

# **Band structure calculations that are accurate, efficient, accessible, and automated**

**Edward Linscott**

Paul Scherrer Institute

MARVEL Review & Retreat | Grindelwald | 14 January 2025

# This talk

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A whistlestop tour of our progress on Koopmans functionals over the past year



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A whistlestop tour of our progress on Koopmans functionals over the past year



Nicola  
Colonna



Marija  
Stojkovic



Giovanni  
Cistaro



Yannick  
Schubert



Junfeng  
Qiao



Miki  
Bonacci



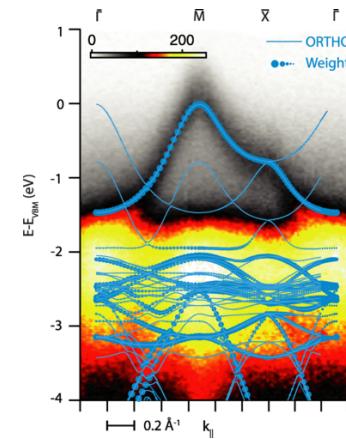
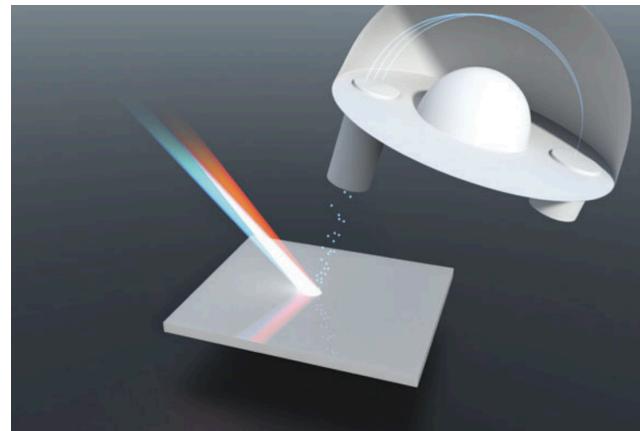
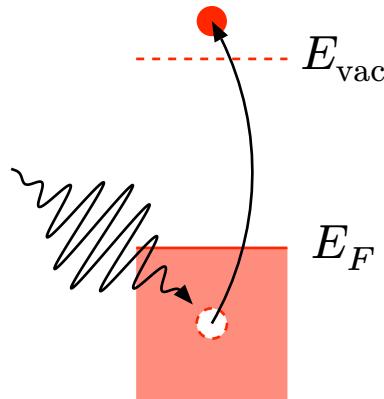
Julian  
Geiger



Nicola  
Marzari

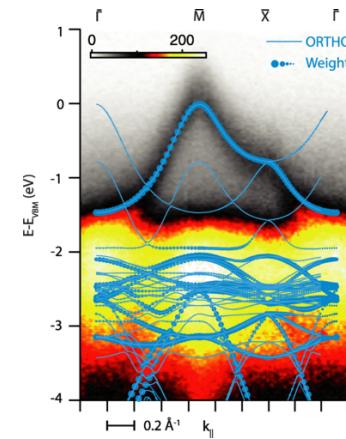
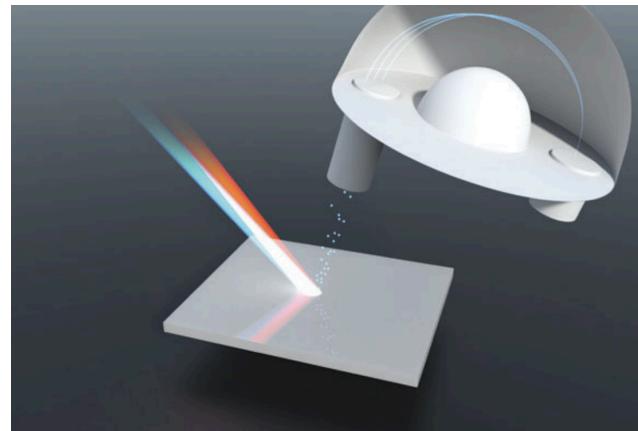
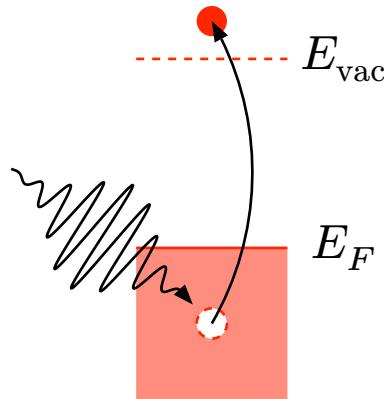
# Koopmans functionals in a nutshell

Spectral properties are fundamental to understanding materials:



# Koopmans functionals in a nutshell

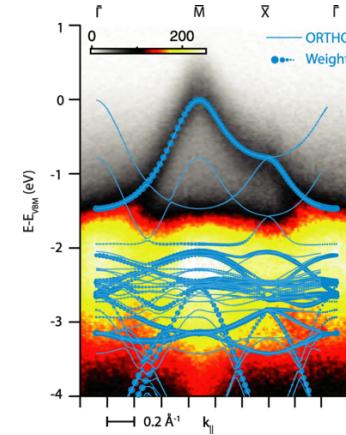
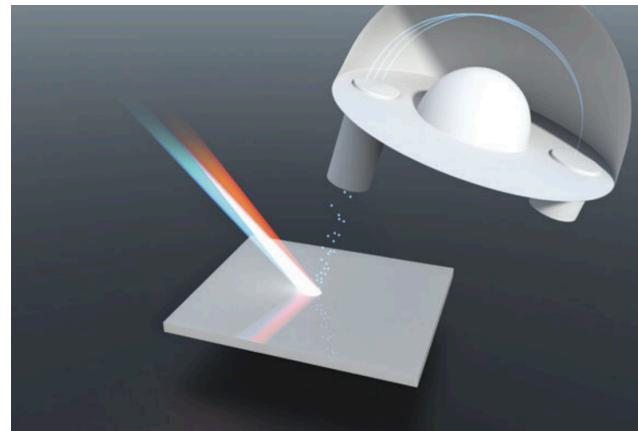
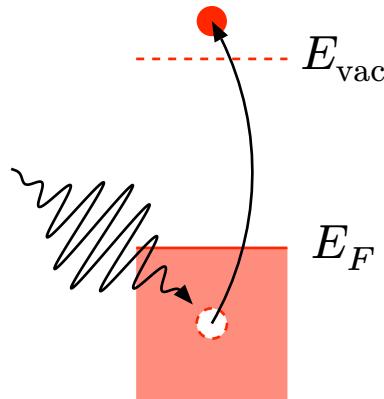
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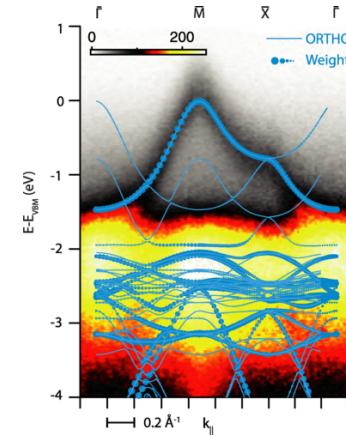
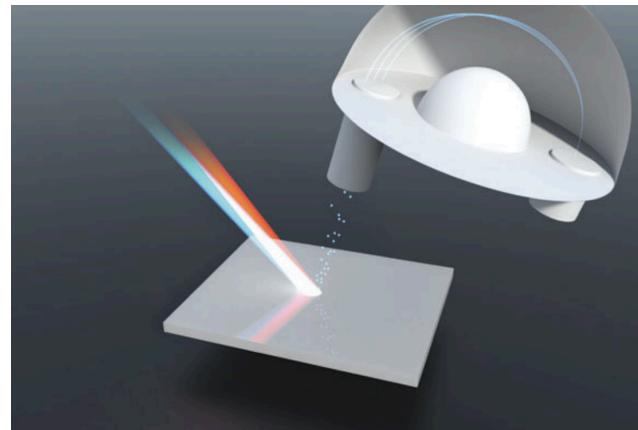
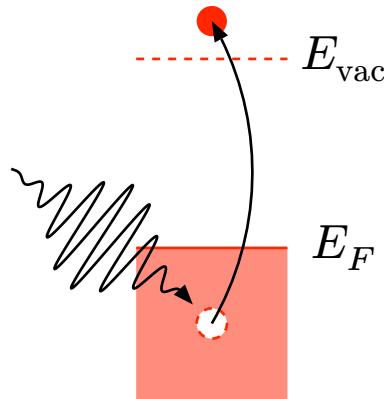


... but how can we routinely compute them?

- GW: accurate but expensive and often ill-behaved; diagrammatic

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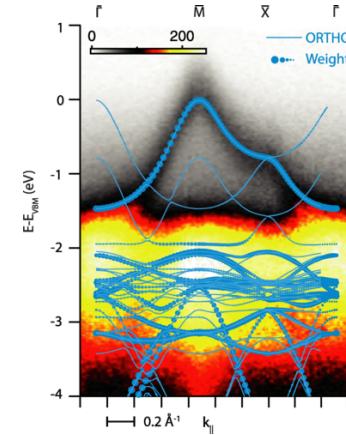
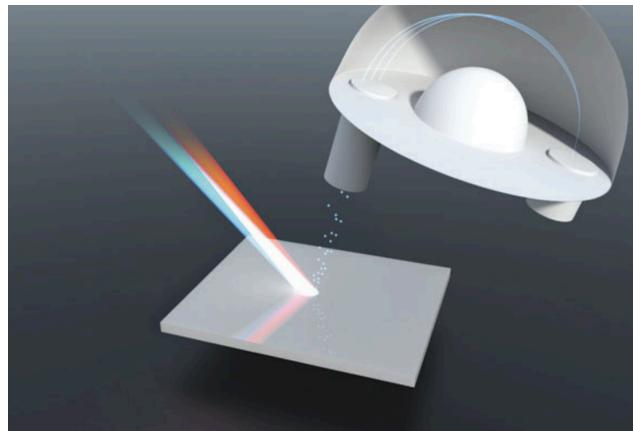
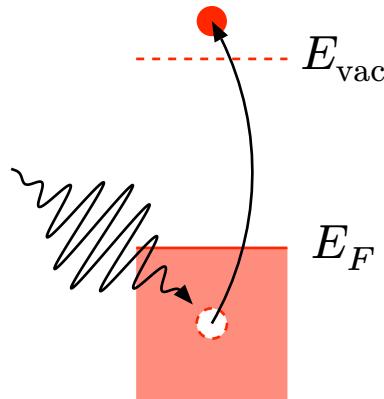


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# Koopmans functionals in a nutshell

Spectral properties are fundamental to understanding materials:



... but how can we routinely compute them?

- GW: accurate but expensive and often ill-behaved; diagrammatic
- DFT: plagued by systematic errors

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

# Koopmans functionals in a nutshell

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

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- screening parameters

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- an orbital-by-orbital correction to DFT
- screening parameters
- orbital-density-dependence

# This talk

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Our goal with Koopmans functionals: band structure calculations that are...

- accurate
- efficient
- accessible
- automated

# Accuracy

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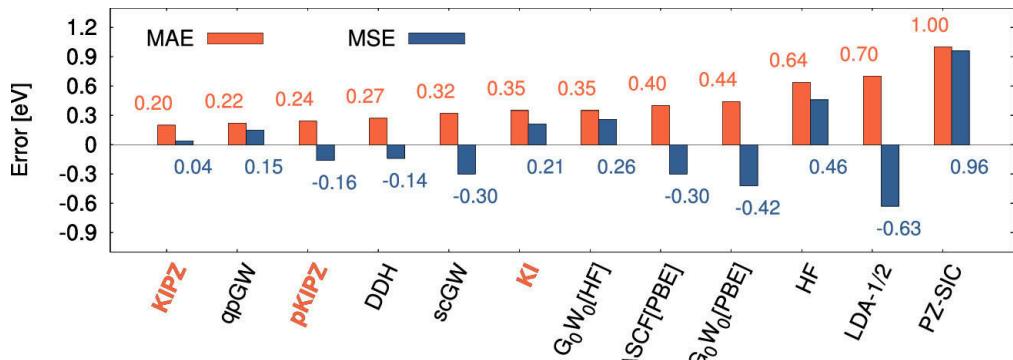


# The accuracy of Koopmans functionals

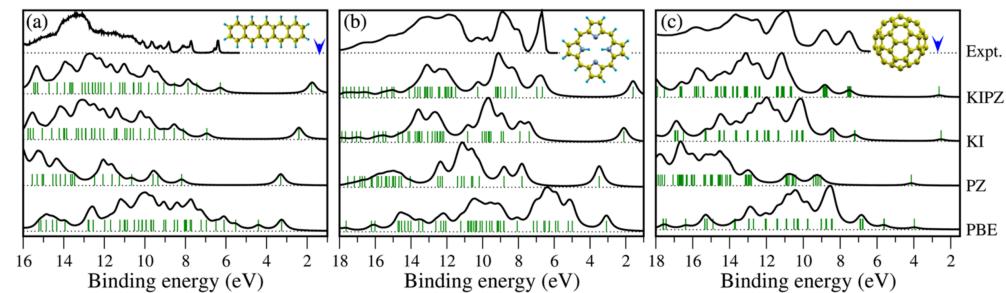
... is well-established

## Molecular systems

Ionisation potentials<sup>1</sup>



UV photoemission spectra<sup>2</sup>



<sup>1</sup>N. Colonna et al. J. Chem. Theory Comput. **15**, 1905–1914 (2019)

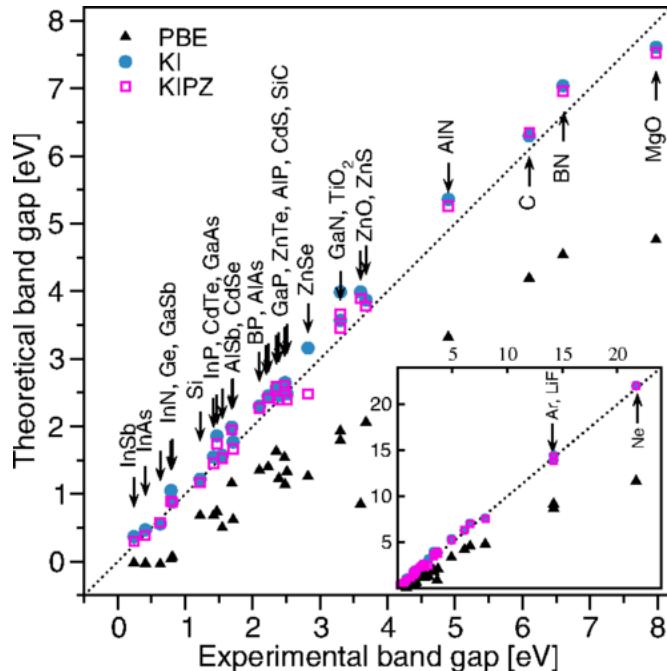
<sup>2</sup>N. L. Nguyen et al. Phys. Rev. Lett. **114**, 166405 (2015)



# The accuracy of Koopmans functionals

## Bulk systems

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

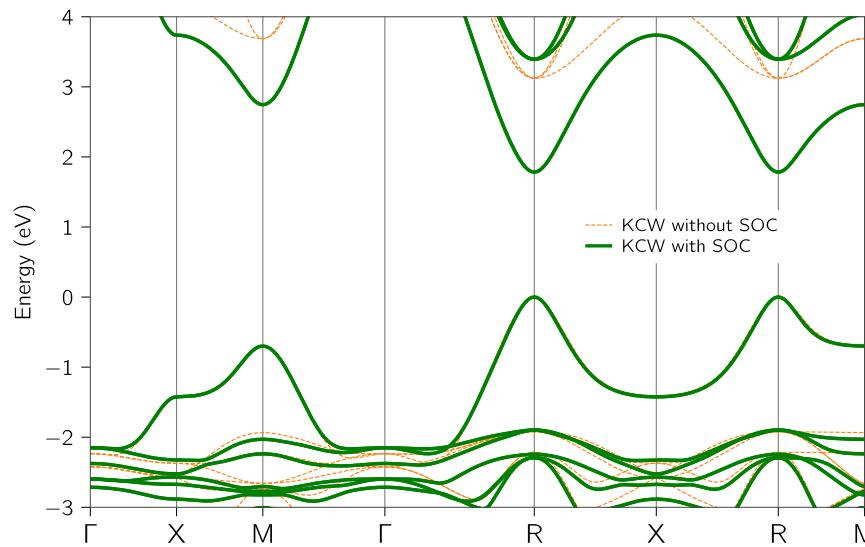


	PBE	$G_0W_0$	KI	KIPZ	$QSG\tilde{W}$
$E_{gap}$	2.54	0.56	<b>0.27</b>	<b>0.22</b>	0.18
IP	1.09	0.39	<b>0.19</b>	<b>0.21</b>	0.49

