

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

Edward Linscott

Paul Scherrer Institute

MARVEL Review & Retreat | Grindelwald | 14 January 2025

This talk



Nicola
Colonna



Marija
Stojkovic



Giovanni
Cistaro



Yannick
Schubert



Junfeng
Qiao



Miki
Bonacci



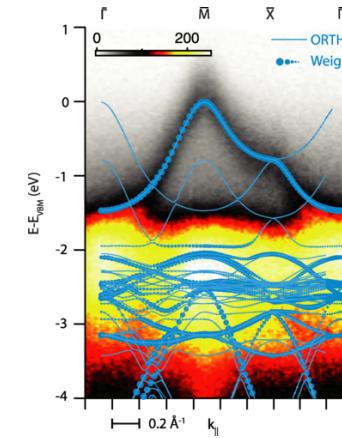
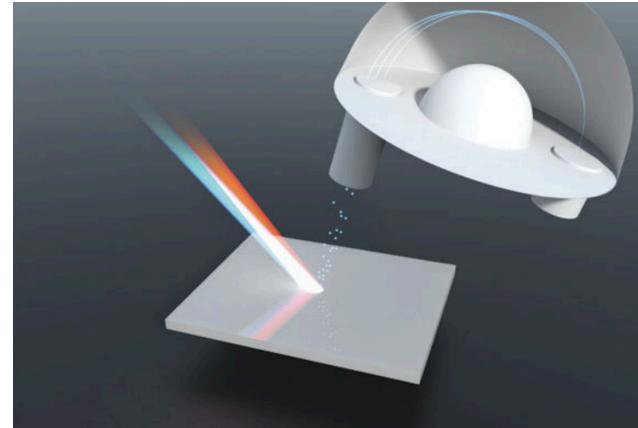
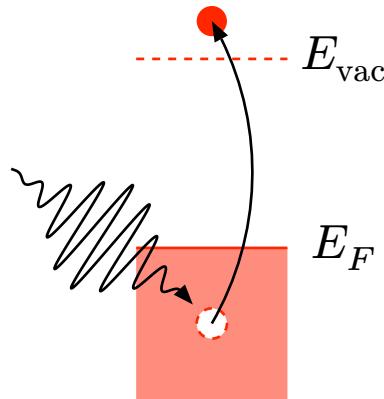
Julian
Geiger



Nicola
Marzari

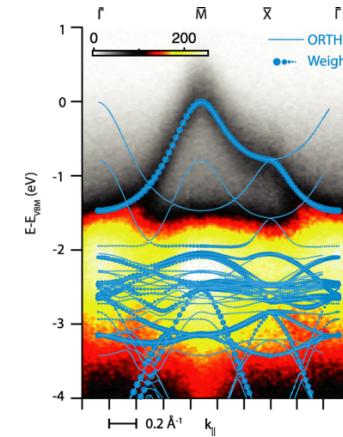
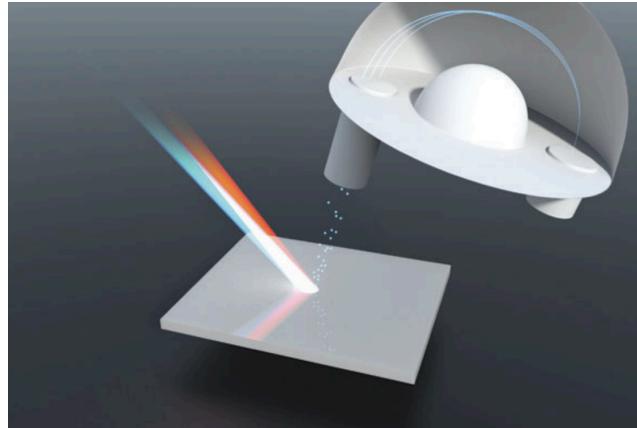
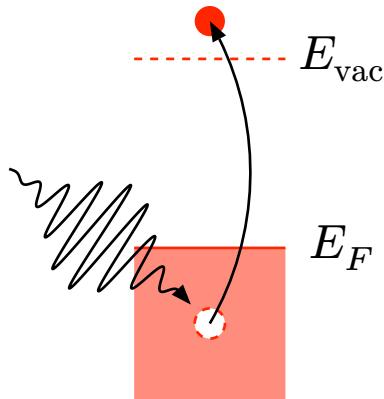
Prologue: Koopmans functionals in a nutshell

Spectral properties are fundamental to understanding materials:



Prologue: Koopmans functionals in a nutshell

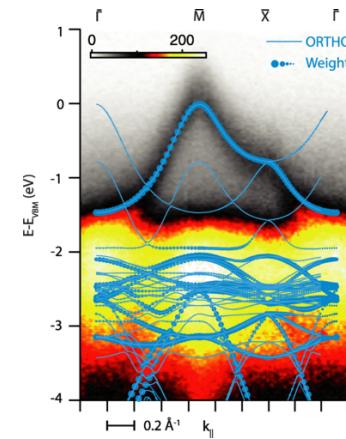
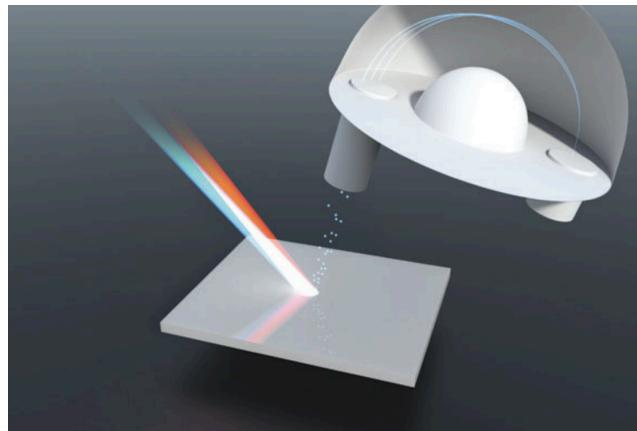
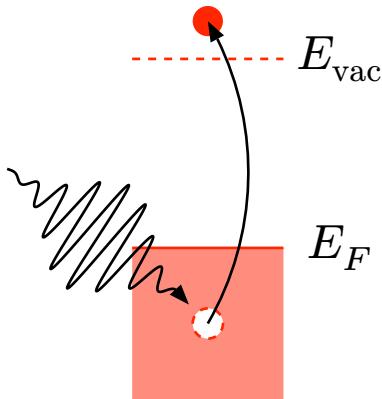
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... but how can we routinely compute them?

Prologue: Koopmans functionals in a nutshell

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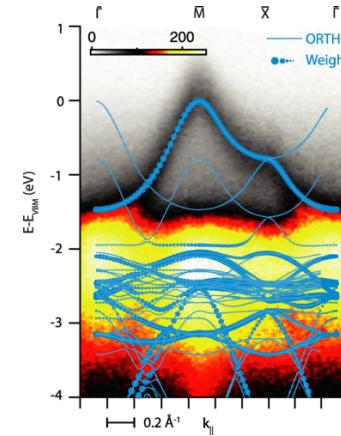
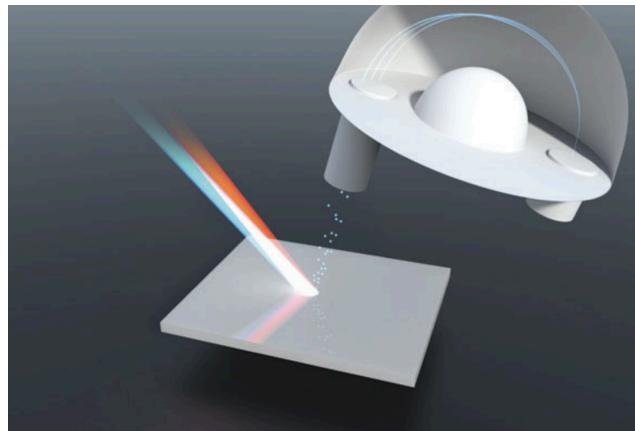
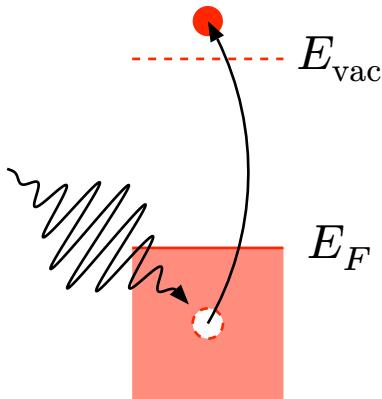


... but how can we routinely compute them?

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

Prologue: Koopmans functionals in a nutshell

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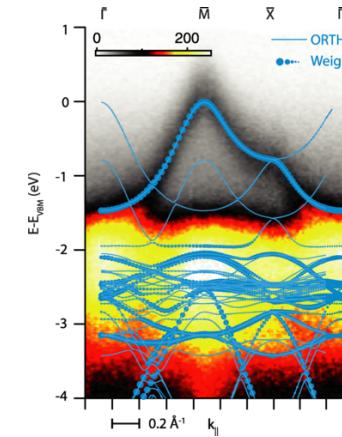
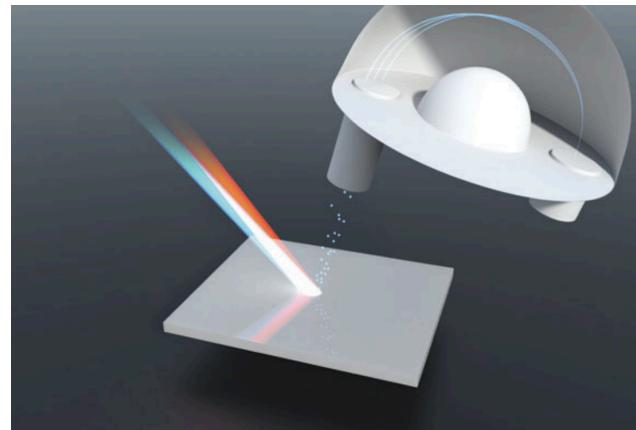
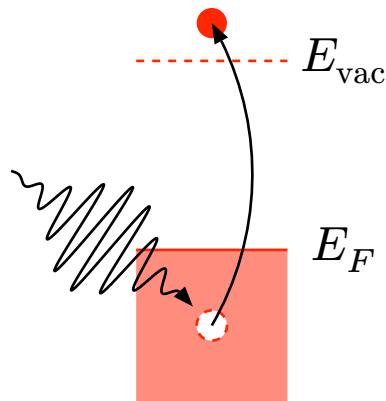


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Prologue: Koopmans functionals in a nutshell

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 systematic errors in DFT → a functional that can accurately predict single-particle excitations

Prologue: Koopmans functionals in a nutshell

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

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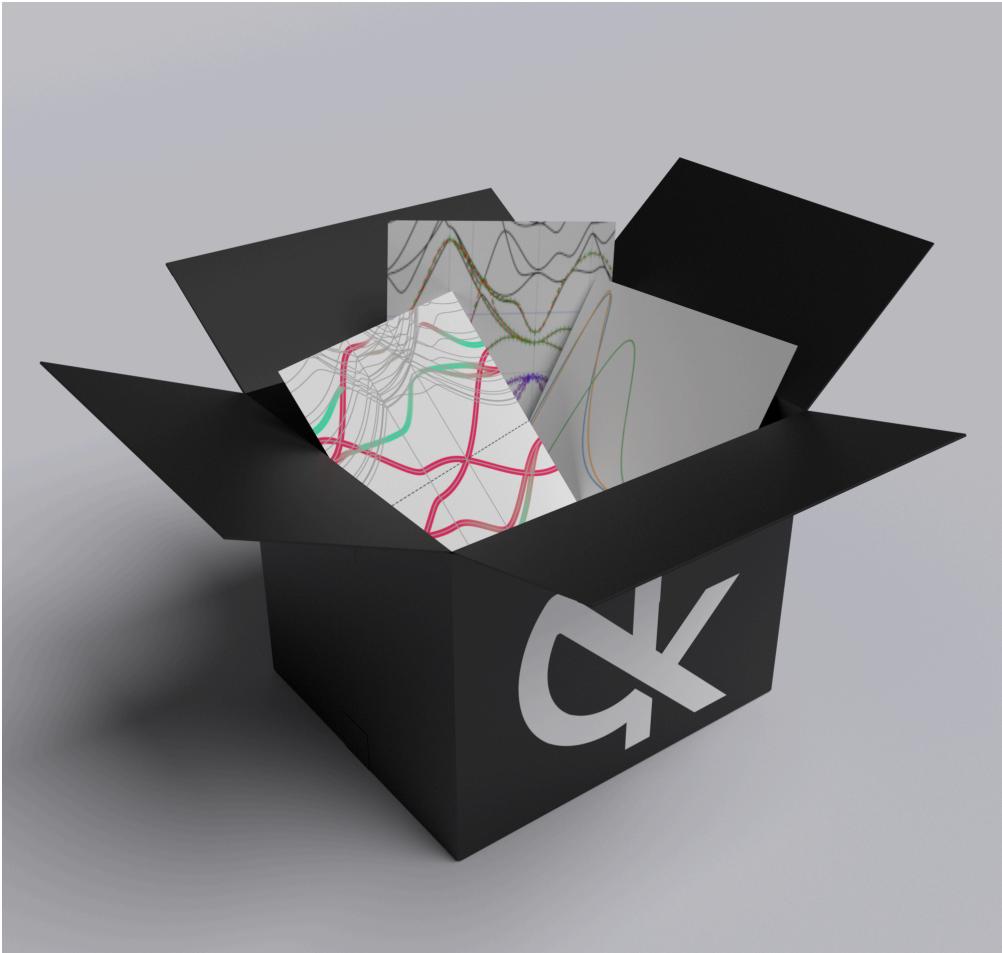
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- screening parameters

