



**PSI**

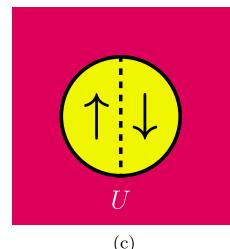
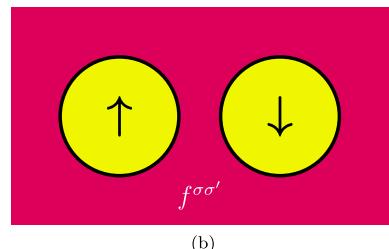
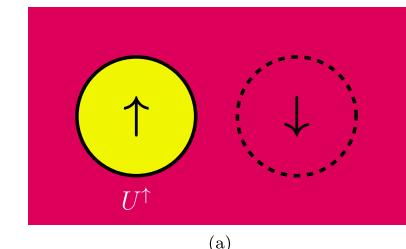
Center for Scientific Computing,  
Theory and Data

# Alternative linear response strategies

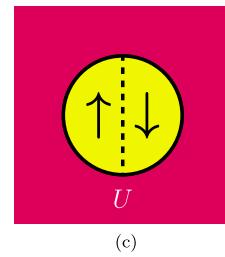
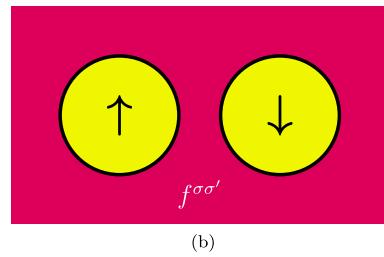
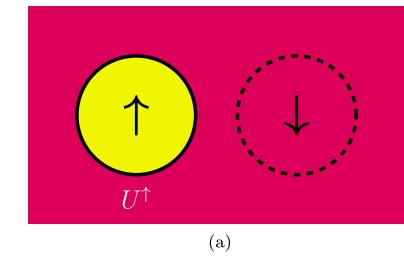
## Spin-resolution and orbital energy/ $\Delta$ SCF equivalence

Edward Linscott

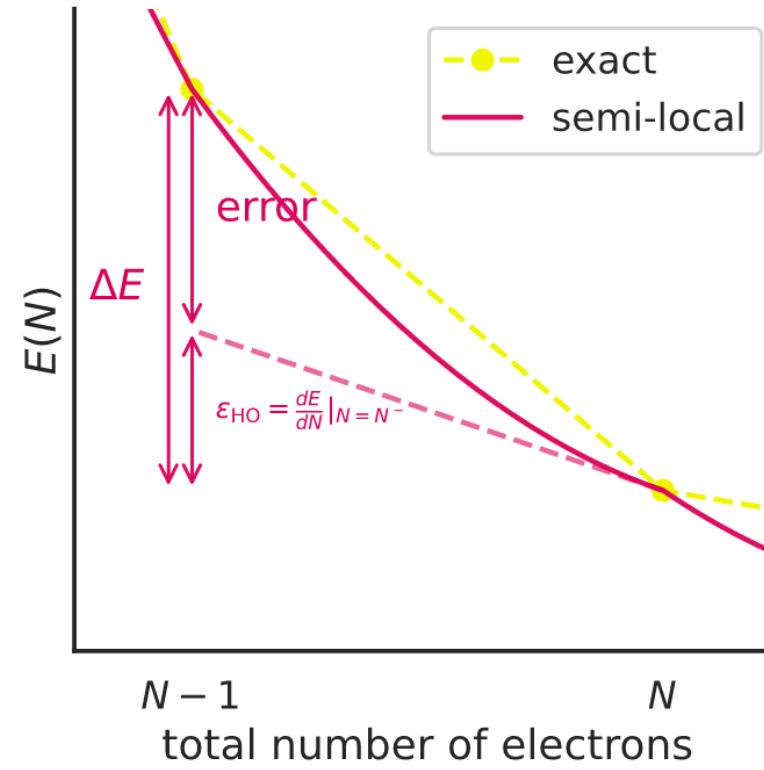
Gandia, 25 September 2025



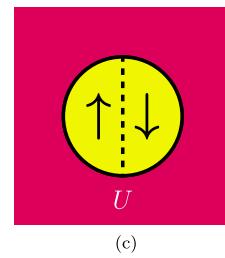
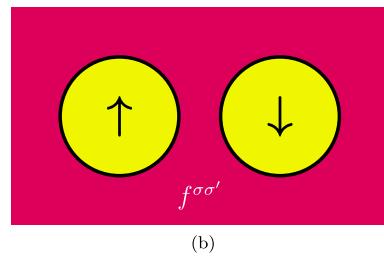
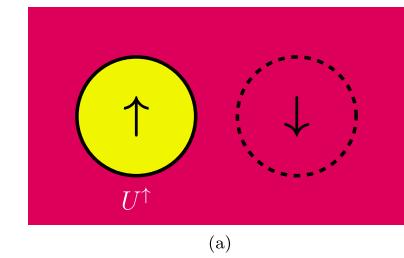
spin-resolved linear response



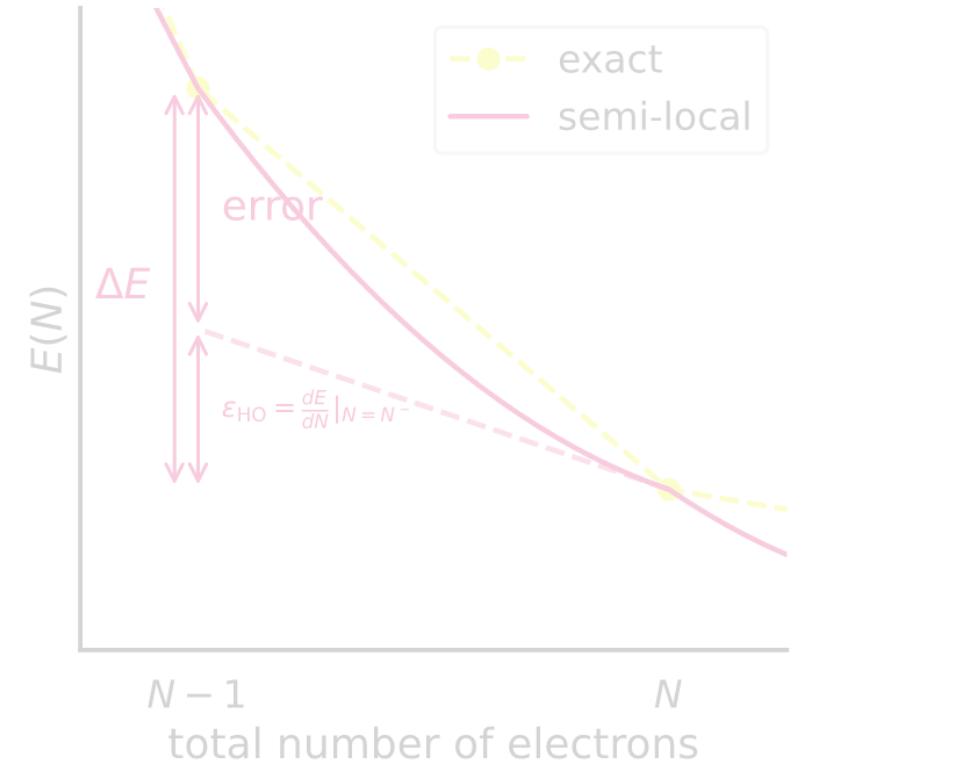
spin-resolved linear response



orbital energy/ΔSCF equivalence  
(Koopmans functionals)



## spin-resolved linear response



orbital energy/ΔSCF equivalence  
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# Spin-resolved linear response

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

$$U^I = [\chi_0^{-1} - \chi^{-1}]_{II}$$

<sup>1</sup>E. B. Linscott *et al.* *Phys. Rev. B* **98**, 235157 (2018)

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LR treats them together

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# Why?

# Role of spin in the calculation of Hubbard $U$ and Hund's $J$ parameters from first principles

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<sup>2</sup>*School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom*

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The density functional theory (DFT) +  $U$  method is a pragmatic and effective approach for calculating the ground-state properties of strongly correlated systems, and linear-response calculations are widely used to determine the requisite Hubbard parameters from first principles. We provide a detailed treatment of spin within the linear-response framework, demonstrating that the conventional Hubbard  $U$  formula, unlike the conventional DFT +  $U$  corrective functional, incorporates interactions that are off-diagonal in the spin indices and places greater weight on one spin channel over the other. We construct alternative definitions for Hubbard and Hund's parameters that are consistent with the contemporary DFT +  $U$  functional, expanding upon the minimum-tracking linear-response method. This approach allows Hund's  $J$  and spin-dependent  $U$  parameters to be calculated with the same ease as for the standard Hubbard  $U$ . Our methods accurately reproduce the experimental band gap, local magnetic moments, and the valence band edge character of manganese oxide, a canonical strongly correlated system. We also apply our approach to a complete series of transition-metal complexes  $[M(\text{H}_2\text{O})_6]^{n+}$  (for  $M = \text{Ti}$  to  $\text{Zn}$ ), showing that Hubbard corrections on oxygen atoms are necessary for preserving bond lengths, and demonstrating that our methods are numerically well behaved even for

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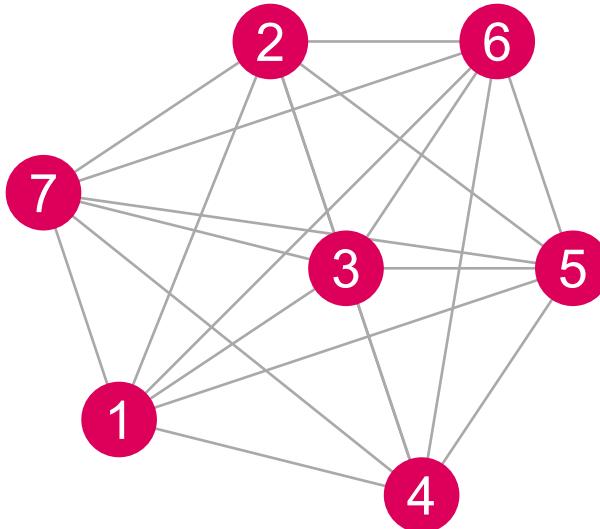
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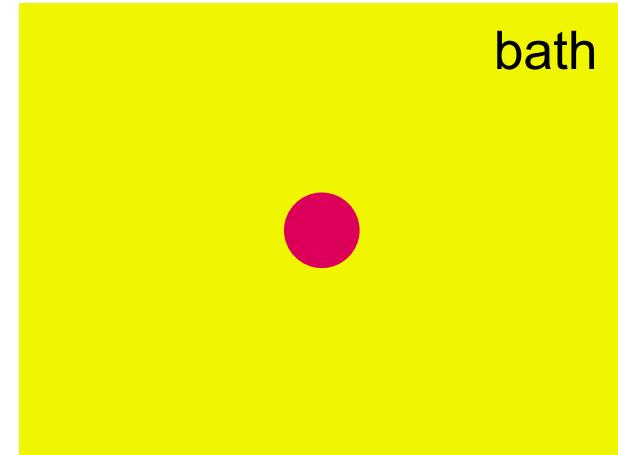
→

$$U^{I\sigma} = ???$$

# What is screening $U$ ?



all sites included in response matrix  
bare  $U$



only one site included in response matrix  
fully-screened  $U$

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# Advantages of spin-resolved linear response

# 1. Conceptual consistency

spin-resolved linear response  $\leftrightarrow$  spin-resolved DFT+ $U$  functional

<sup>1</sup>A. C. Burgess *et al.* *Phys. Rev. B* **107**, L121115 (2023)

spin-resolved linear response  $\leftrightarrow$  spin-resolved DFT+ $U$  functional

... we didn't explore DFT+ $U^\sigma$ ; instead see BLOR<sup>1</sup>)

<sup>1</sup>A. C. Burgess *et al.* *Phys. Rev. B* **107**, L121115 (2023)

## 2. Unconstrained constrained linear response

# Unconstrained constrained linear response

Suppose we want to compute  $\frac{d^2 E_{\text{Hxc}}}{d(n^I)^2} \Big|_{\mu^I}$

This is easy with spin-resolved LR:

$$\frac{d^2 E_{\text{Hxc}}}{d(n^I)^2} = \frac{1}{2} \frac{dv_{\text{Hxc}}^\uparrow + dv_{\text{Hxc}}^\downarrow}{d(n^\uparrow + n^\downarrow)} = \frac{1}{2} \frac{f^{\uparrow\uparrow}dn^\uparrow + f^{\uparrow\downarrow}dn^\downarrow + f^{\downarrow\uparrow}dn^\uparrow + f^{\downarrow\downarrow}dn^\downarrow}{dn^\uparrow + dn^\downarrow}$$

“Impose” the constraint by setting  $dn^\uparrow = dn^\downarrow$  to get...

$$\frac{d^2 E_{\text{Hxc}}}{dn^2} \Big|_{\mu} = \frac{1}{4} (f^{\uparrow\uparrow} + f^{\downarrow\downarrow} + f^{\uparrow\downarrow} + f^{\downarrow\uparrow})$$

This simple average is one choice (of many) for  $M : f_I^{\sigma\sigma'} \rightarrow U^I$

**3. We can recover conventional linear response**

# Conventional linear response

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$$dn = \sum_{\sigma} dn^{\sigma} = \sum_{\sigma\sigma'} \chi^{\sigma\sigma'} dv^{\sigma'} = \sum_{\sigma\sigma'} \chi^{\sigma\sigma'} dv \implies \chi_{\text{conv}} = \frac{dn}{dv} = \sum_{\sigma\sigma'} \chi^{\sigma\sigma'}$$

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And thus

$$U = (\varepsilon^{-1} - 1) \chi^{-1} = \frac{1}{2} \frac{\sum_{\sigma\sigma'} (f\chi)^{\sigma\sigma'}}{\sum_{\sigma\sigma'} \chi^{\sigma\sigma'}}$$

**4.  $J$  is free**

As defined by

$$J = -\frac{1}{2} \frac{dv_{\text{Hxc}}^{\uparrow} - dv_{\text{Hxc}}^{\downarrow}}{d(n^{\uparrow} - n^{\downarrow})} = -\frac{1}{4} \frac{(f^{\uparrow\uparrow} - f^{\downarrow\uparrow})dn^{\uparrow} - (f^{\downarrow\downarrow} - f^{\uparrow\downarrow})dn^{\downarrow}}{d(n^{\uparrow} - n^{\downarrow})}$$

Different ways to define  $J$ :

1. while keeping  $n = n^{\uparrow} + n^{\downarrow}$  fixed:

$$J = -\frac{1}{4}(f^{\uparrow\uparrow} - f^{\downarrow\uparrow} - f^{\uparrow\downarrow} + f^{\downarrow\downarrow})$$

2. for a perturbation where  $dv^{\uparrow} = -dv^{\downarrow}$

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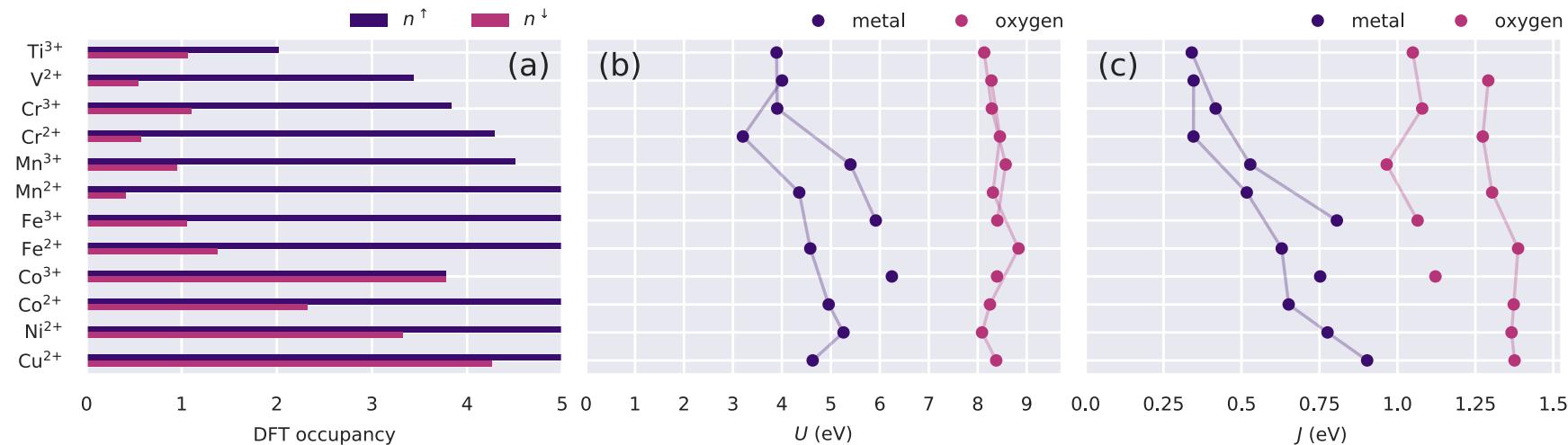
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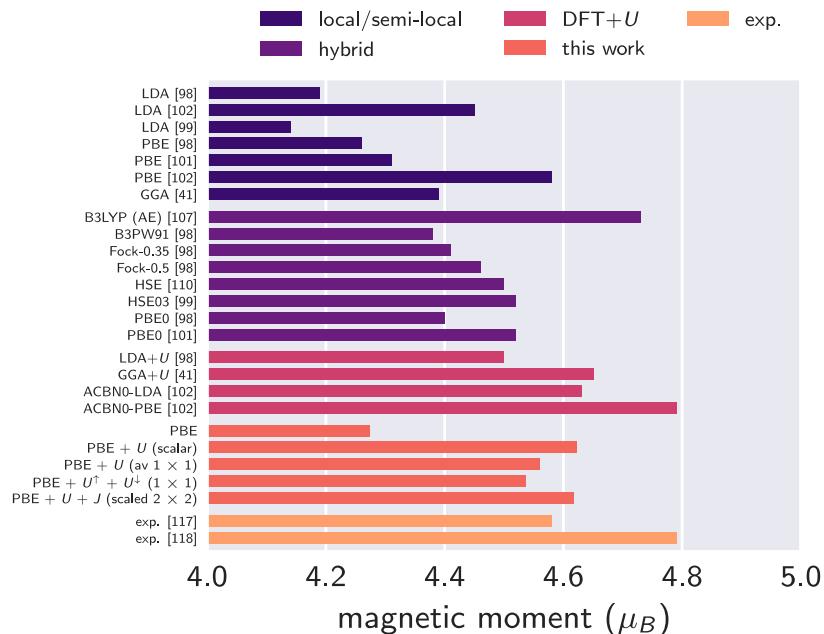
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## **5. Easy to implement**