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

# The accuracy of Koopmans functionals

CsPbBr<sub>3</sub>

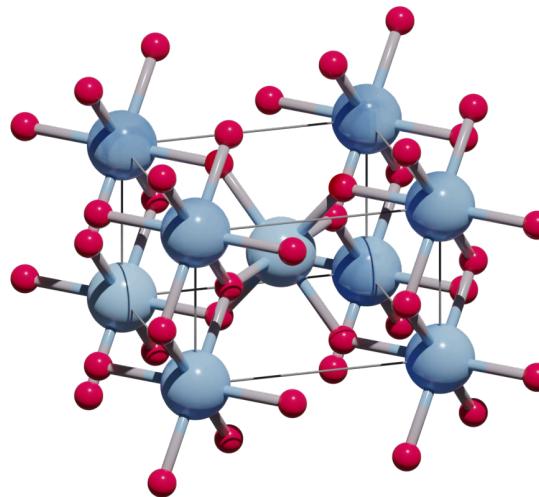


	LDA	HSE	G <sub>0</sub> W <sub>0</sub>	scG $\tilde{W}$	KI	exp
<b>with SOC</b>	0.18	0.78	0.94	1.53	<b>1.78</b>	
without SOC	1.40	2.09	2.56	3.15	3.12	1.85

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

# The accuracy of Koopmans functionals

TiO<sub>2</sub>



	PBE	HSE06	$G_0W_0$ @PBE	$scQPG\tilde{W}$	KI	exp - ZPR
$E_{\text{gap}}$	1.73	3.39	3.46	5.18	<b>3.29</b>	3.34 to 3.41
IP	7.22	8.66	7.29	8.77	<b>8.00</b>	8.5
EA	5.55	4.99	3.03	3.59	<b>4.71</b>	5.0

<sup>1</sup>M. Stojkovic et al. (2024)

# Efficiency

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# Screening parameters

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A key ingredient of Koopmans functional calculations:

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

<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. **14**, 2549–2557 (2018), N. Colonna et al. J. Chem. Theory Comput. **18**, 5435–5448 (2022)



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- a local measure of the degree by which electronic interactions are screened

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- one screening parameter per (non-equivalent) orbital

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- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital
- must be computed ab initio via  $\Delta\text{SCF}$ <sup>1</sup> or DFPT<sup>2</sup>
- corresponds to the vast majority of the computational cost of Koopmans functional calculation

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# Taking advantage of symmetries

---

```
1: function CalculateAlpha( $n$ )
2:   for  $q \in \text{BZ}$  do
3:      $\triangleright$  NSCF at  $k, k + q$ 
4:     for  $k \in \text{BZ}$  do
5:        $\triangleright$  Linear system  $Ax = b$  with  $\dim(A) = n_{\text{pw}}^2$ 
6:        $\Pi_{0n,q}^{(r)} \leftarrow \langle \Delta\rho_q^{0n} \mid f_{\text{Hxc}} \mid \rho_q^{0n} \rangle$ 
7:        $\Pi_{0n,q}^{(u)} \leftarrow \langle \rho_q^{0n} \mid f_{\text{Hxc}} \mid \rho_q^{0n} \rangle$ 
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- $q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$

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- $k \in \text{BZ} \rightarrow k \in \text{IBZ}(q)$

TODO DOUBLE-CHECK THIS WITH NICOLA

# Taking advantage of symmetries

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TODO

Inner sum

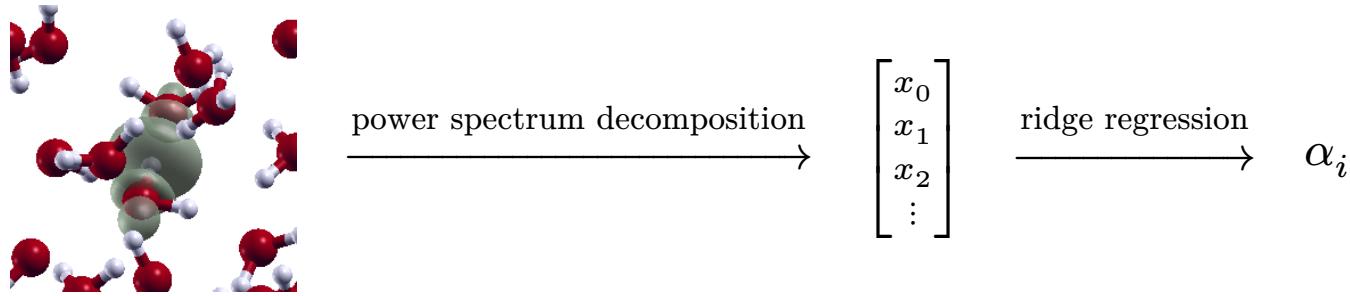
Outer sum

Speedup figure



# Electronic screening via machine learning

## The ML framework



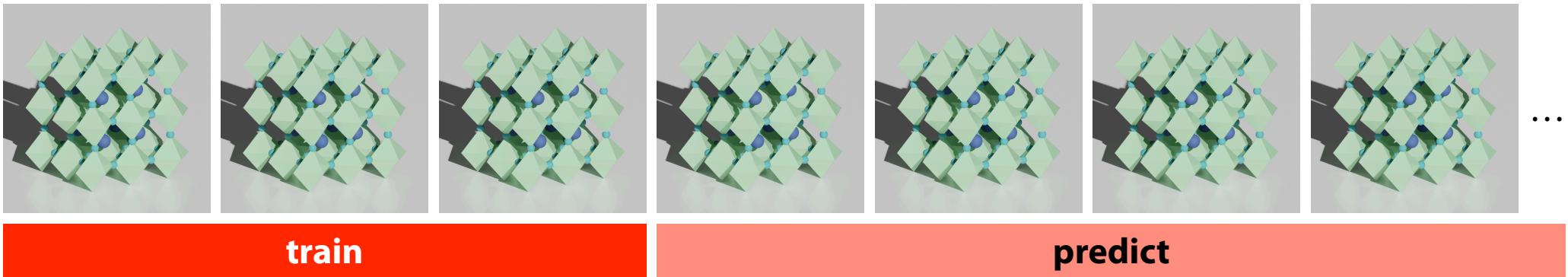
$$c_{nlm,k}^i = \int dr g_{nl}(r) Y_{lm}(\theta, \varphi) n_i(\mathbf{r} - \mathbf{R}_i)$$

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

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

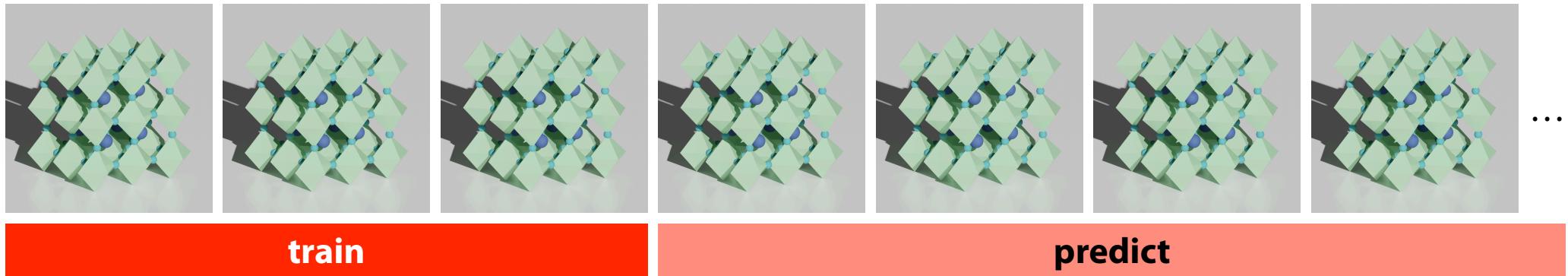
# Electronic screening via machine learning

The use-case



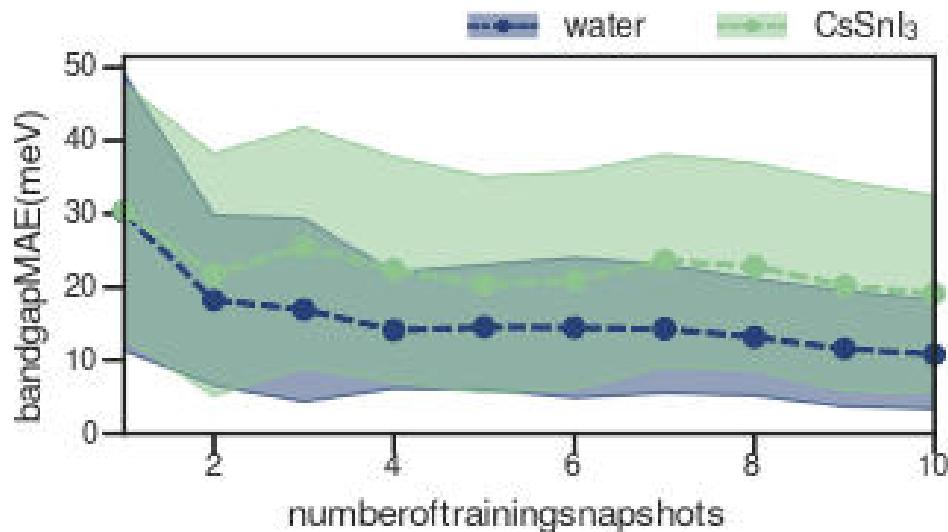
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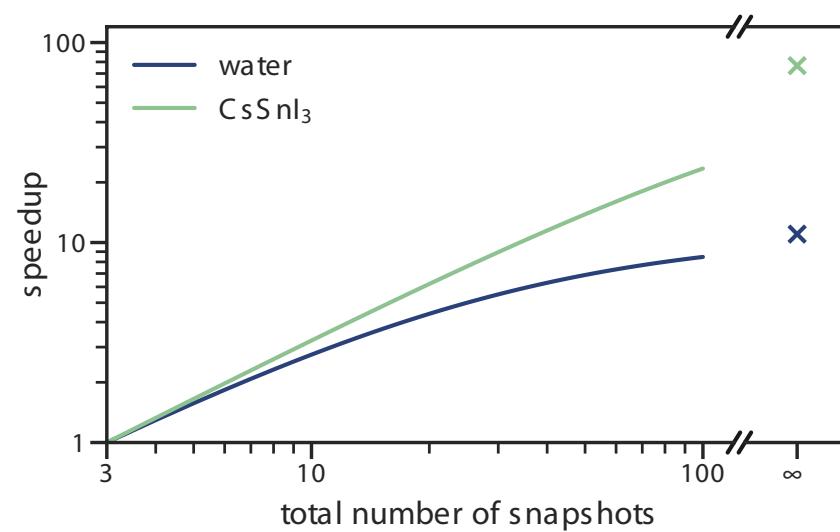


N.B. not a general model

# Electronic screening via machine learning



**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  $\mathcal{O}(100)$

TODO REPLACE WITH UPDATED FIGURES

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



# Accessibility

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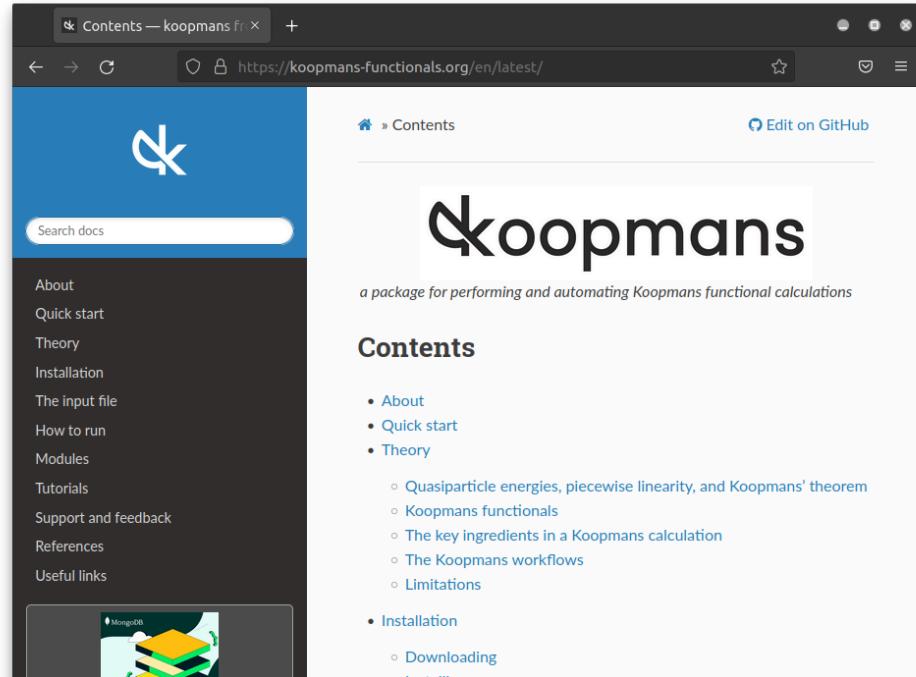
# Barriers to accessibility

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- non-standard functionals
- (some) bespoke code
- complicated workflows



koopmans



An ongoing effort to make Koopmans functional calculations straightforward for non-experts<sup>1</sup>

- easy installation
- automated workflows
- minimal knowledge required from the user

See koopmans - functionals .org

<sup>1</sup>E. B. Linscott et al. J. Chem. Theory Comput. **19**, 7097–7111 (2023)

# Automation

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# AiiDA integration

---

Koopmans

Simple by design

# AiiDA integration

---

Koopmans

Simple by design

- local execution only

# AiiDA integration

---

## Koopmans

Simple by design

- local execution only
- serial step execution (even when steps are independent!)

# AiiDA integration

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Powerful by design

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Powerful by design

- remote execution

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Powerful by design

- remote execution
- parallel step execution

# AiiDA integration

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Powerful by design

- remote execution
- parallel step execution
- outputs stored in a database

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# AiiDA integration

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## Koopmans

Simple by design

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- serial step execution (even when steps are independent!)
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## AiiDA

Powerful by design

- remote execution
- parallel step execution
- outputs stored in a database
- installation more involved

We could really benefit from a lot of these features

# Introducing...

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koopmans

# What's new

---

UI practically unchanged:

```
$ koopmans tio2.json
```

# What's new

---

UI practically unchanged:

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

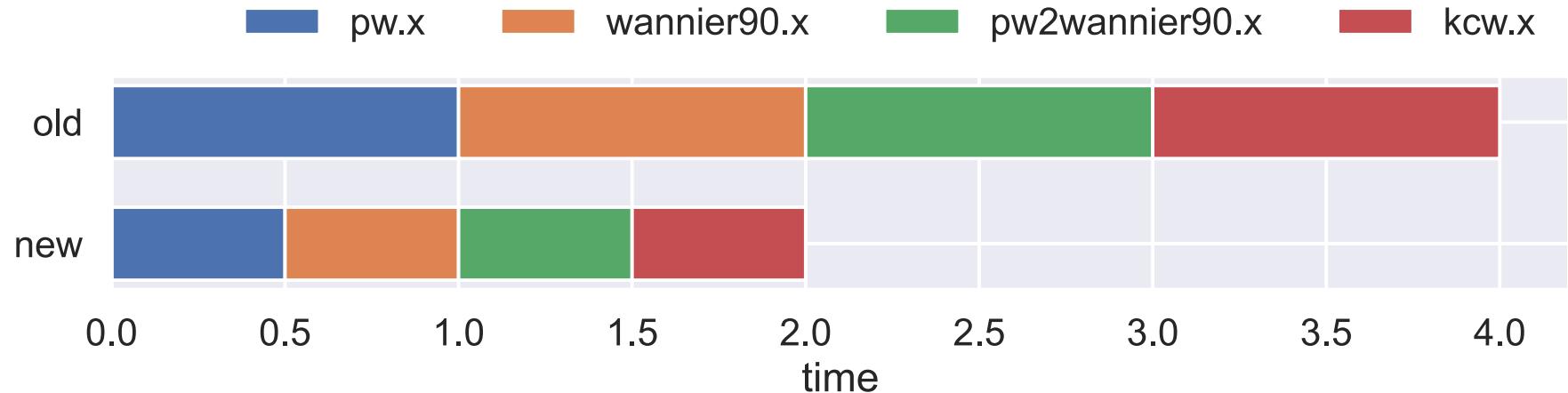
# What's new

---

UI practically unchanged:

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

but executed remotely and in parallel:



# What did this require?

---



# What did this require?

---

- aiida-blitz for simplified AiiDA setup



# What did this require?

---

- aiida-blitz for simplified AiiDA setup
- ? for dumping contents of AiiDA database to a local file structure



# What did this require?

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- aiida-blitz for simplified AiiDA setup
- ? for dumping contents of AiiDA database to a local file structure
- substantial refactoring of the koopmans code base

# What did this require?

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- aiida-blitz for simplified AiiDA setup
- ? for dumping contents of AiiDA database to a local file structure
- substantial refactoring of the koopmans code base
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# What did this require?

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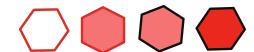
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  - ▶ removing all reliance on shared directories

TODO WORK OUT WHAT ARE THE PROPER NAMES FOR THESE AiiDA TOOLS



# Automated Wannierization

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Koopmans functionals rely heavily on Wannier functions...

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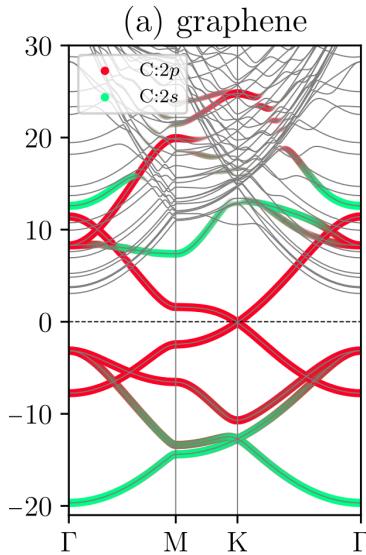
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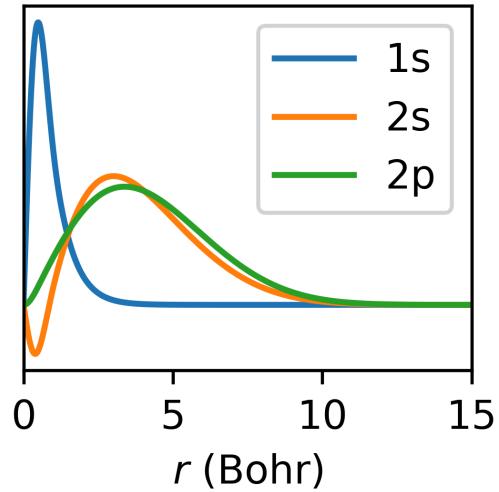
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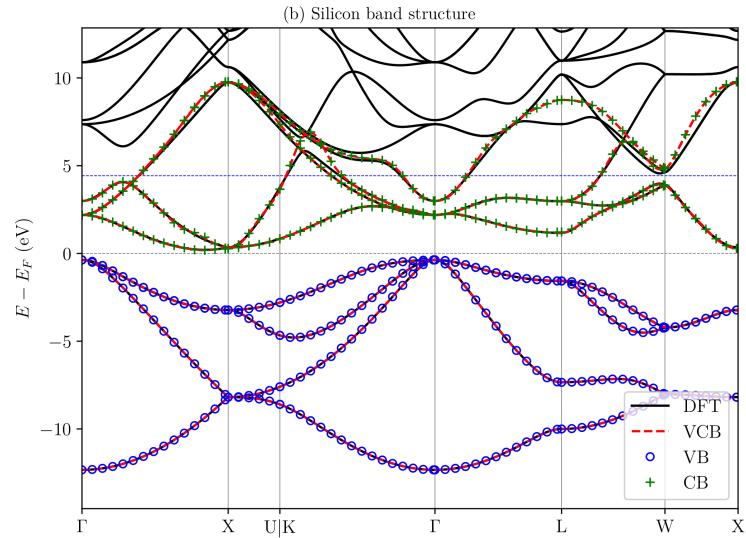
# Automated Wannierization



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)



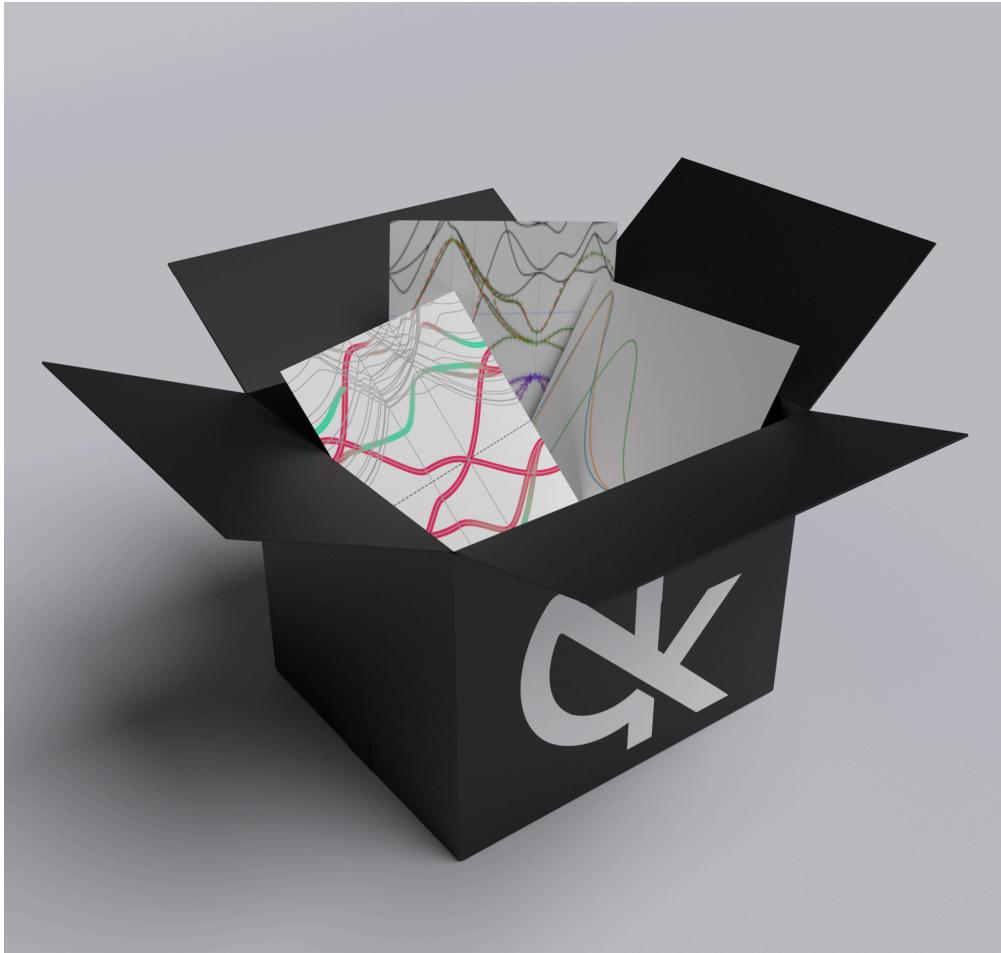
# Summary

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# Summary

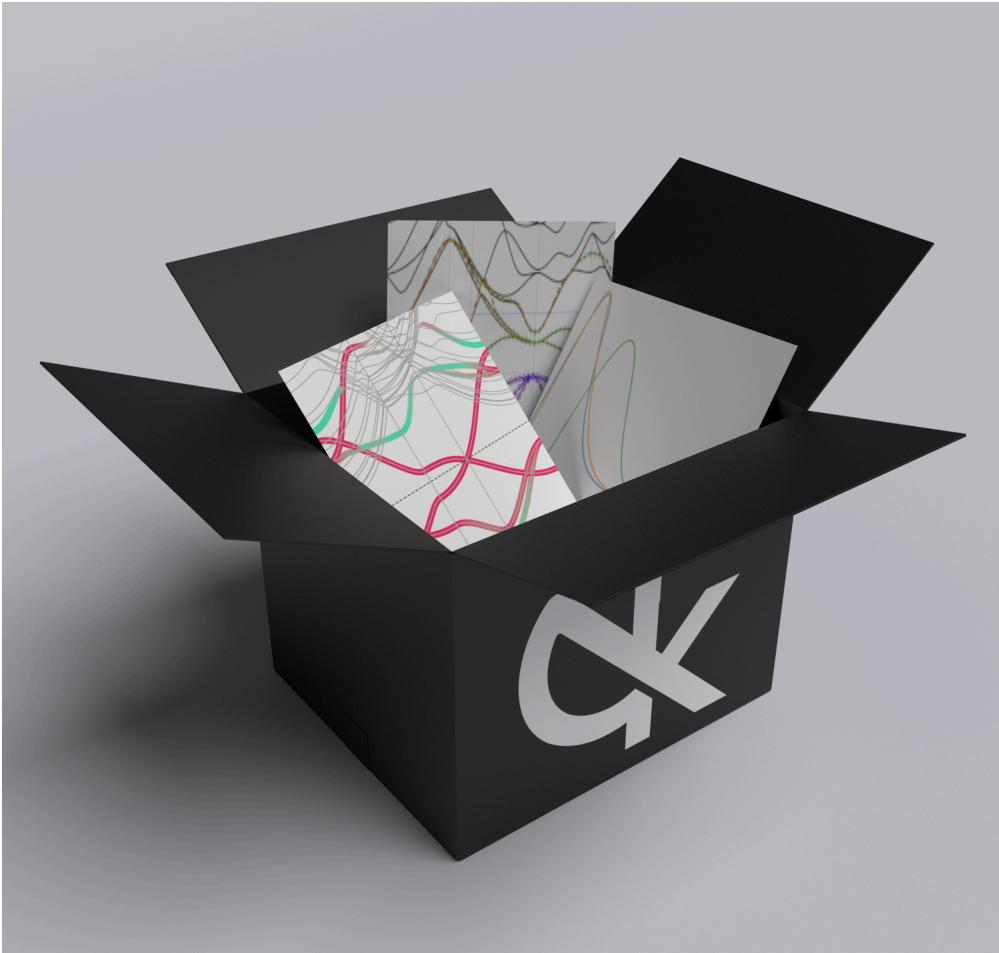
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Koopmans functionals are...

# Summary

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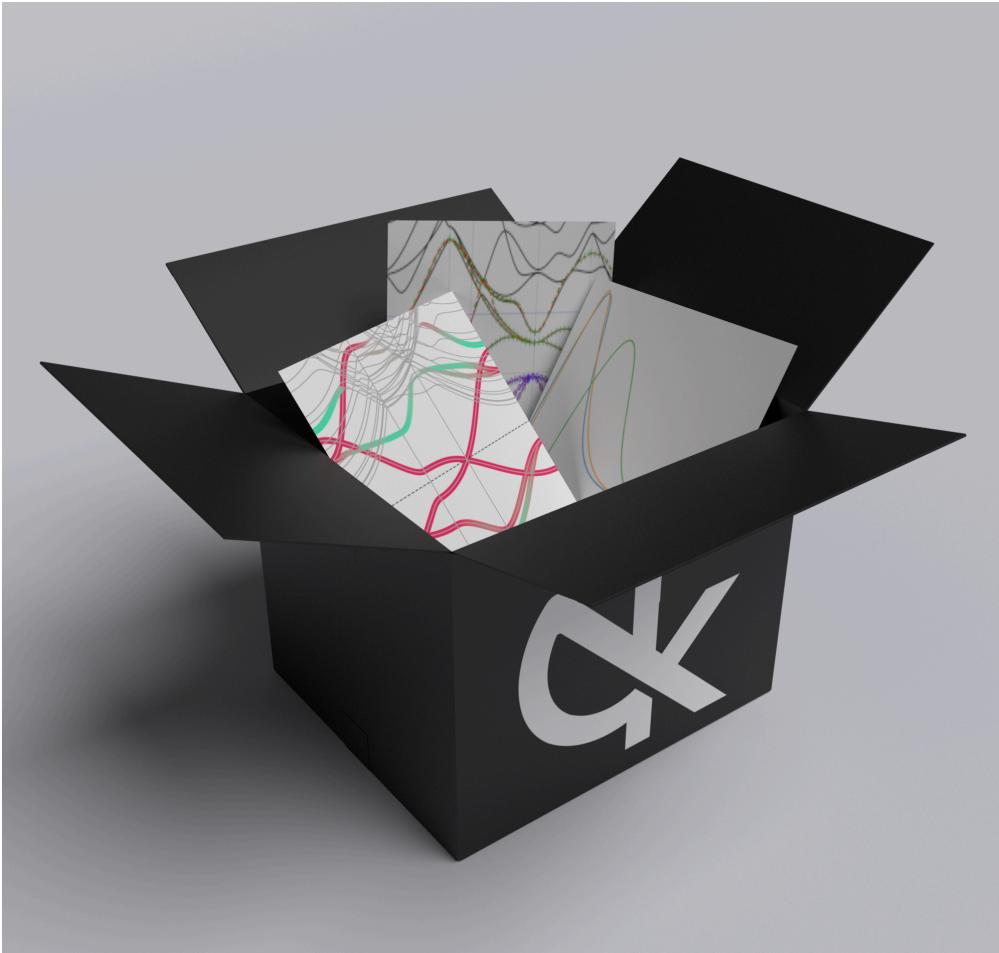


Koopmans functionals are...

- **accurate**, with band structures comparable to state-of-the-art GW
  - ▶ now also for systems with strong SOC

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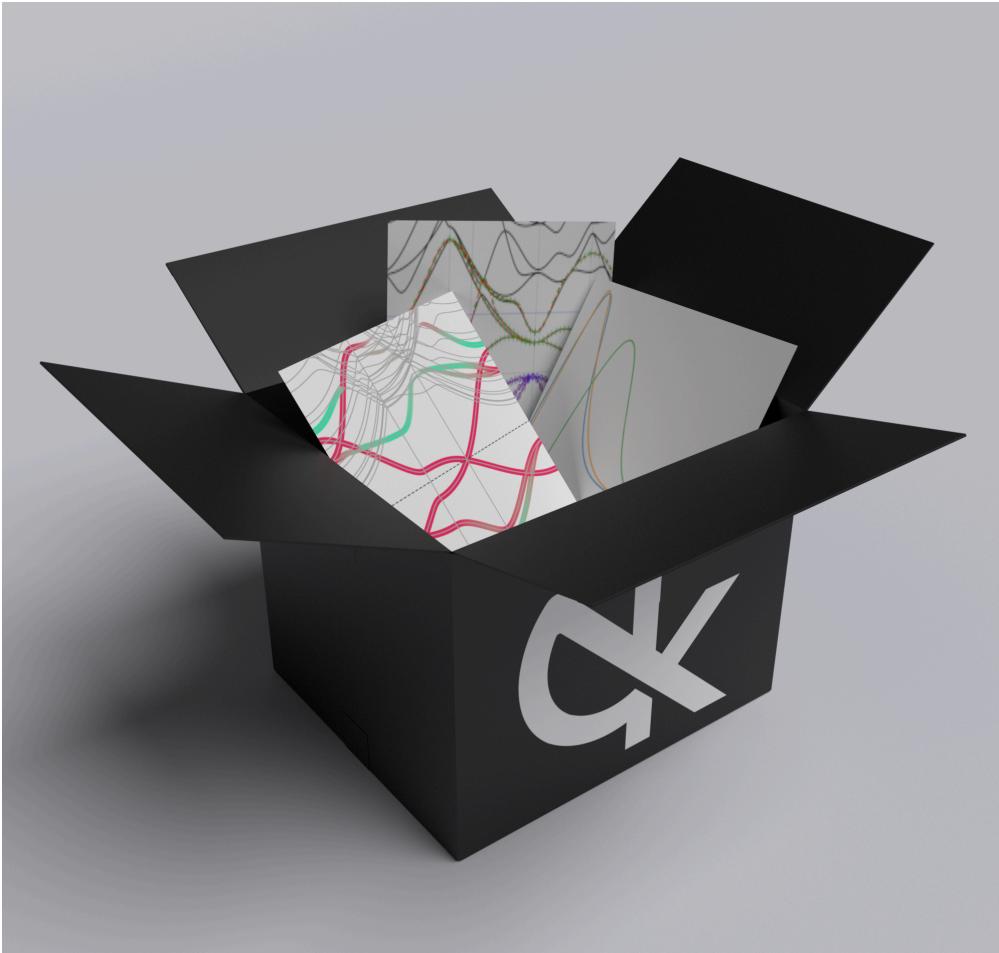