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

This talk



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

- accurate
- efficient
- accessible
- automated

Accuracy

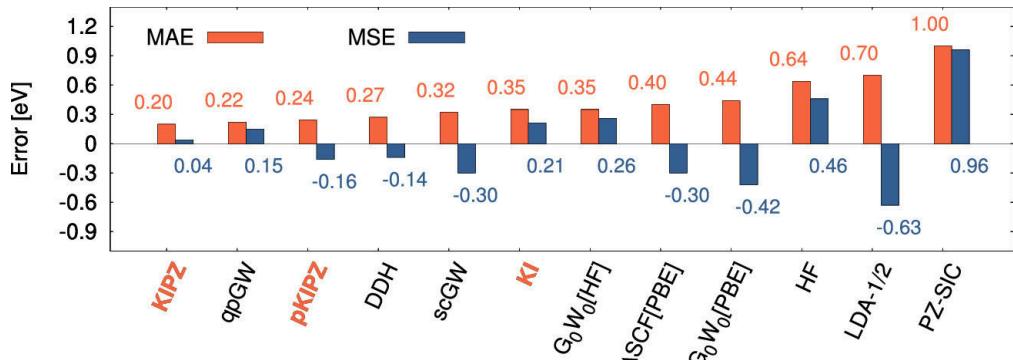


The accuracy of Koopmans functionals

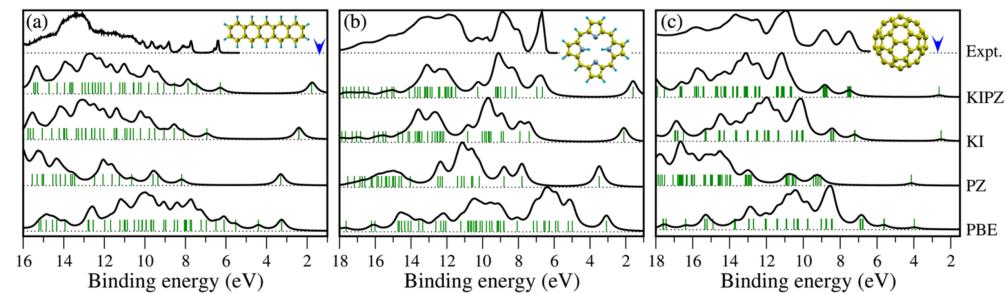
... is well-established

Molecular systems

Ionisation potentials¹



UV photoemission spectra²



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

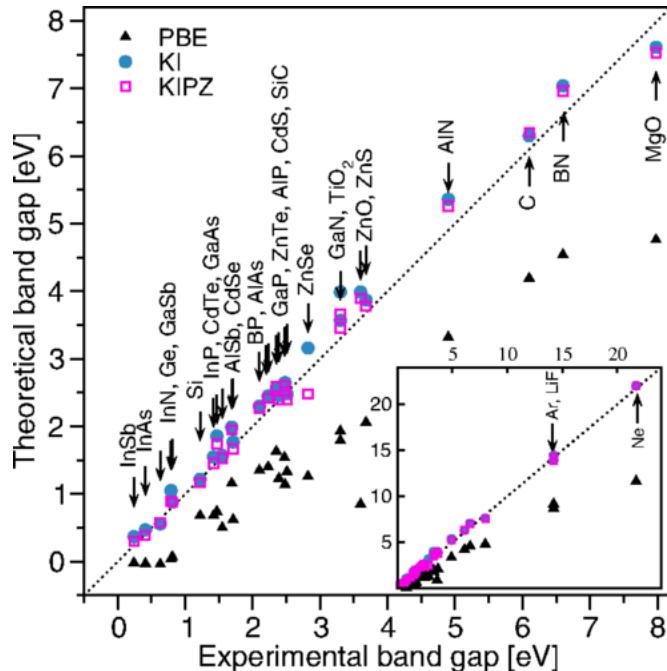
²N. L. Nguyen et al. Phys. Rev. Lett. **114**, 166405 (2015)



The accuracy of Koopmans functionals

Bulk systems

Prototypical semiconductors and insulators¹

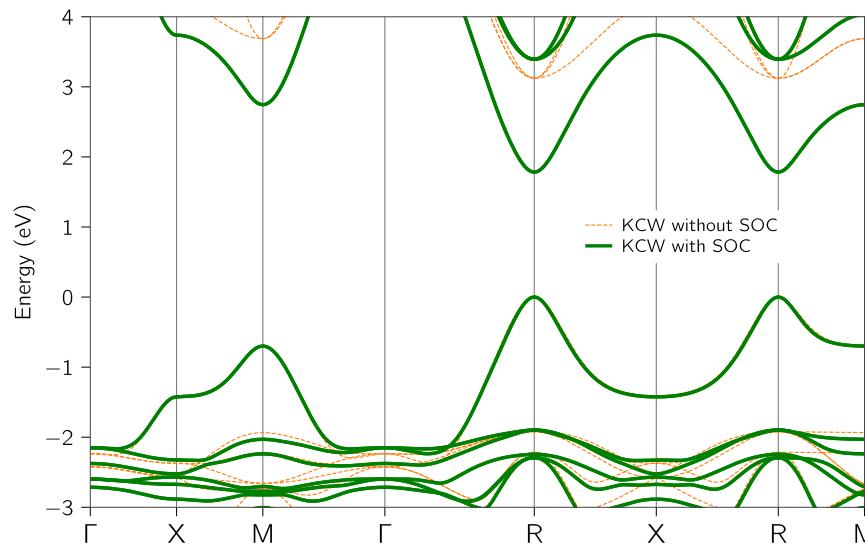


	PBE	G_0W_0	KI	KIPZ	$QSG\tilde{W}$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

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

The accuracy of Koopmans functionals

CsPbBr₃



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

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

Efficiency



Screening parameters

A key ingredient of Koopmans functional calculations:

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

¹N. 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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- a local measure of the degree by which electronic interactions are screened

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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 ΔSCF ¹ or DFPT²
- corresponds to the vast majority of the computational cost of Koopmans functional calculation