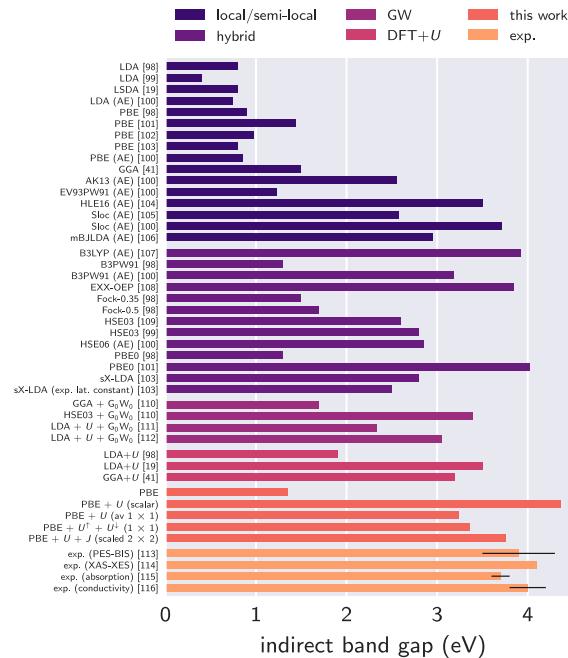
<sup>1</sup>O. K. Orhan *et al.* *Phys. Rev. B* **101**, 245137 (2020), D. S. Lambert *et al.* *Phys. Rev. Research* **5**, 13160 (2023), L. MacEnulty *et al.* *Phys. Rev. B* **108**, 245137 (2023), L. MacEnulty *et al.* *Electron. Struct.* **6**, 37003 (2024), G. C. Moore *et al.* *Phys. Rev. Mater.* **8**, 14409 (2024)

<sup>2</sup>A. C. Burgess *et al.* *Phys. Rev. B* **107**, L121115 (2023), A. C. Burgess *et al.* (2024) doi:10.48550/arXiv.2408.08391



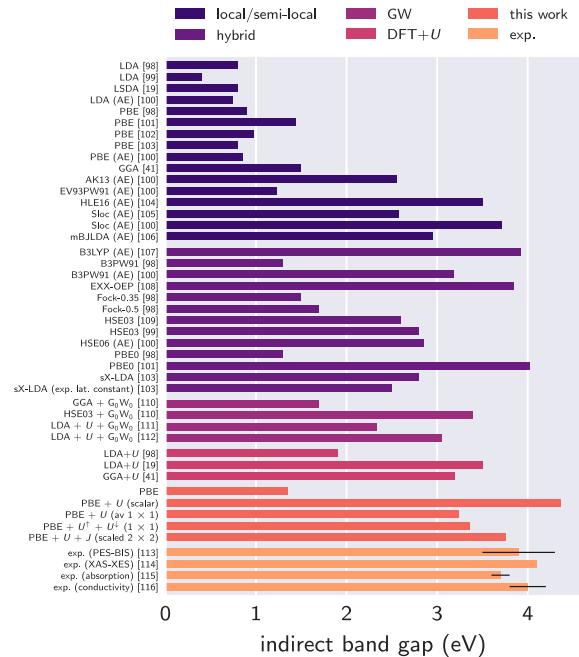
<sup>1</sup>O. K. Orhan *et al.* *Phys. Rev. B* **101**, 245137 (2020), D. S. Lambert *et al.* *Phys. Rev. Research* **5**, 13160 (2023), L. MacEnulty *et al.* *Phys. Rev. B* **108**, 245137 (2023), L. MacEnulty *et al.* *Electron. Struct.* **6**, 37003 (2024), G. C. Moore *et al.* *Phys. Rev. Mater.* **8**, 14409 (2024)

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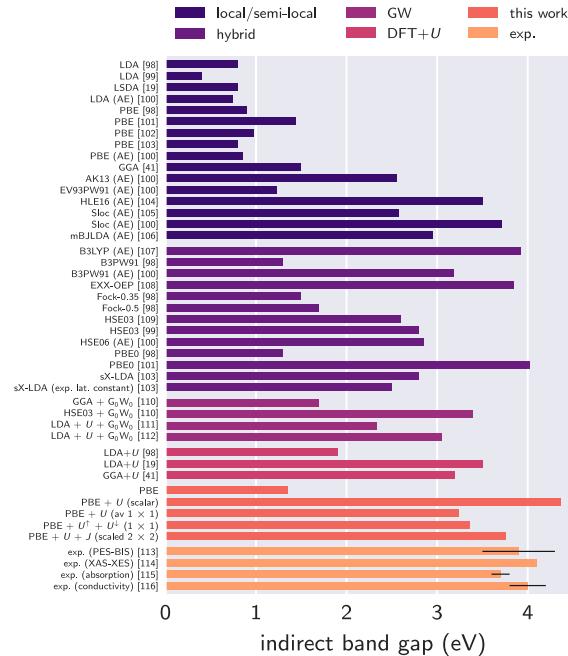
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... for more details see Linscott et al. 2018.

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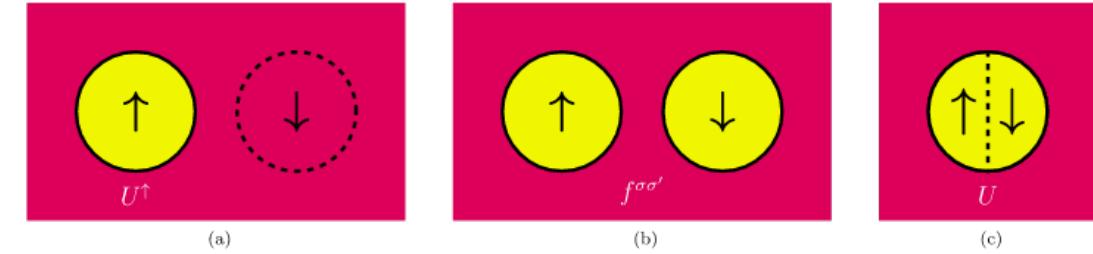
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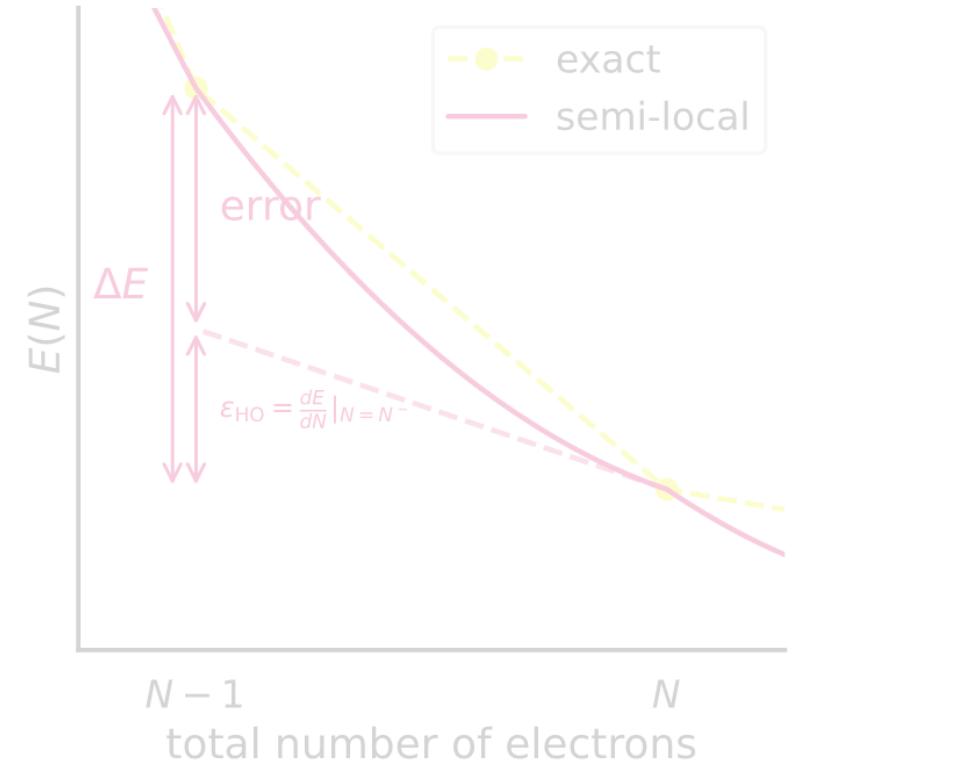
... for more details see Linscott et al. 2018. Since then used by many authors<sup>1</sup> and opened the door to DFT+U-inspired approaches<sup>2</sup>

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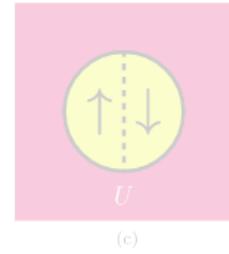
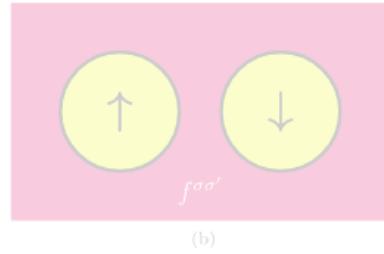
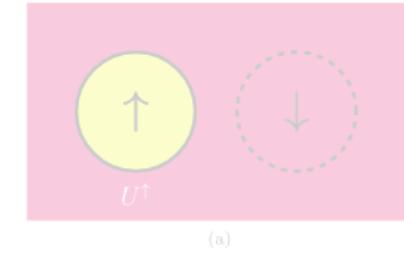
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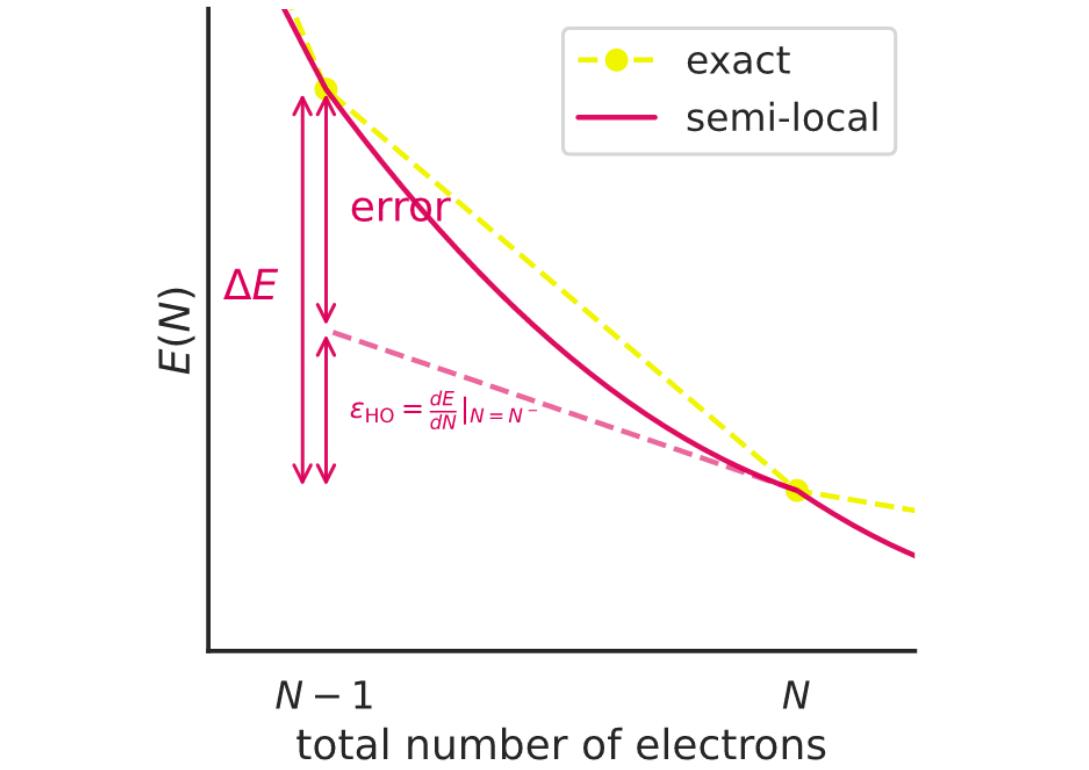
spin-resolved linear response



orbital energy/ $\Delta$ SCF equivalence  
(Koopmans functionals)



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# Koopmans functionals

# Total energy differences vs. eigenvalues

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

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

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

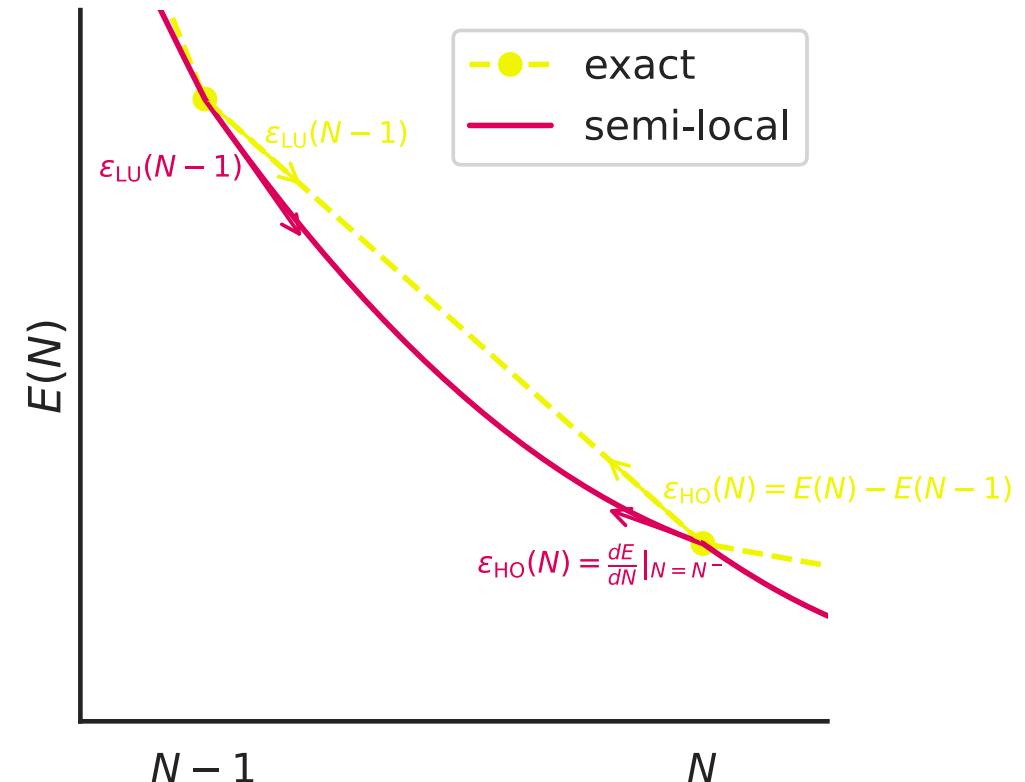
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but DFT does *not*



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

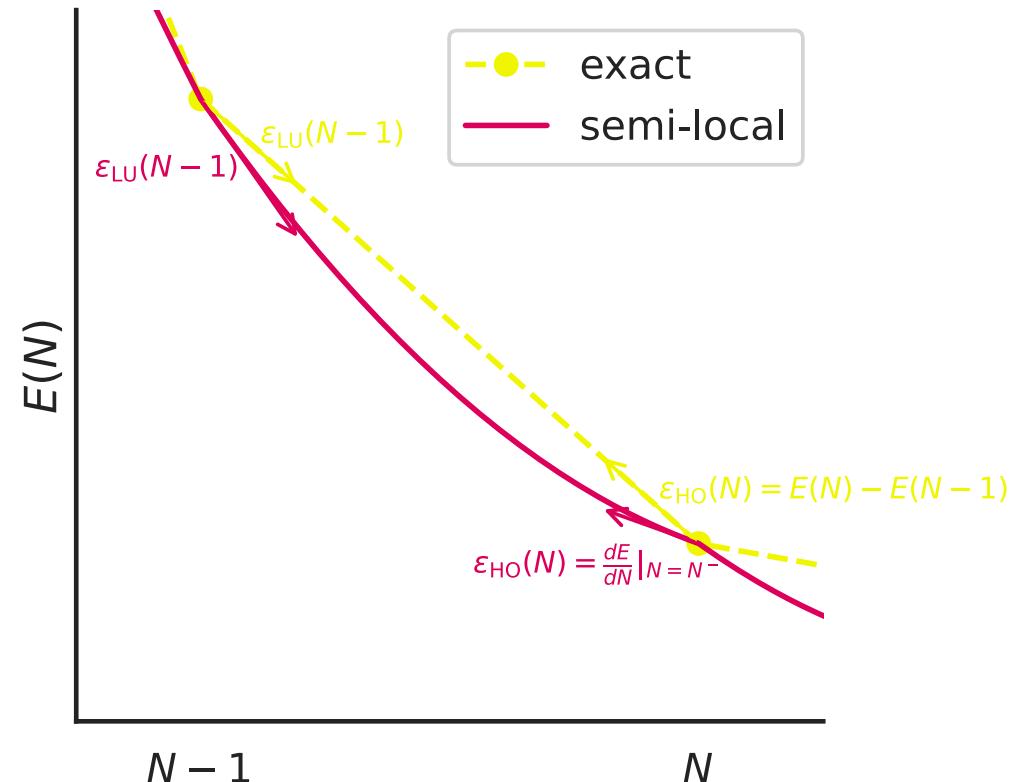
# Imposing generalised piecewise linearity