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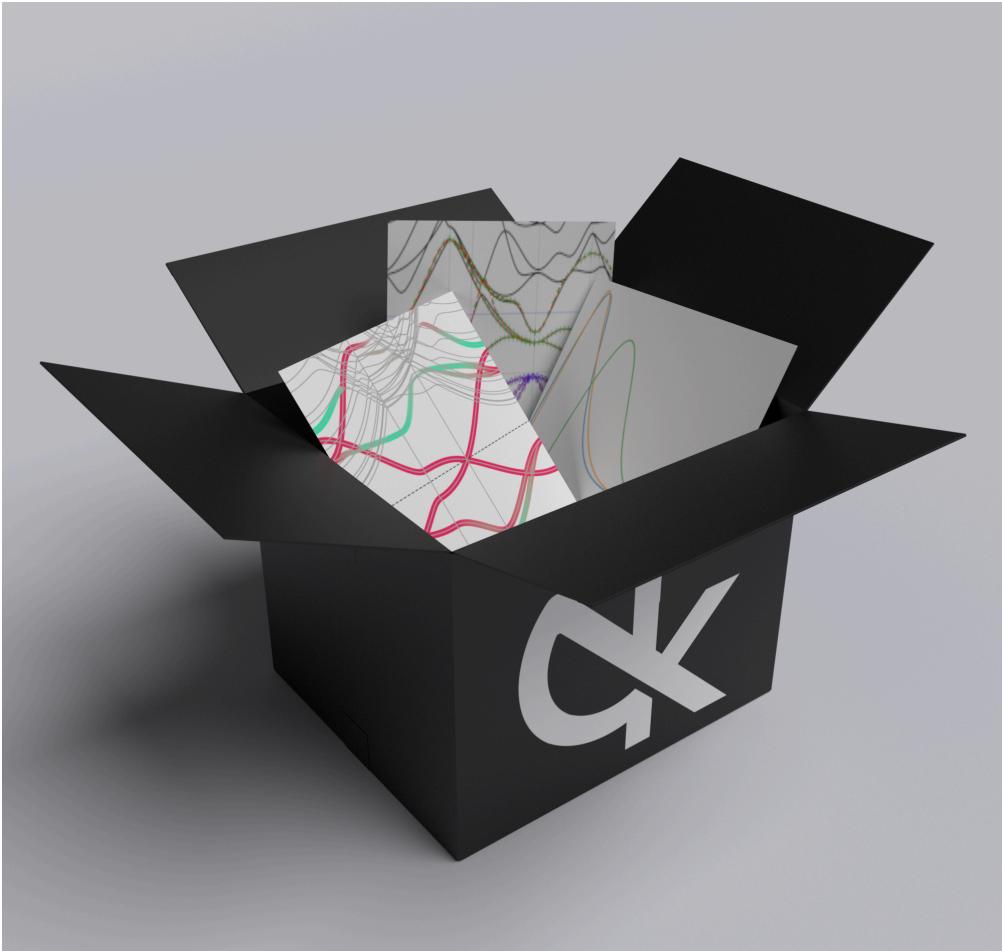


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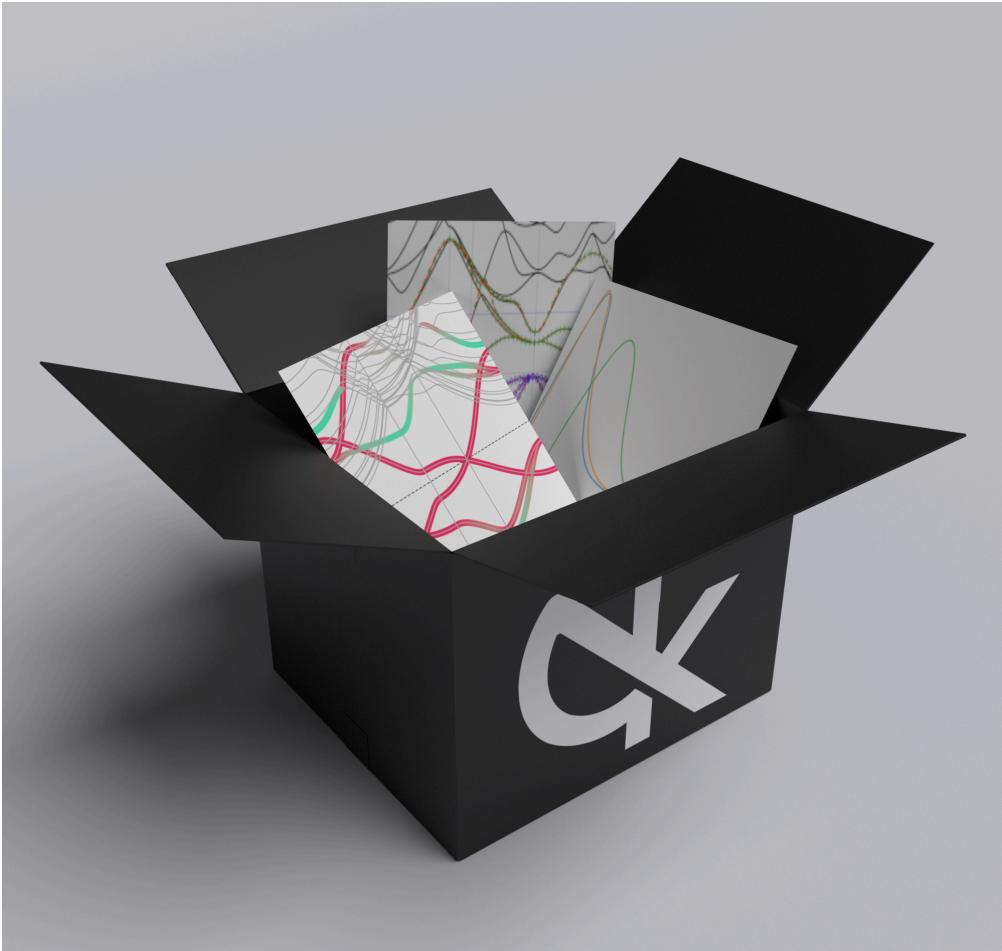


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- more **automated** thanks to
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# Summary

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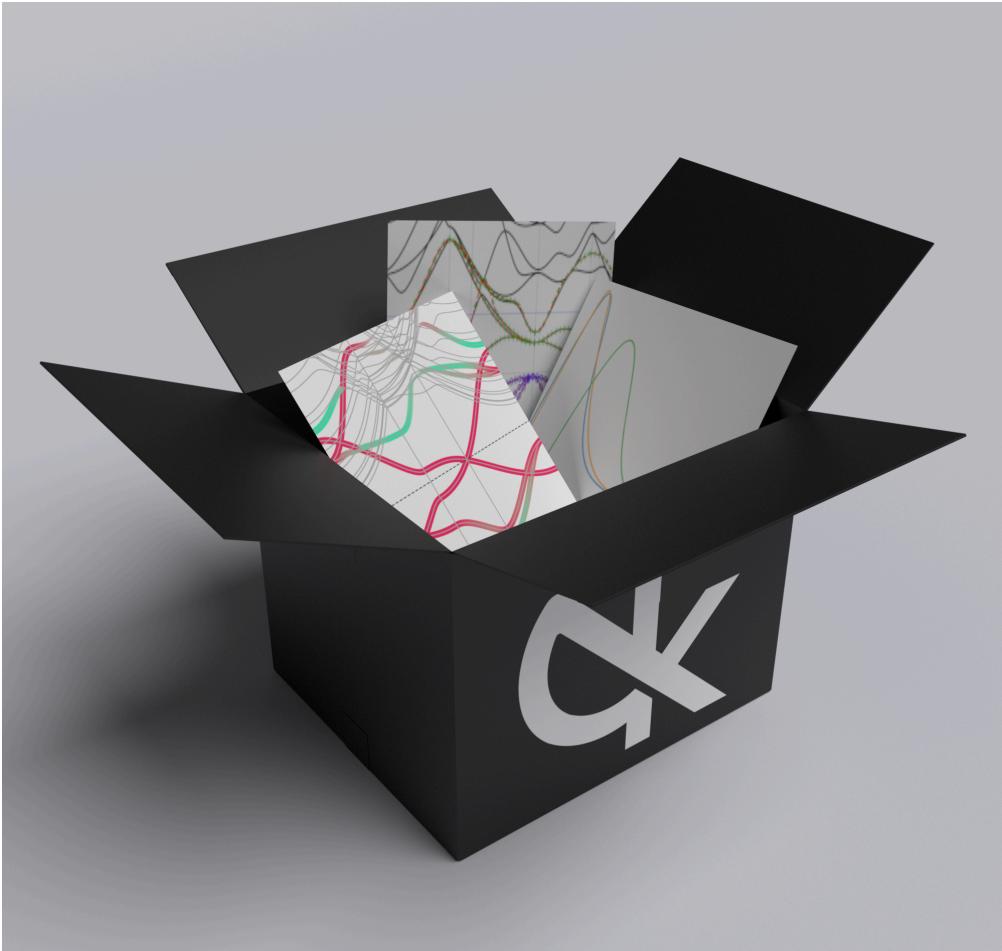


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  - ▶ automated Wannierization

**Thank you!**

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**spare slides**

# Detailed Theory

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# Total energy differences vs. eigenvalues

---

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

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

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

but DFT does not

**Core idea: impose this condition to DFT to improve its description of spectral properties**

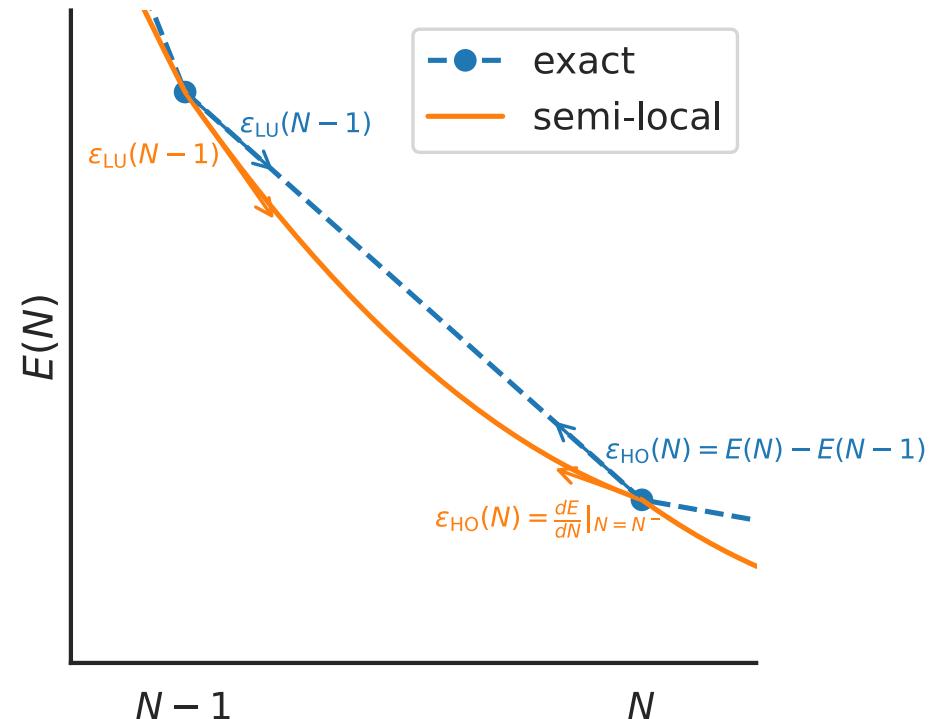
# Total energy differences vs. eigenvalues

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



# Total energy differences vs. eigenvalues

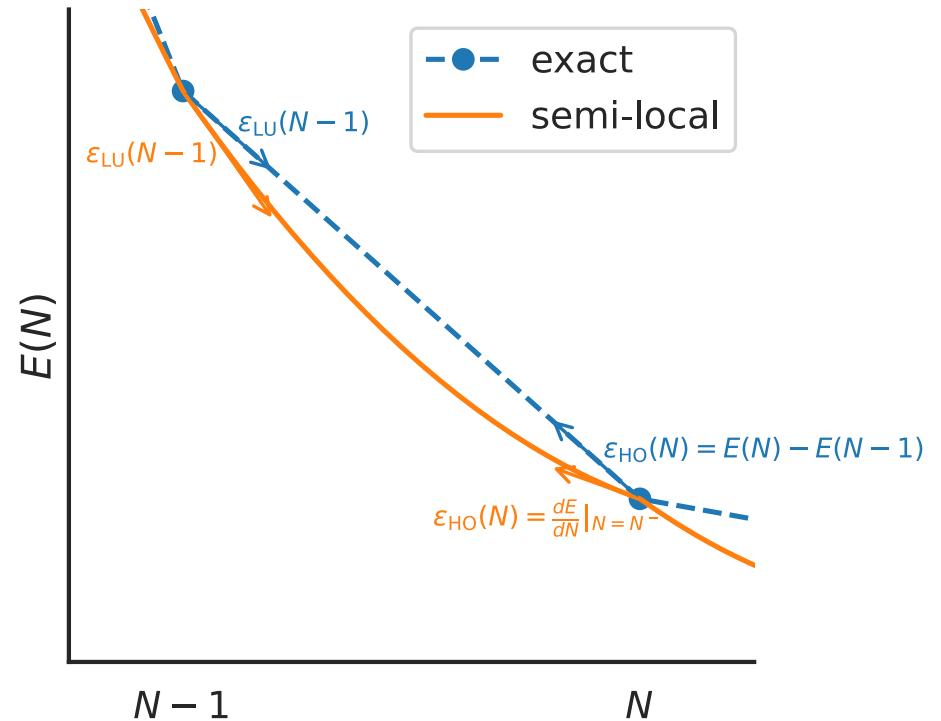
$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

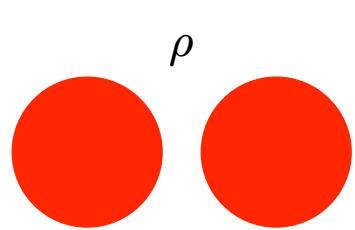
$$+ \sum_i \left\{ - \underbrace{(E^{\text{DFT}}[\rho] - E[\rho^{f_i \rightarrow 0}])}_{\text{remove non-linear dependence}} + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}$$

restore linear dependence

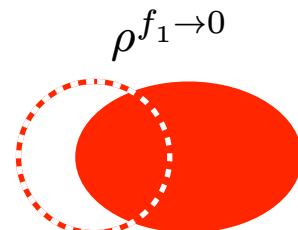
Bakes the total energy differences

$E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]$  into the functional

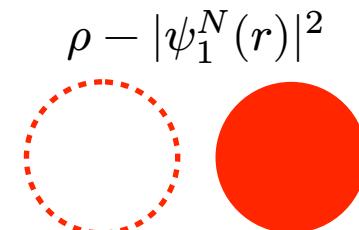




$N$ -electron solution



what we'd like to evaluate



what we can quickly evaluate



---

$$\begin{aligned} E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] &= E^{\text{DFT}}[\rho] \\ &\quad + \sum_i \left\{ -\left( E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right) + f_i \left( E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right) \right\} \\ &\approx E^{\text{DFT}}[\rho] \\ &\quad + \sum_i \alpha_i \left\{ -\left( E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i] \right) + f_i \left( E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i] \right) \right\} \end{aligned}$$

---

$$H_{ij}^{\text{KI}} = \langle \varphi_j | \hat{h}^{\text{DFT}} + \alpha_i \hat{v}_i^{\text{KI}} | \varphi_i \rangle$$

For e.g. occupied orbitals

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