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



Taking advantage of symmetries

```
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  $\Delta\psi_{k+q,v}(r)$ 
5:        $\Delta\rho_q^{0n} \leftarrow \sum_{kv} \psi_{kv}^*(r) \Delta\psi_{k+q,v}(r) + c.c.$ 
6:        $\Pi_{0n,q}^{(r)} \leftarrow \langle \Delta\rho_q^{0n} | f_{\text{Hxc}} | \rho_q^{0n} \rangle$ 
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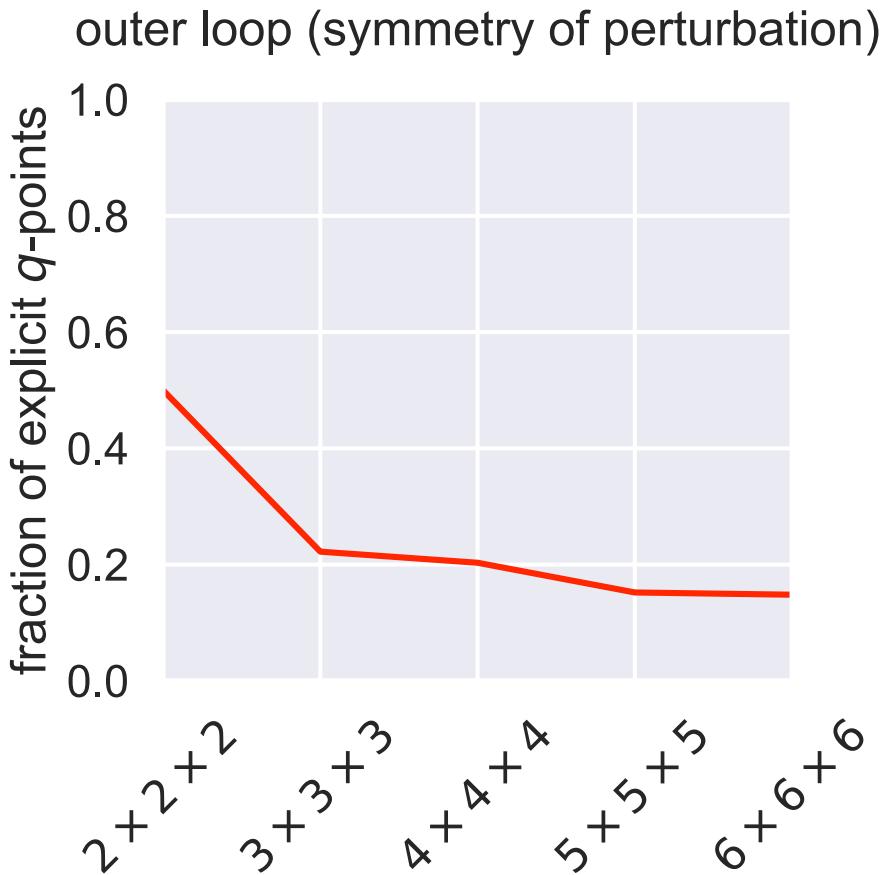
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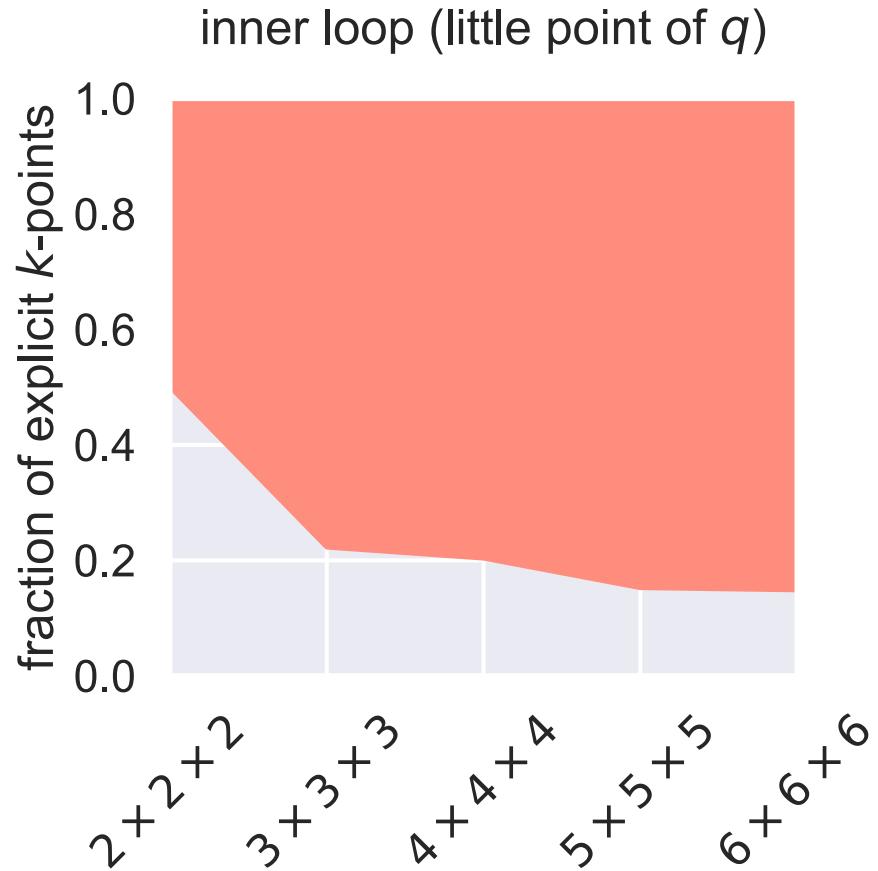
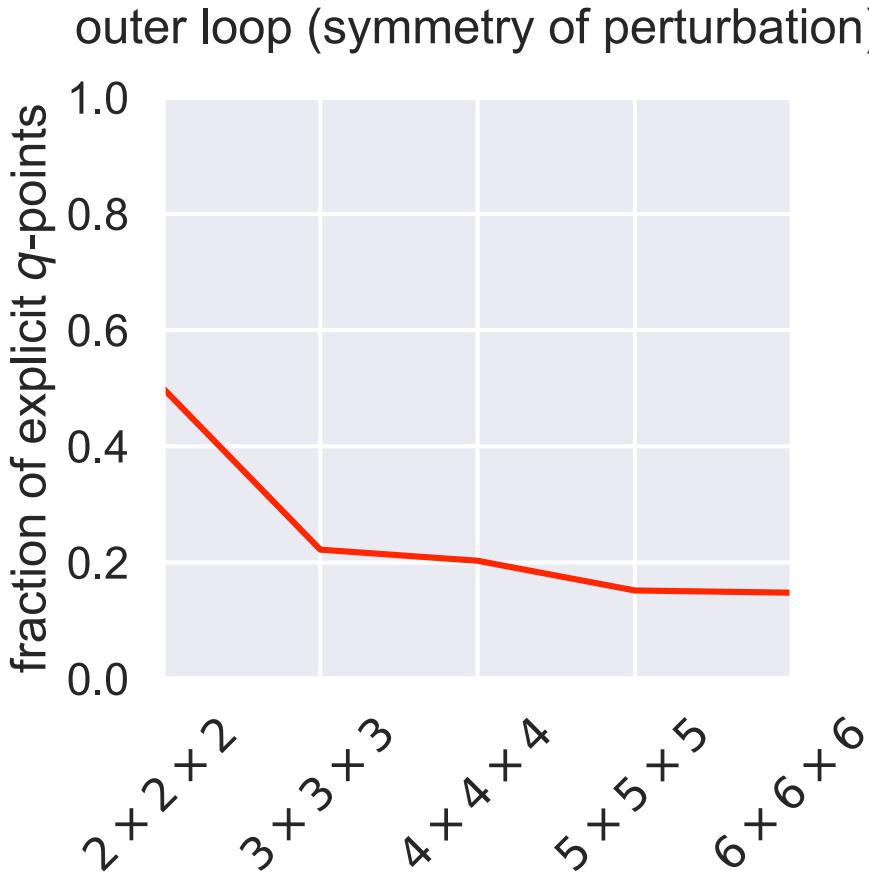
Use symmetry to reduce the terms in the sums:

- $q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$ (the symmetry of the perturbation; lower than that of the primitive cell)
- $k \in \text{BZ} \rightarrow k \in \text{IBZ}(q)$ (can only use symmetries that leave q invariant)

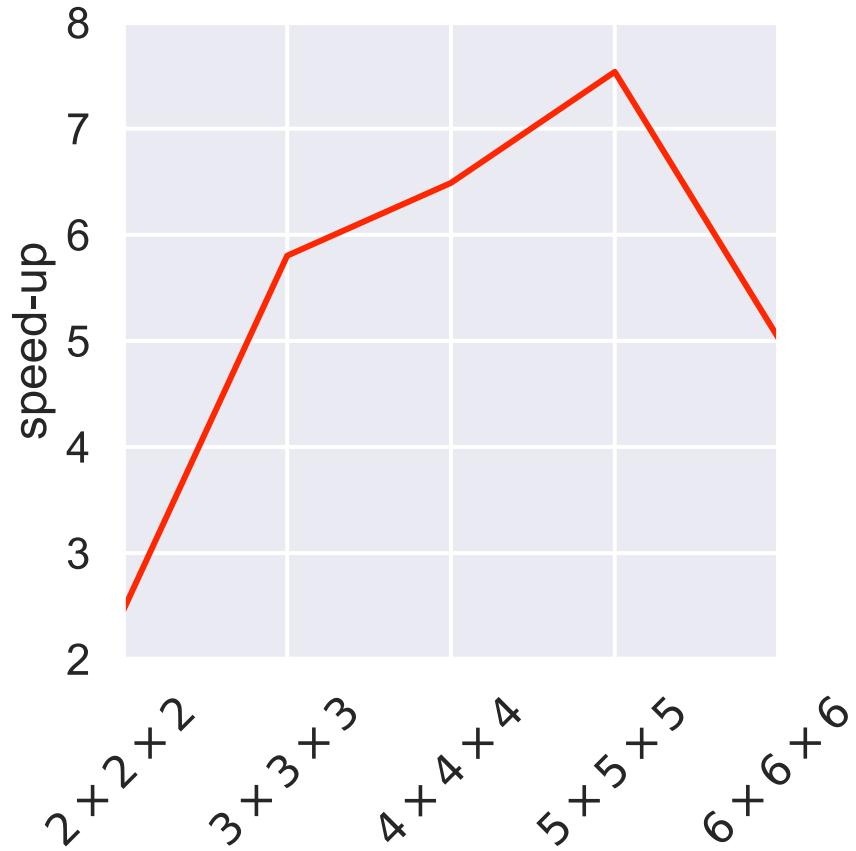
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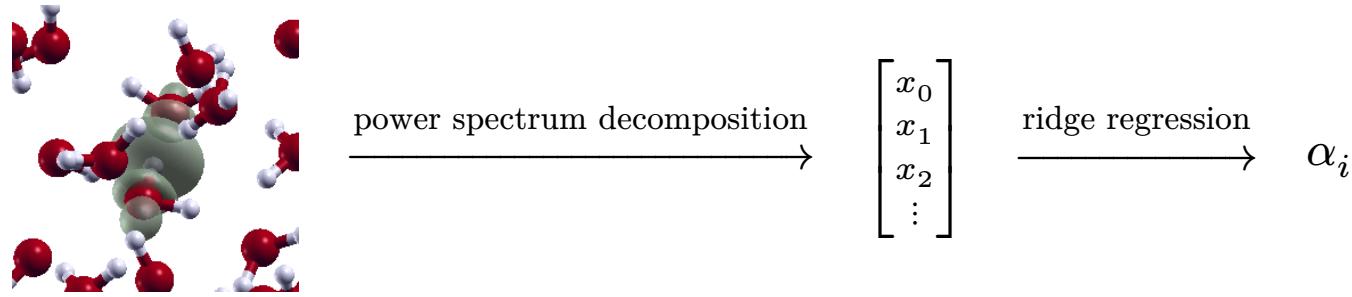


Taking advantage of symmetries



Electronic screening via machine learning

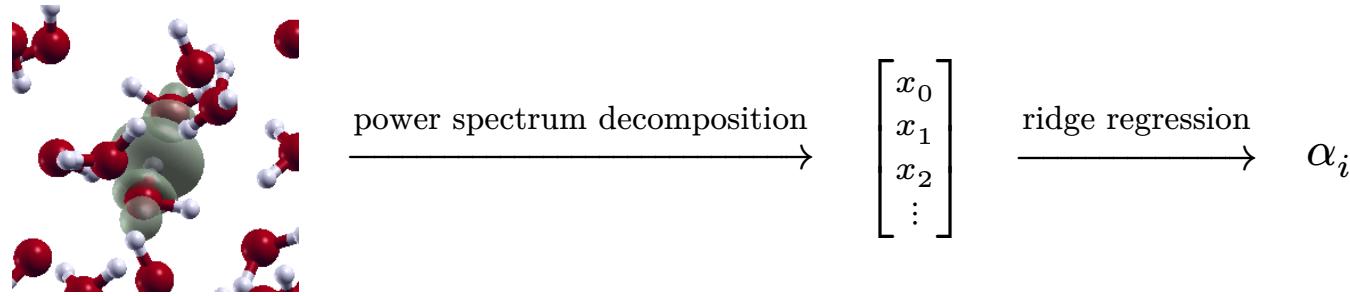
The ML framework



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

Electronic screening via machine learning

The ML framework



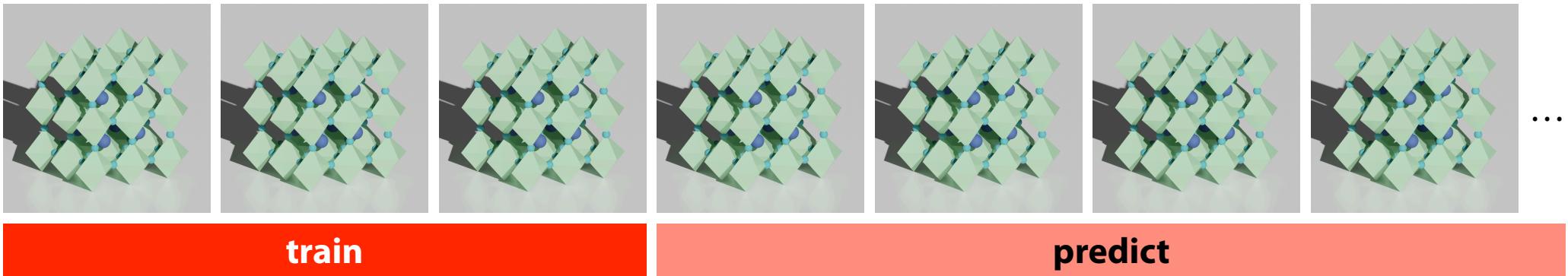
$$c_{nlm,k}^i = \int dr g_{nl}(r) Y_{lm}(\theta, \varphi) n_i(\mathbf{r} - \mathbf{R}_i)$$

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

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

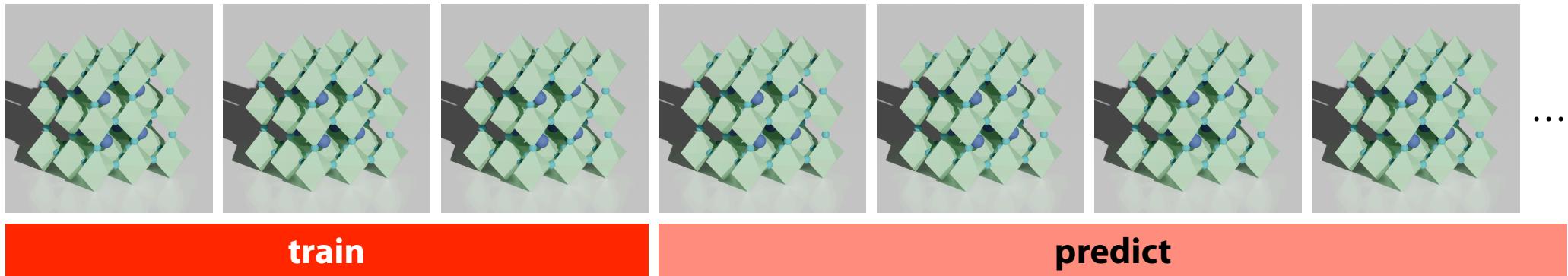
Electronic screening via machine learning

The use-case



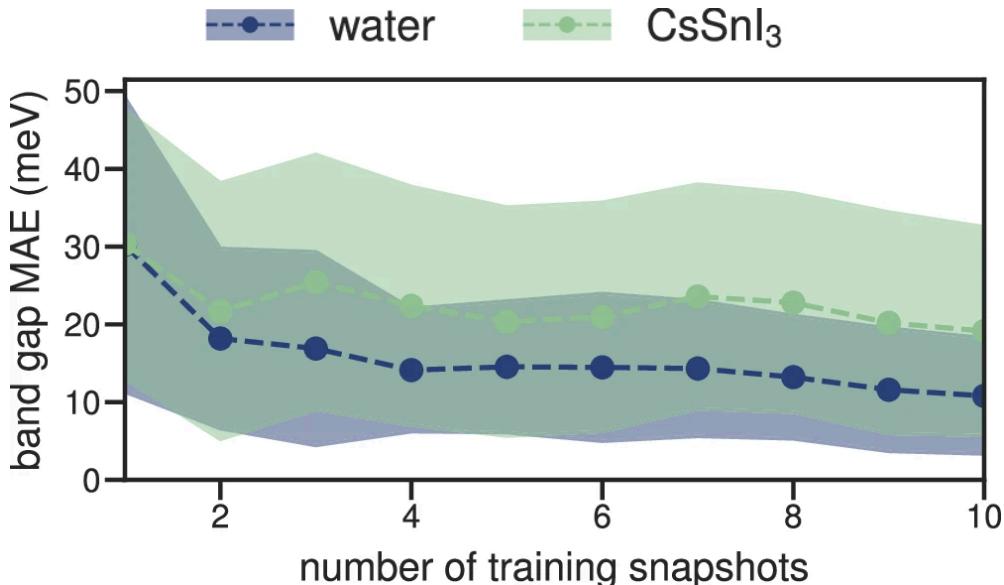
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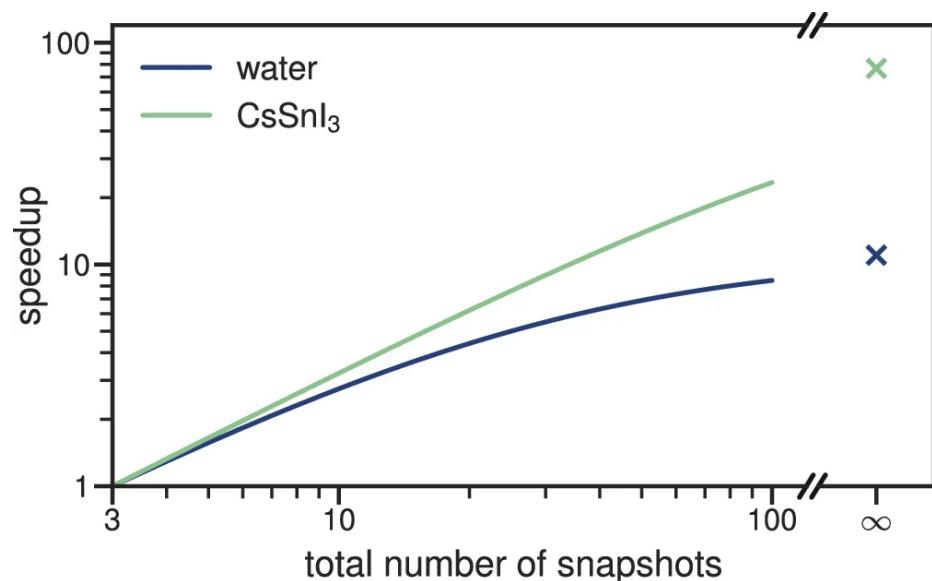


N.B. not a general model

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 $\mathcal{O}(100)$

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



Accessibility

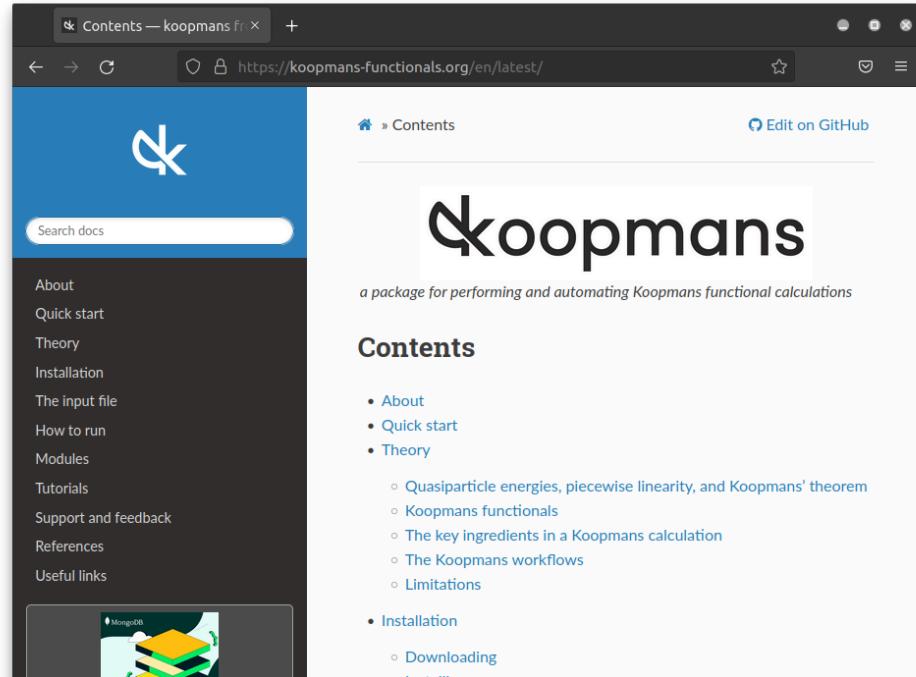


Barriers to accessibility

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