Formally, every orbital  $i$  should have an eigenenergy

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

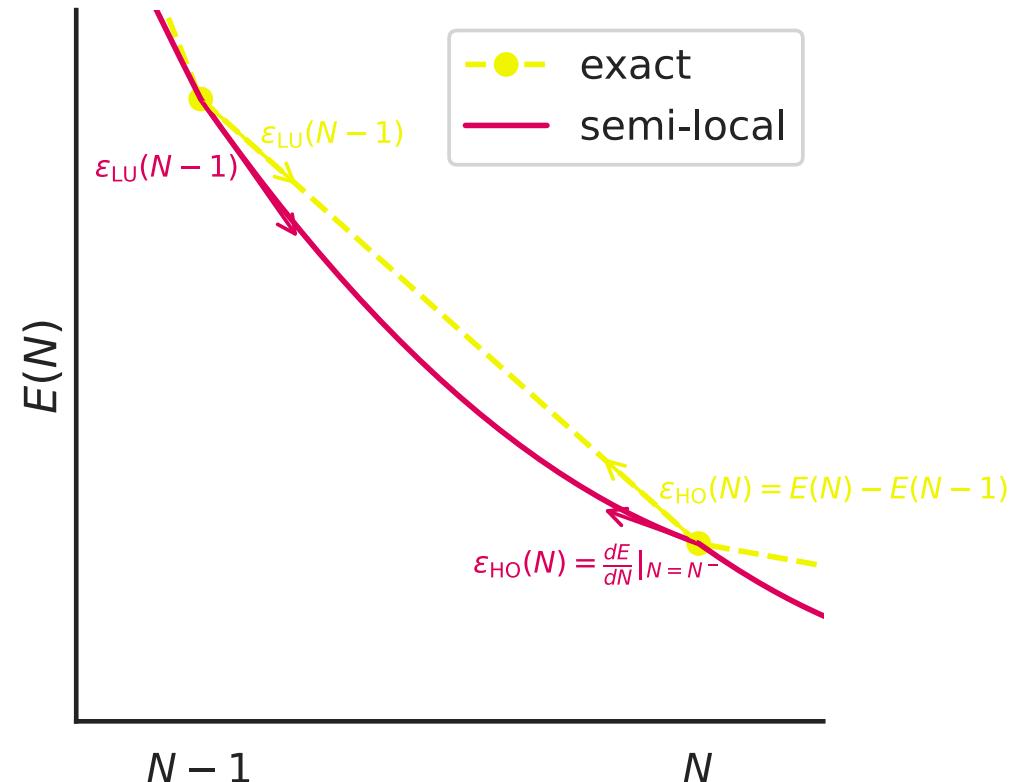
that is

- independent of  $f_i$
- equal to  $\Delta E$  of explicit electron addition/  
removal



# Imposing generalised piecewise linearity

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

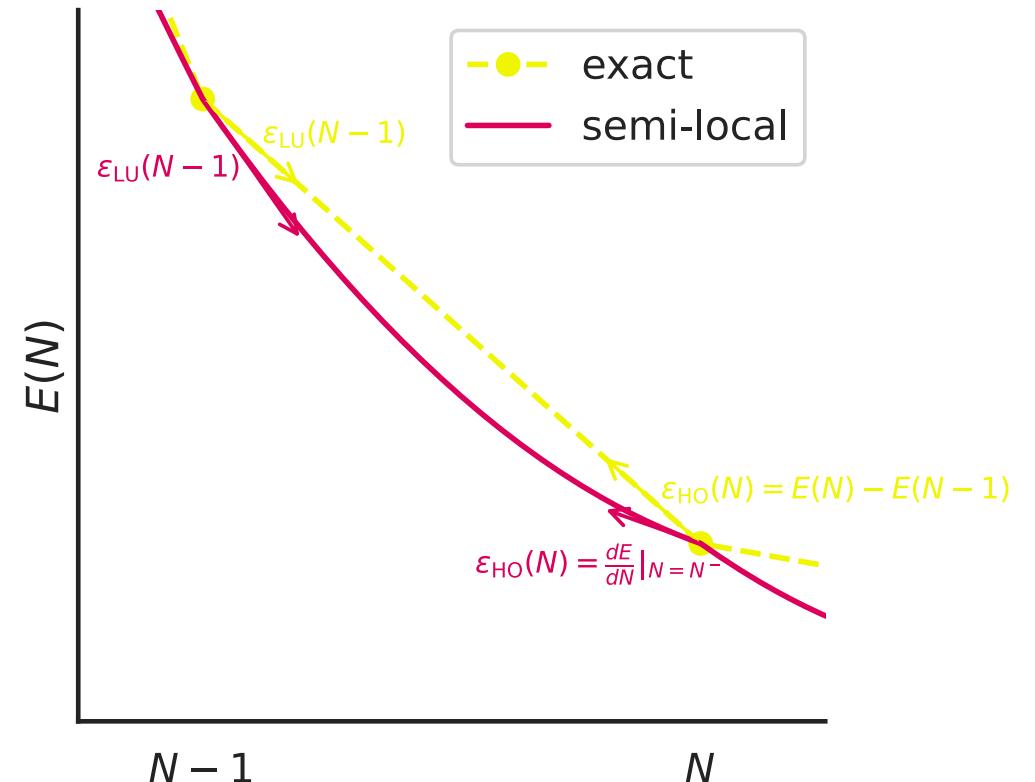


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removes dependence on  $f_i$



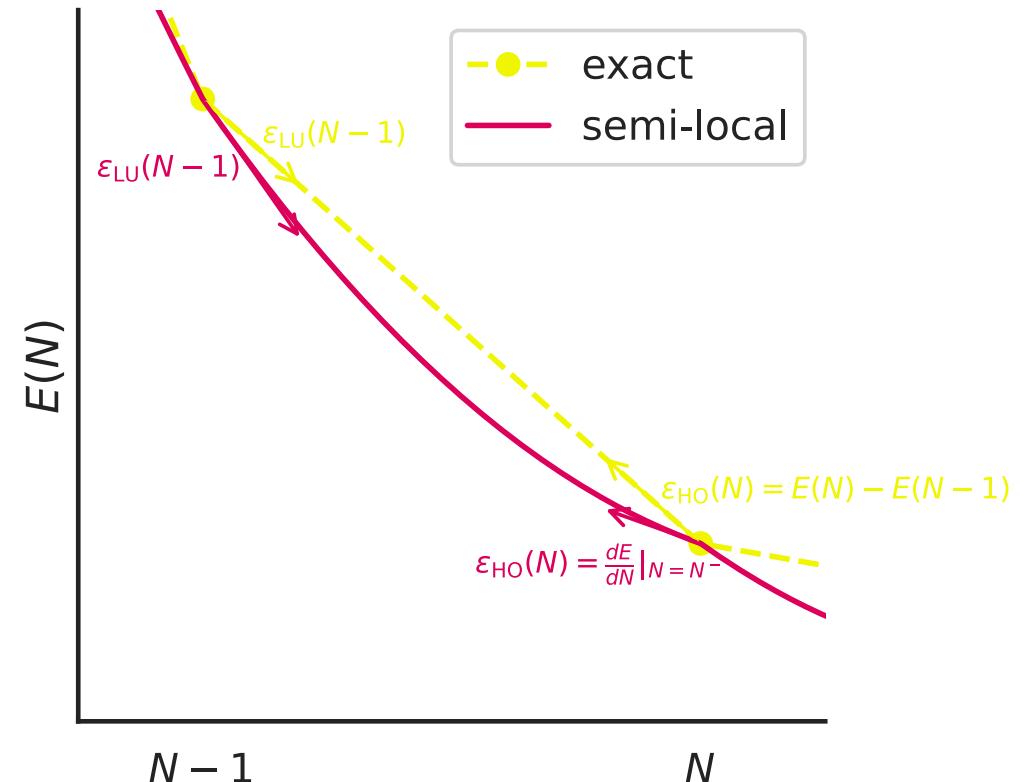
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removes dependence on  $f_i$

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>	

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# Comparison with DFT+ $U$ (and BLOR)

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seeks to correct...	erroneous curvature in total energies w.r.t. $N$	erroneous curvature in total energies w.r.t. $f_i \forall i$
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<i>correction applied to...</i>		
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# Electronic screening via parameters

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

# Electronic screening via parameters

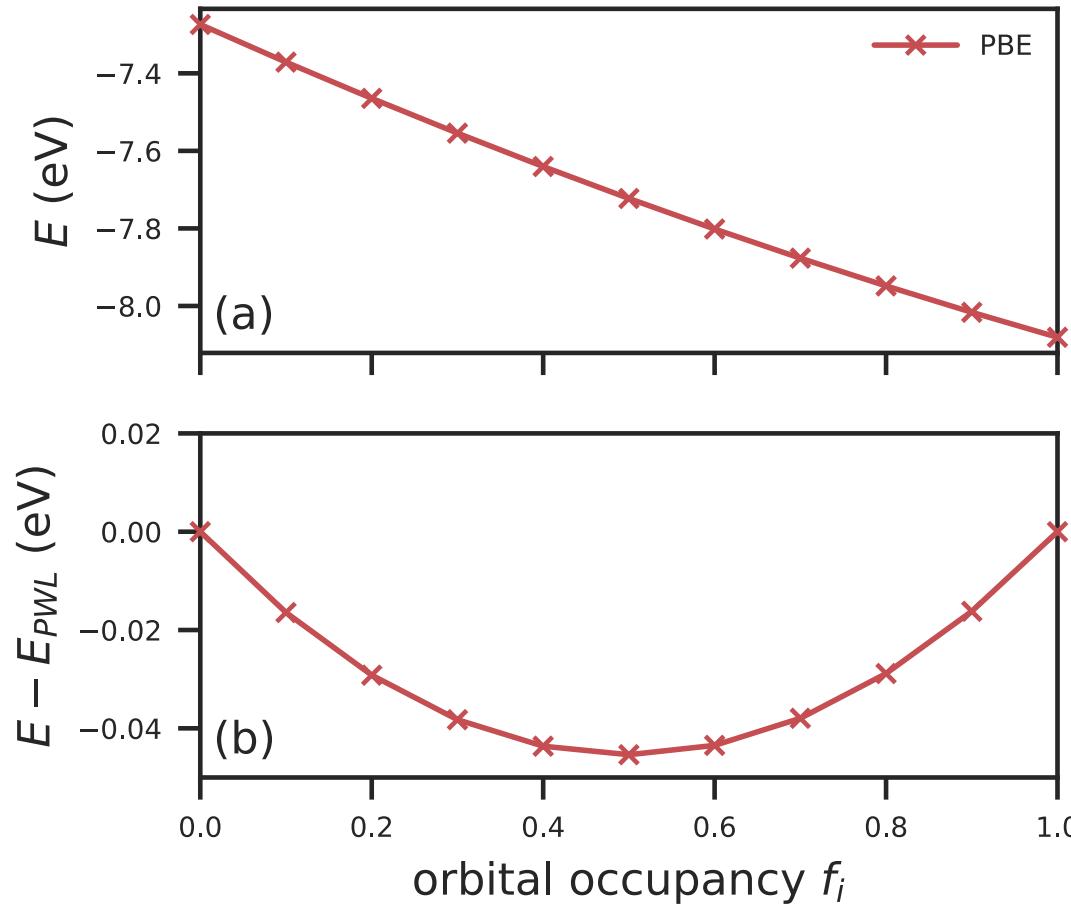
$$\begin{aligned}
 E^{\text{KI}}[\{\rho_i\}] &= E^{\text{DFT}}[\rho] + \sum_i \left( - \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right) \\
 &= E^{\text{DFT}}[\rho] + \sum_i \left\{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

# Electronic screening via parameters

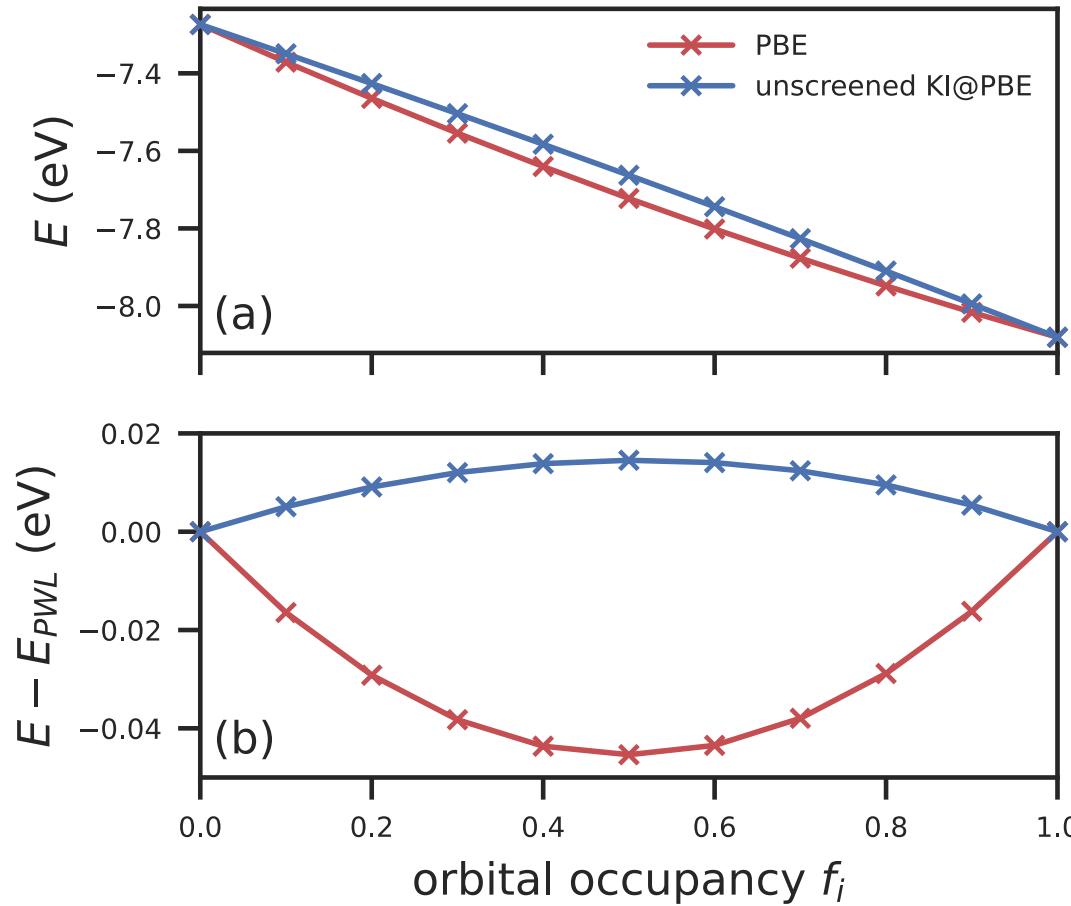
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 \end{aligned}$$

cannot evaluate directly      cannot evaluate directly      cannot evaluate directly

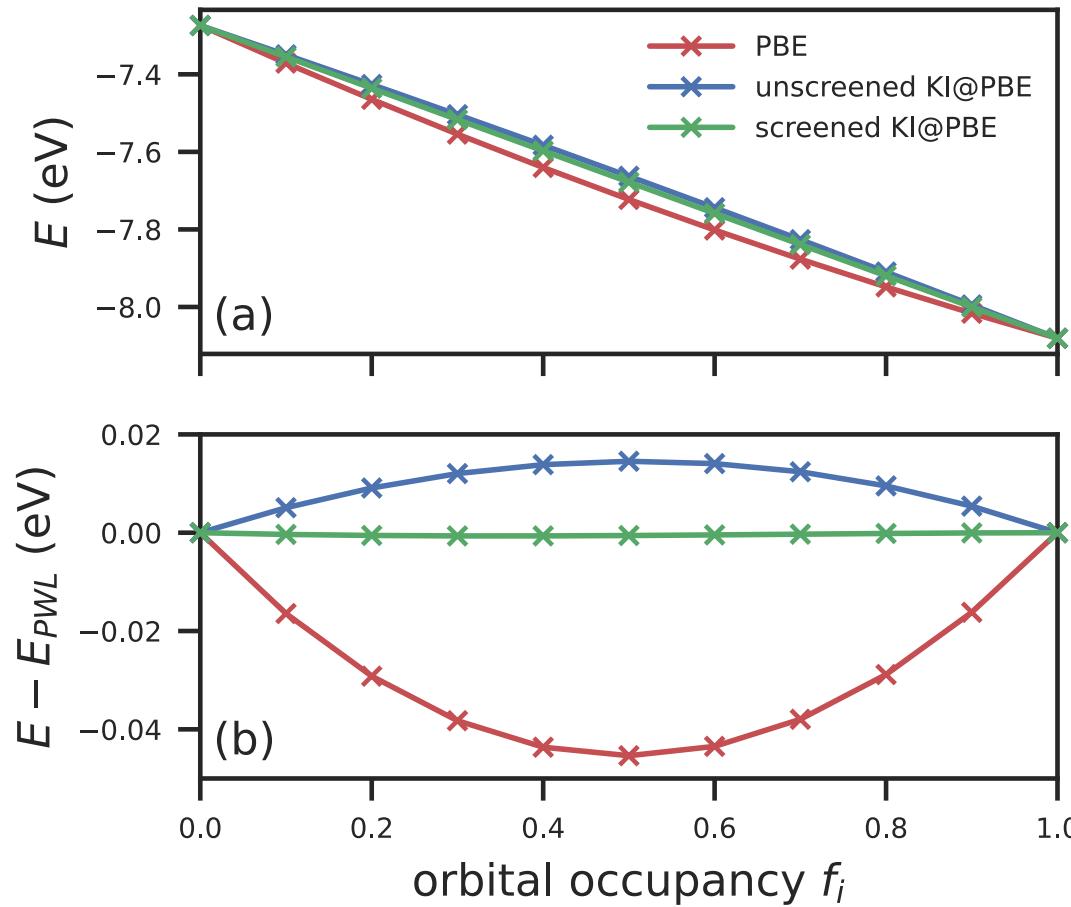
# Electronic screening via parameters



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

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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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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!