# Screening

---

Construct  $\alpha_i$  from explicit  $\Delta$ SCF calculations<sup>1</sup>

$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)} \text{ where } \lambda_{ii}(\alpha) = \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}_i^{\text{KI}} | \varphi_i \rangle$$

Recast via linear response<sup>2</sup>:

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

which can be efficiently computed via DFPT<sup>3</sup>

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which can be efficiently computed via DFPT<sup>3</sup> ... but is still the bulk of the computational cost (can use machine-learning)

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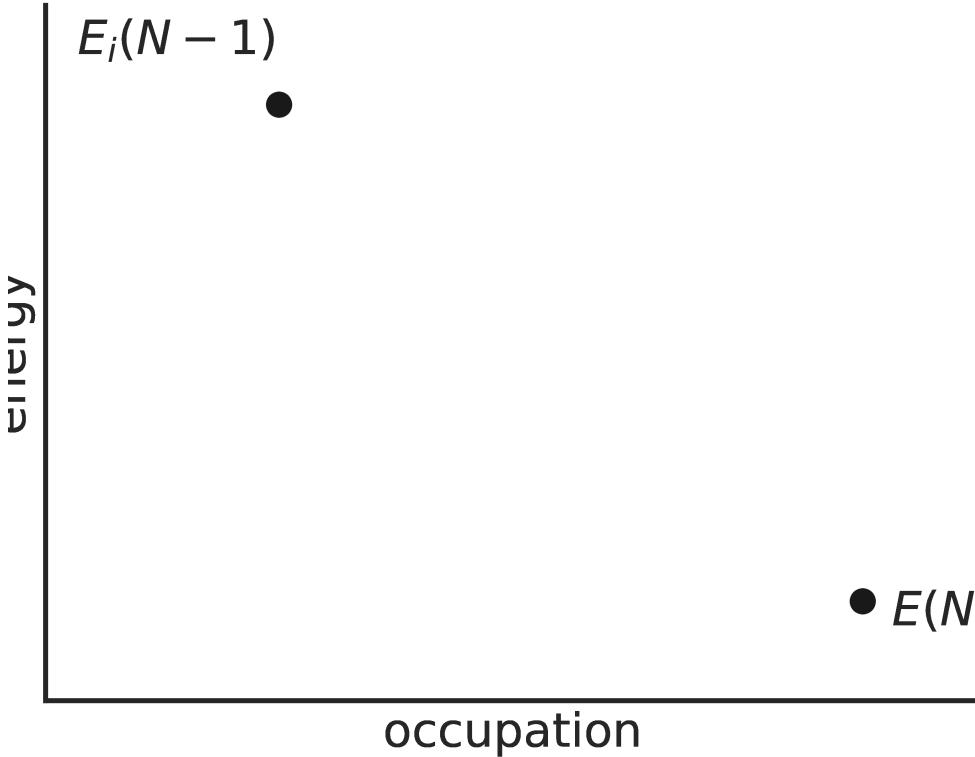
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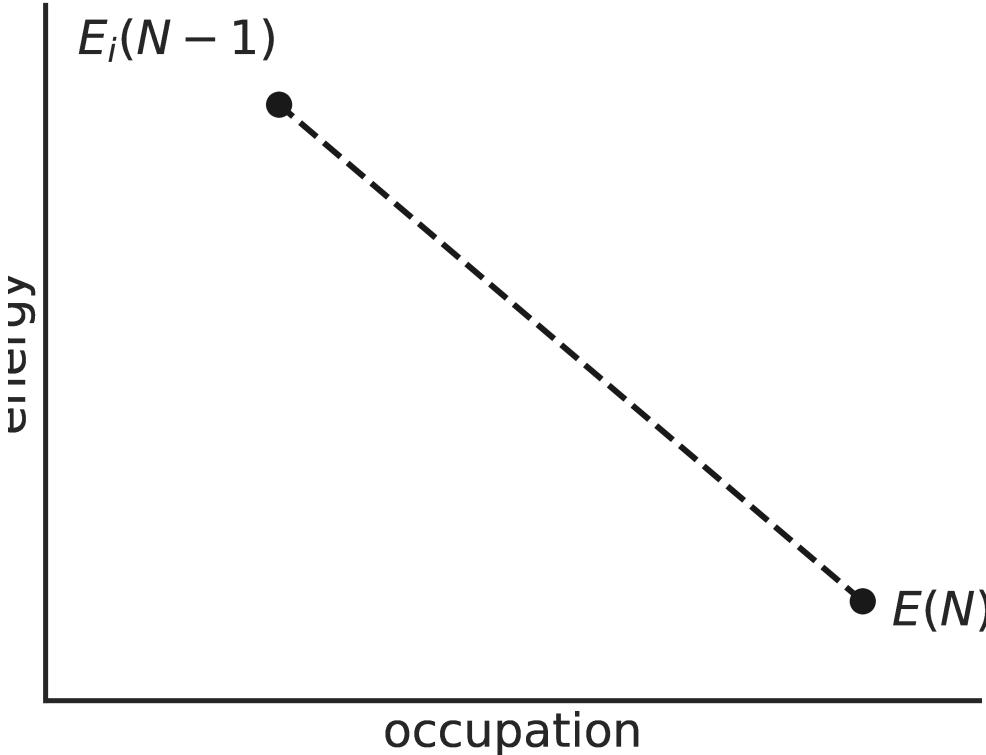
# Calculating screening parameters via SCF

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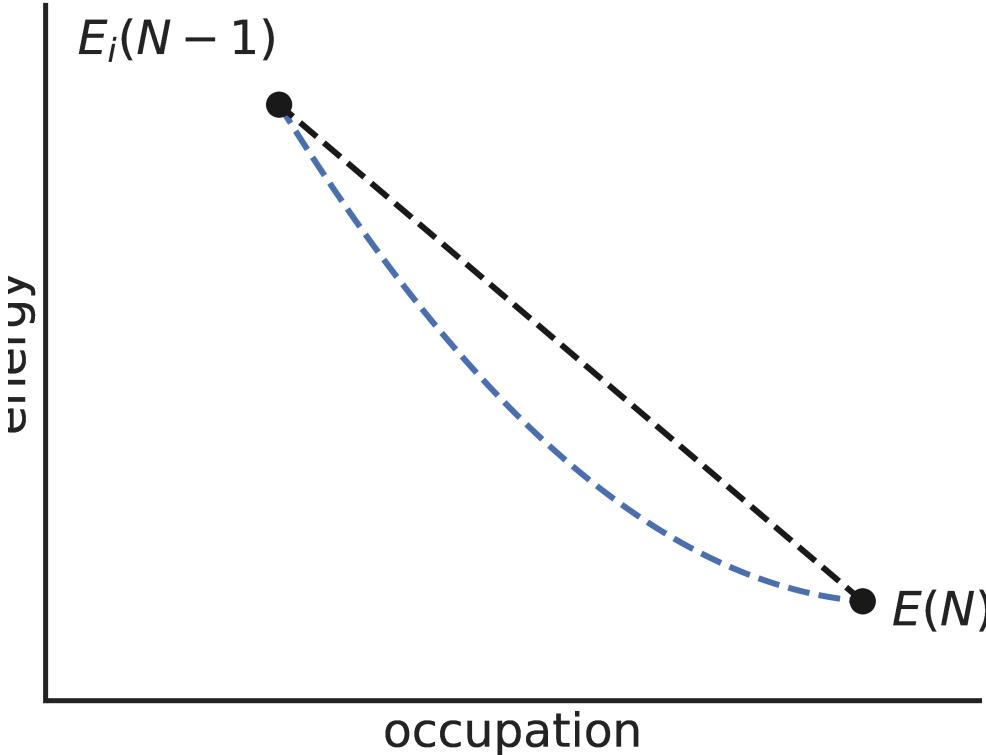
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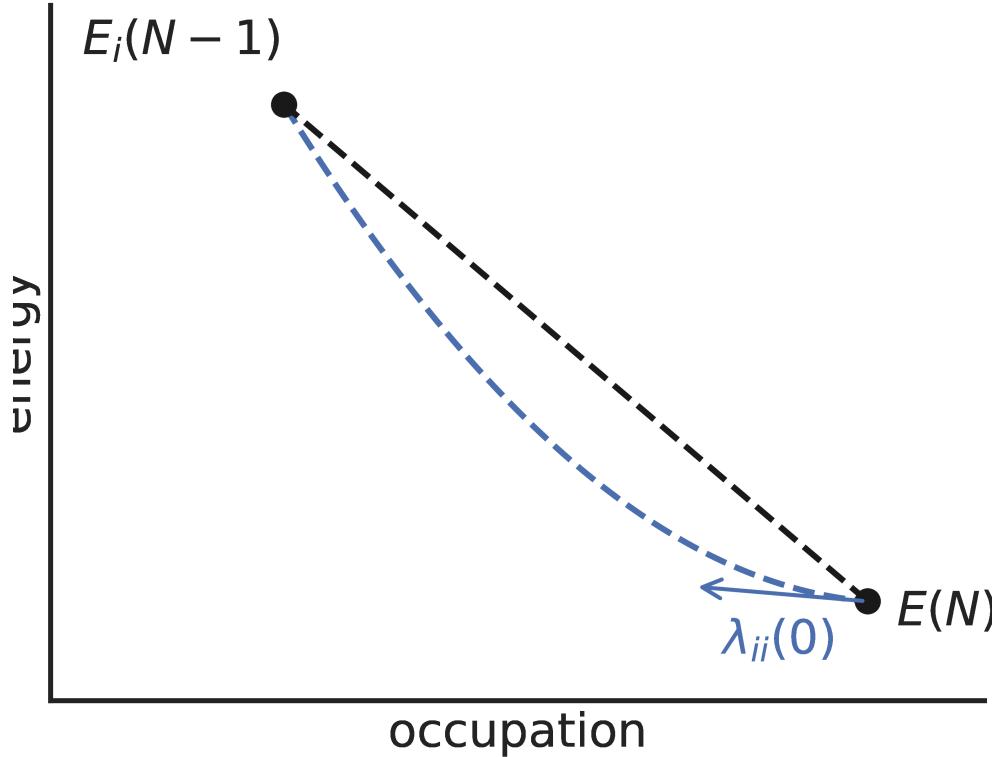
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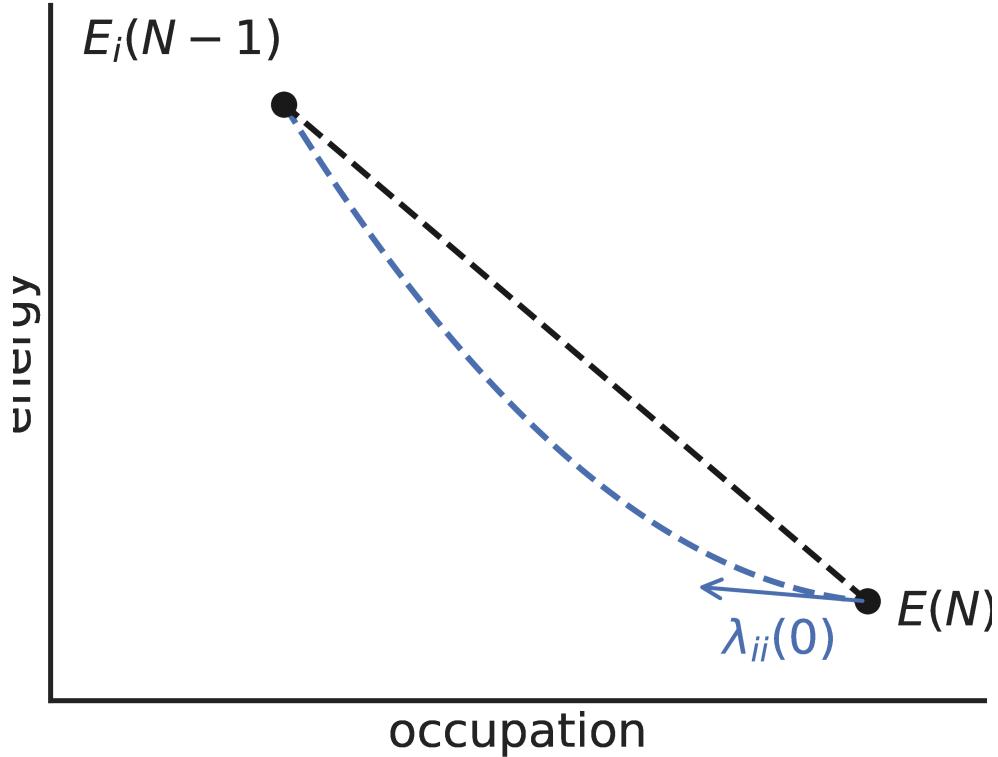
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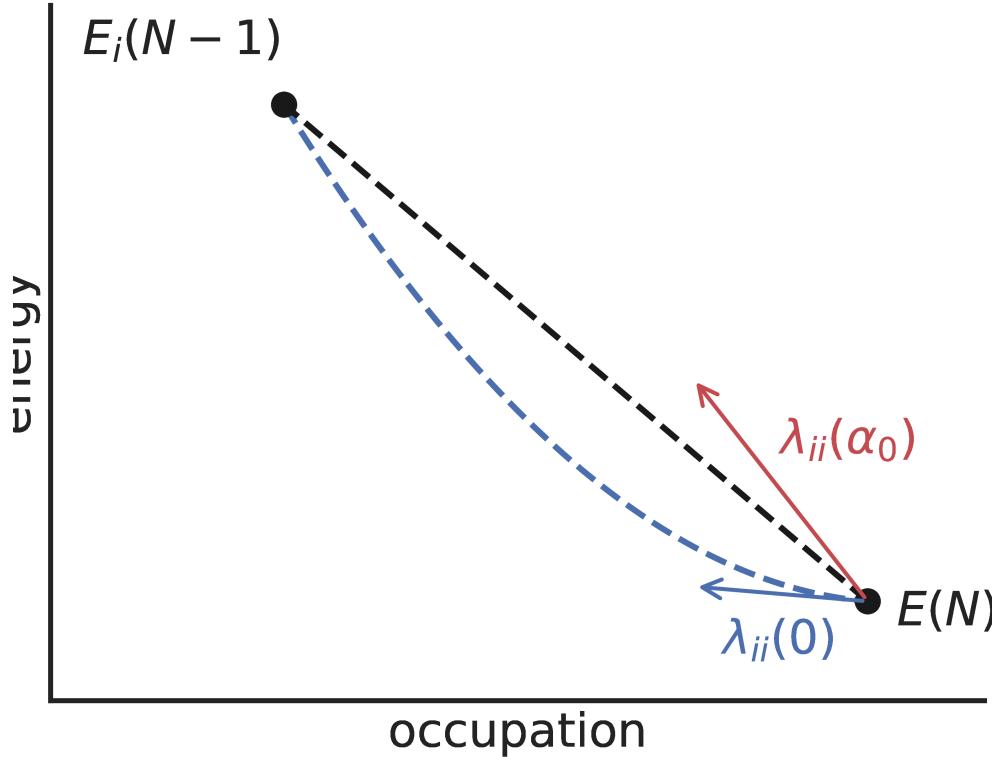
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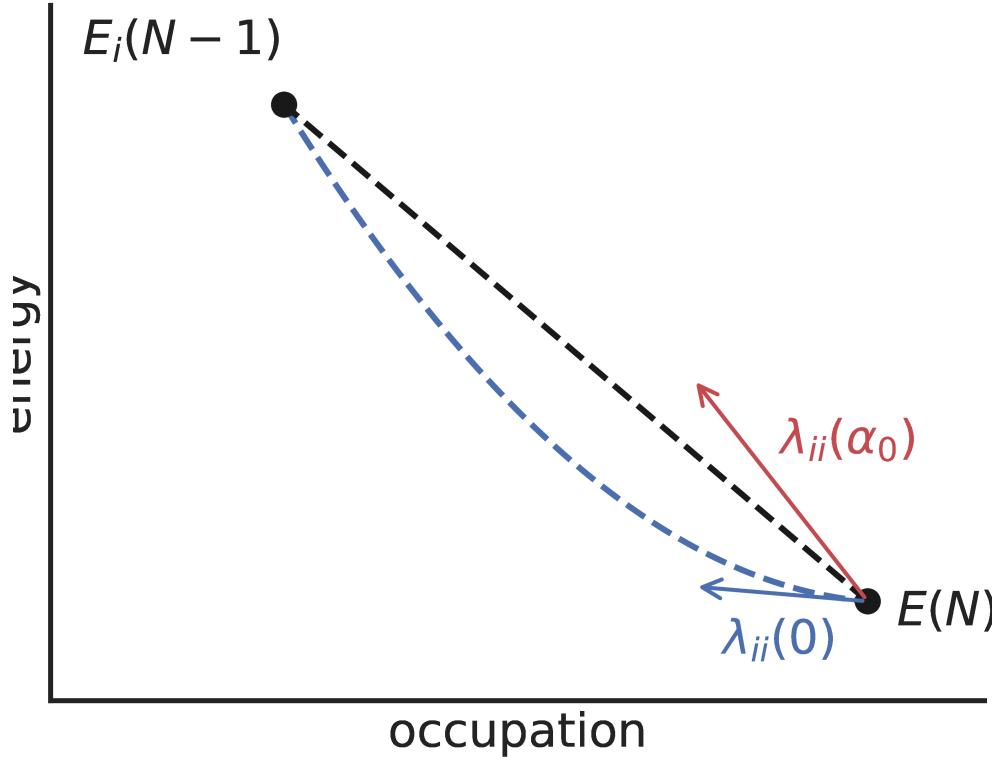
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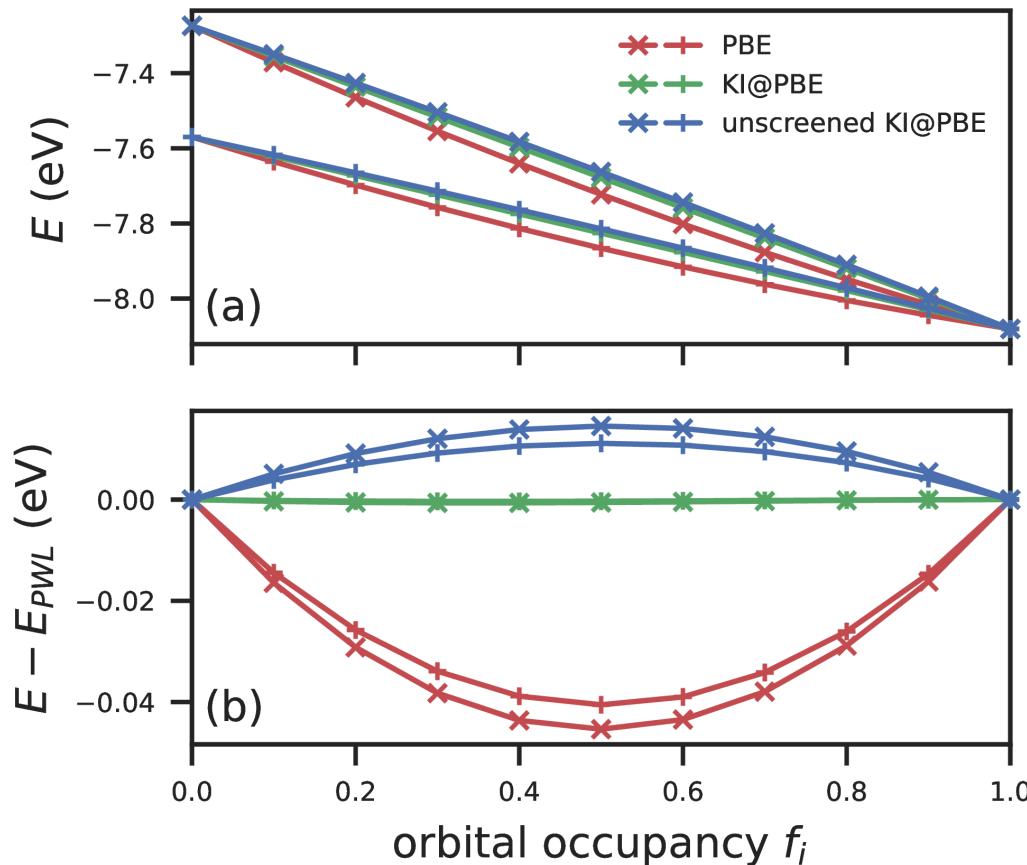
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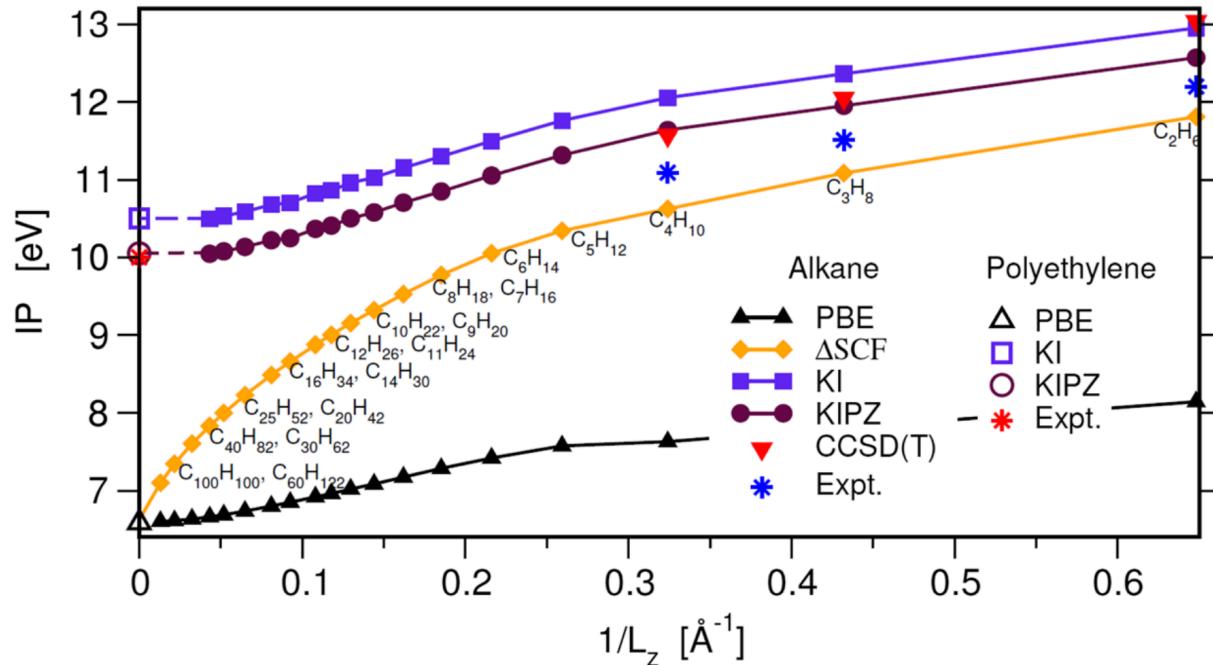
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# Calculating screening parameters via SCF



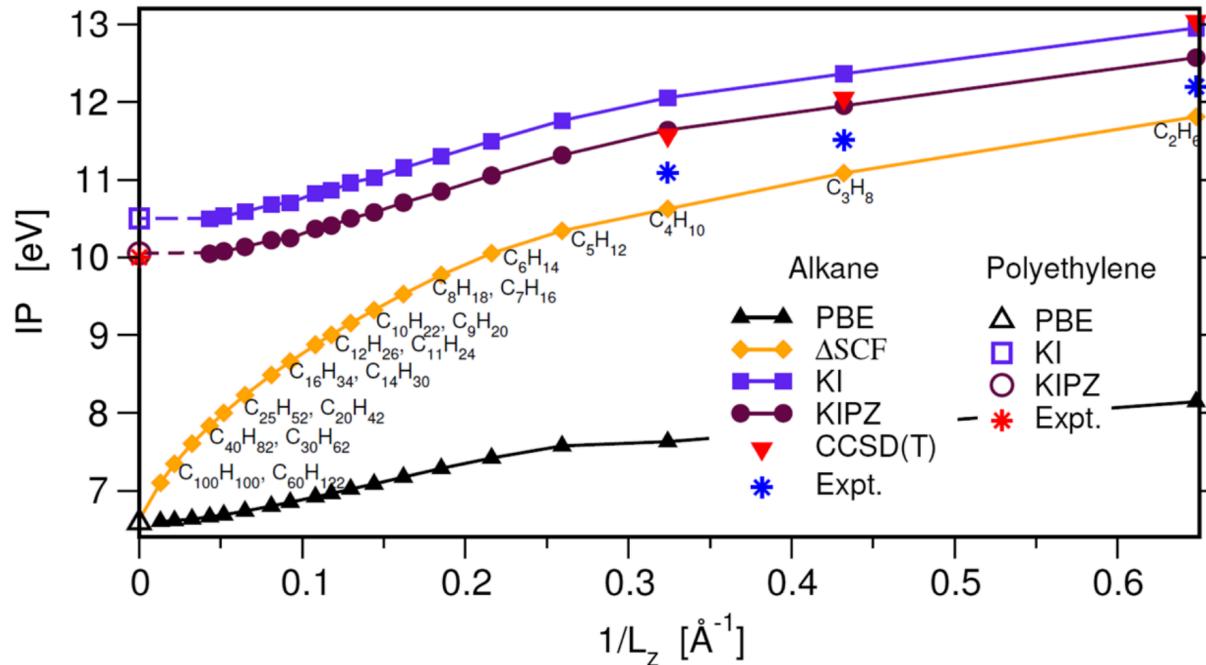
# Issues with extended systems



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



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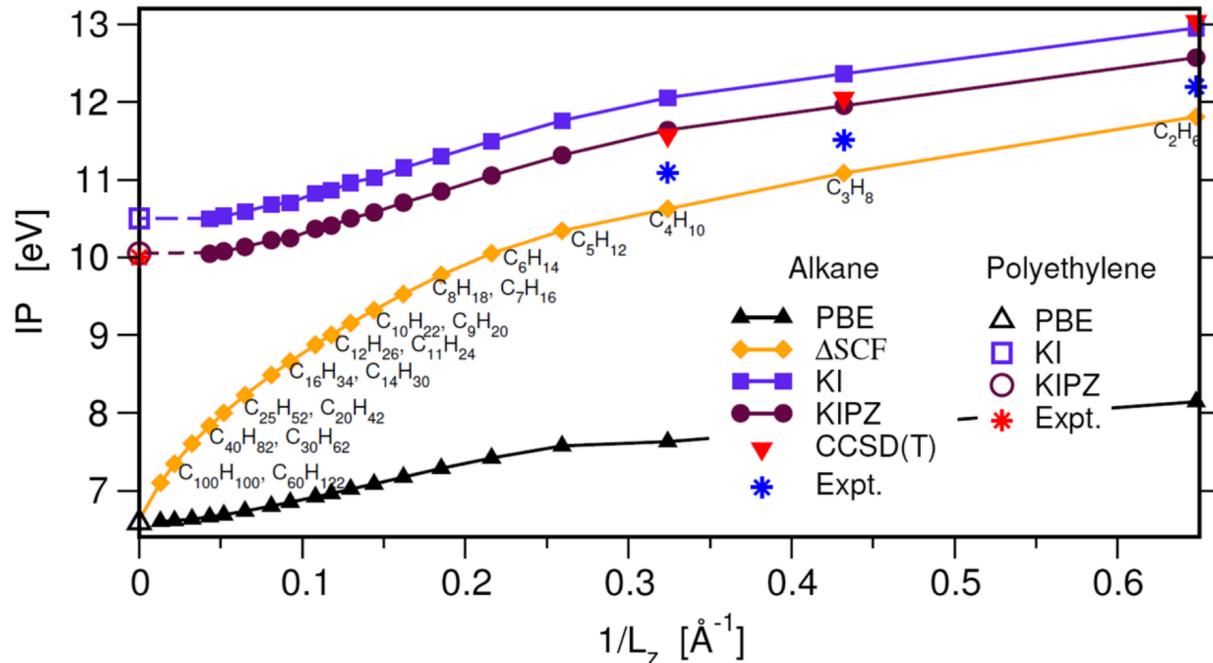


One cell:  $E(N + \delta N) - E(N)$

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



# Issues with extended systems

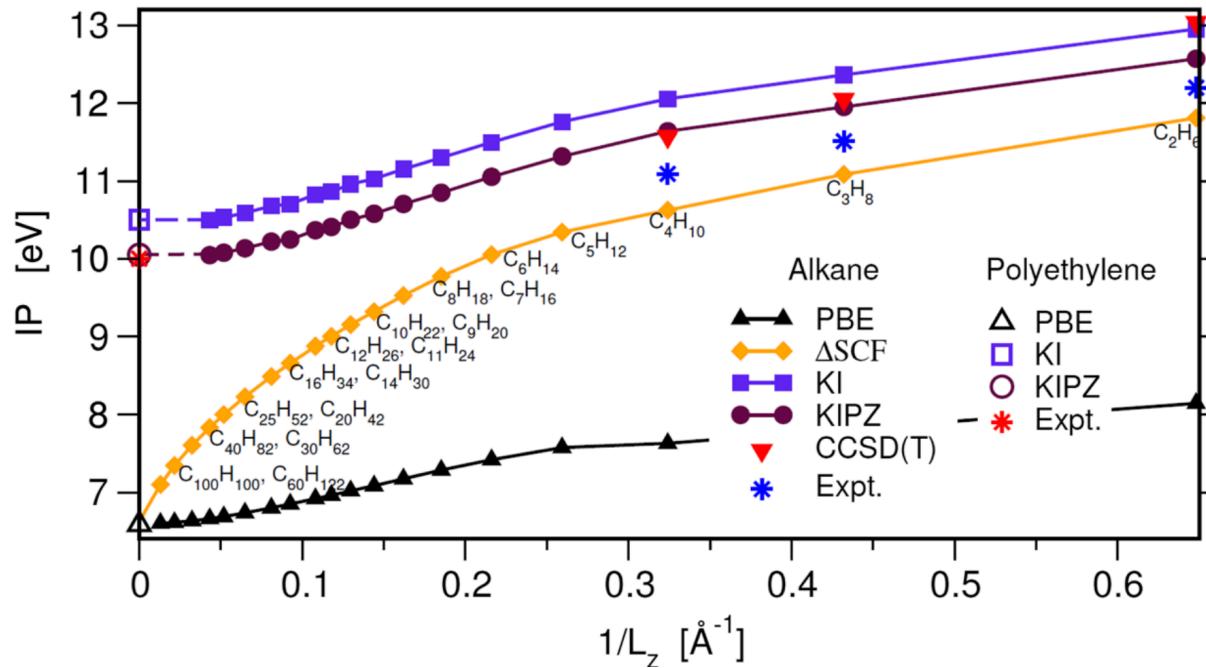


One cell:  $E(N + \delta N) - E(N)$  all cells:  $\Delta E = \frac{1}{\delta N} (E(N + \delta N) - E(N)) = \frac{dE}{dN} = -\varepsilon_{HO}$ <sup>1</sup>

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

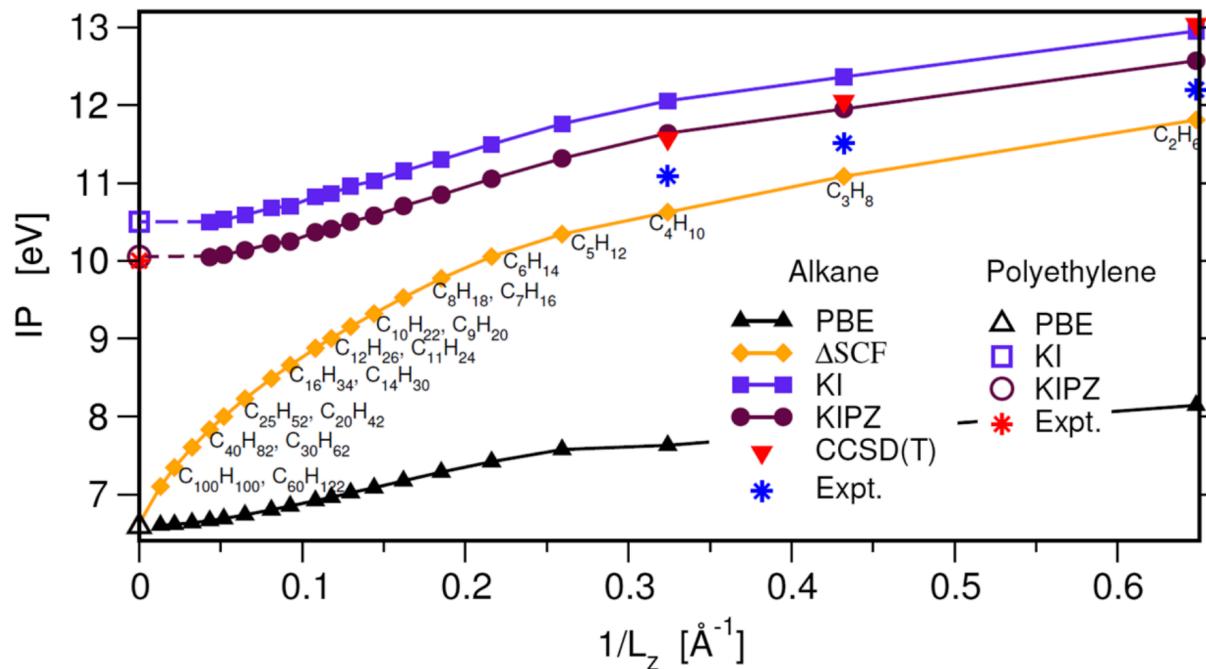


# Issues with extended systems



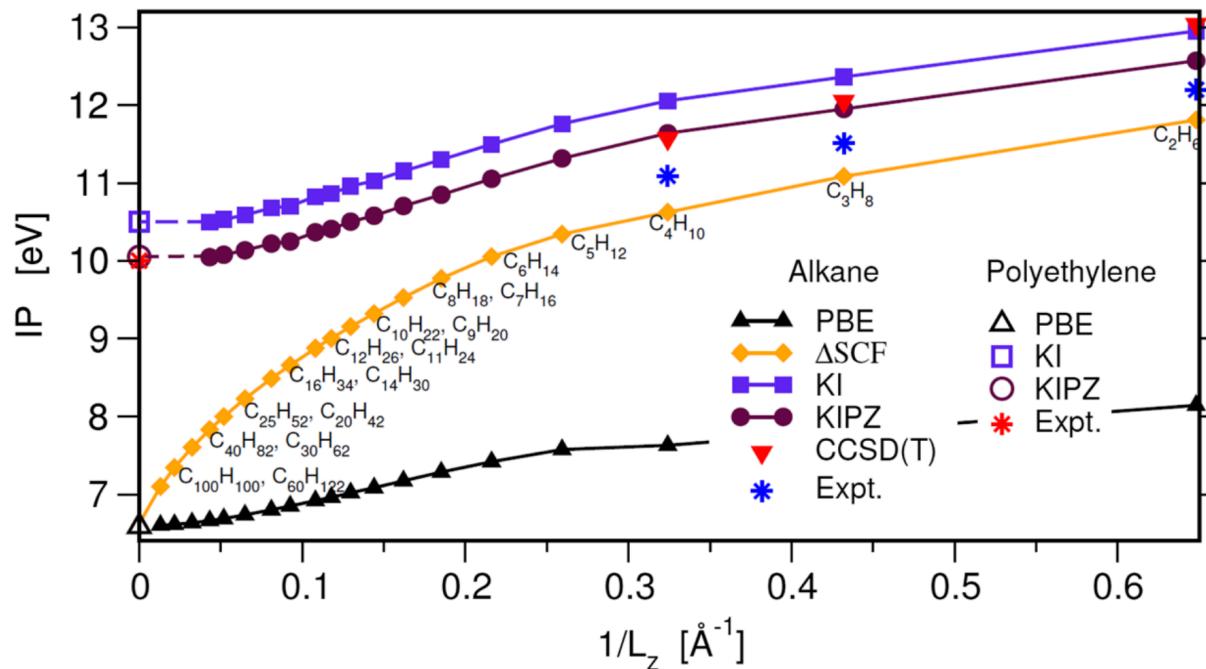
Two options:

# Issues with extended systems



Two options: 1. use a more advanced functional

# Issues with extended systems



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