koopmans



- automated workflows that wrap Quantum ESPRESSO
- easy installation
- minimal technical knowledge required from the user

See koopmans-functionals.org

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

Automation



AiiDA integration

Koopmans

Simple by design

- local execution only
- serial step execution (even when steps are independent!)
- direct access to input/output files
- simple installation



Powerful by design

AiiDA integration

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Powerful by design

- remote execution

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Powerful by design

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- parallel step execution

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Powerful by design

- remote execution
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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...

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:

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

but executed remotely and in parallel:



What did this require?



What did this require?

- new tools in aiida-core
 - ▶ presto for simplified AiiDA setup
 - ▶ dump for dumping contents of AiiDA database to a local directory

What did this require?

- new tools in aiida-core
 - presto for simplified AiiDA setup
 - dump for dumping contents of AiiDA database to a local directory
- substantial refactoring of the koopmans code base
 - abstraction of various operations (e.g. reading/writing files)
 - conversion of steps to pure functions e.g. removing all reliance on shared directories



Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

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

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

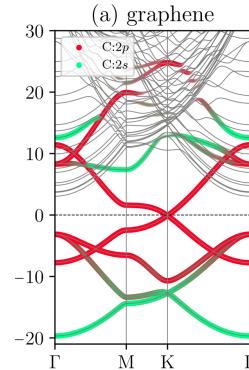
²J. Qiao et al. npj Comput Mater **9**, 206 (2023)



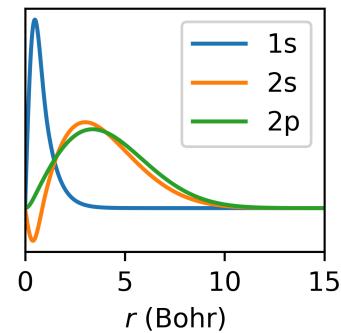
Automated Wannierisation

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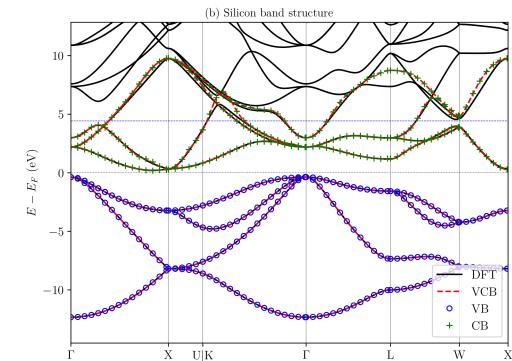
- to initialize the minimising orbitals, or
