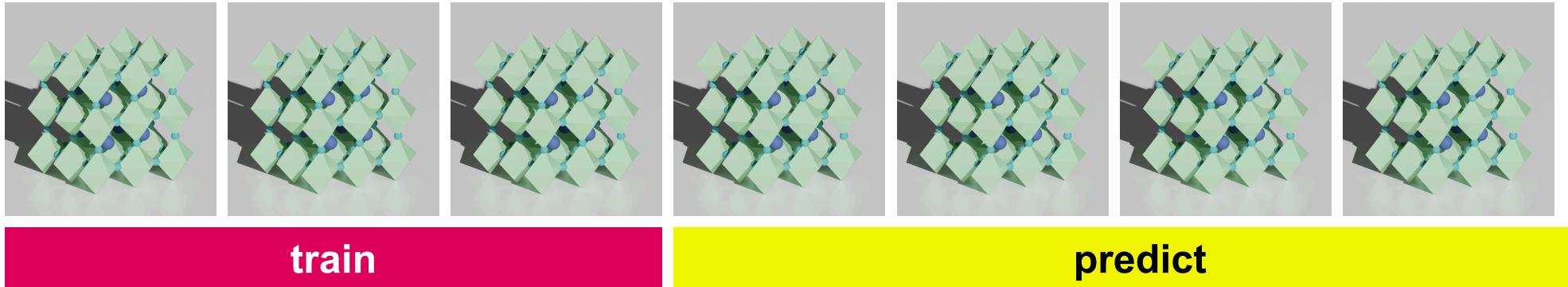


train

predict

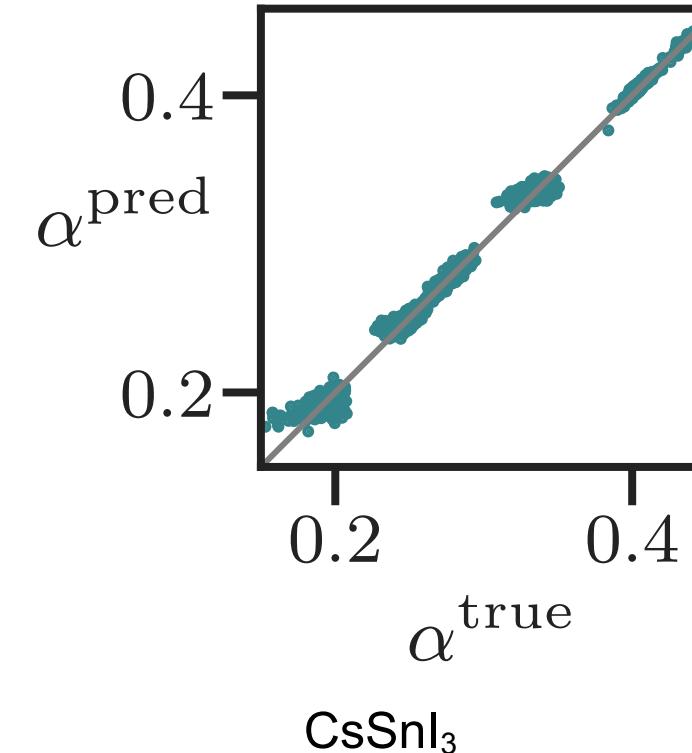
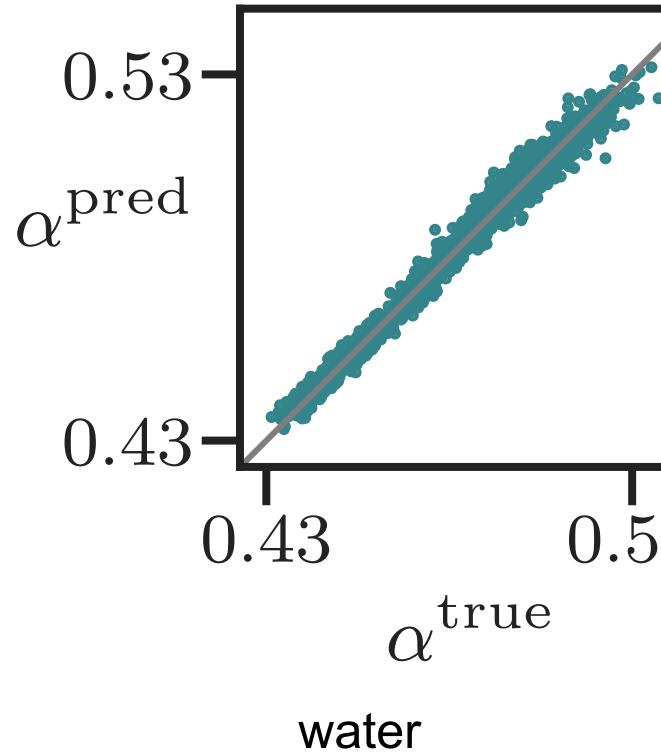
Machine-learned electronic screening