# Orbital-density dependence

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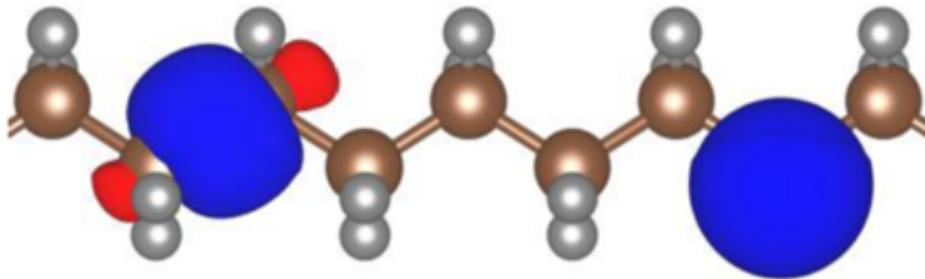
The potential is orbital-dependent!

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

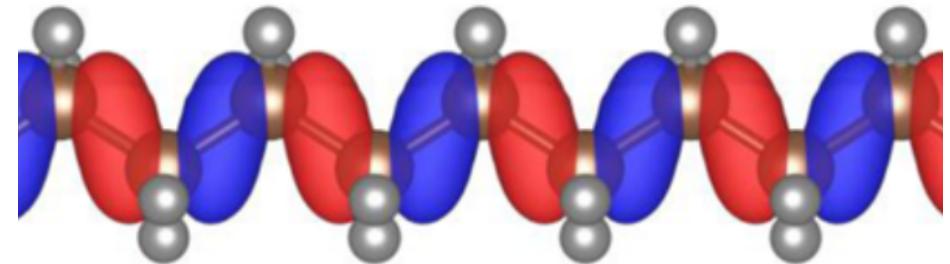
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two variational orbitals



a canonical orbital

# Orbital-density dependence

---

Because we have an ODD...

- 

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

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



# Orbital-density dependence

---

Because we have an ODD...

- minimisation gives rise to localised orbitals, so we can use MLWFs<sup>1</sup>
- we know  $\hat{H}|\varphi_i\rangle$  but we don't know  $\hat{H}$

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# Orbital-density dependence

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- minimisation gives rise to localised orbitals, so we can use MLWFs<sup>1</sup>
- we know  $\hat{H}|\varphi_i\rangle$  but we don't know  $\hat{H}$
- we have a natural generalisation of DFT in the direction of spectral functional theory<sup>2</sup>

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

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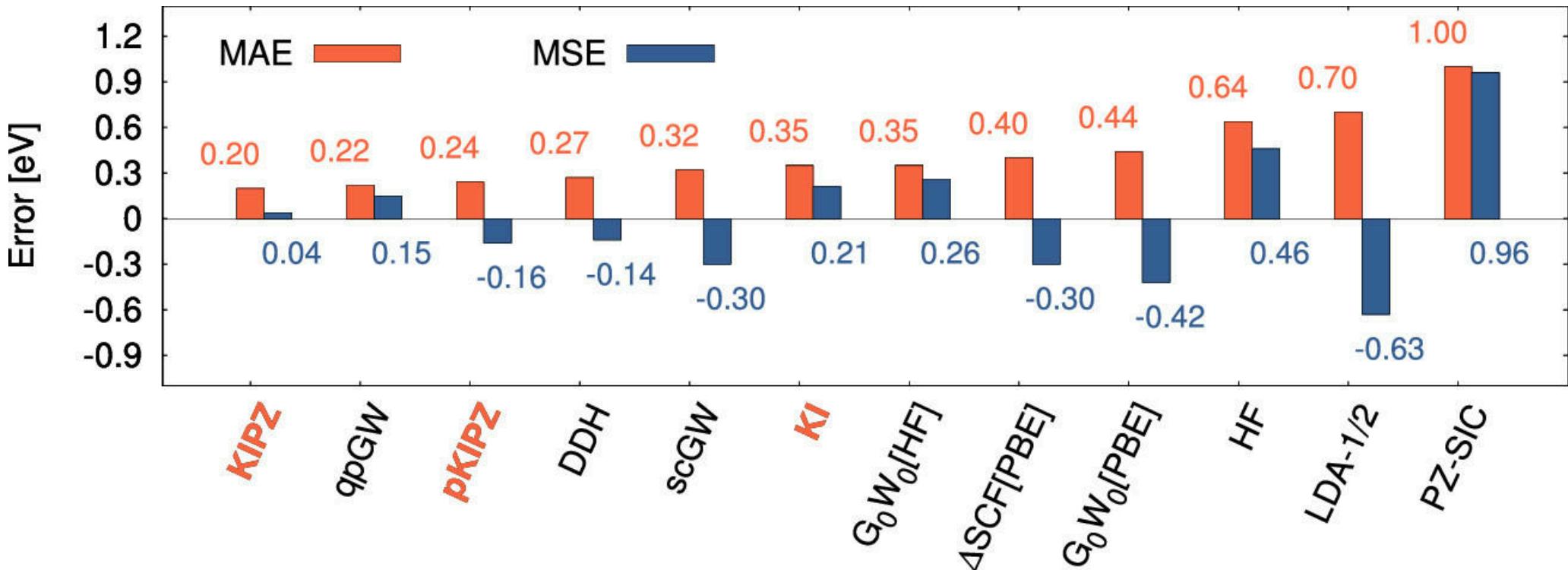
# Exhaustive Results

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# Molecular systems

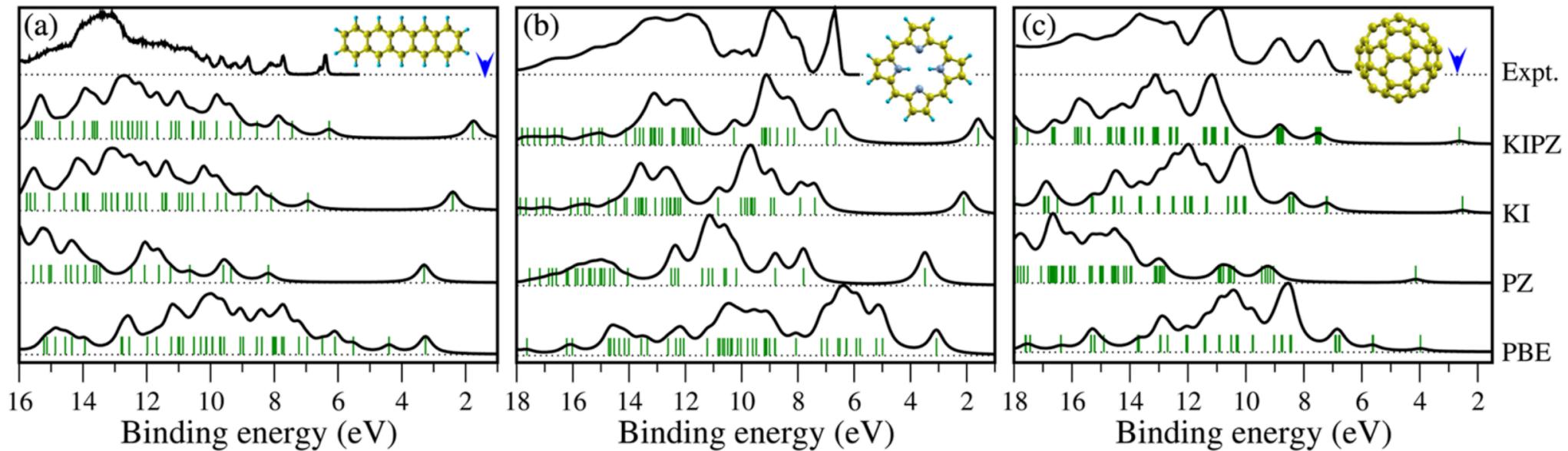
## Ionisation potentials<sup>1</sup>



<sup>1</sup>N. Colonna et al. J. Chem. Theory Comput. **15**, 1905–1914 (2019)

# Molecular systems

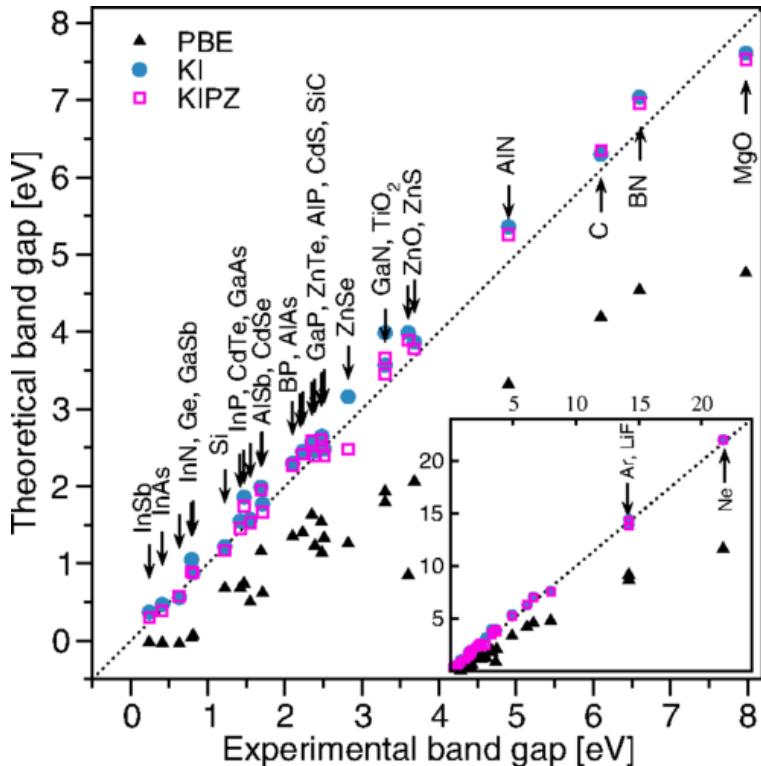
## UV photoemission spectra<sup>1</sup>



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

# Extended systems

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

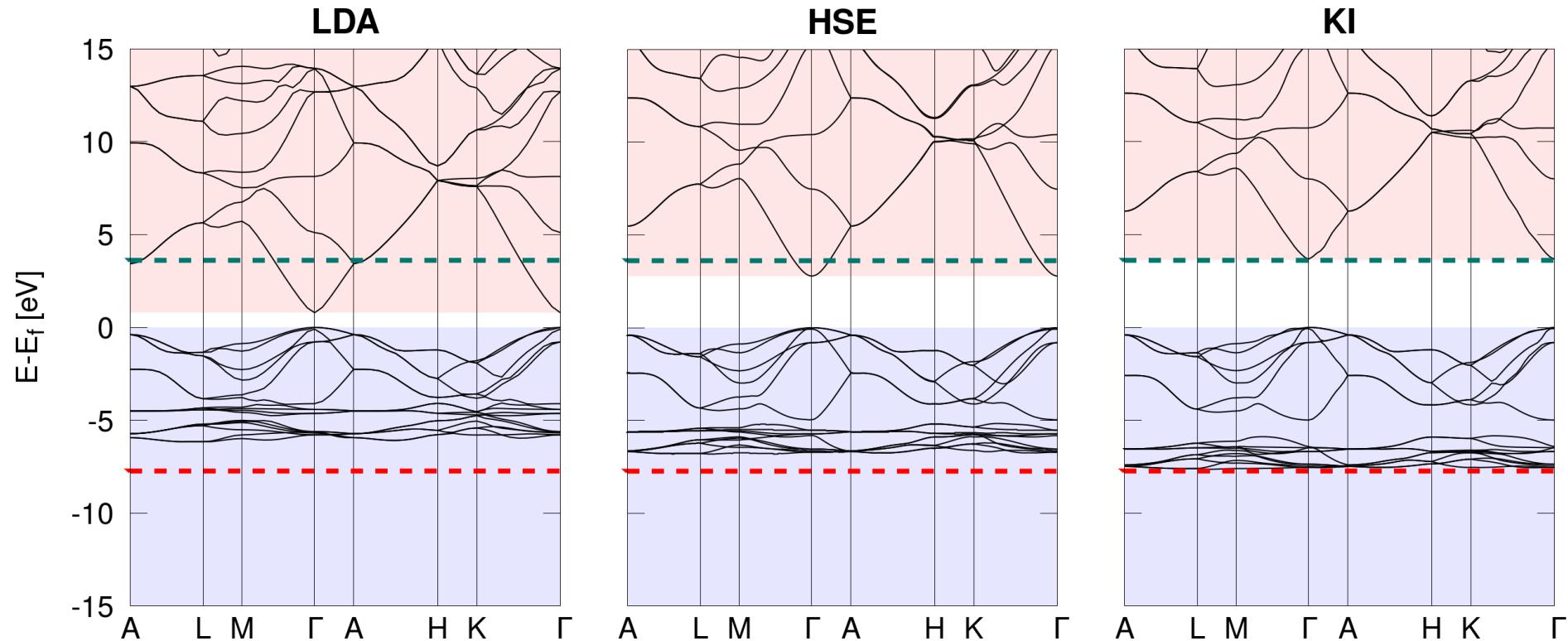


	PBE	$G_0W_0$	KI	KIPZ	$QS\tilde{G}W$
$E_{\text{gap}}$	2.54	0.56	<b>0.27</b>	<b>0.22</b>	0.18
IP	1.09	0.39	<b>0.19</b>	<b>0.21</b>	0.49

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

# Extended systems

ZnO



<sup>1</sup>N. Colonna et al. J. Chem. Theory Comput. **18**, 5435–5448 (2022)



# Extended systems

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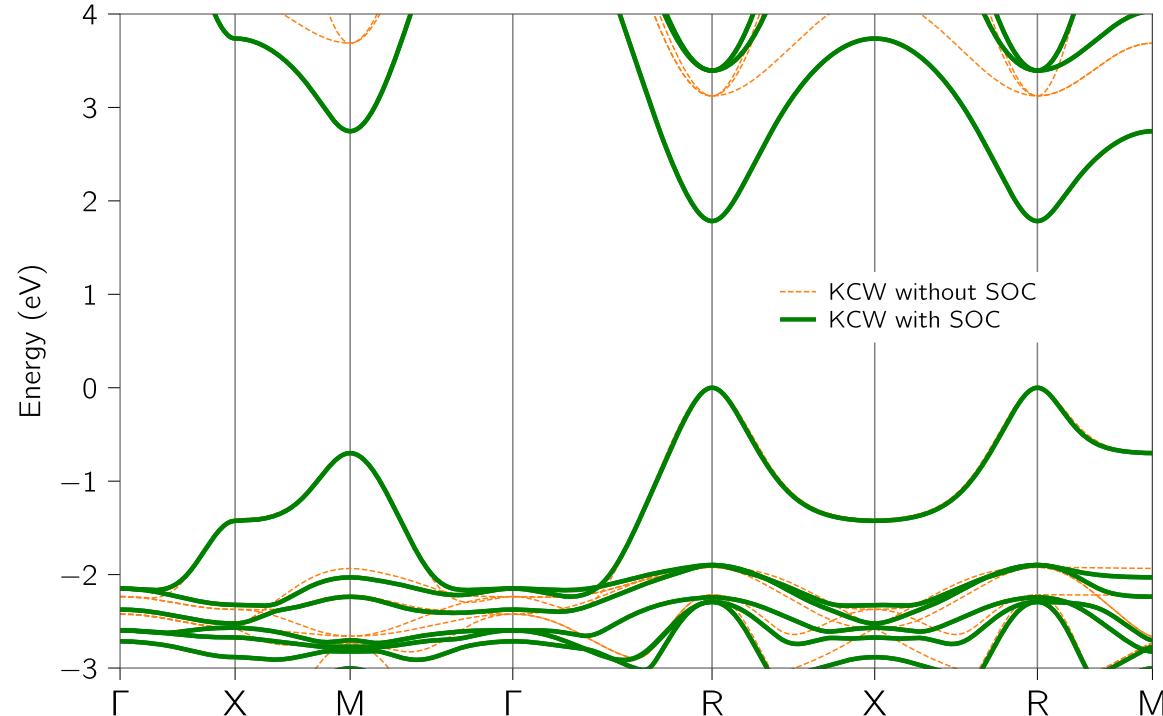
ZnO

	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	-6.9	-7.5 to -8.81
$\Delta$	4.15				4.99	5.3

<sup>1</sup>N. Colonna et al. J. Chem. Theory Comput. **18**, 5435–5448 (2022)

# Extended systems

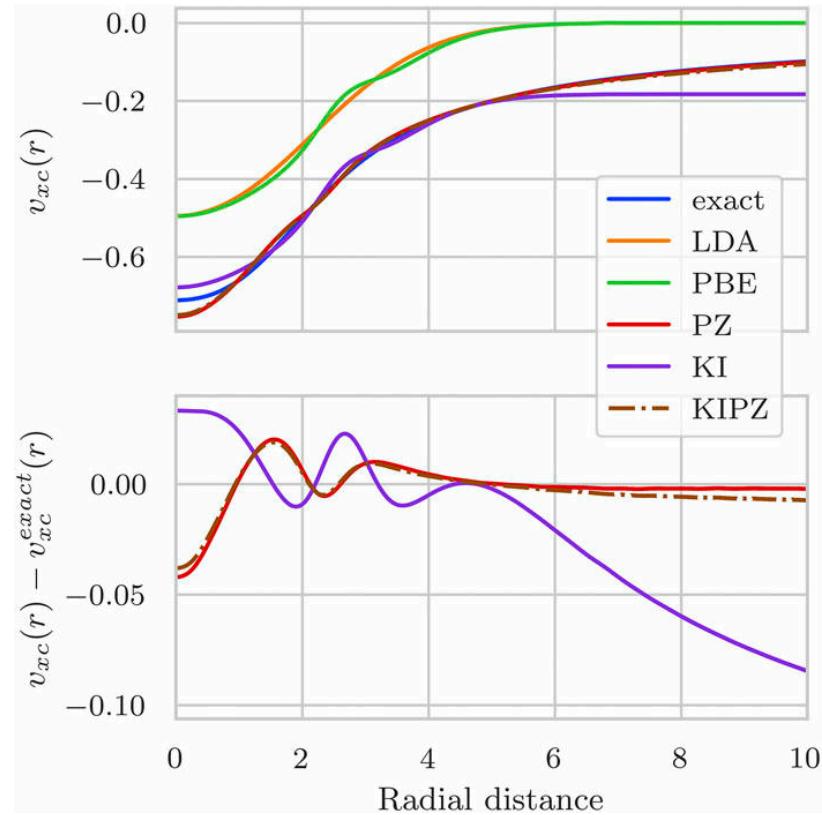
## Spin-orbit coupling



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