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projectability-based
disentanglement¹



use PAOs found in
pseudopotentials



parallel transport to separate manifolds²

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

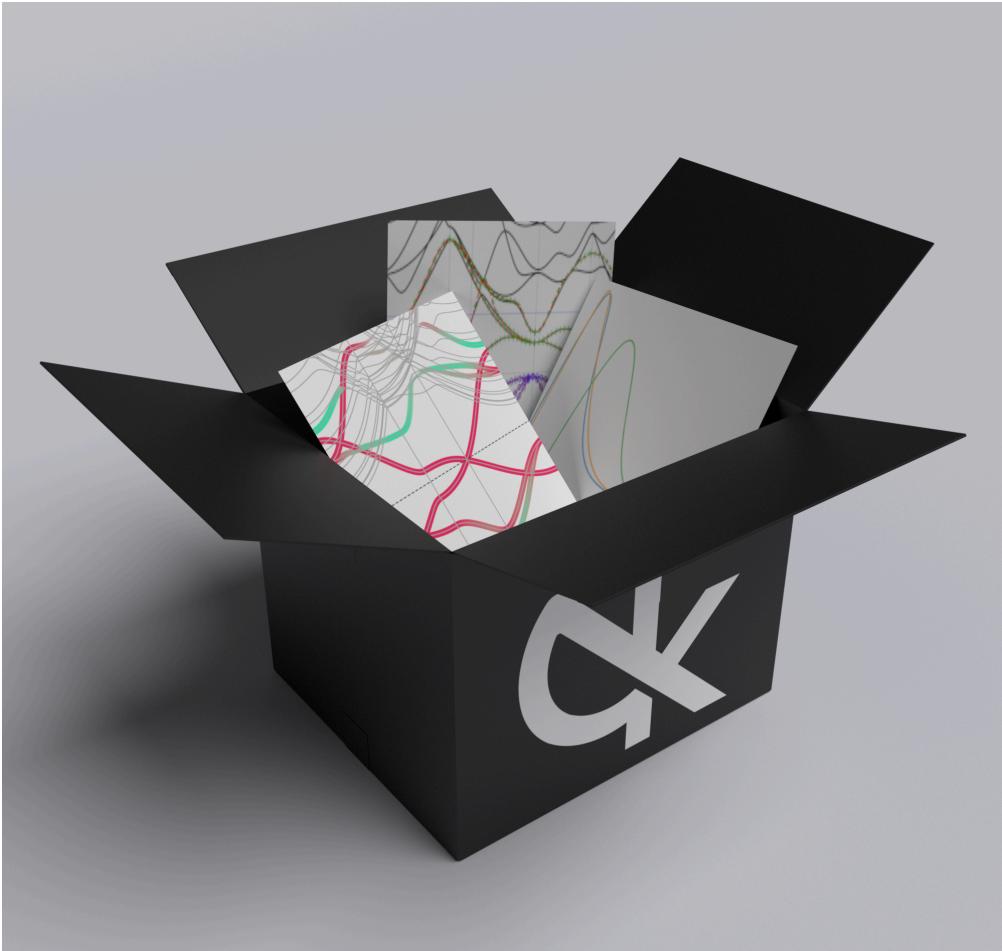
²J. Qiao et al. npj Comput Mater **9**, 206 (2023)



Summary



Summary



Koopmans functionals are...

- **accurate**, with band structures comparable to state-of-the-art GW
 - ▶ now also for systems with strong SOC
- more **efficient** thanks to
 - ▶ DFPT that now takes advantage of symmetries
 - ▶ a new machine learning framework for predicting screening parameters
- more **accessible** thanks to ongoing work on the koopmans package
- more **automated** thanks to
 - ▶ a new AiiDA backend ... with an AiiDALab app on the horizon!
 - ▶ automated Wannierisation

Thank you!

References

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spare slides

Detailed Theory



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

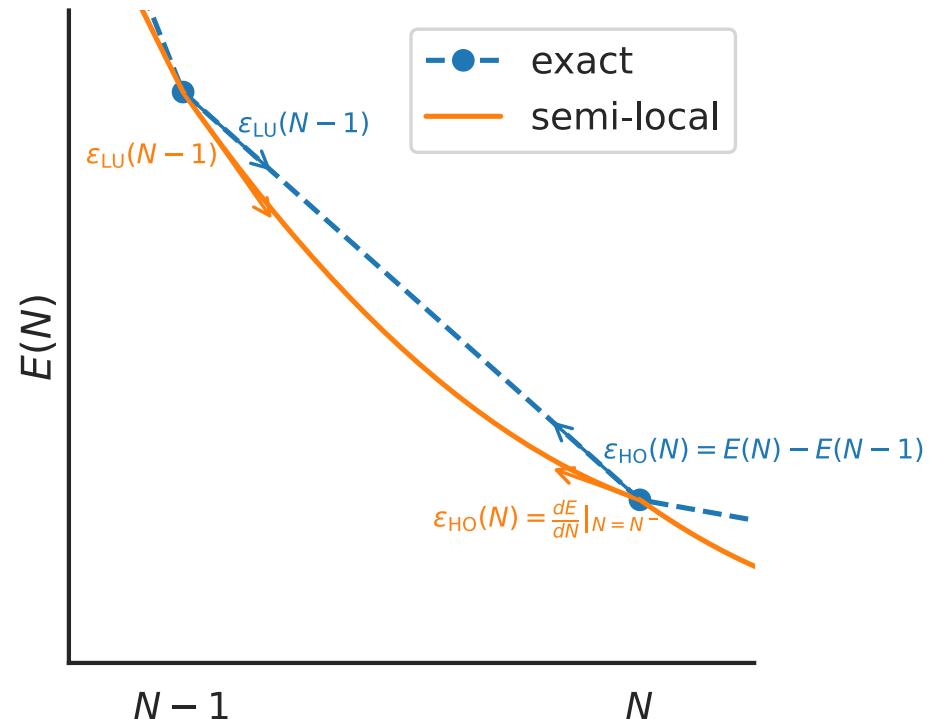
Total energy differences vs. eigenvalues

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 ΔE of explicit electron addition/
removal



Total energy differences vs. eigenvalues

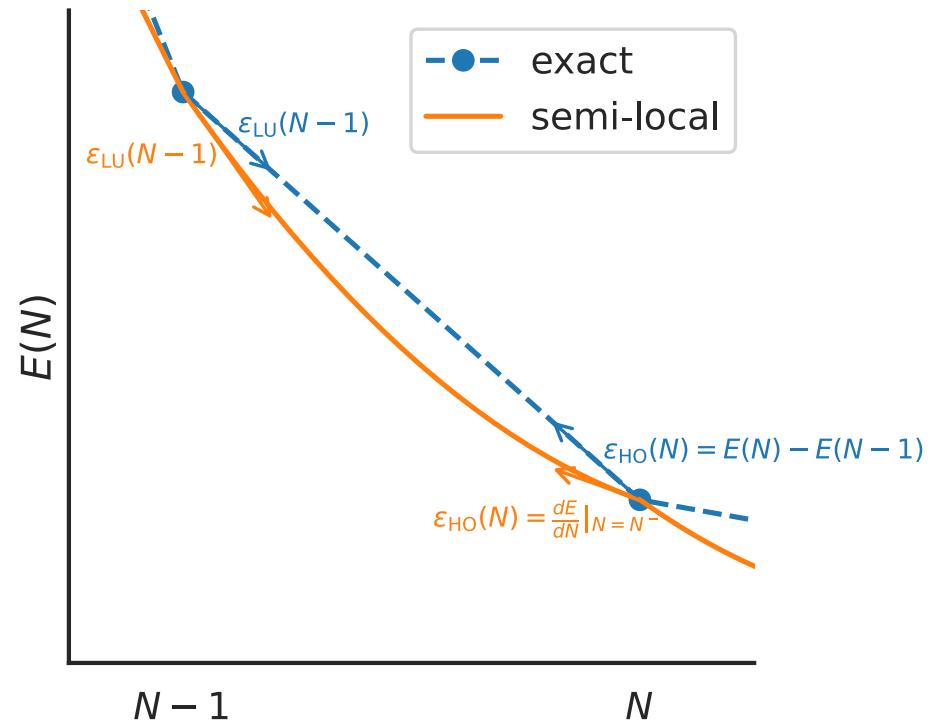
$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

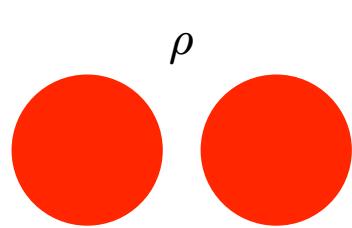
$$+ \sum_i \left\{ - \underbrace{(E^{\text{DFT}}[\rho] - E[\rho^{f_i \rightarrow 0}])}_{\text{remove non-linear dependence}} + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}$$

restore linear dependence

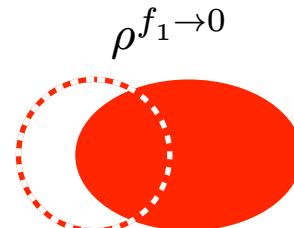
Bakes the total energy differences

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

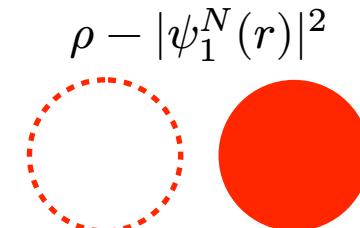




N -electron solution



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 α_i from explicit Δ SCF calculations¹

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

Recast via linear response²:

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

which can be efficiently computed via DFPT³