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

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<sup>2</sup>N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

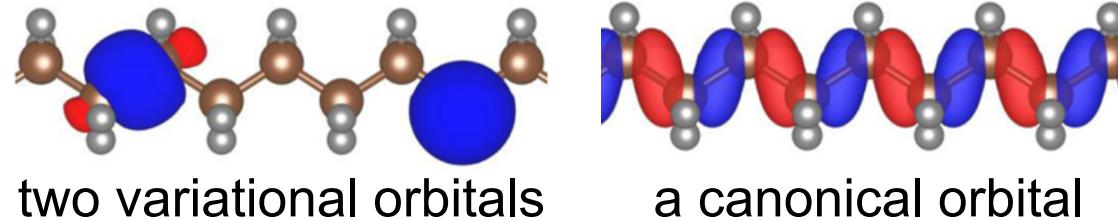
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- loss of unitary invariance<sup>1</sup>



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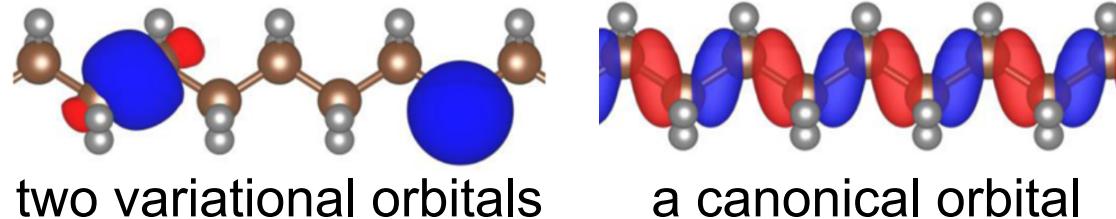
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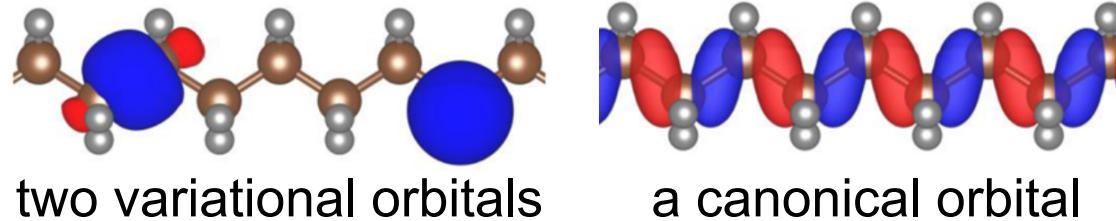
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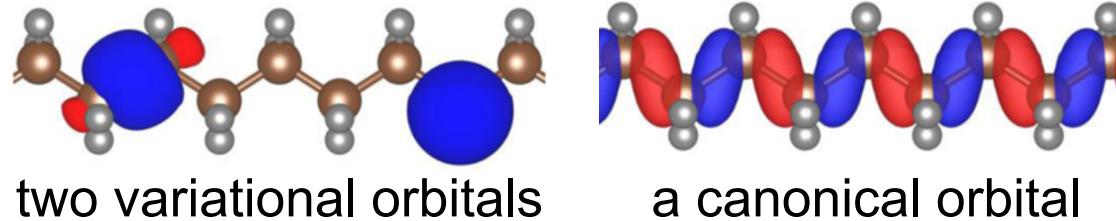
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- we can use MLWFs<sup>2</sup>
- we know  $\hat{H}|\varphi_i\rangle$  but not  $\hat{H}$
- a natural generalisation of DFT towards spectral functional theory<sup>3</sup>

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# 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 at integer occupations 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 manifold (BLOR does so more faithfully)	removes dependence of $\varepsilon_i$ on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
<i>correction applied to...</i>		
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<i>orbitals defined by...</i>		
<i>parametrised by...</i>		

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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)	
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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)	
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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
seeks to correct...	erroneous global curvature in total energies w.r.t. $N$	erroneous global curvature in total energies w.r.t. <b>canonical</b> orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local manifold (BLOR does so more faithfully)	removes dependence of $\varepsilon_i$ 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. <b>canonical</b> orbital occupancies
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# 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. <b>canonical</b> orbital occupancies
<i>in practice...</i>	corrects curvature in total energies w.r.t. local manifold (BLOR does so more faithfully)	removes dependence of $\varepsilon_i$ on <b>variational</b> 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>	$\{U_I\}$	

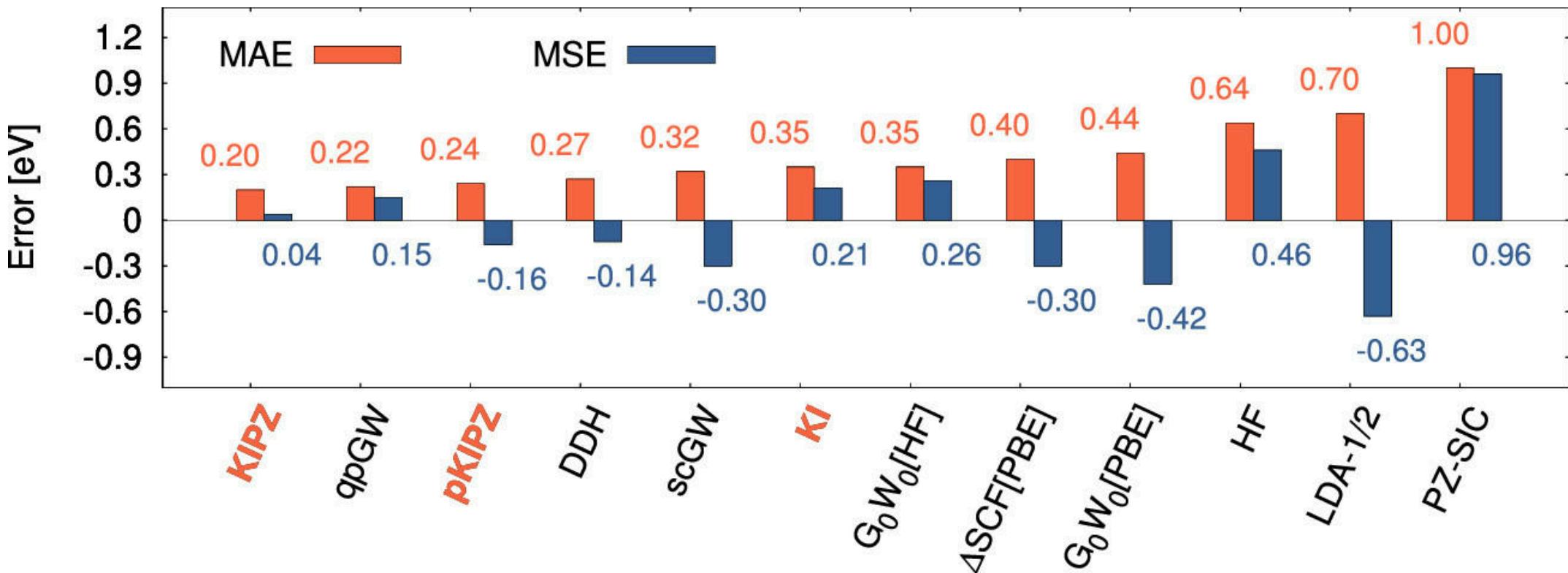
# Comparison with DFT+ $U$ (and BLOR)

	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. <b>canonical</b> orbital occupancies
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<i>parametrised by...</i>	$\{U_I\}$	$\{\alpha_i\}$

# Results

# Molecular systems

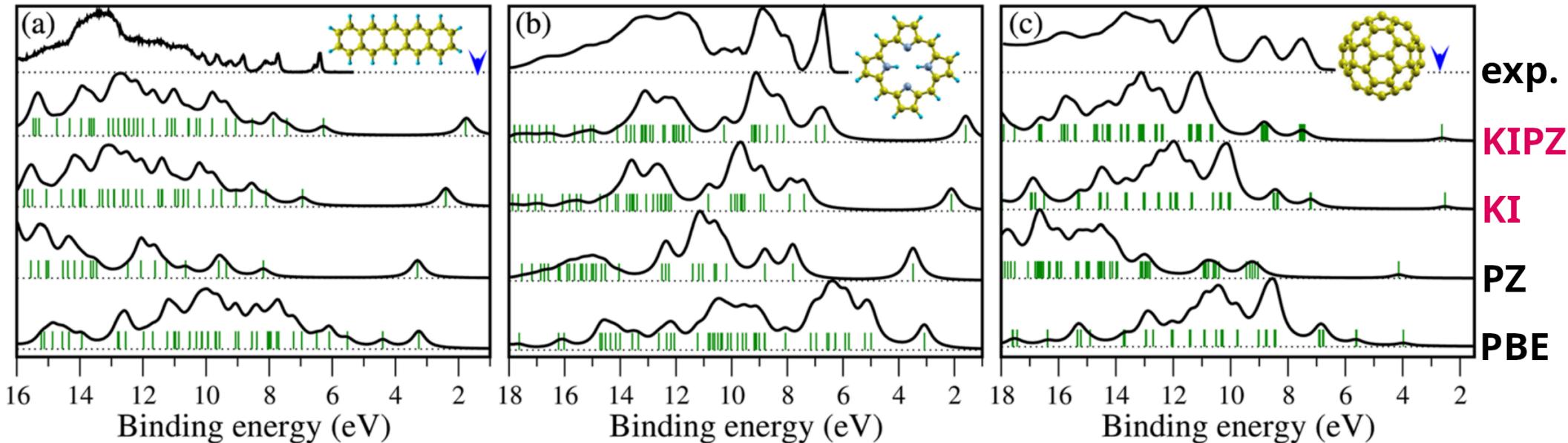
## Ionisation potentials<sup>1</sup>



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

# Molecular systems

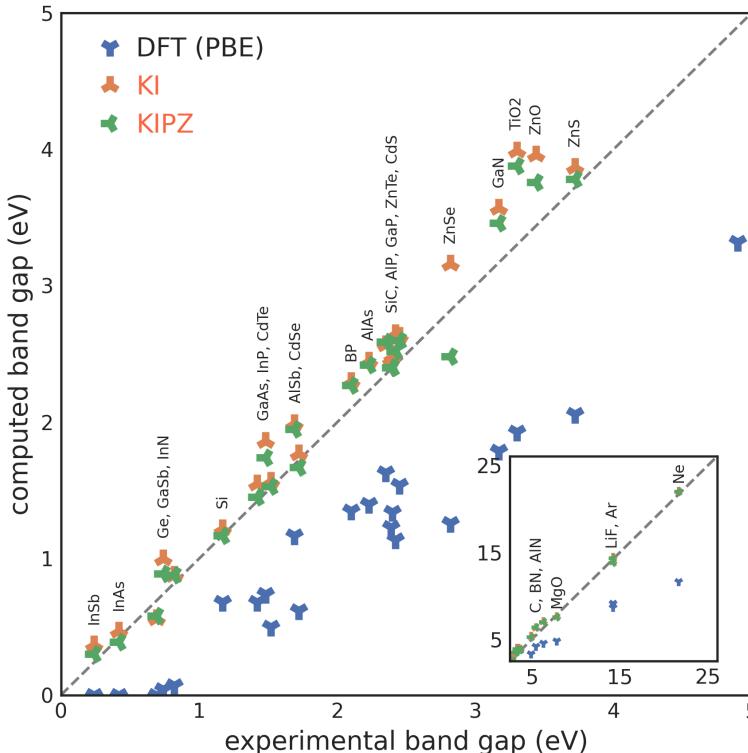
## UV photoemission spectra<sup>1</sup>



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

# Extended systems

## Prototypical semiconductors and insulators<sup>1</sup>

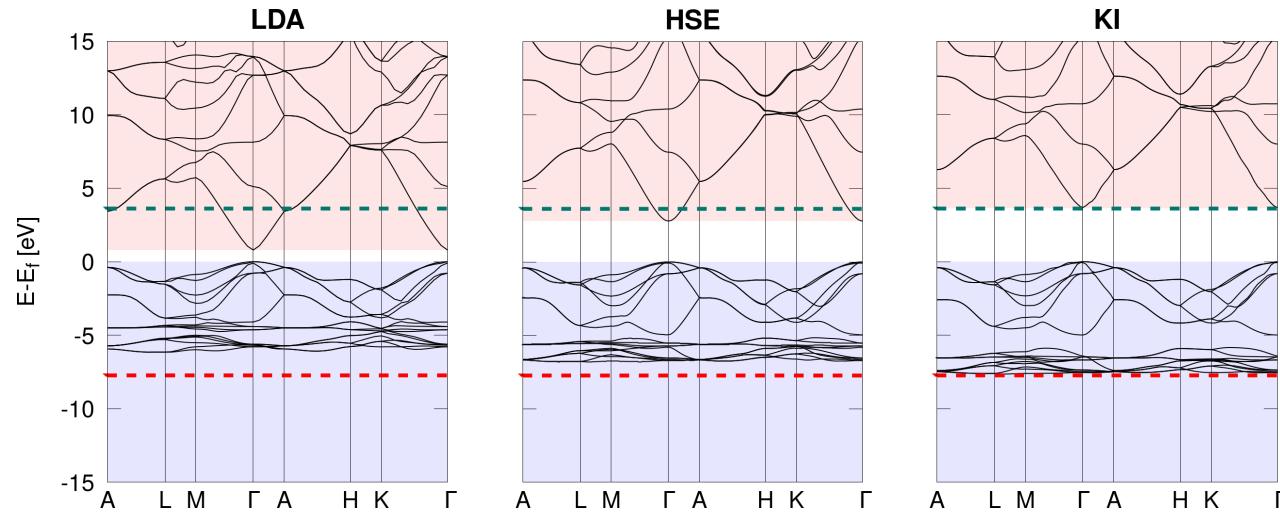


	PBE	$G_0W_0$	KI	KIPZ	$QSG\tilde{W}$
$E_{gap}$	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

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

# Extended systems

ZnO<sup>1</sup>



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

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

# Caveats

# Limitations

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

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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 Kozhevnikov<sup>1</sup>
- Optimally-tuned range-separated hybrid functionals of Kronik, Pasquarello, and others<sup>2</sup>
- Ensemble DFT of Kraisler and Kronik<sup>3</sup>
- Koopmans-Wannier method of Wang and co-workers<sup>4</sup>
- Dielectric-dependent hybrid functionals of Galli and co-workers<sup>5</sup>
- Scaling corrections of Yang and co-workers<sup>6</sup>

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

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

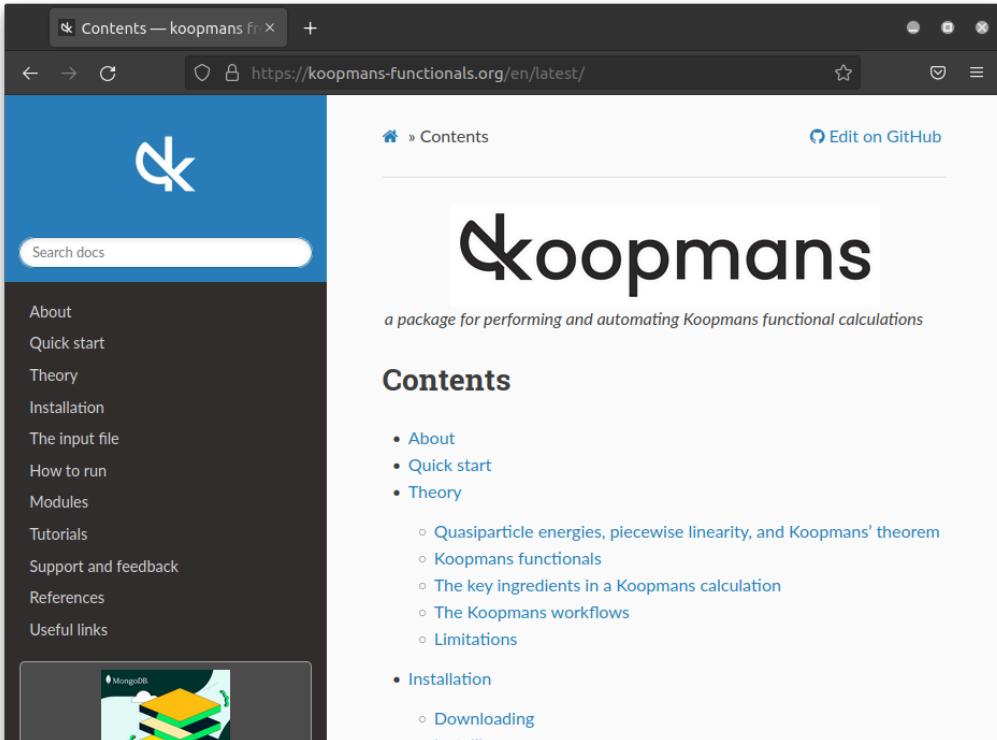
<sup>3</sup>E. Kraisler *et al.* *Phys. Rev. Lett.* **110**, 126403 (2013)

<sup>4</sup>J. Ma *et al.* *Sci. Rep.* **6**, 24924 (2016)

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

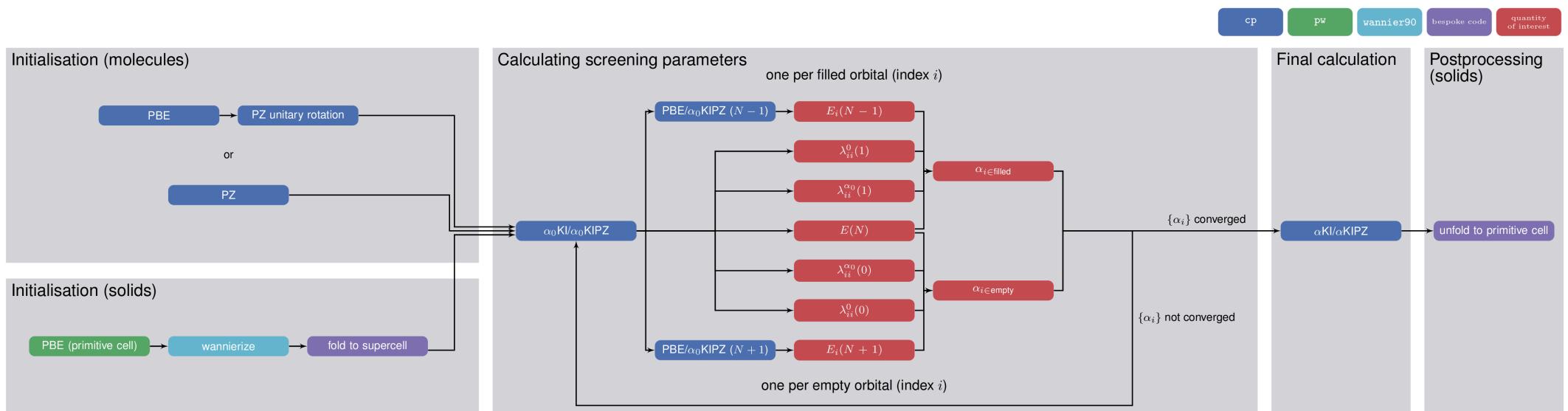
<sup>6</sup>C. Li *et al.* *Natl. Sci. Rev.* **5**, 203–215 (2018)