# Model systems

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



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



# Caveats

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# Limitations

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



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- empty state localisation in the bulk limit



# Limitations

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

# Resonance with other efforts

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- 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)



# **Electronic screening via machine learning**

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# Electronic screening via machine learning

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A key ingredient of Koopmans functional calculations are the 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. **14**, 2549–2557 (2018), N. Colonna et al. J. Chem. Theory Comput. **18**, 5435–5448 (2022)



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- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital

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- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital
- must be computed ab initio via  $\Delta\text{SCF}$ <sup>1</sup> or DFPT<sup>2</sup>
- corresponds to the vast majority of the computational cost of Koopmans functional calculation

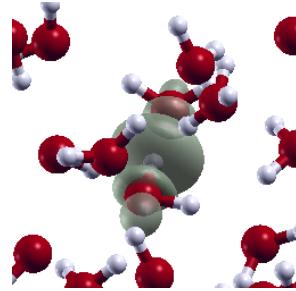
<sup>1</sup>N. L. Nguyen et al. Phys. Rev. X **8**, 21051 (2018), R. De Gennaro et al. Phys. Rev. B **106**, 35106 (2022)

<sup>2</sup>N. Colonna et al. J. Chem. Theory Comput. **14**, 2549–2557 (2018), N. Colonna et al. J. Chem. Theory Comput. **18**, 5435–5448 (2022)



# The machine-learning framework

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power spectrum decomposition

$$\begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix} \xrightarrow{\text{ridge regression}} \alpha_i$$

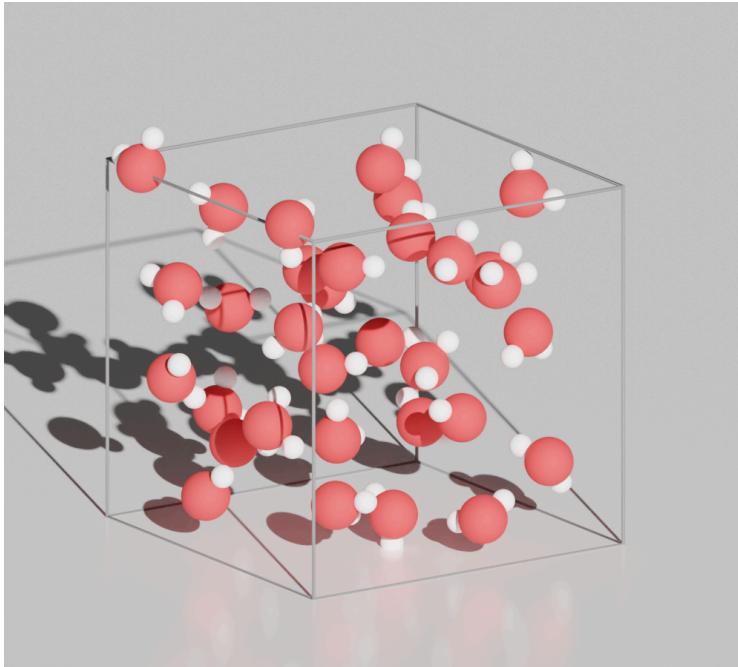
$$c_{nlm,k}^i = \int dr g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

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

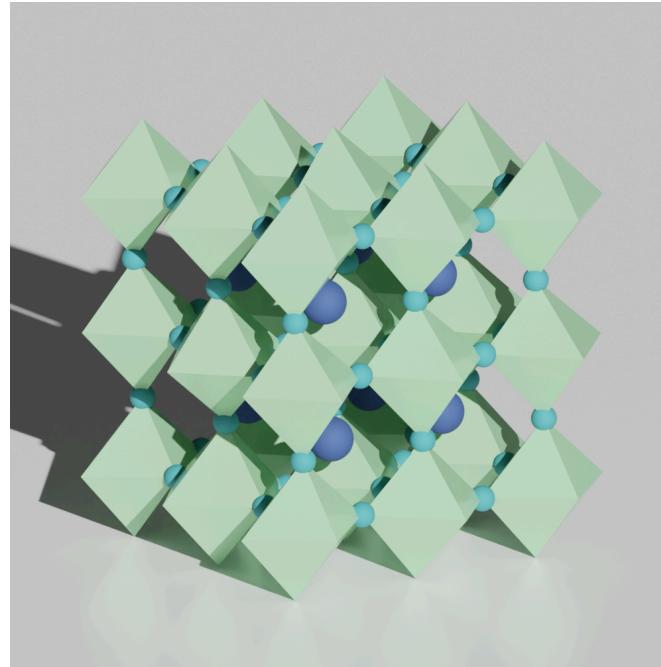
<sup>1</sup>Y. Schubert et al. npj Comput Mater **10**, 1–12 (2024)

## Two test systems

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water

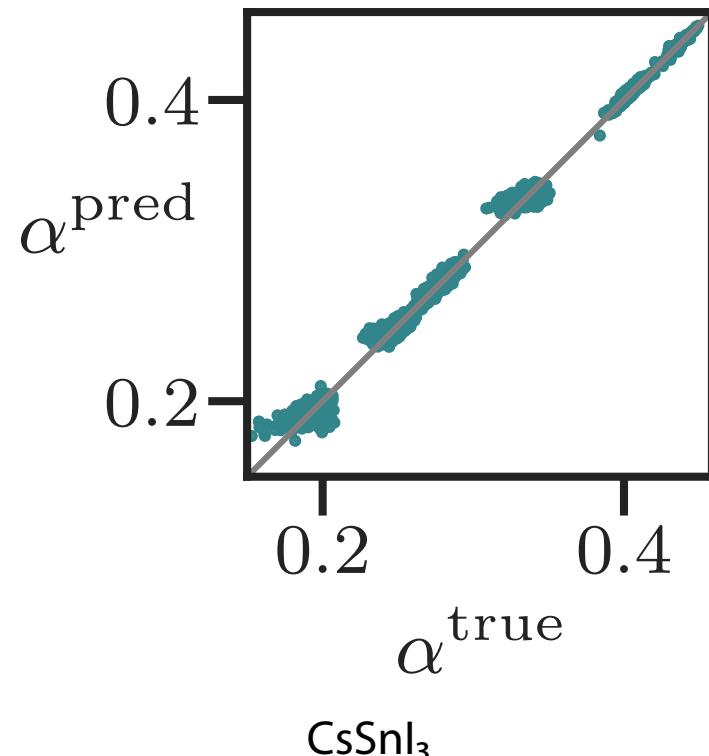
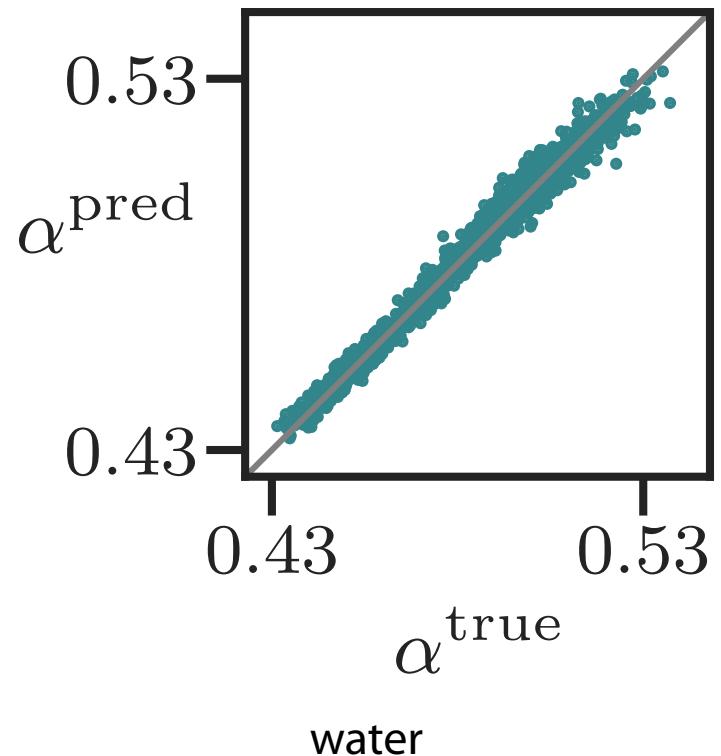


CsSnI<sub>3</sub>

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

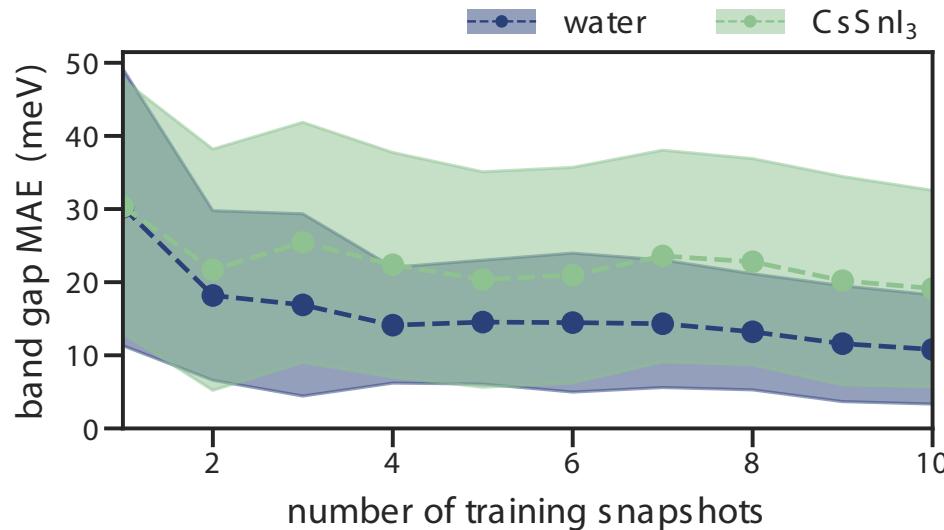