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

²N. Colonna et al. J. Chem. Theory Comput. **14**, 2549–2557 (2018)

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Recast via linear response²:

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

which can be efficiently computed via DFPT³ ... but is still the bulk of the computational cost (can use machine-learning)

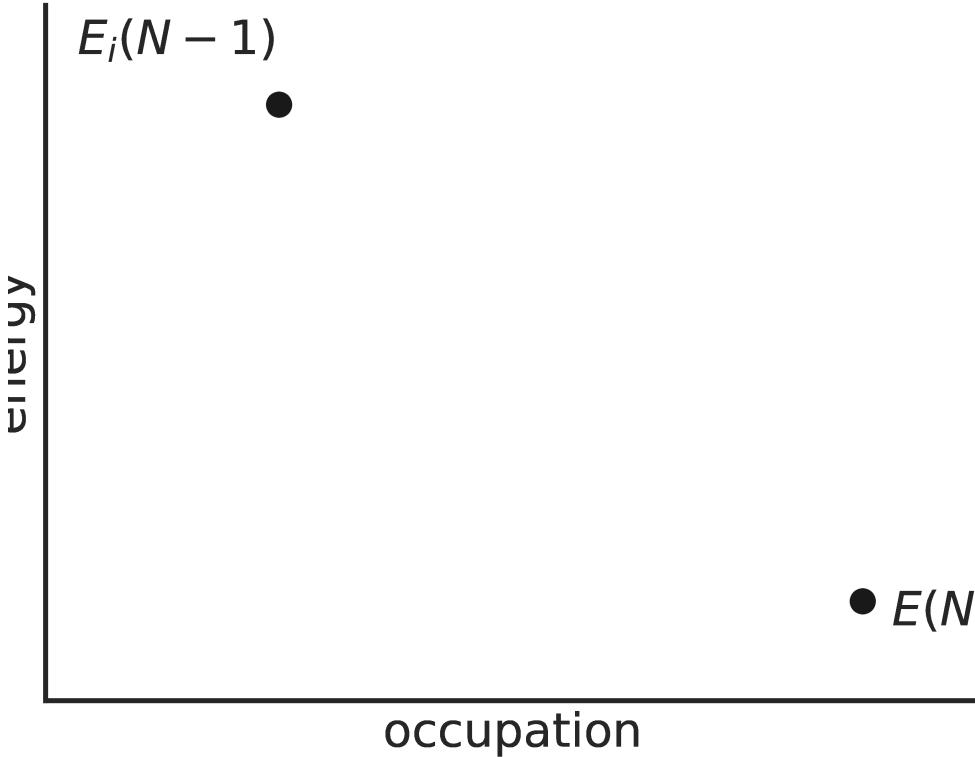
¹N. L. Nguyen et al. Phys. Rev. X **8**, 21051 (2018), R. De Gennaro et al. Phys. Rev. B **106**, 35106 (2022)

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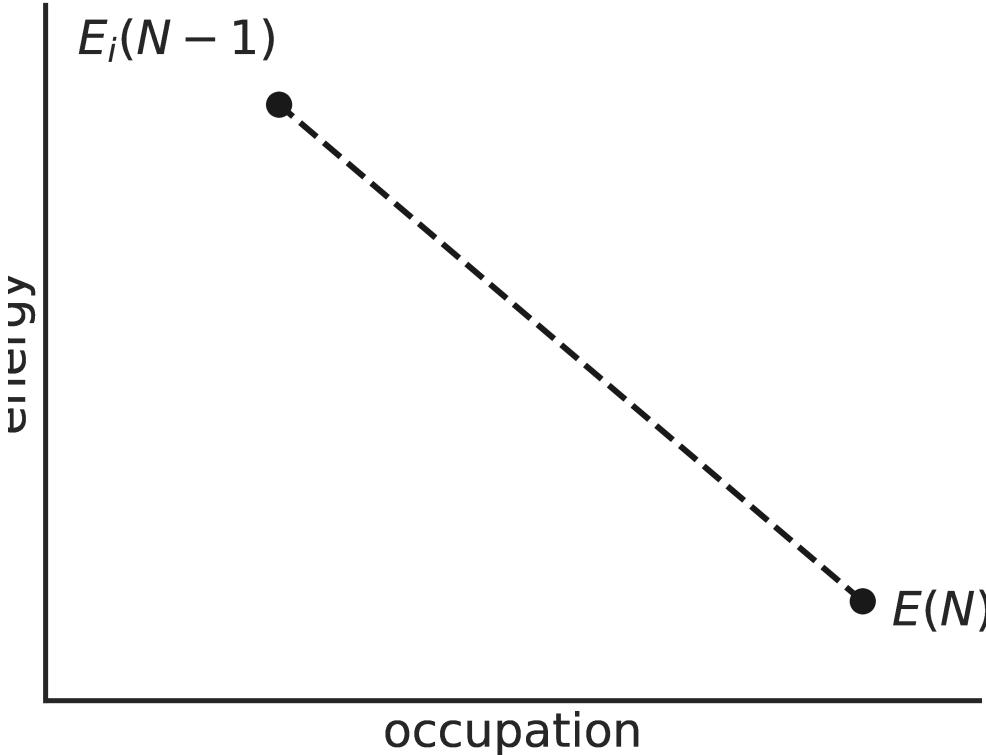
³N. Colonna et al. J. Chem. Theory Comput. **18**, 5435–5448 (2022)



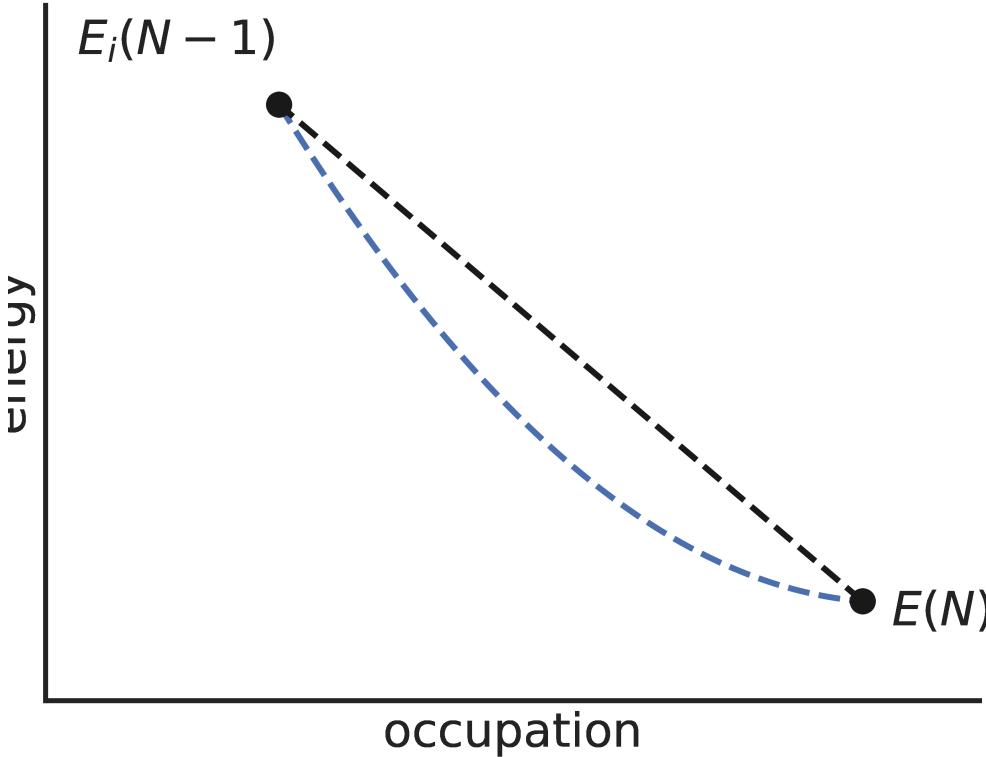
Calculating screening parameters via SCF



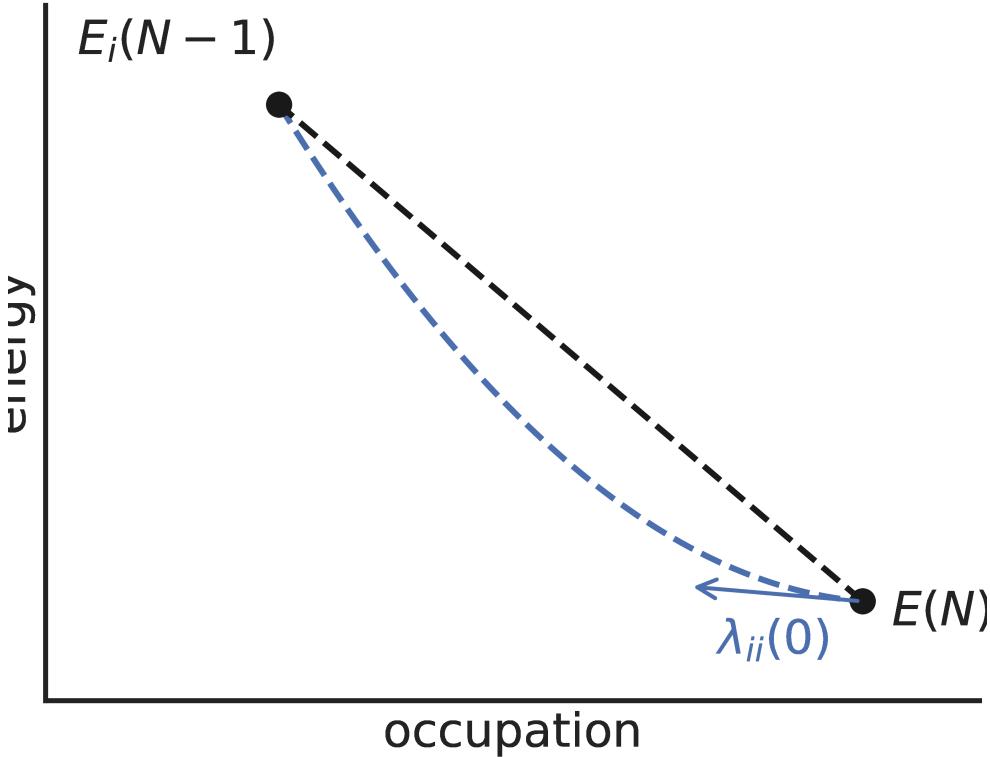
Calculating screening parameters via SCF



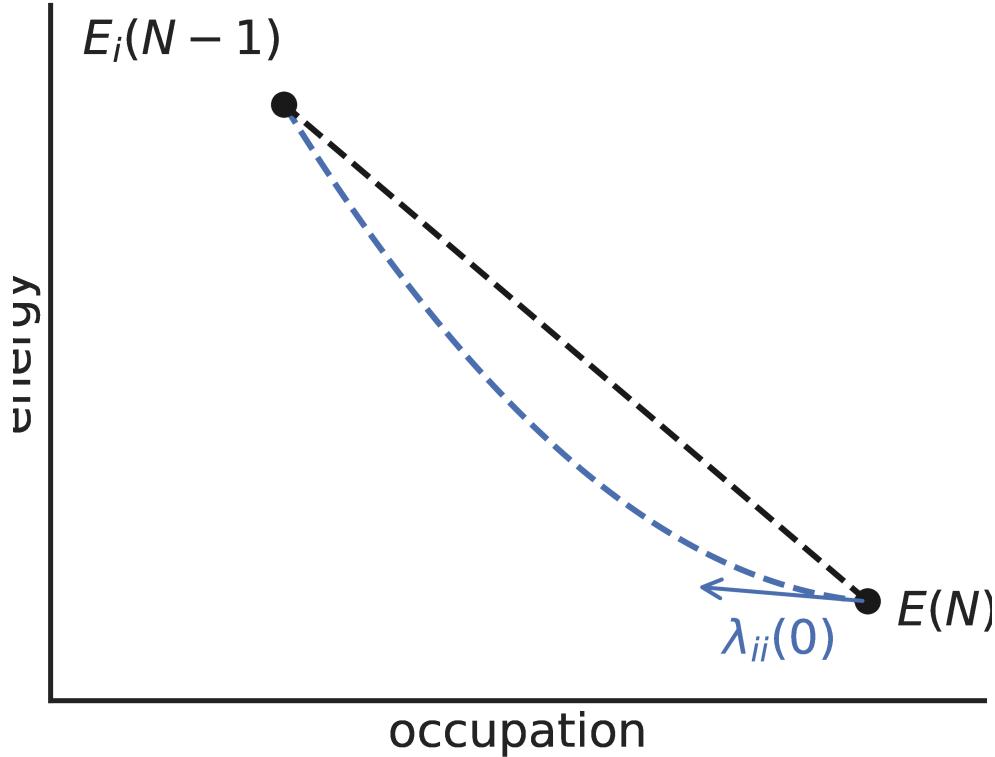
Calculating screening parameters via SCF



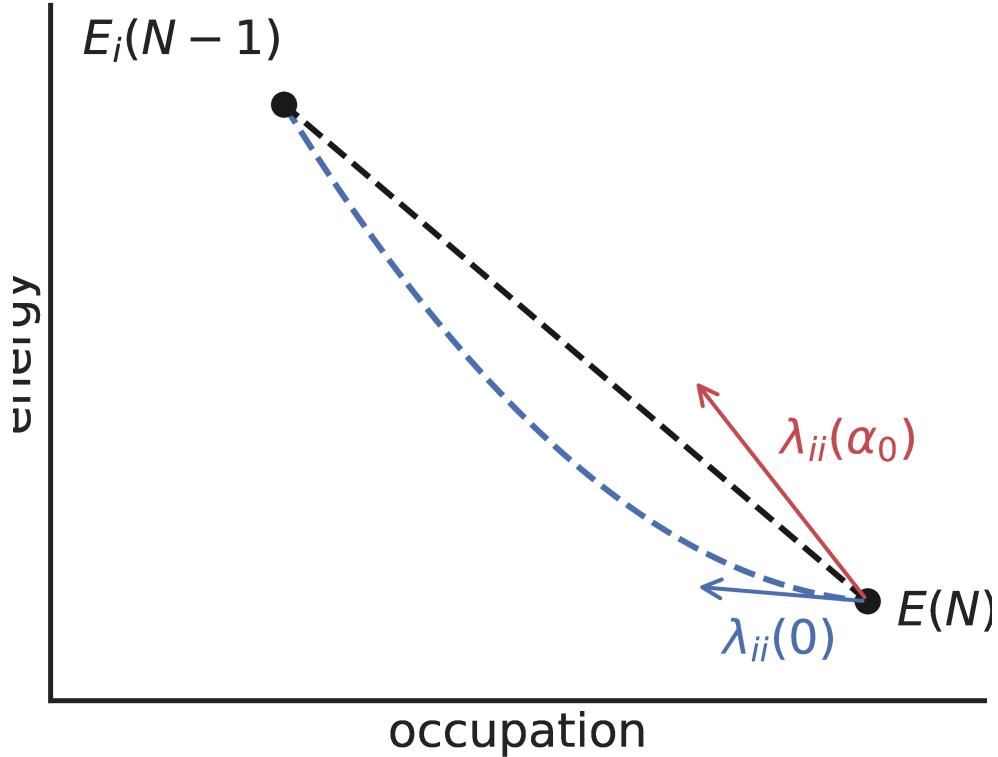
Calculating screening parameters via SCF



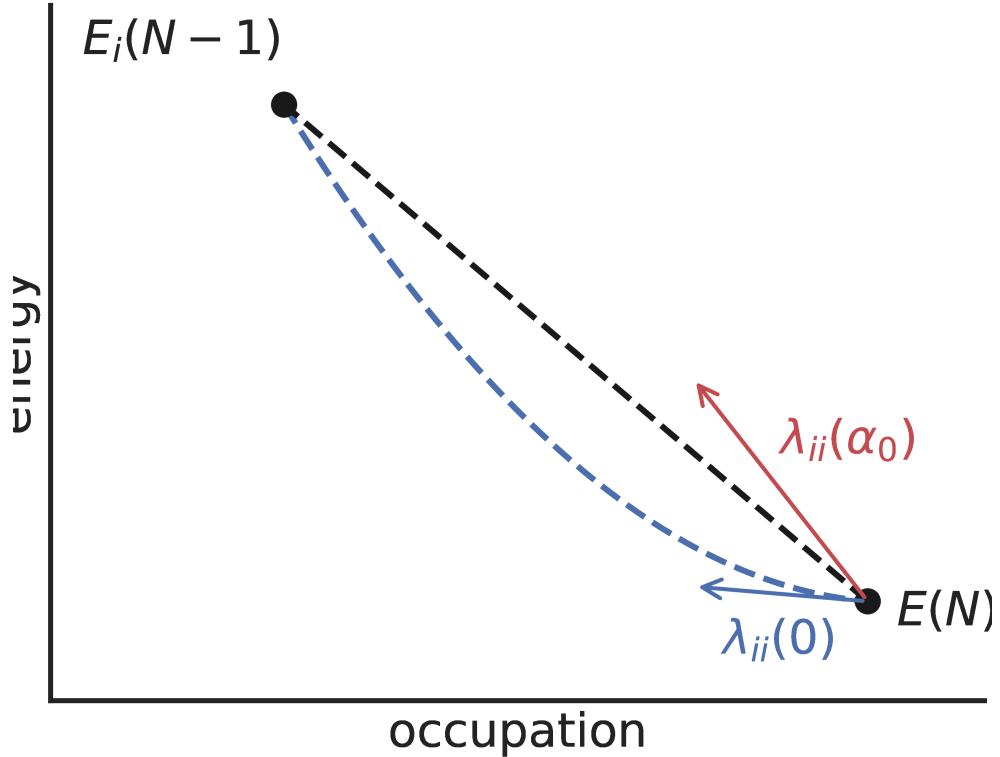
Calculating screening parameters via SCF



Calculating screening parameters via SCF



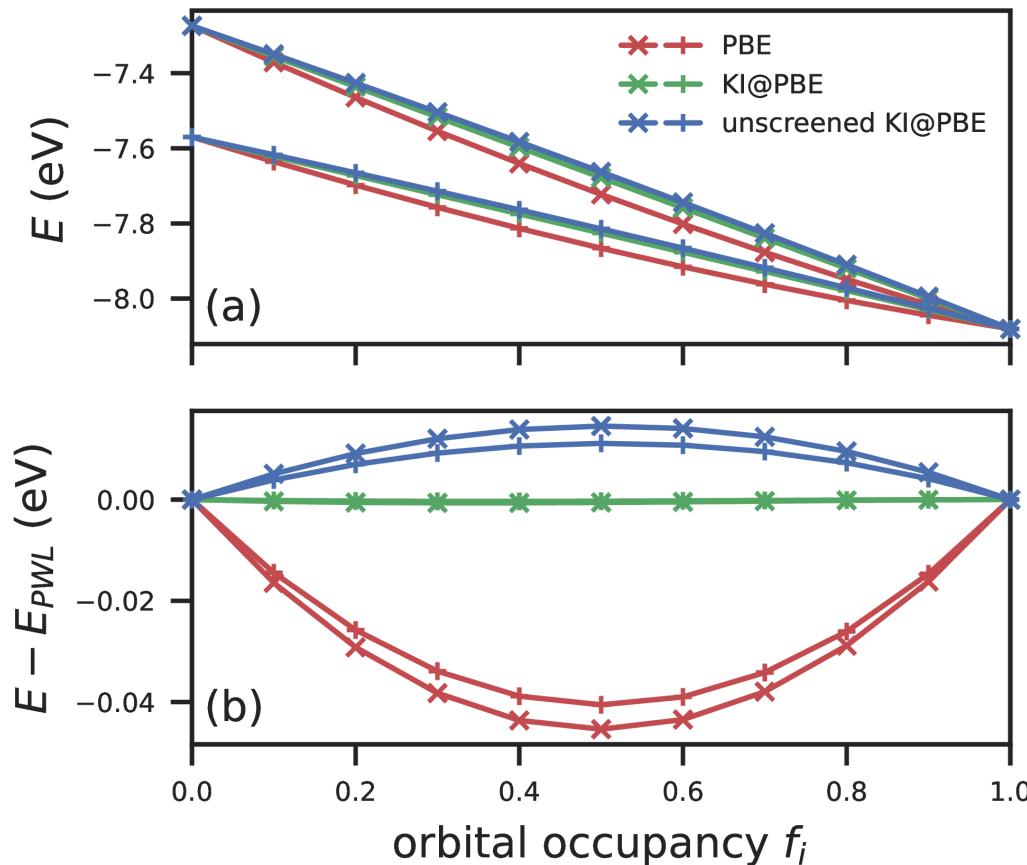
Calculating screening parameters via SCF



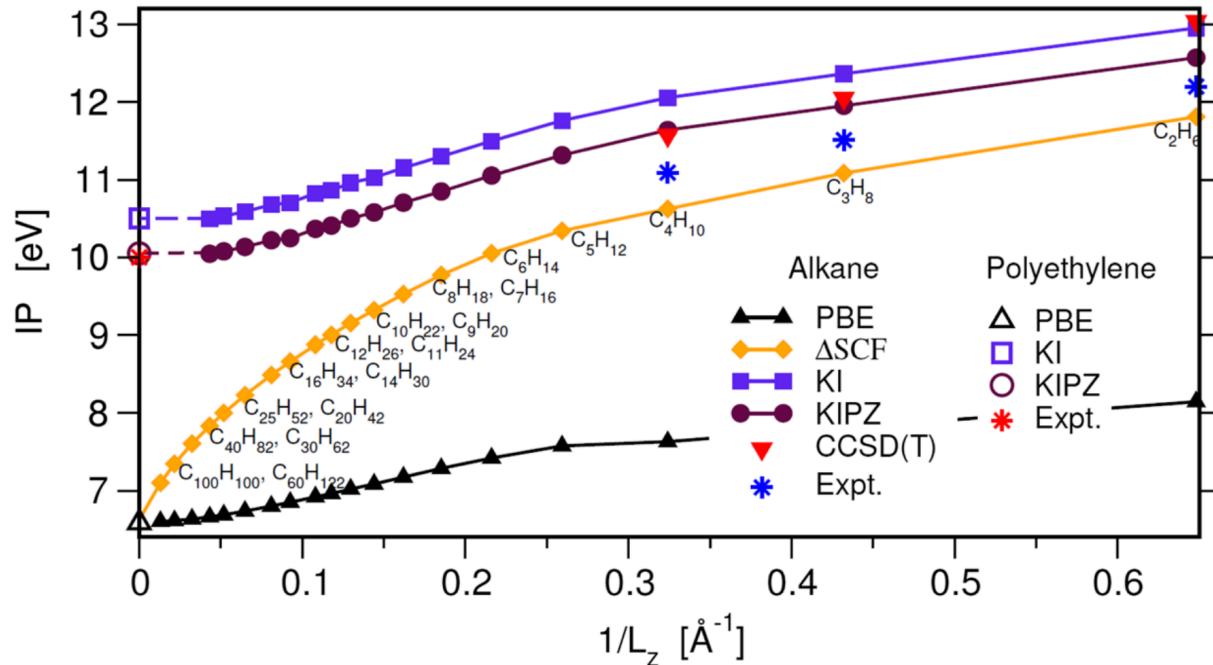
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$$\lambda_{ii}(\alpha) = \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}_i^{\text{KI}} | \varphi_i \rangle$$

Calculating screening parameters via SCF



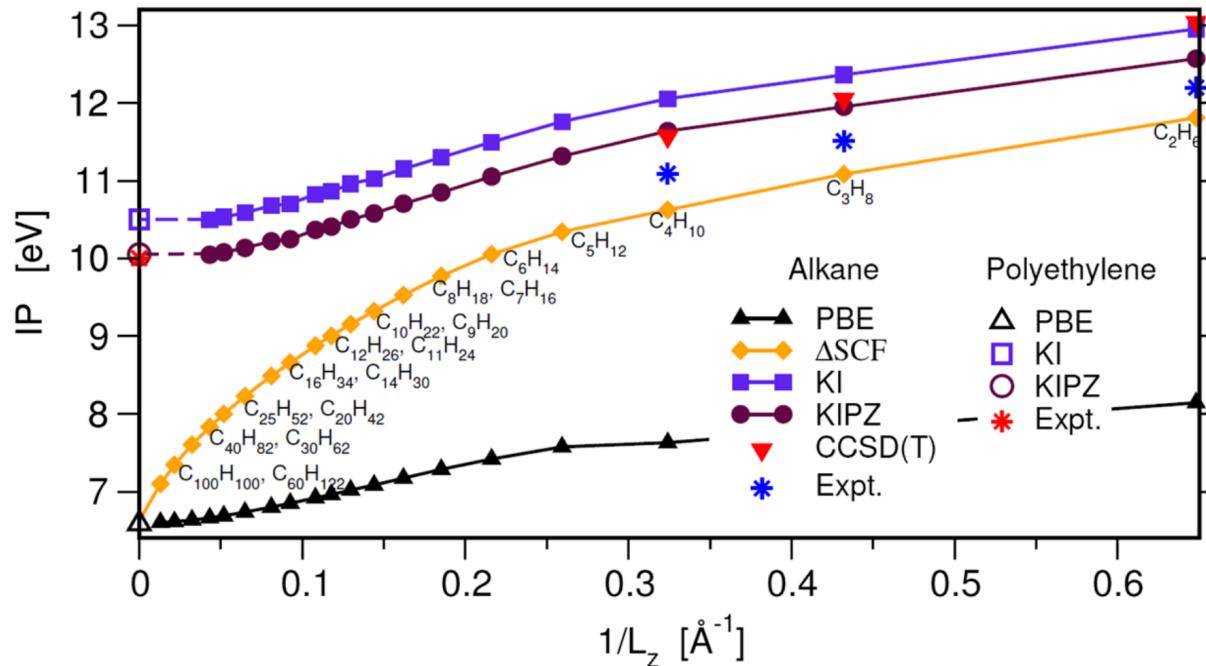
Issues with extended systems



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



Issues with extended systems

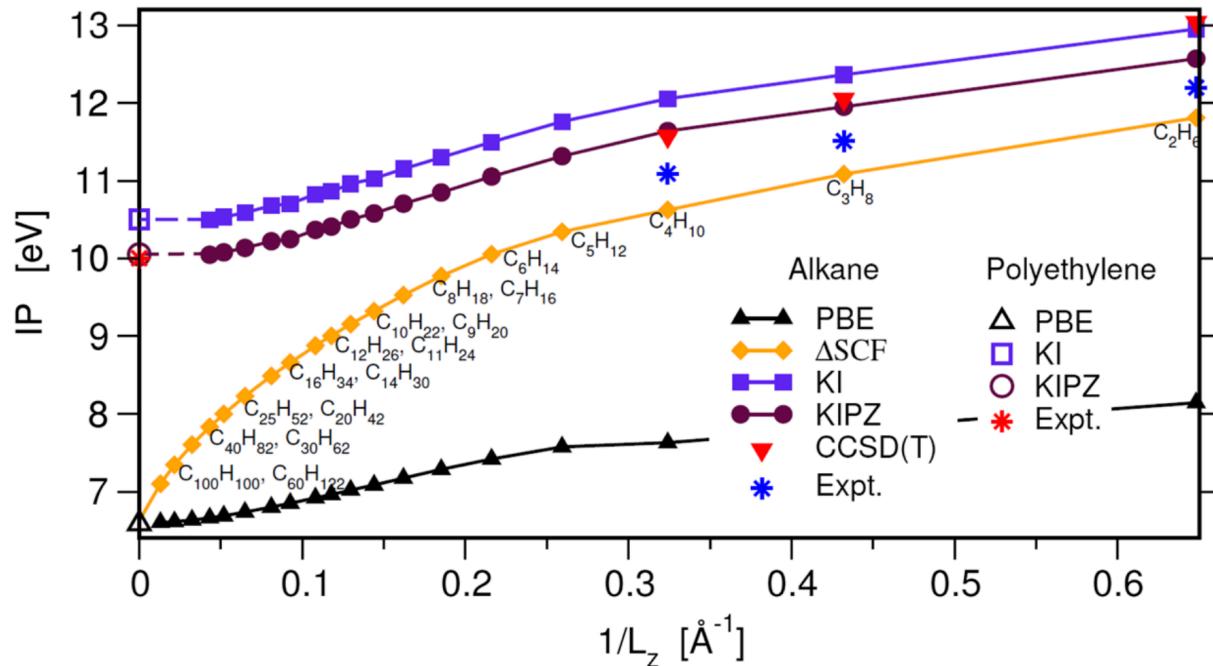


One cell: $E(N + \delta N) - E(N)$

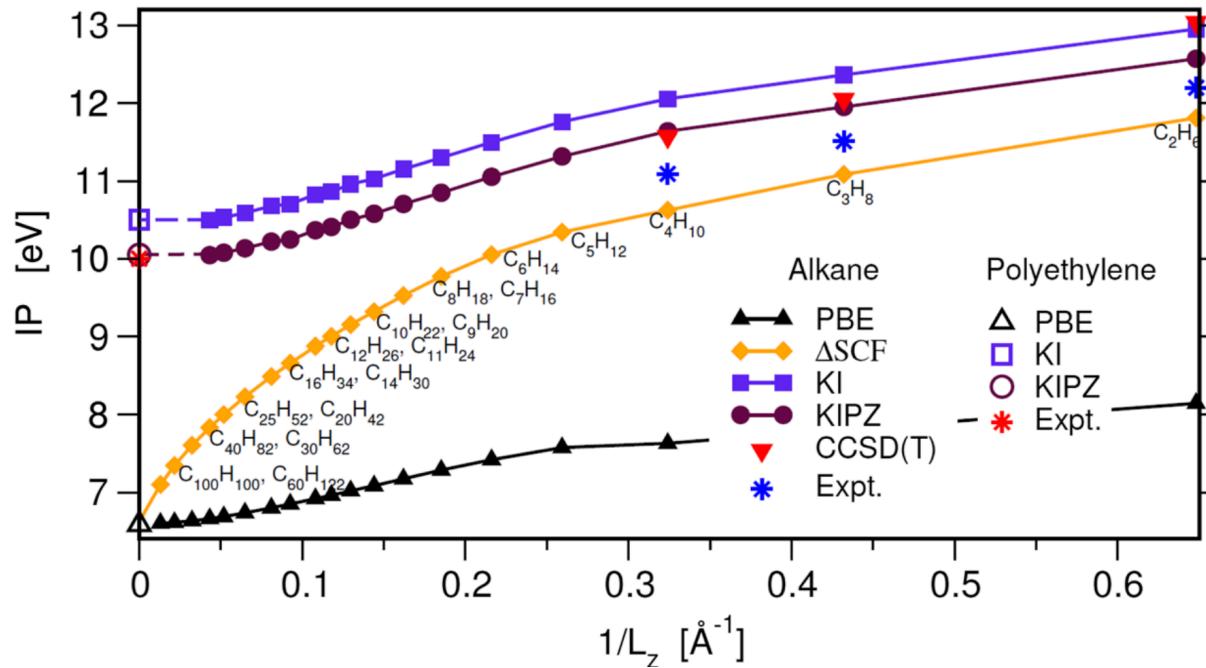
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Issues with extended systems

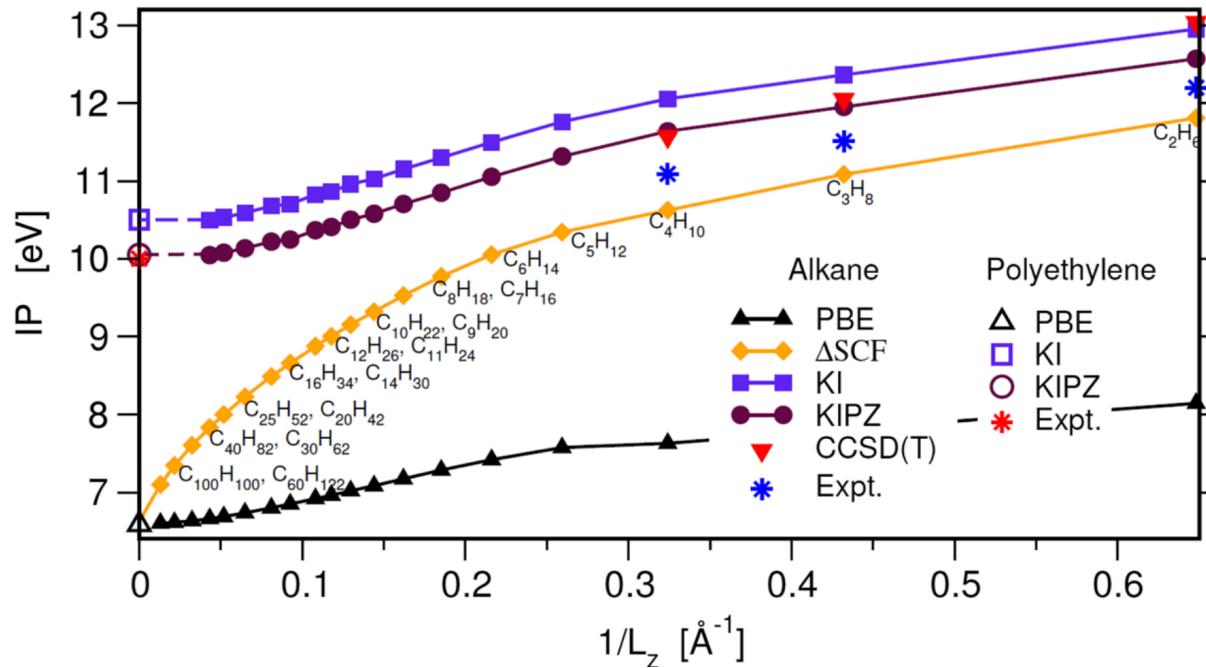


Issues with extended systems

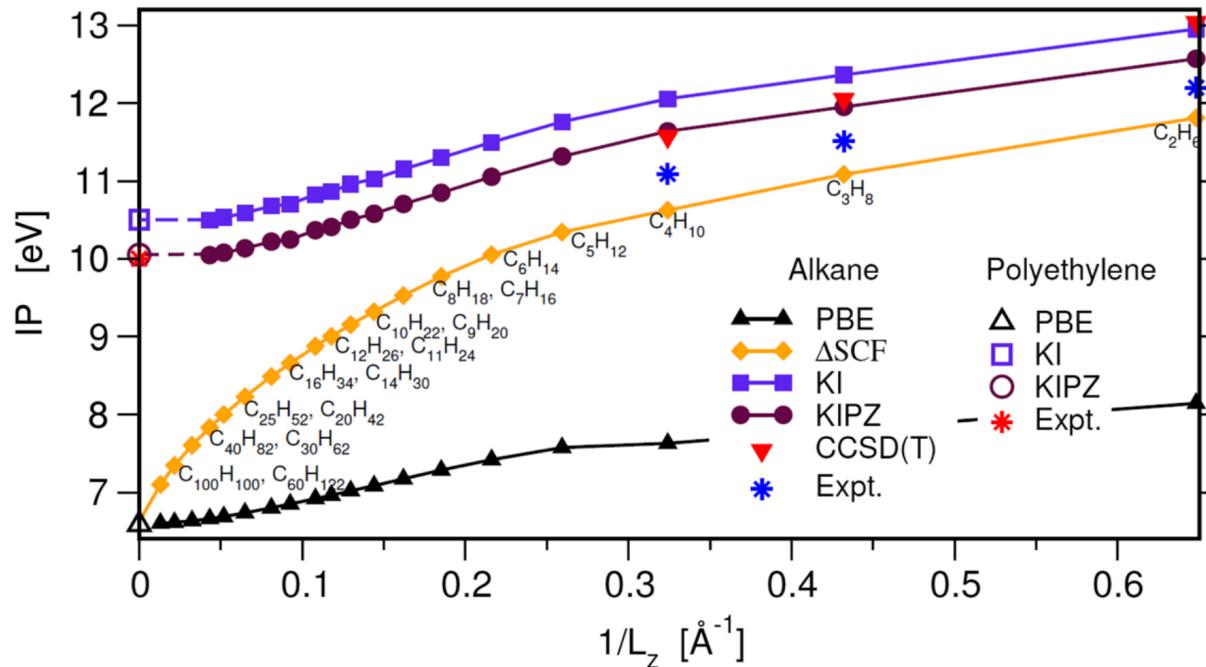


Two options:

Issues with extended systems