The use-case

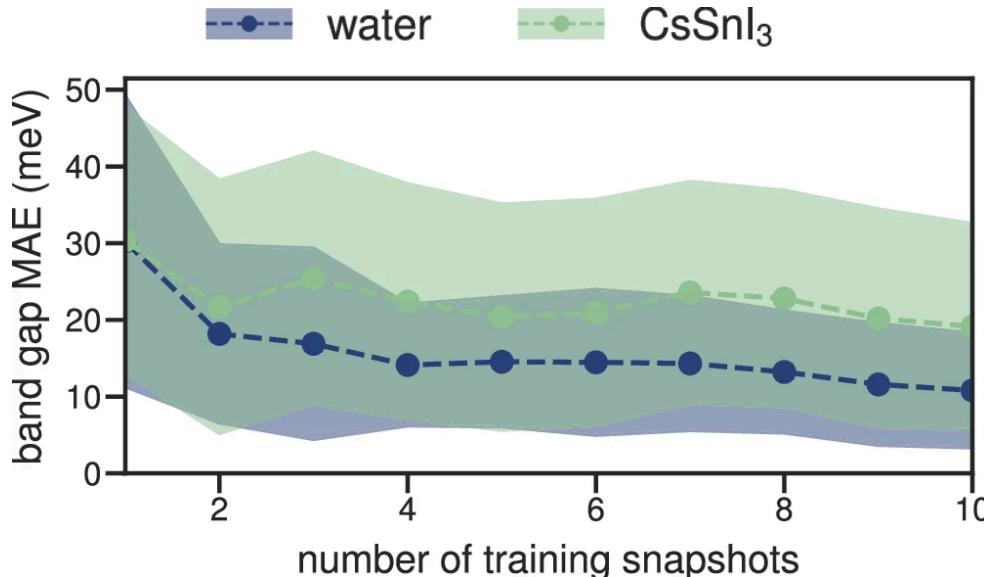


N.B. not a general model

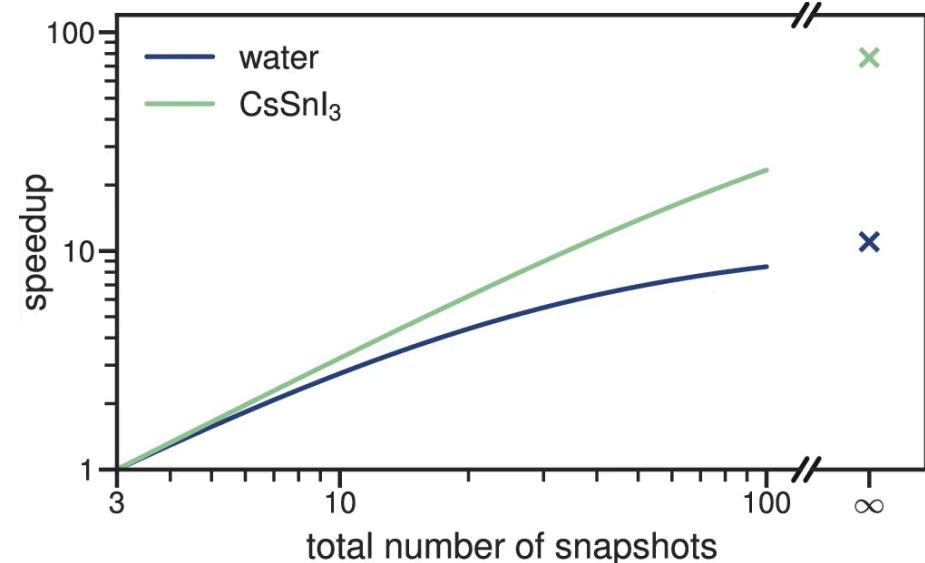
Machine-learned electronic screening



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

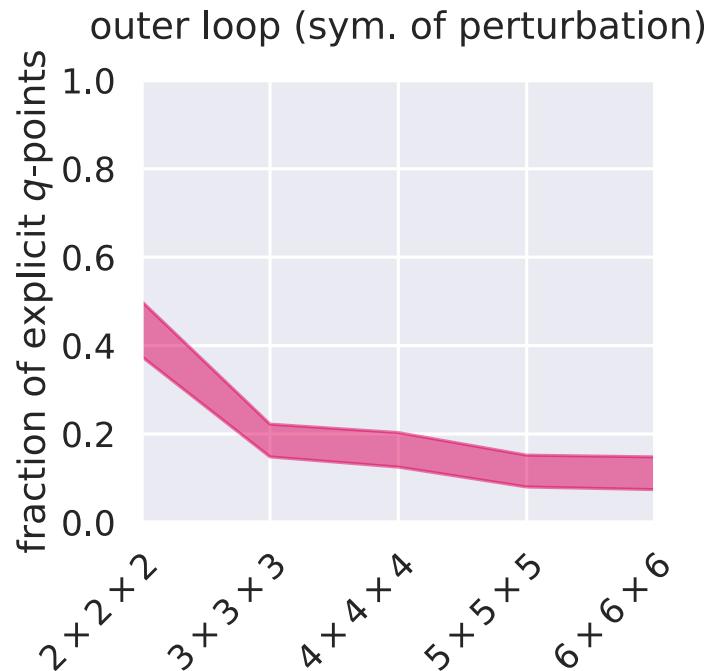
To compute screening parameters via DFPT...

```

1:function CalculateAlpha( $n$ )
2:   for  $q \in \text{BZ}$  do