# Results: screening parameters

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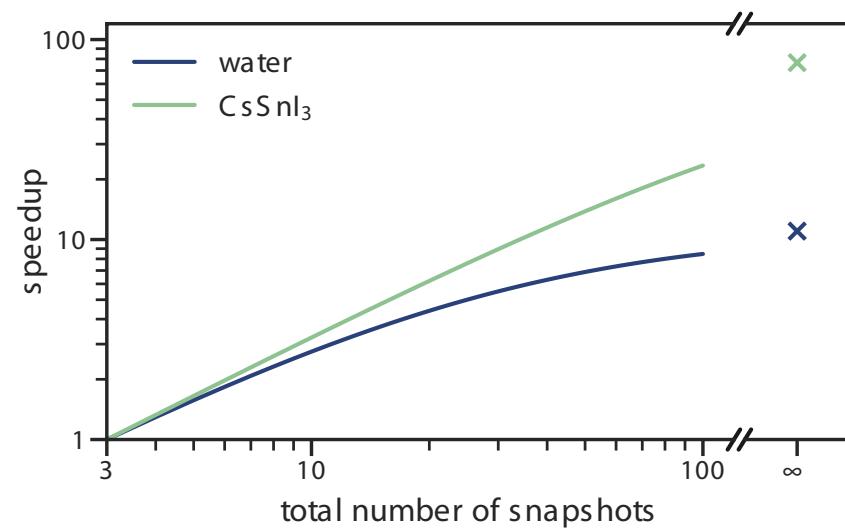


<sup>1</sup>Y. Schubert et al. npj Comput Mater **10**, 1–12 (2024)

# Results: balancing accuracy and speedup



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)



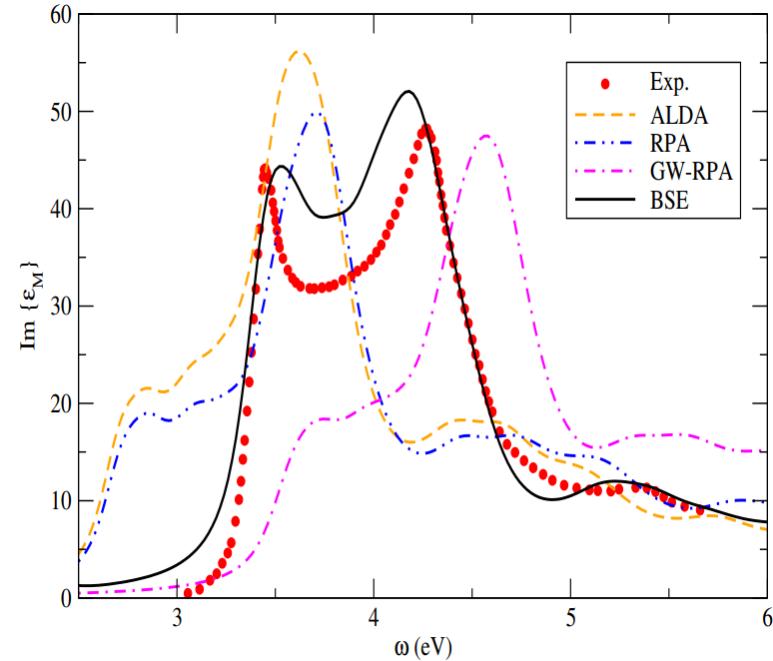
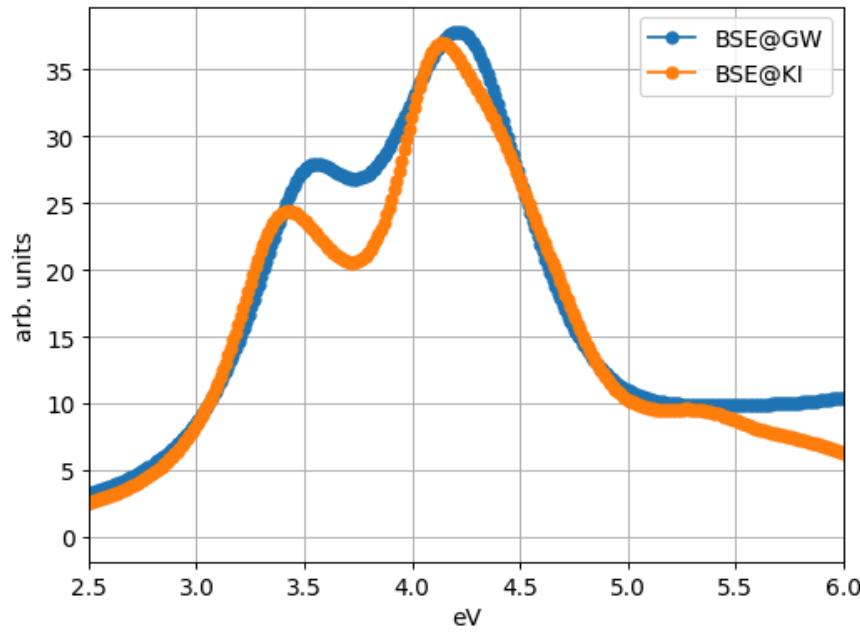
# Going beyond single-particle excitations

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# Preliminary results

The idea: solve the BSE, skipping GW and instead using Koopmans eigenvalues<sup>1</sup>



N.B. using DFT response

<sup>1</sup>P. Lautenschlager et al. Phys. Rev. B **36**, 4821–4830 (1987), F. Sottile. (École Polytechnique, 2003).

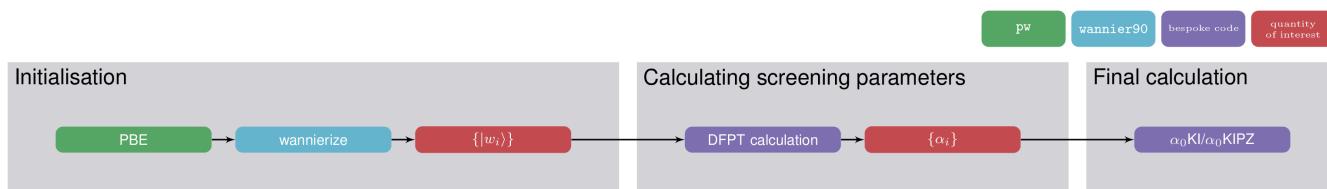
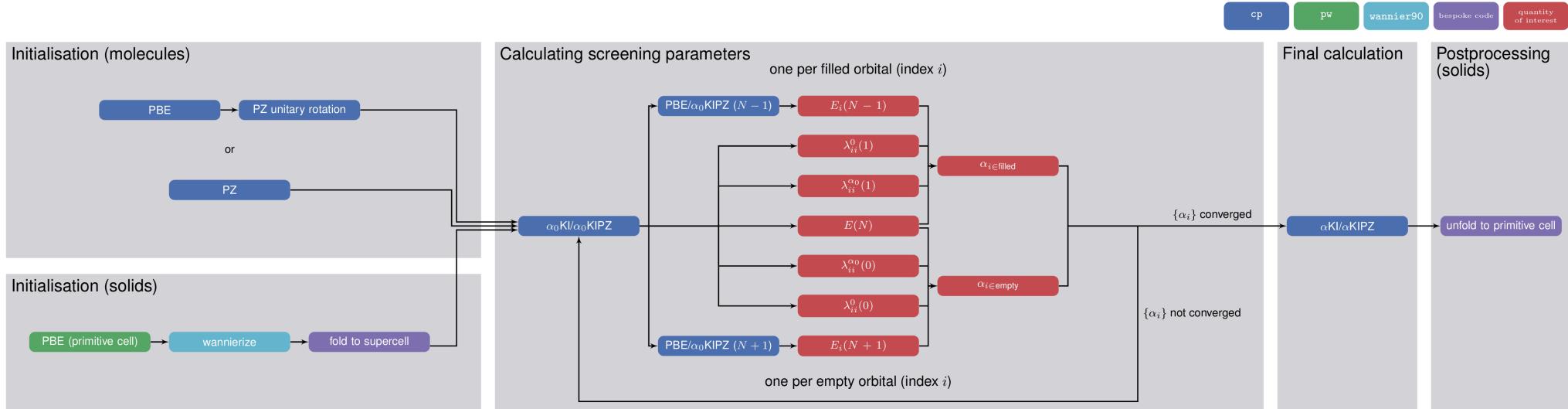


# Miscellaneous

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# The general workflows



# Connections with approximate self-energies<sup>1</sup>

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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

# Connections with approximate self-energies<sup>1</sup>

---

Orbital-density functional theory:

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

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

cf. Green's function theory:

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

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

# Connections with approximate self-energies<sup>1</sup>

---

Hartree-Fock self-energy in localized representation

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

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 approximate self-energies<sup>1</sup>

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Screened exchange plus Coulomb hole (COHSEX)

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

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

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

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 approximate self-energies<sup>1</sup>

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Static  $GW\Gamma_{xc}$  — local (DFT-based) vertex corrections<sup>1</sup>

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

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

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

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

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

<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)