Issues with extended systems



Orbital-density dependence

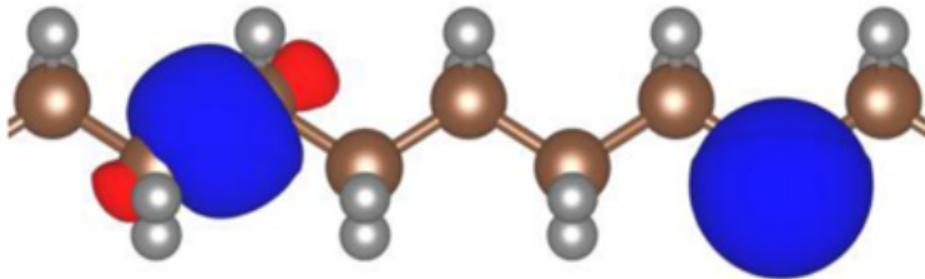
The potential is orbital-dependent!

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

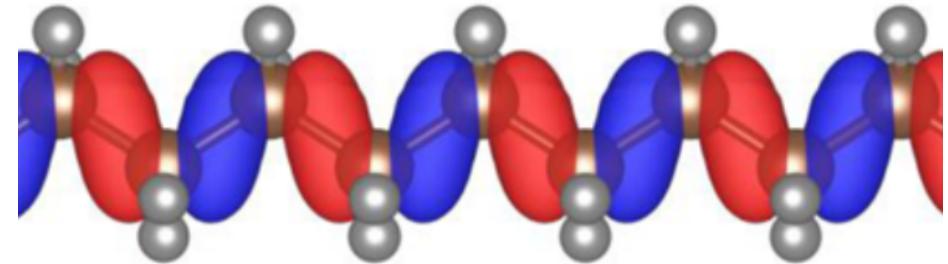
Orbital-density dependence

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



two variational orbitals



a canonical orbital

Orbital-density dependence

Because we have an ODD...

-

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

²A. 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 MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but we don't know \hat{H}

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Orbital-density dependence

Because we have an ODD...

- minimisation gives rise to localised orbitals, so we can use MLWFs¹
- 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 theory²

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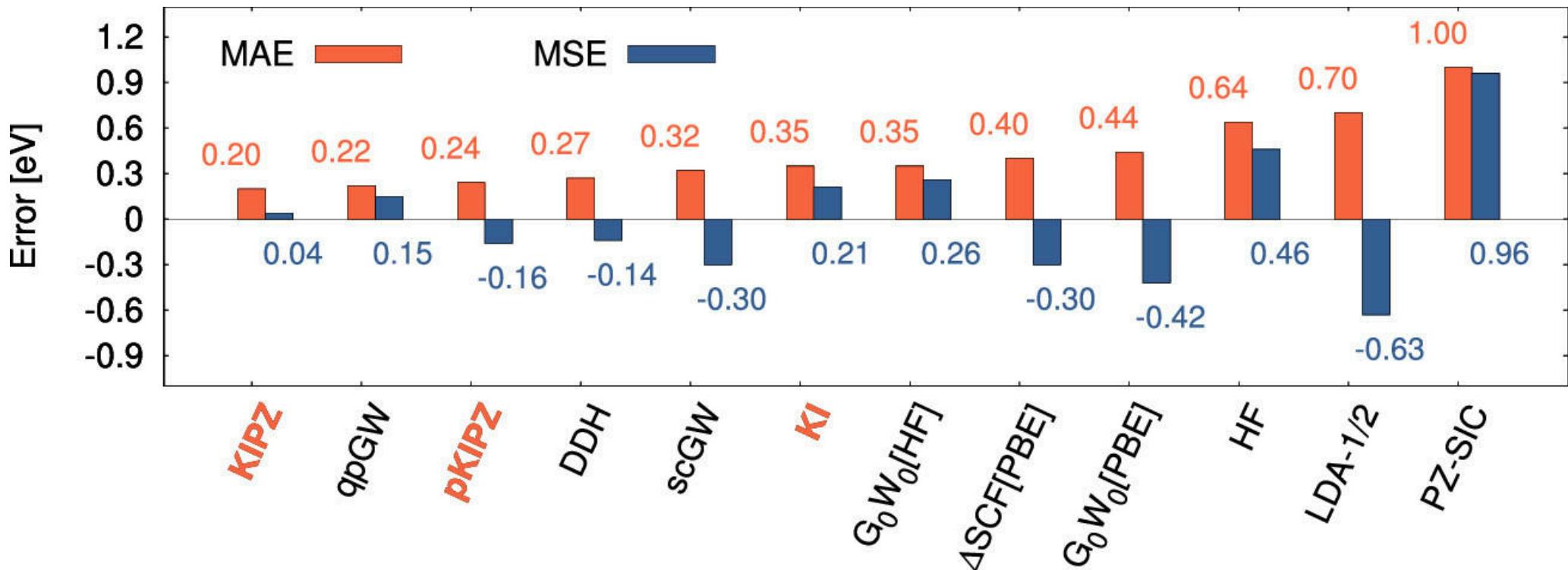


Exhaustive Results



Molecular systems

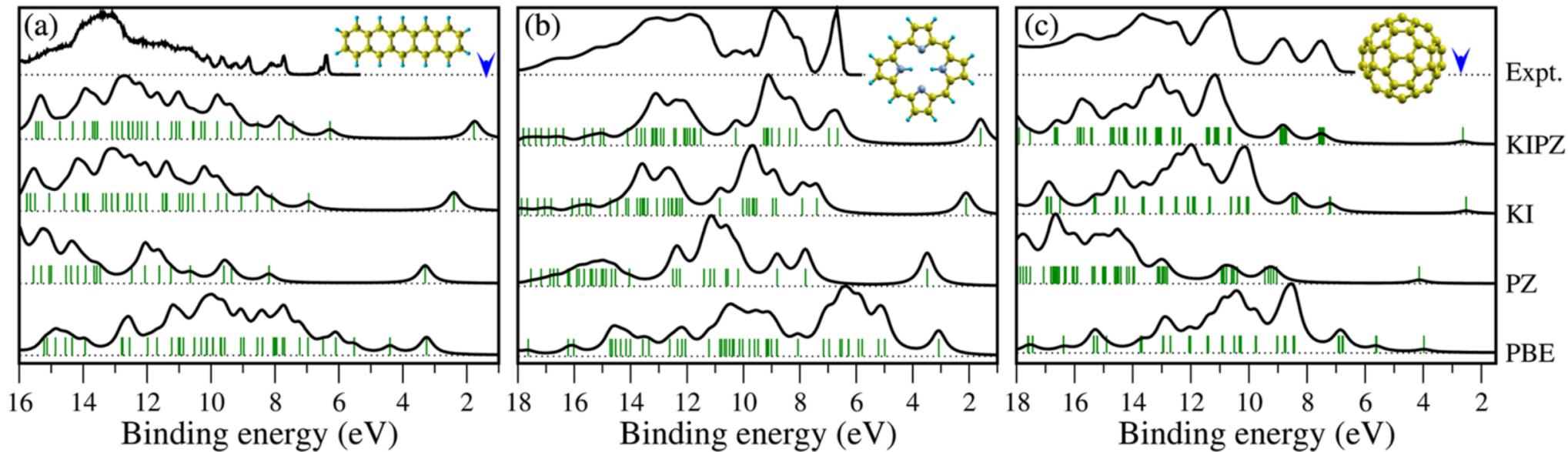
Ionisation potentials¹



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

Molecular systems

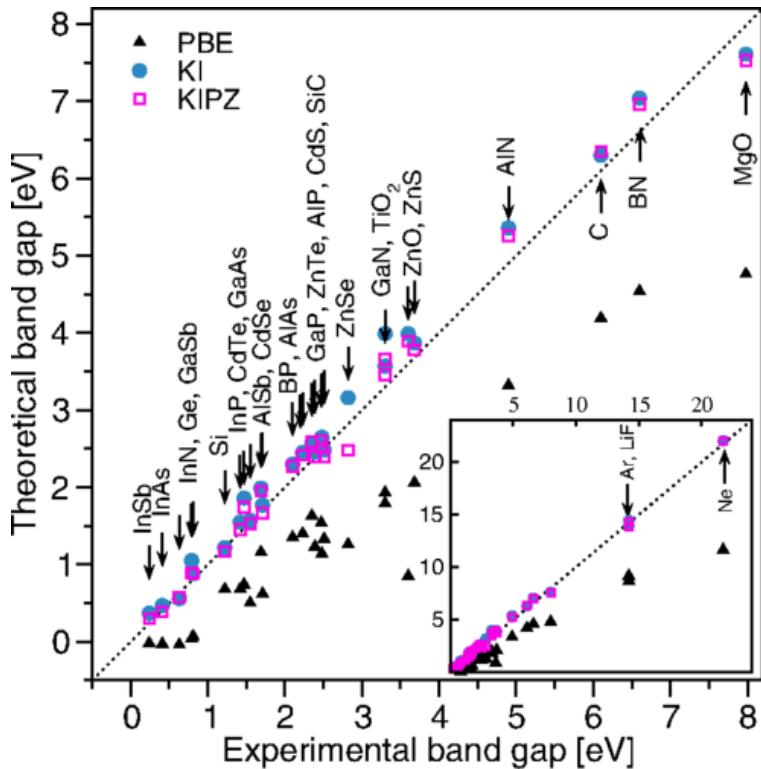
UV photoemission spectra¹



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

Extended systems

Prototypical semiconductors and insulators¹



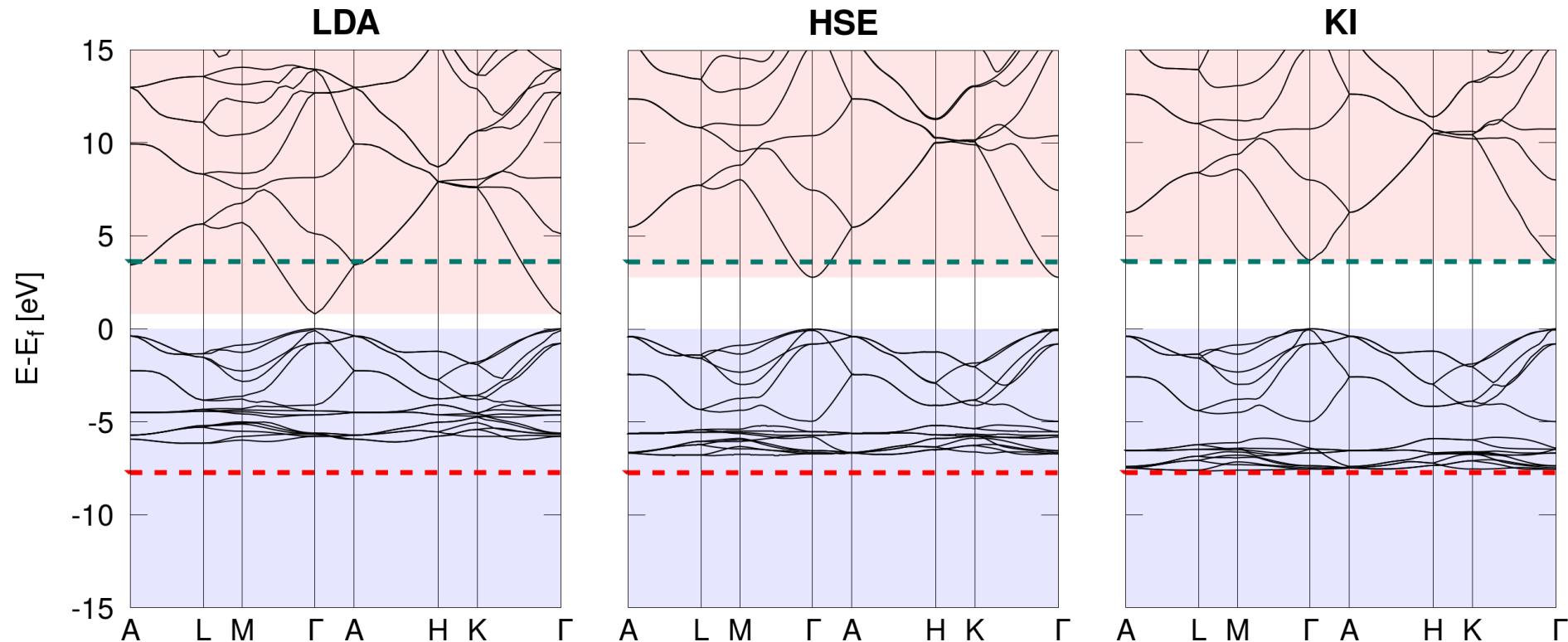
	PBE	G_0W_0	KI	KIPZ	$QS\tilde{G}W$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

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



Extended systems

ZnO



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



Extended systems

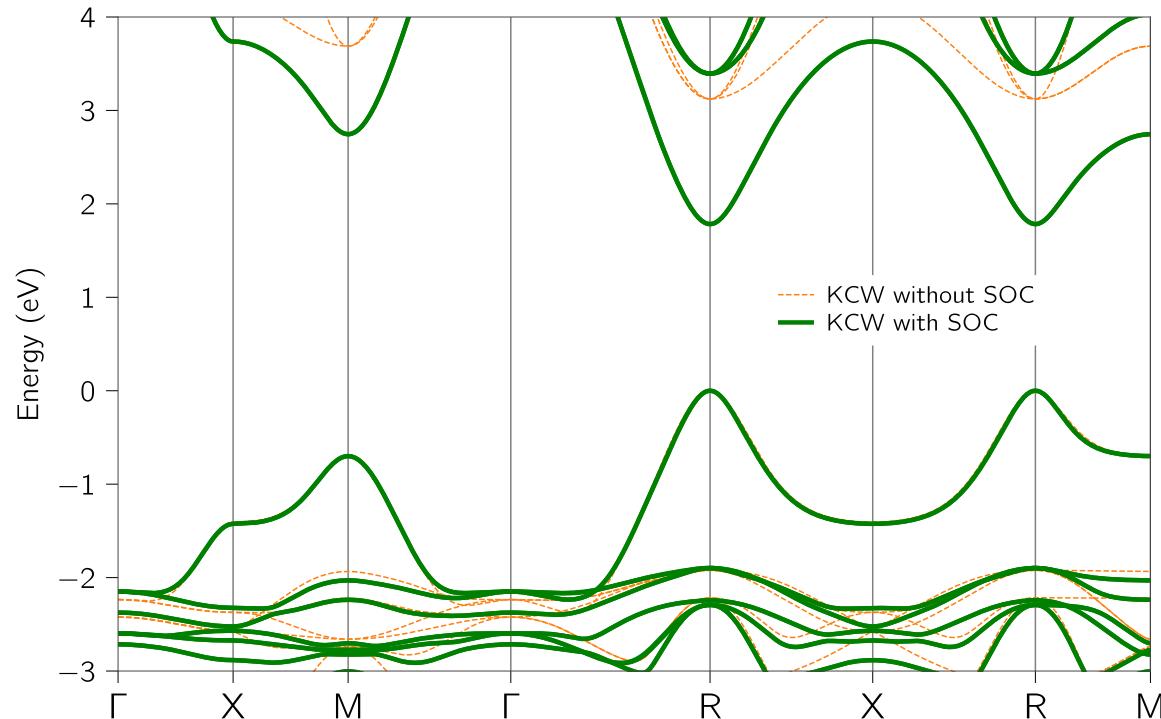
ZnO

	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
Δ	4.15				4.99	5.3

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

Extended systems

Spin-orbit coupling

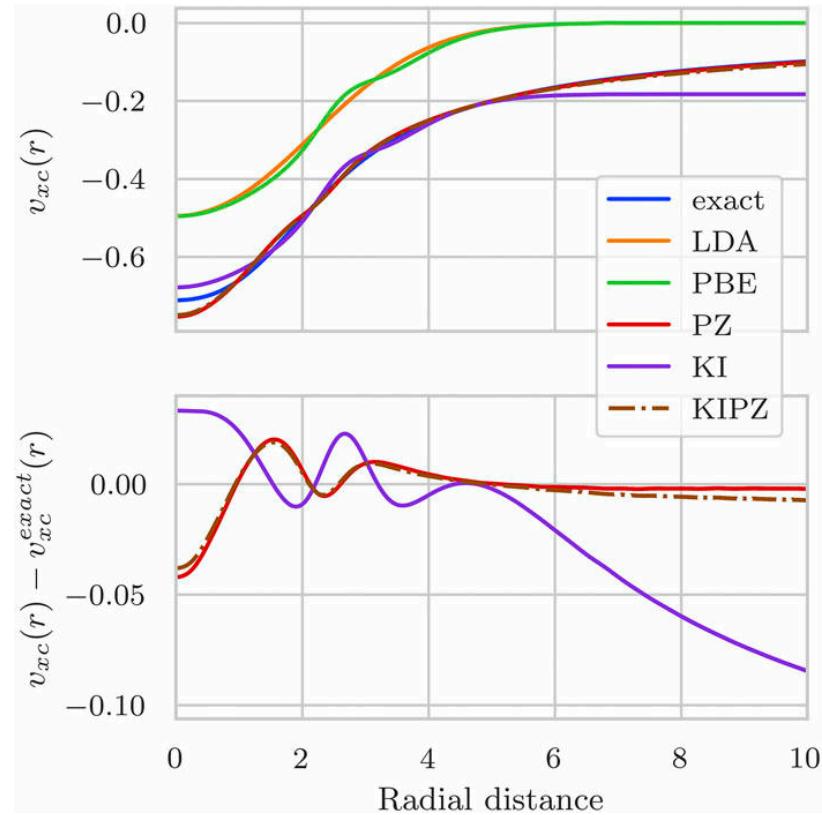


¹A. Marrazzo et al. Phys. Rev. Res. **6**, 33085 (2024)



Model systems

Hooke's atom¹



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

Caveats



Limitations