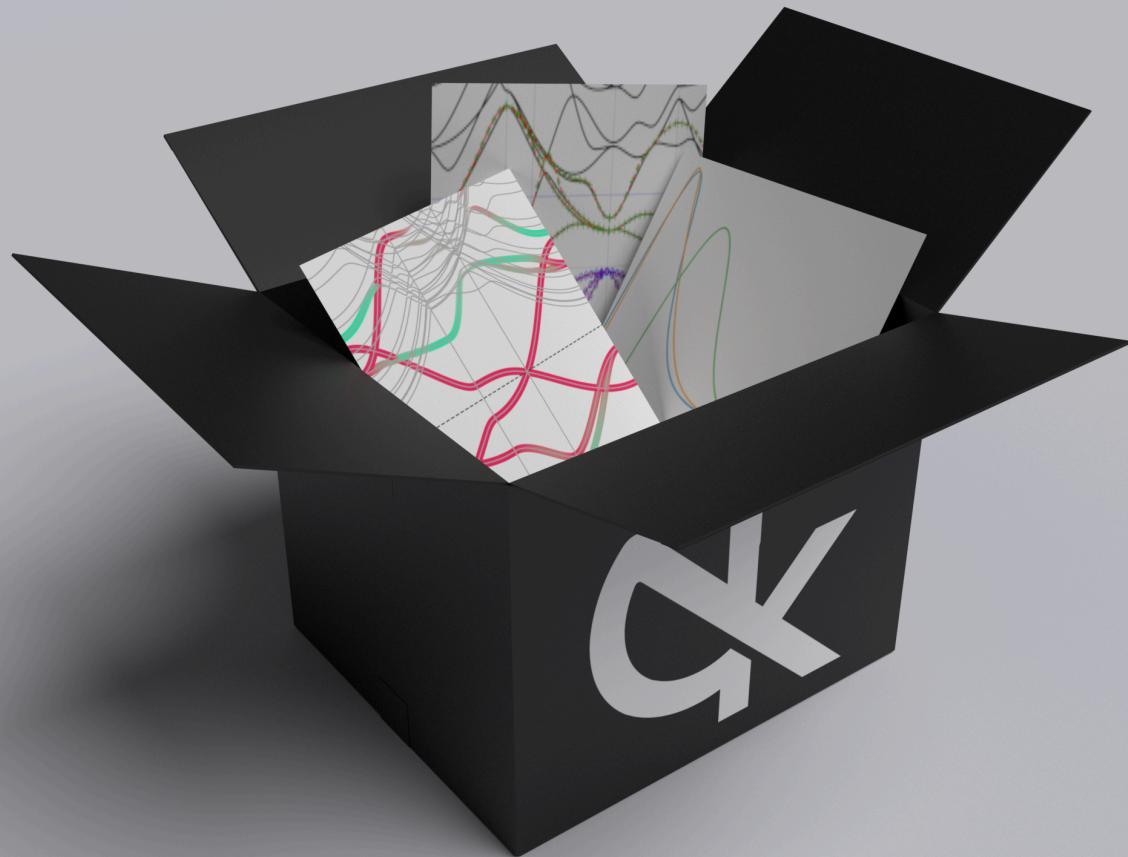
koopmans



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

See [koopmans-functionals.org](https://koopmans-functionals.org)

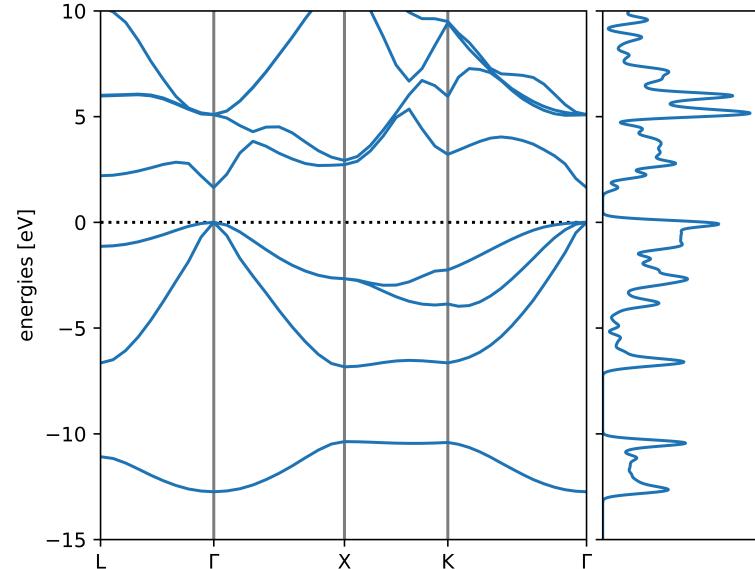




Our goal:

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

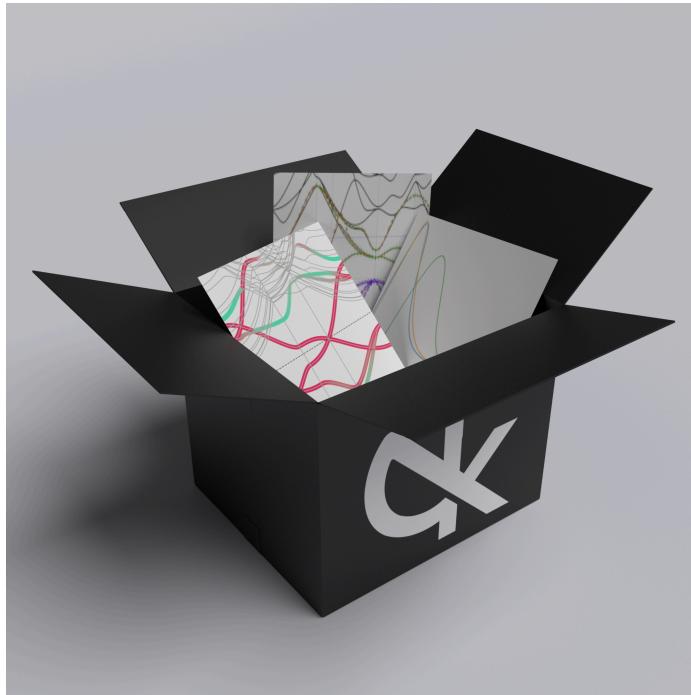
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```



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

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

# Open questions

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

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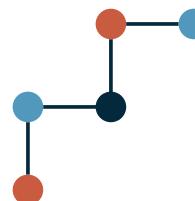
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- how to extend to metallic systems?
- can we provide a formal basis for the Koopmans correction?
  - GKS
  - spectral functional theory<sup>1</sup>
  - ensemble DFT
  - RDMFT

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

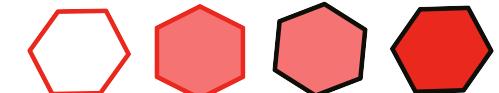
# Acknowledgements



David Andrew Nicola Miki Aleksandr Marija Junfeng Yannick Nicola  
O'Regan Burgess Colonna Bonacci Poliukhin Stojkovic Qiao Schubert Marzari



**Swiss National  
Science Foundation**

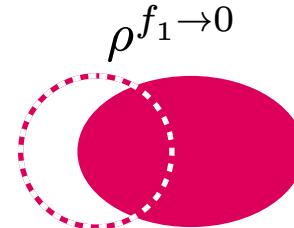
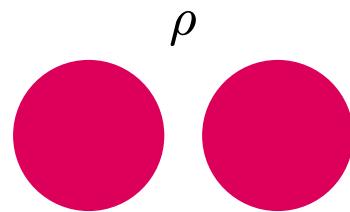
MARVEL  


# Thank you!

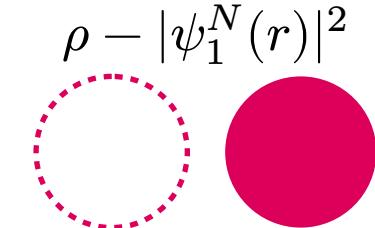
*these slides are available at*  [\*elinscott-talks\*](https://github.com/elinscott-talks)