3:     for  $k \in \text{BZ}$  do
4:        $\triangleright$  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:      $\Pi_{0n,\mathbf{q}}^{(r)} \leftarrow \langle \Delta\rho_{\mathbf{q}}^{0n} | f_{\text{Hxc}} | \rho_{\mathbf{q}}^{0n} \rangle$ 
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

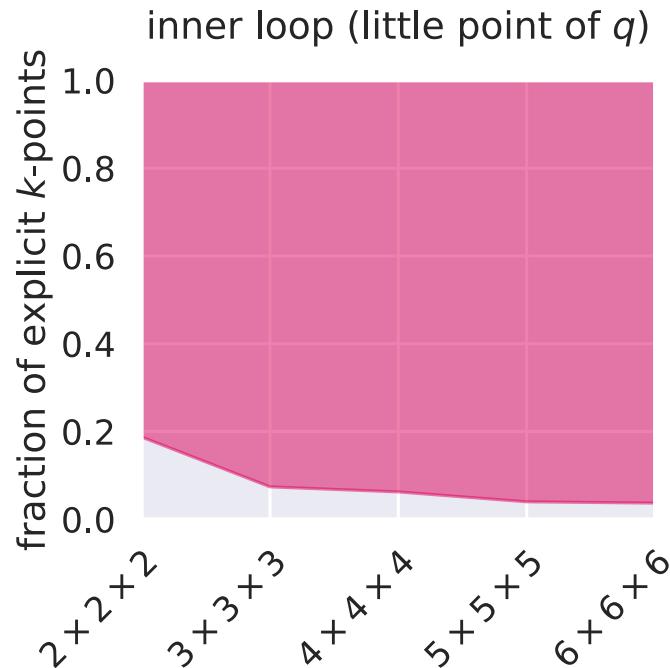
```