spare slides

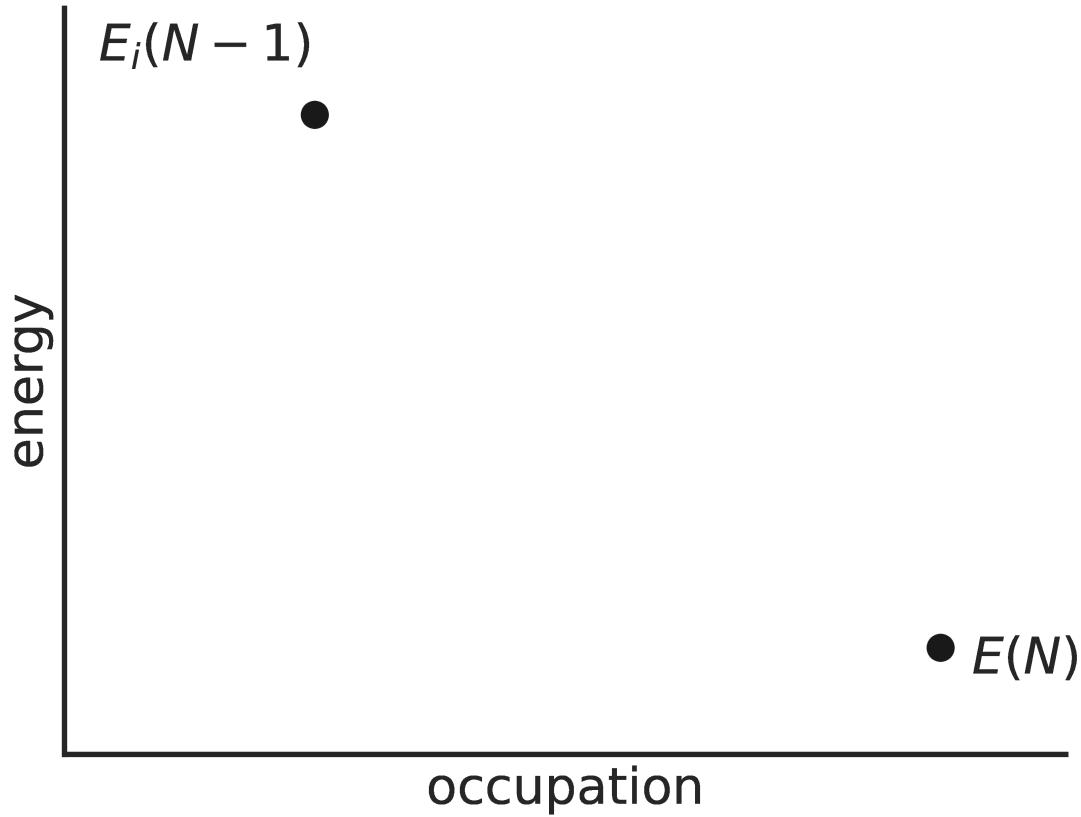
# Frozen orbital approximation

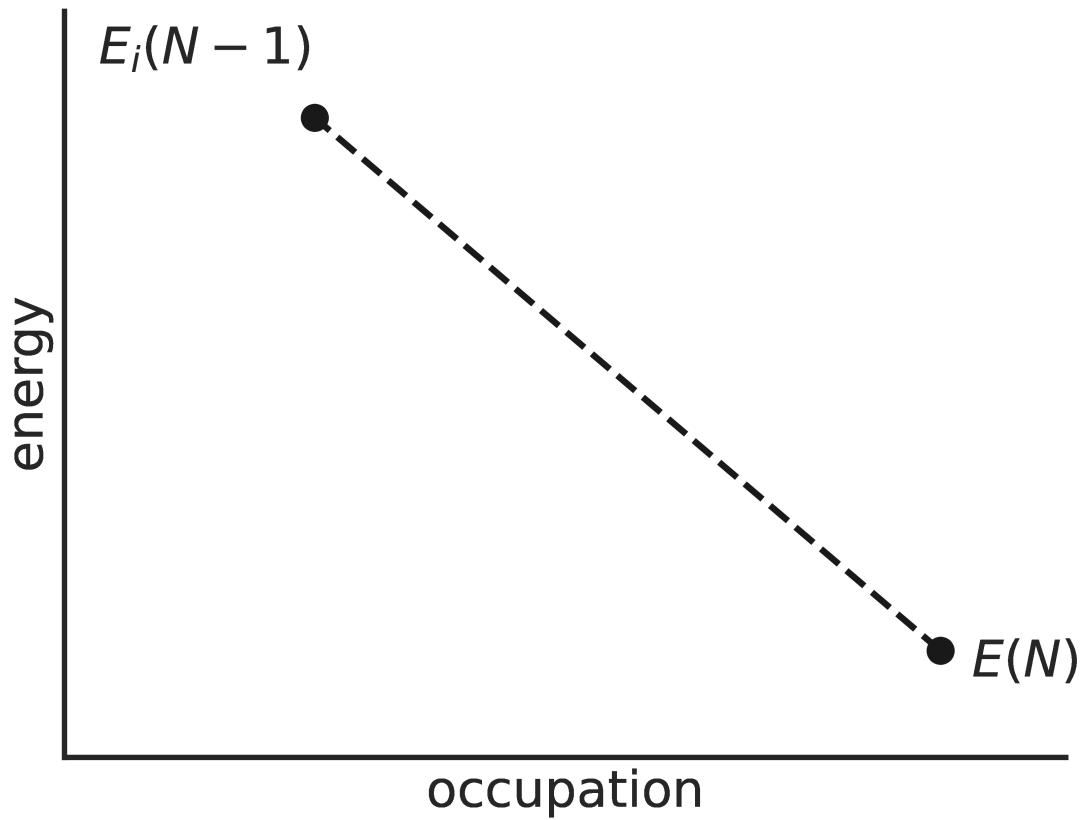


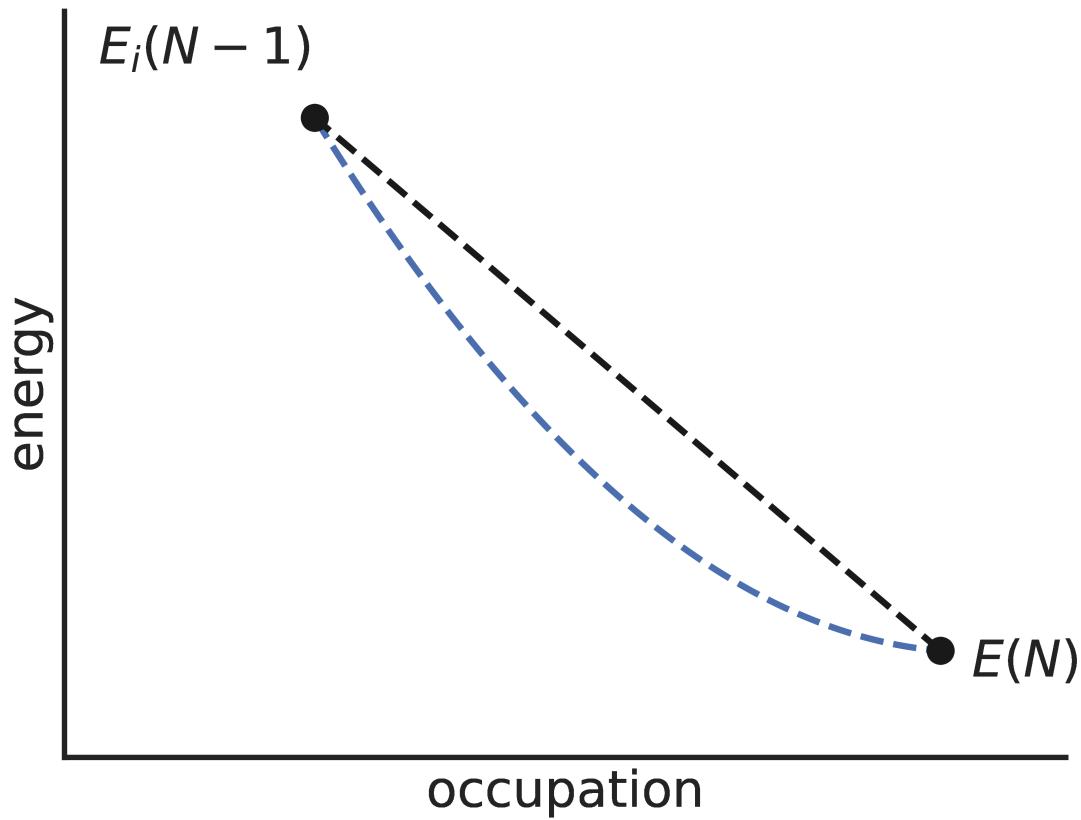
2-electron solution

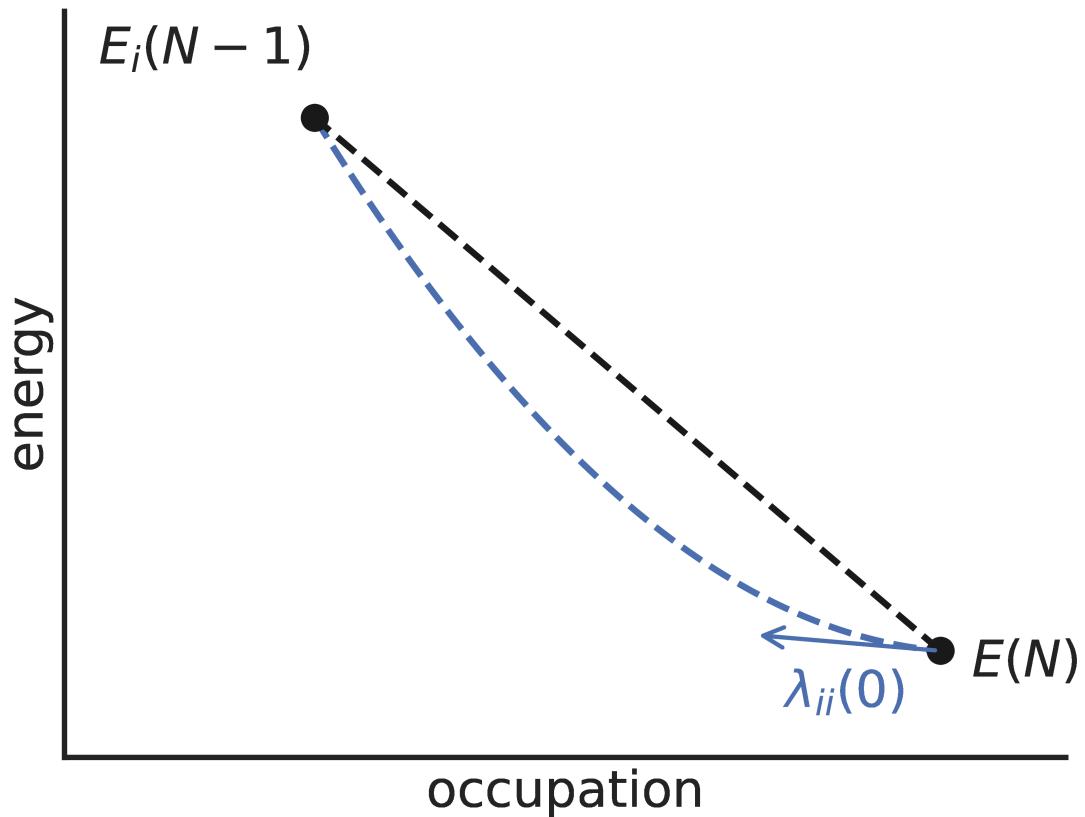


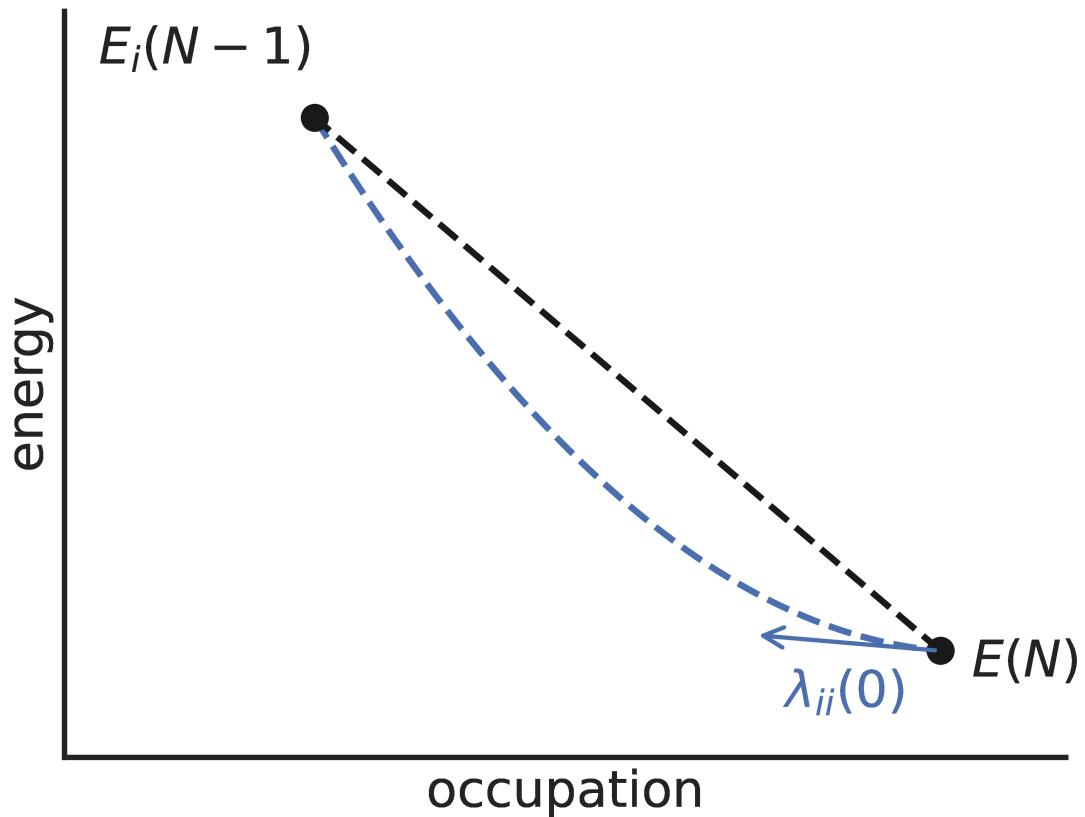
what we can quickly evaluate

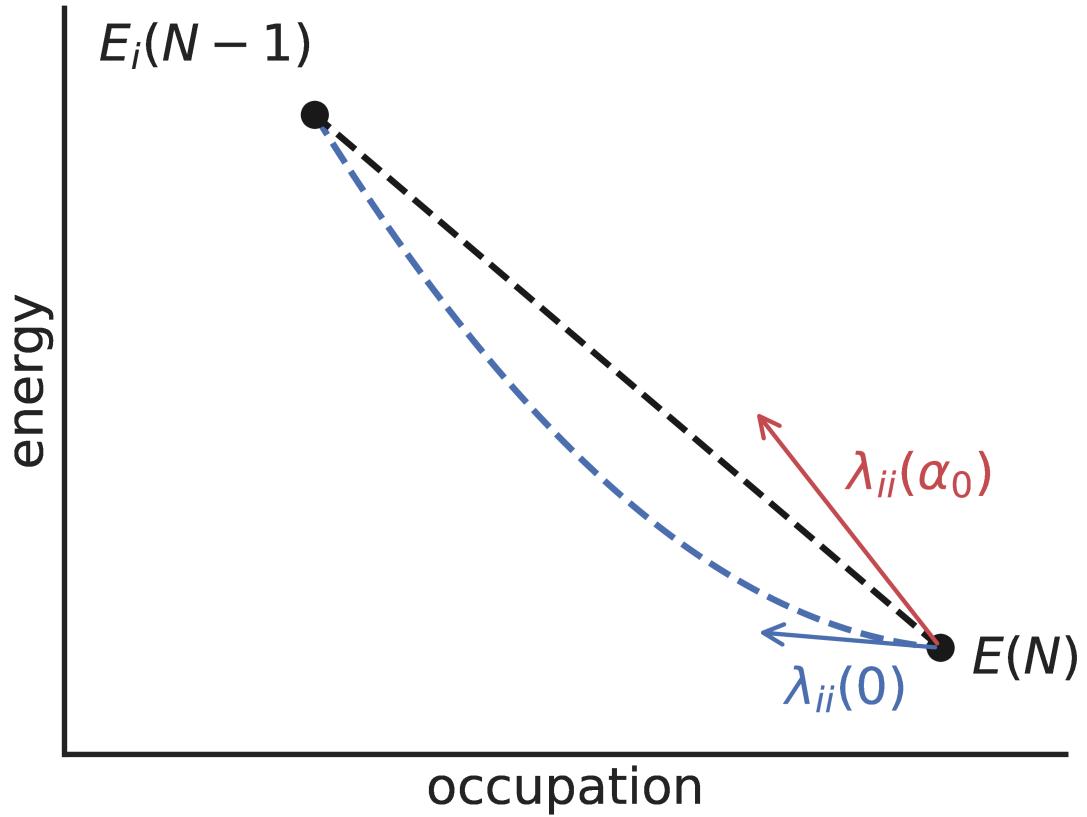


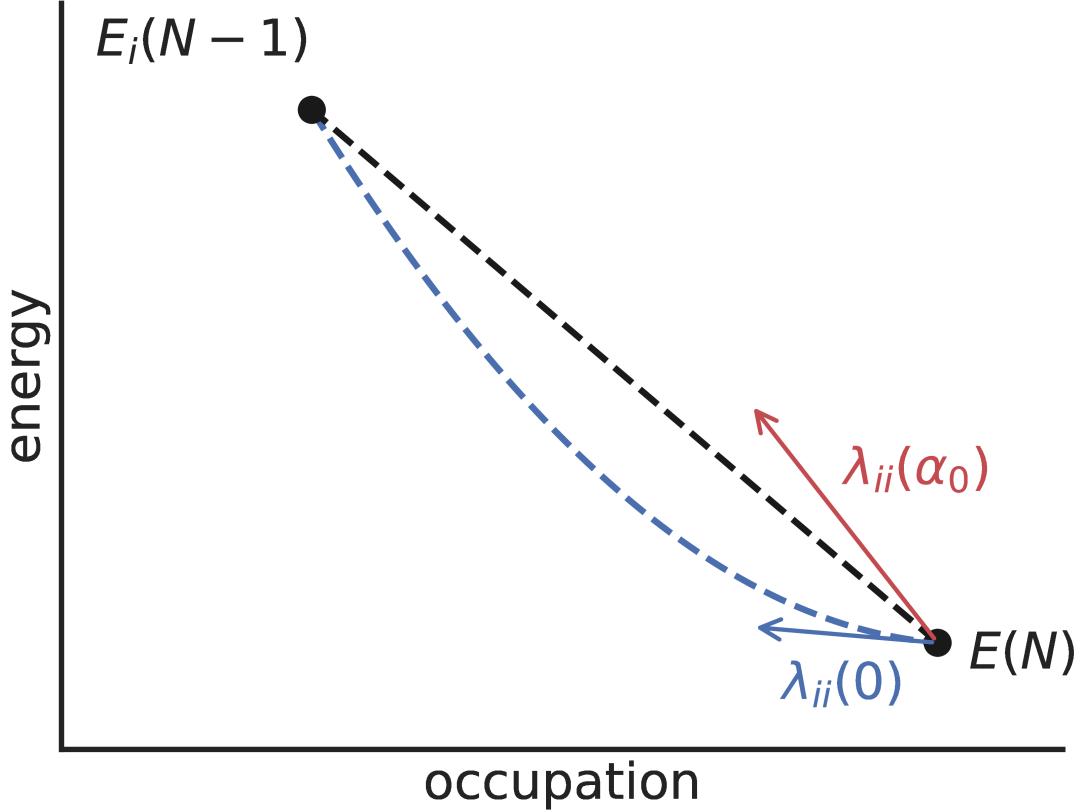








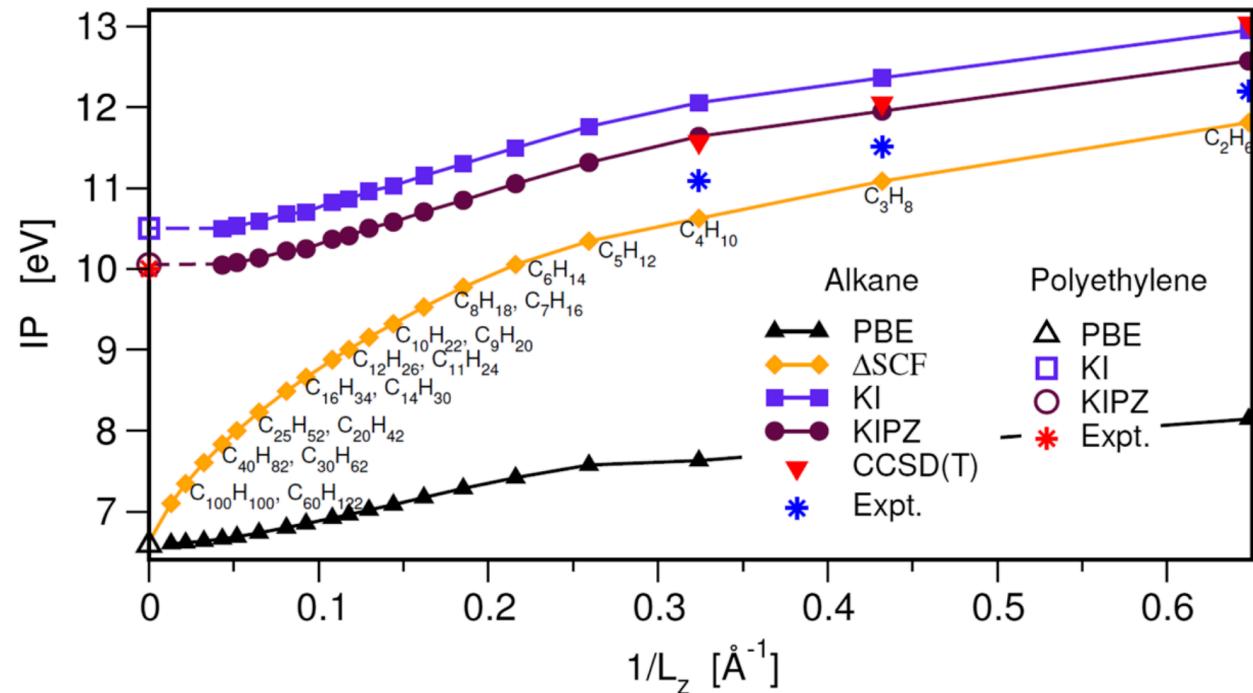




$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

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

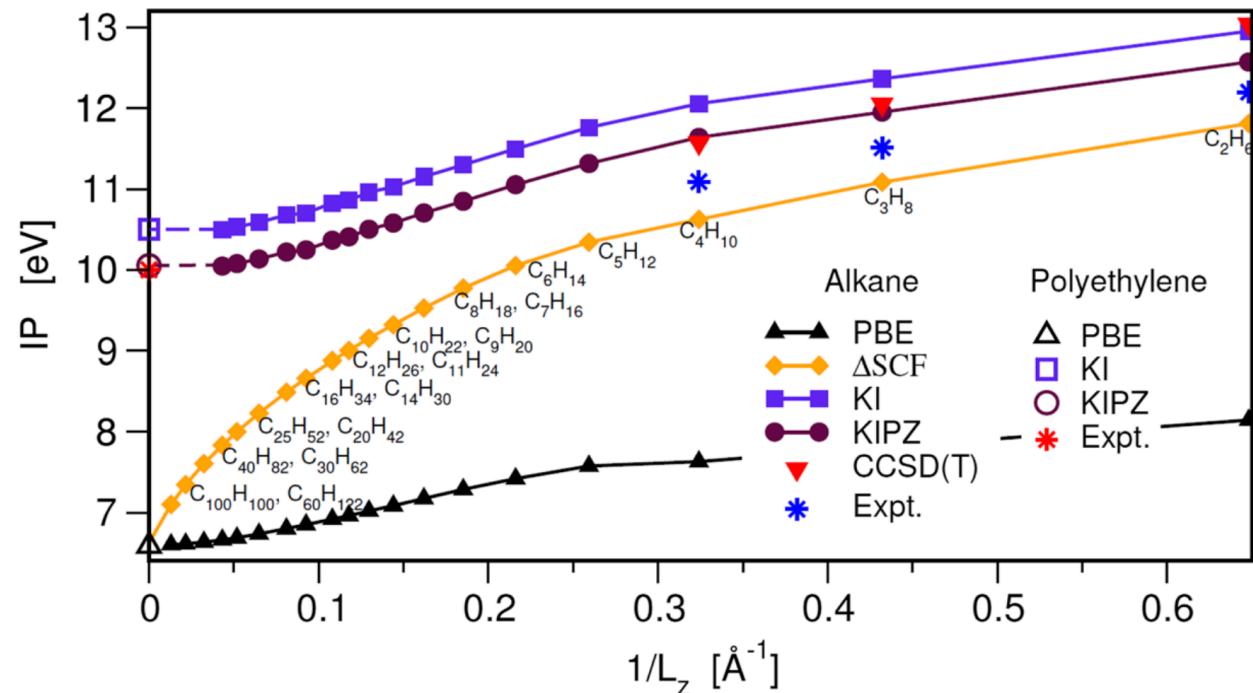
# Issues with extended systems



Two options:

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

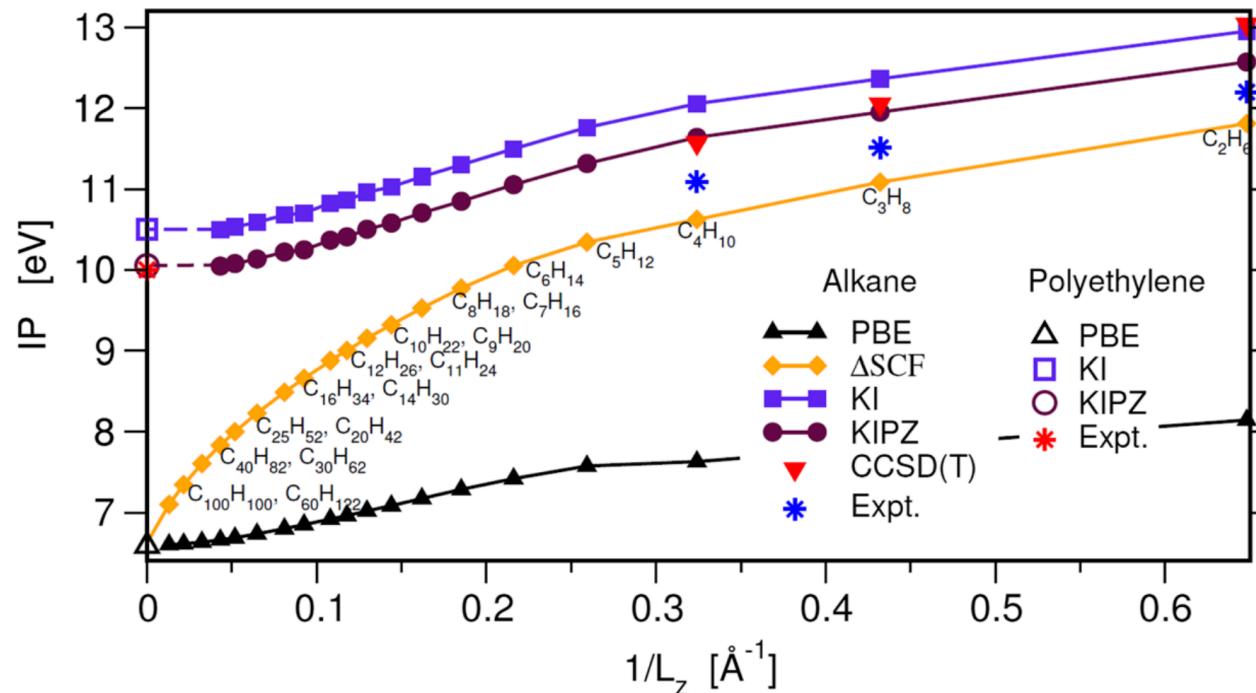
# Issues with extended systems



Two options: 1. use a more advanced functional

<sup>1</sup>N. 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

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

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# Extensions

# Non-collinear spin

# Non-collinear spin

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

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

# Non-collinear spin

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

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e.g. for the corrective potential