Taking advantage of symmetries



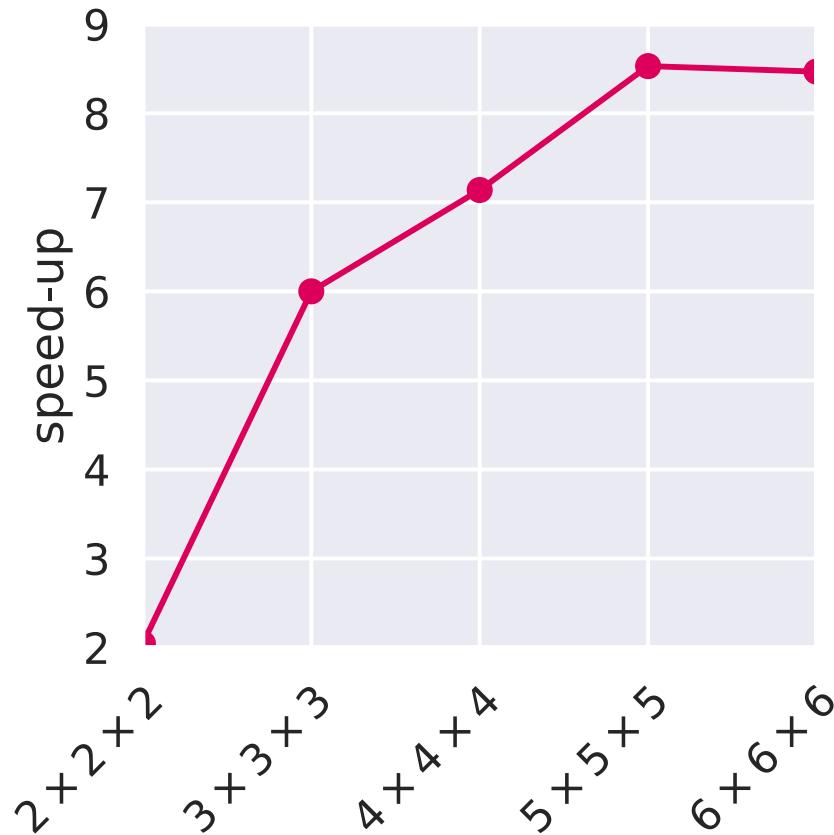
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$ (the symmetry of the perturbation; lower than that of the primitive cell)

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





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

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



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

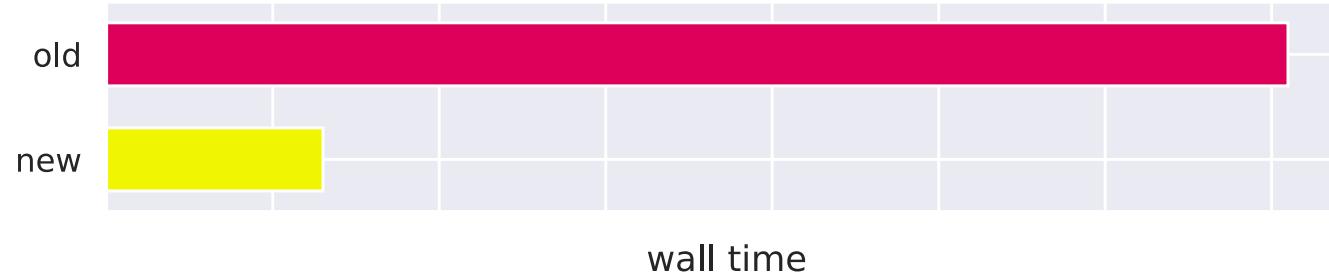
remote compute, parallel step execution, provenance-tracking, (requires configuration, WIP...)

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)

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)

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

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

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

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

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

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

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

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

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

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

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