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

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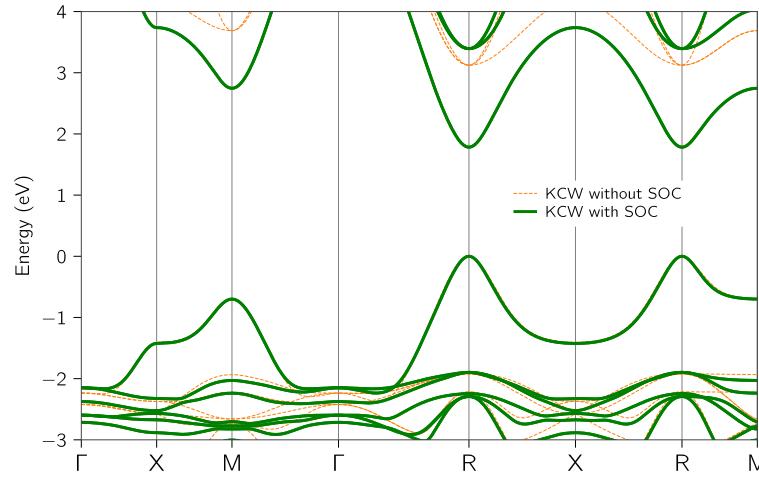
↓

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

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

# Non-collinear spin

CsPbBr<sub>3</sub>



	LDA	HSE	$G_0W_0$	$scG\tilde{W}$	KI	exp
<b>with SOC</b>	0.18	0.78	0.94	1.53	<b>1.78</b>	1.85
without SOC	1.40	2.09	2.56	3.15	3.12	

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

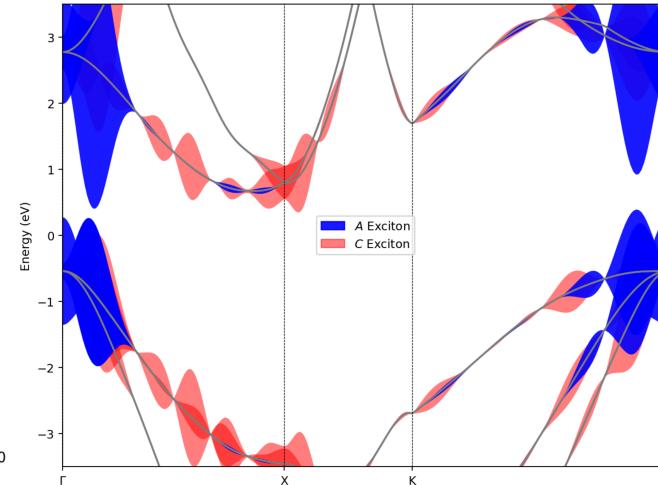
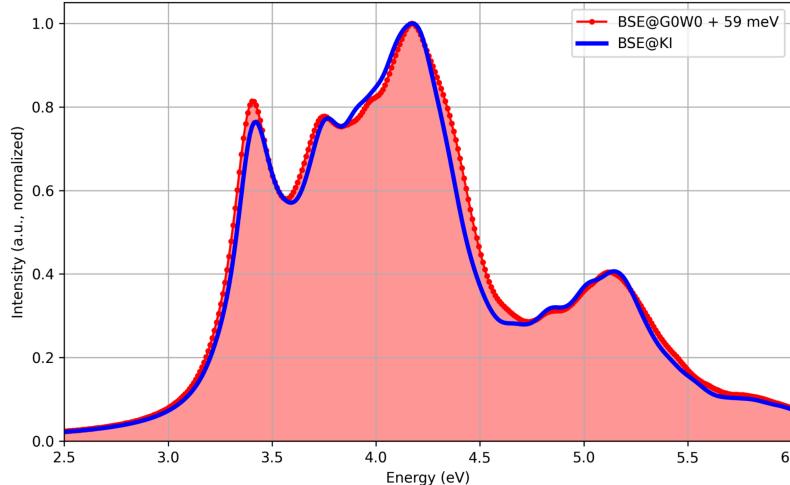
# Optical spectra

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Solve the BSE, using Koopmans eigenvalues in lieu of GW

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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

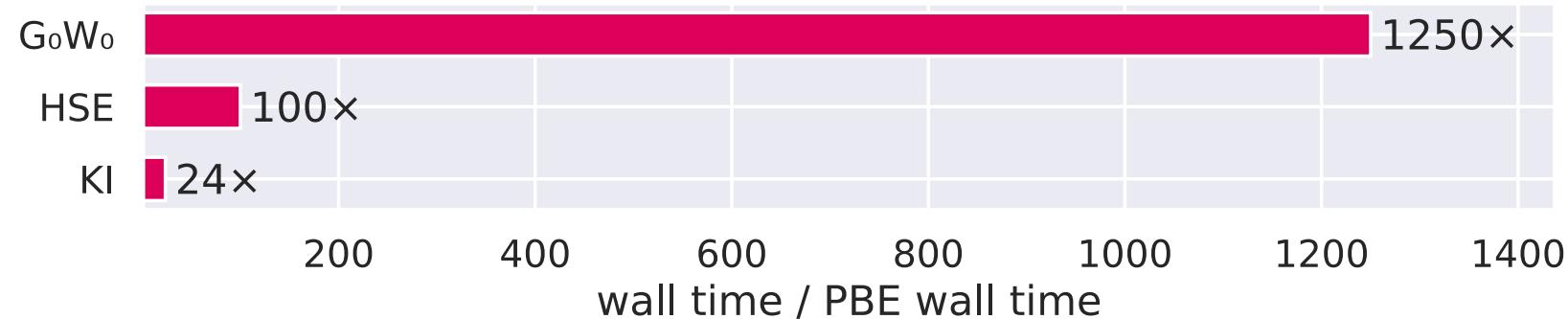
3.25

3.34

0.09

# Computational cost and scaling

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# Computational cost and scaling

The vast majority of the computational cost: determining screening parameters

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

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

<sup>2</sup>N. 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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- a local measure of screening of electronic interactions
- one screening parameter per orbital
- must be computed *ab initio* via...

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

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

- a local measure of screening of electronic interactions
- one screening parameter per orbital
- must be computed *ab initio* via...
  - ΔSCF<sup>1</sup>: embarrassingly parallel steps which each cost  $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$

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

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

# Computational cost and scaling

The vast majority of the computational cost: determining screening parameters

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

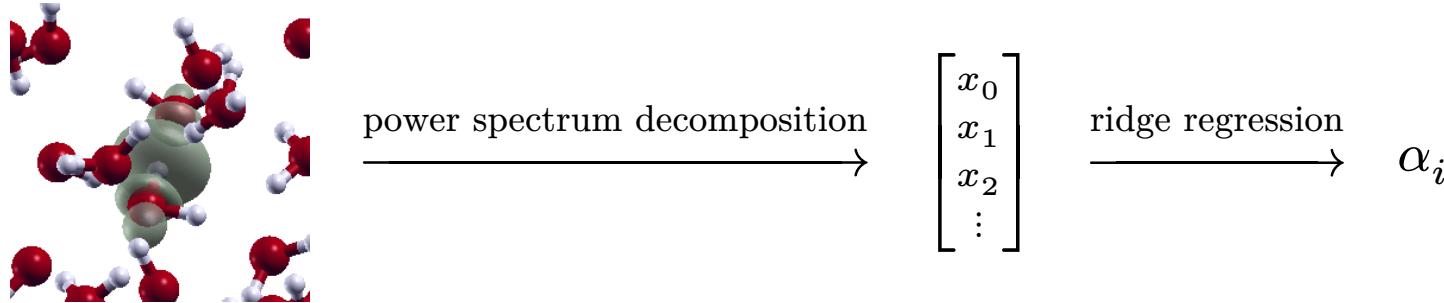
- a local measure of screening of electronic interactions
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  - ΔSCF<sup>1</sup>: embarrassingly parallel steps which each cost  $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$
  - DFPT<sup>2</sup>:  $\mathcal{O}(N_{\mathbf{k}}^2 N^3)$

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

<sup>2</sup>N. 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

# Machine-learned electronic screening

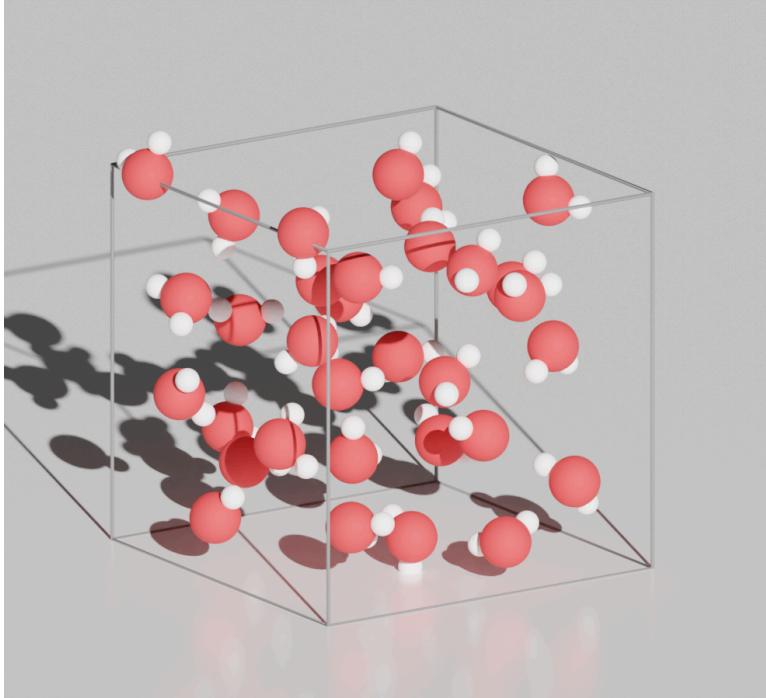


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

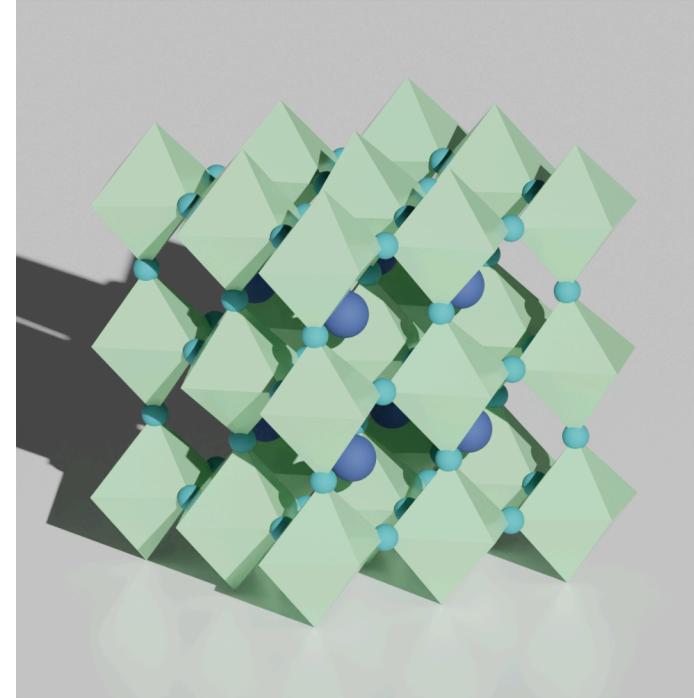
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

# Machine-learned electronic screening



water

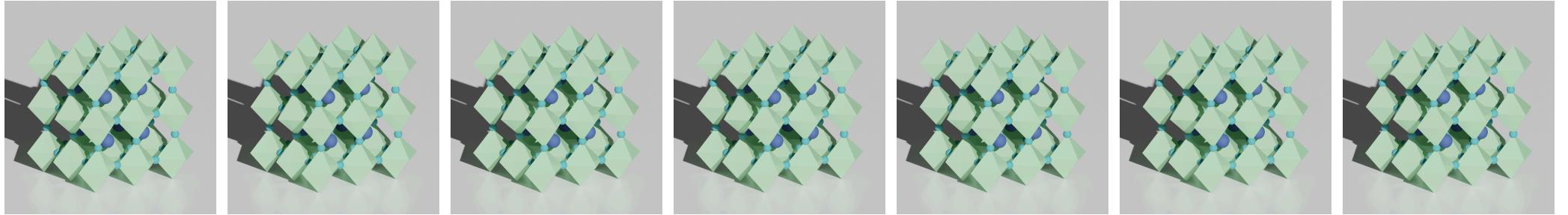


CsSnI<sub>3</sub>

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

# Machine-learned electronic screening

The use-case

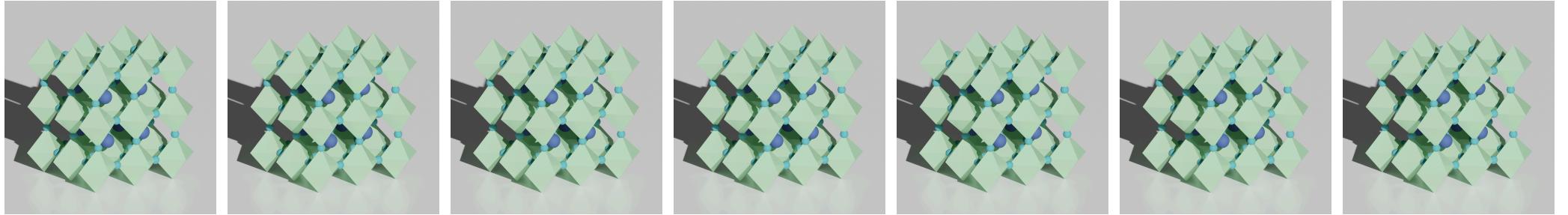


train

predict

# Machine-learned electronic screening

The use-case

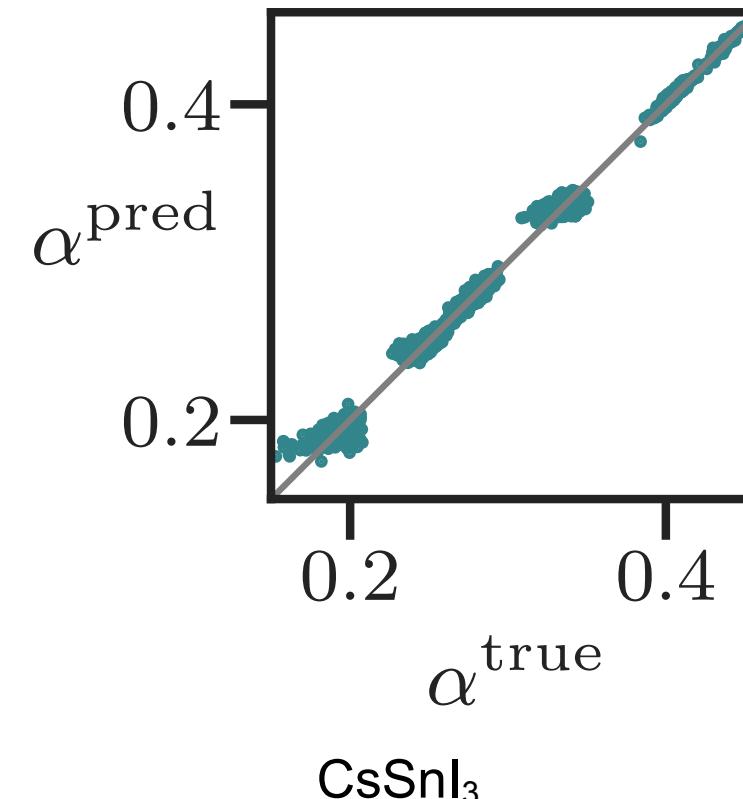
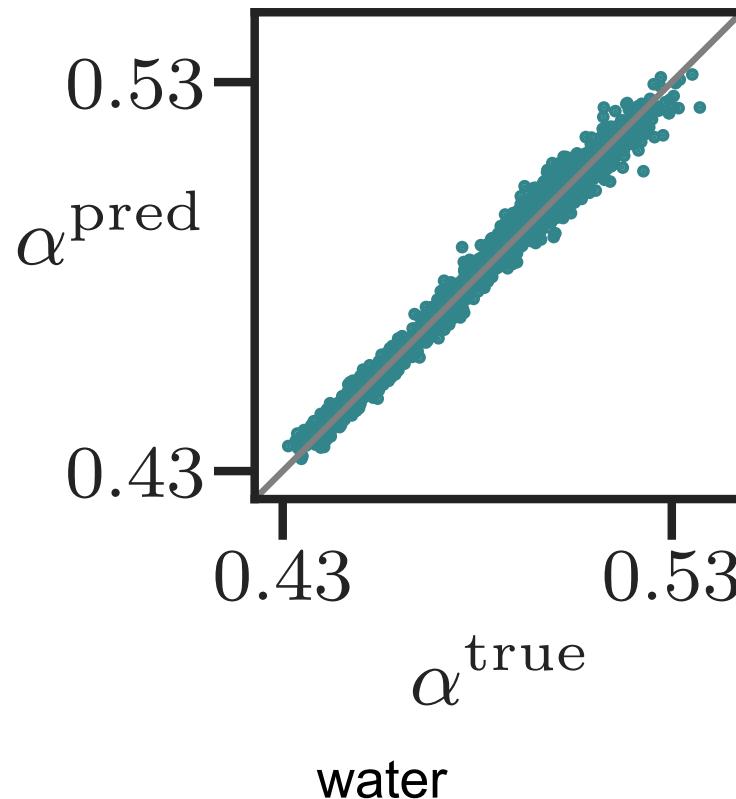


train

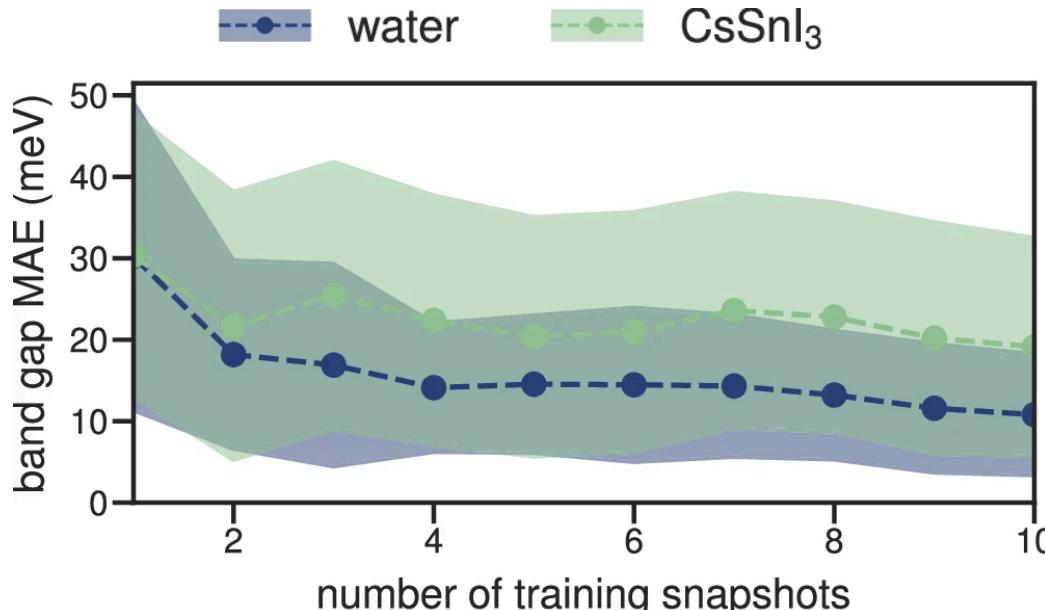
predict

N.B. not a general model

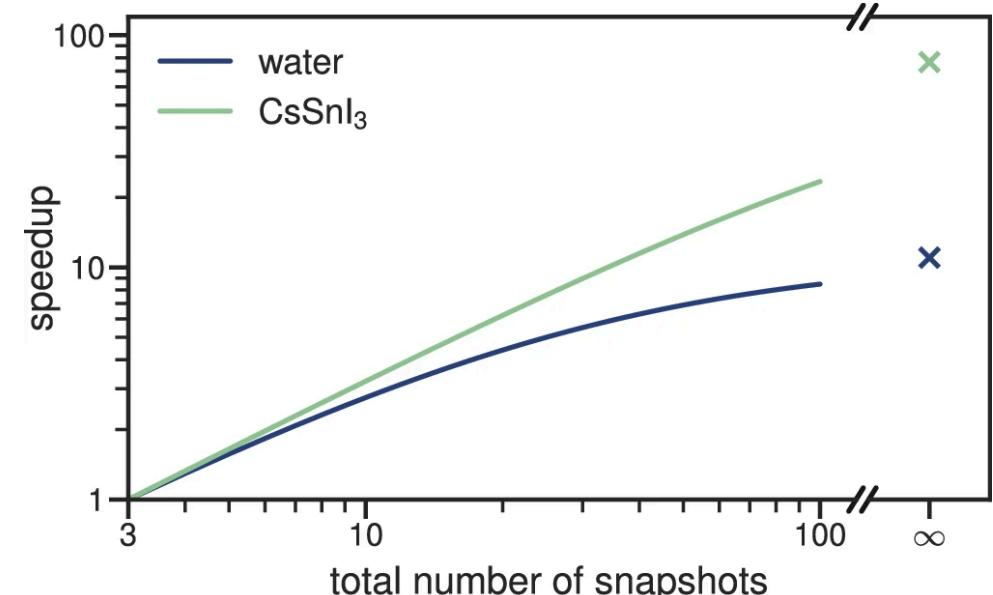
# Machine-learned electronic screening



# 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  $\mathcal{O}(100)$

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

# Symmetries

# Taking advantage of symmetries

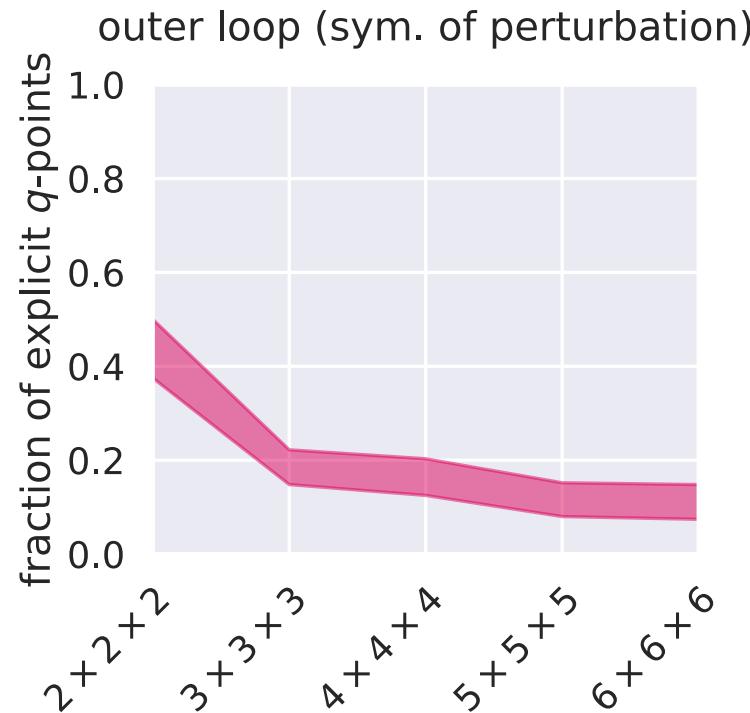
To compute screening parameters via DFPT...

```

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

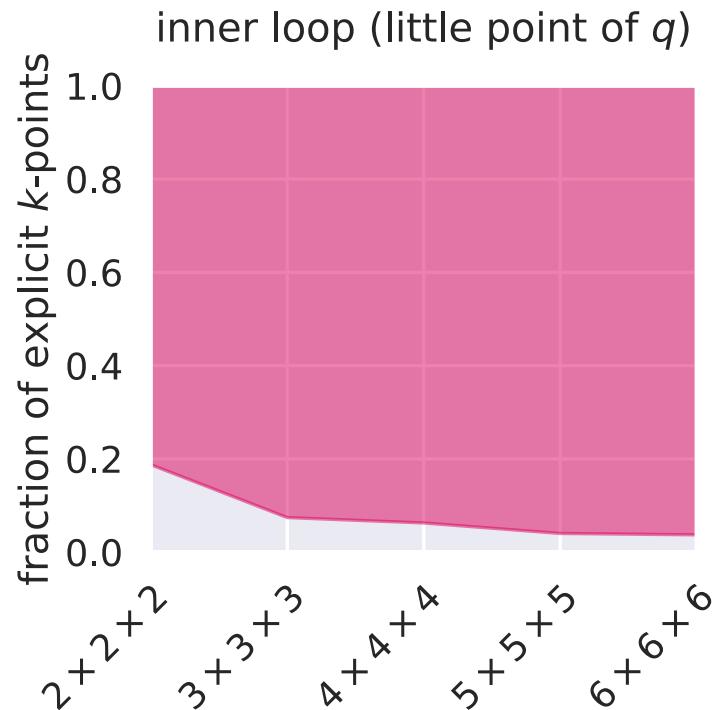
```

# Taking advantage of symmetries



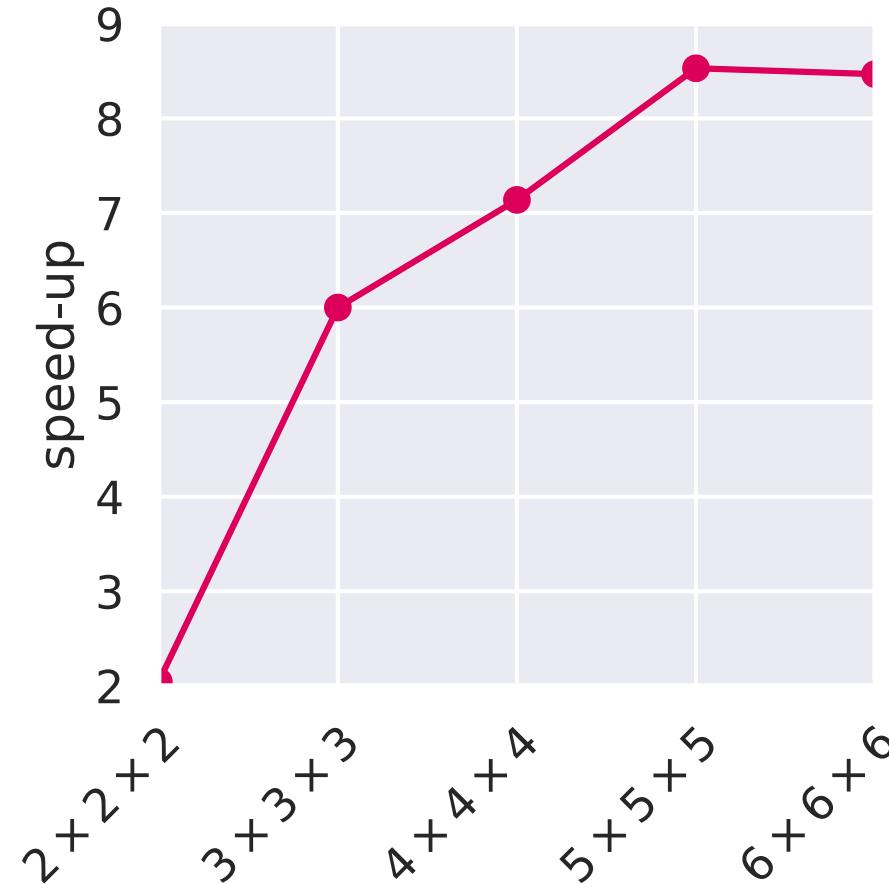
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$  (the symmetry of the perturbation; lower than that of the primitive cell)

# 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



# Automated Wannierisation

# Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

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

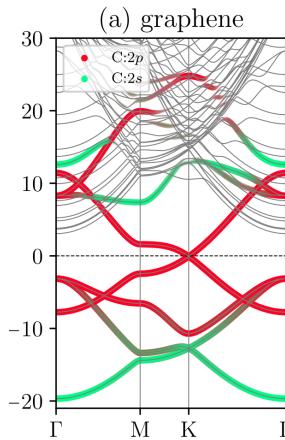
<sup>1</sup>J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

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

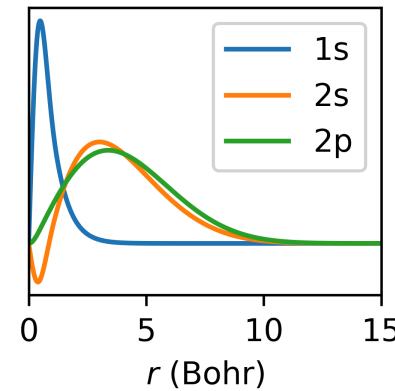
# Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

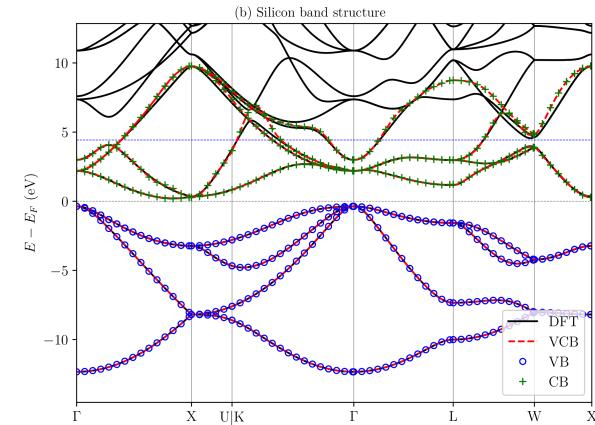
- to initialise the minimising orbitals, or
- in place of the minimising orbitals entirely



projectability-based  
disentanglement<sup>1</sup>



use PAOs found in  
pseudopotentials



parallel transport to separate  
manifolds<sup>2</sup>

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

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

# koopmans 🤝 AiiDA

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



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

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



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

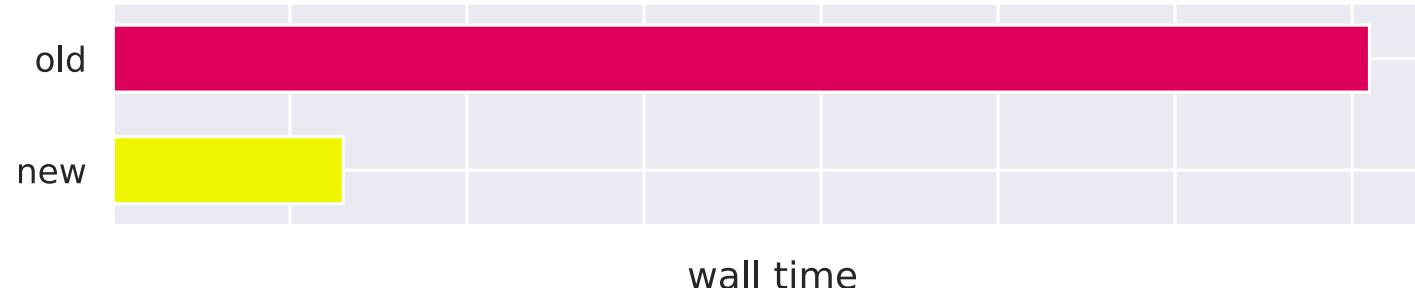
remote compute, parallel step execution, provenance-tracking, (requires configuration,  
WIP...)

<sup>1</sup>S. 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...)



<sup>1</sup>S. 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

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

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$v_i^{KI}(\mathbf{r})$  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

<sup>1</sup>A. 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 corrections<sup>1</sup>

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

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

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

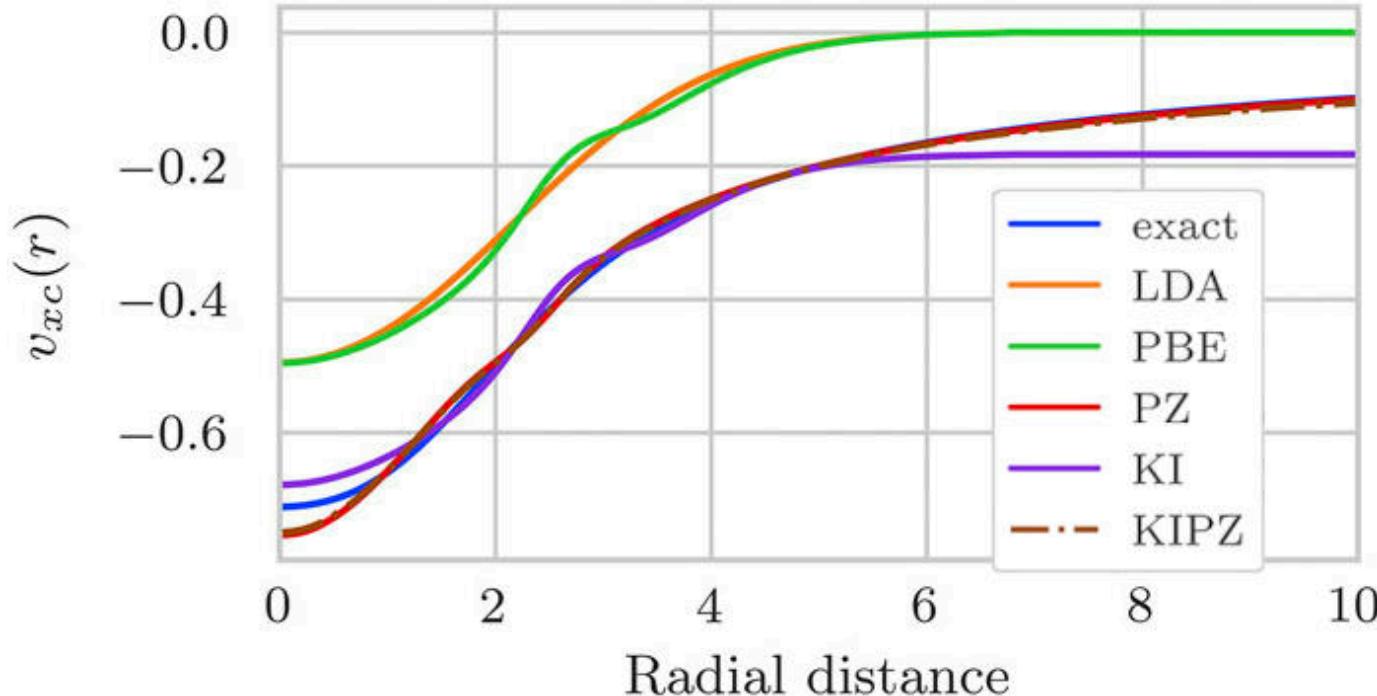
KIPZ@ DFT ( $v_{\text{xc}} \rightarrow \text{DFT}$ ;  $f_{\text{Hxc}} \rightarrow \text{DFT}$ ;  $\varepsilon^{-1} \rightarrow \text{DFT}$ )

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

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

# Model systems

## Hooke's atom<sup>1</sup>



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

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