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



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- empty state localisation in the bulk limit



Limitations

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



Resonance with other efforts

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

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

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

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

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

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



Electronic screening via machine learning



Electronic screening via machine learning

A key ingredient of Koopmans functional calculations are the screening parameters:

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

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

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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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- must be computed ab initio via ΔSCF ¹ or DFPT²

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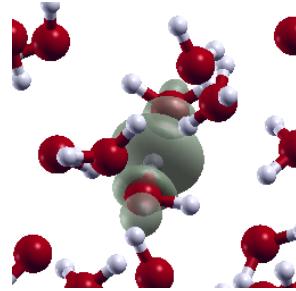
- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital
- must be computed ab initio via ΔSCF ¹ or DFPT²
- corresponds to the vast majority of the computational cost of Koopmans functional calculation

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²N. 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



power spectrum decomposition

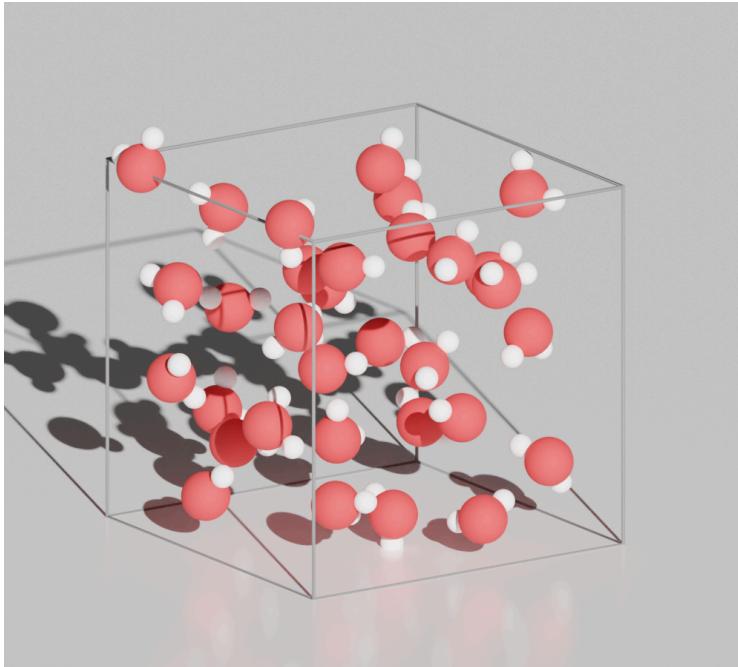
$$\begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix} \xrightarrow{\text{ridge regression}} \alpha_i$$

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

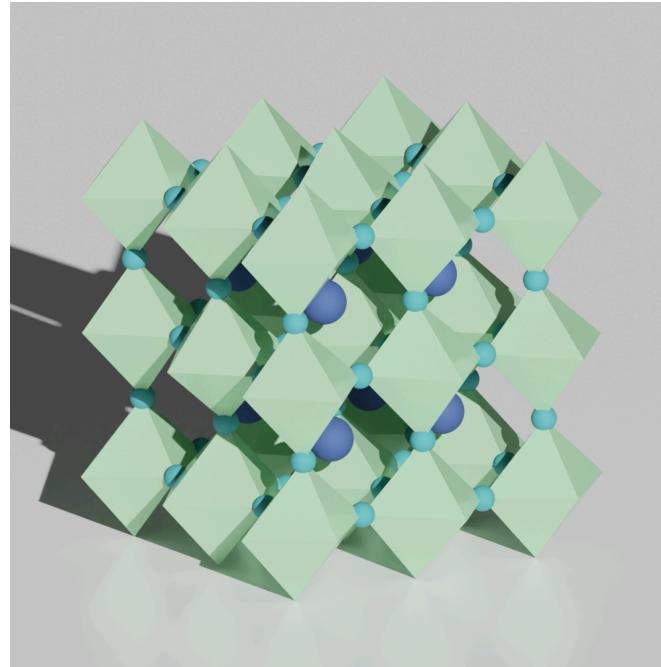
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

Two test systems



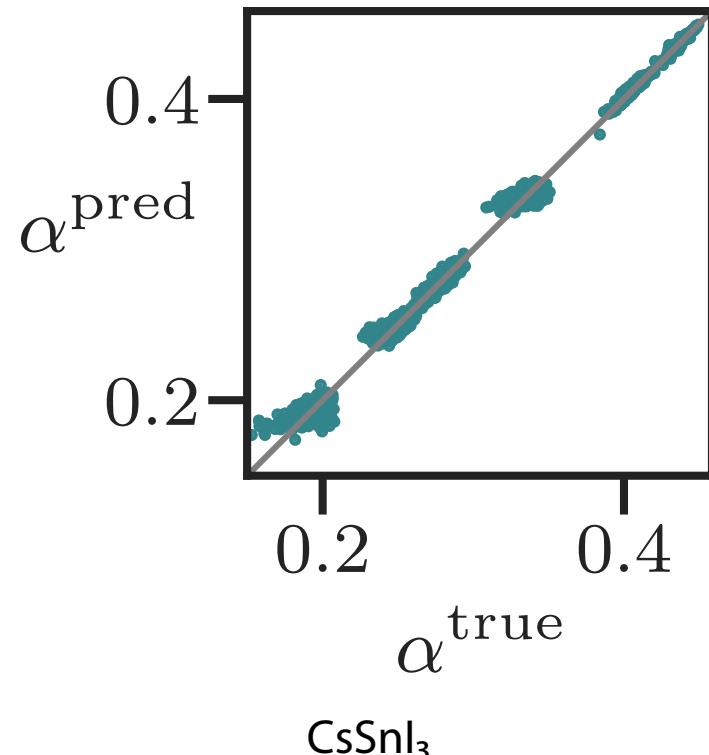
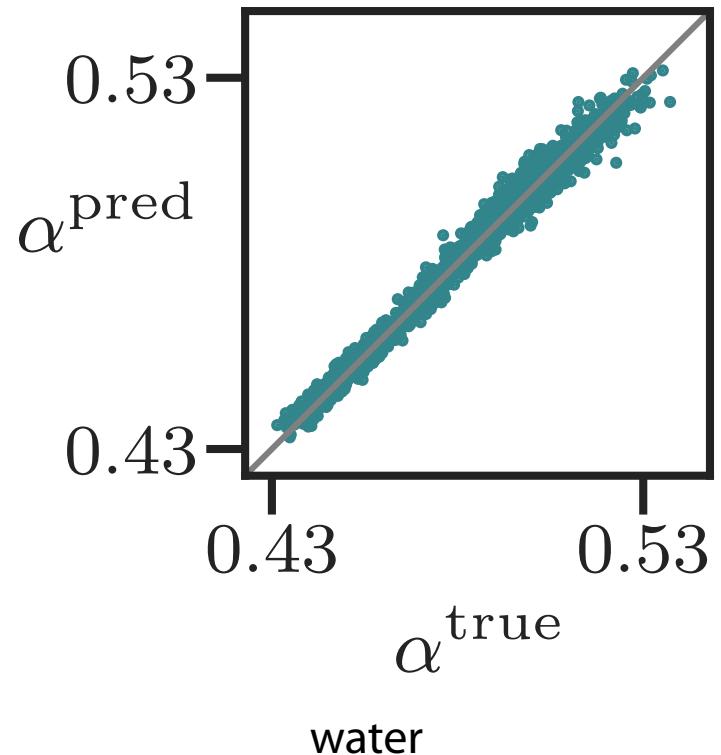
water



CsSnI₃

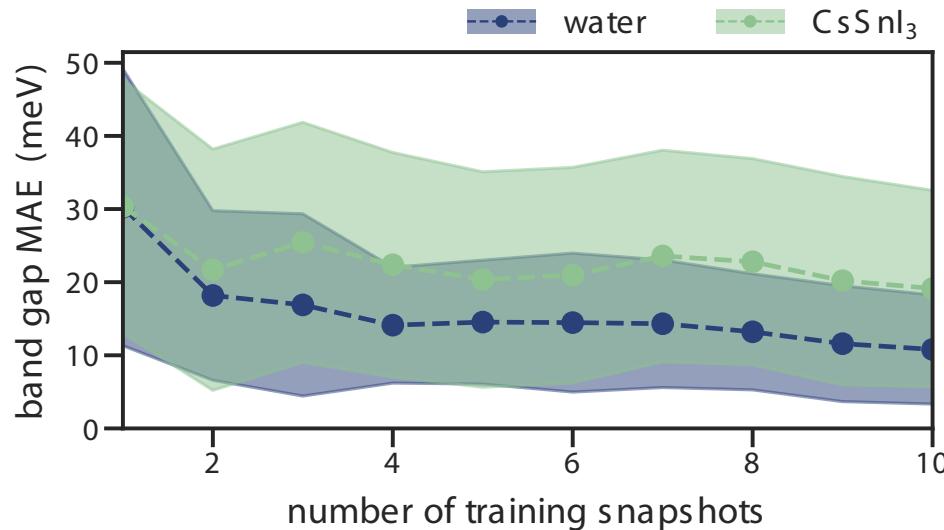
¹Y. Schubert et al. npj Comput Mater **10**, 1–12 (2024)

Results: screening parameters

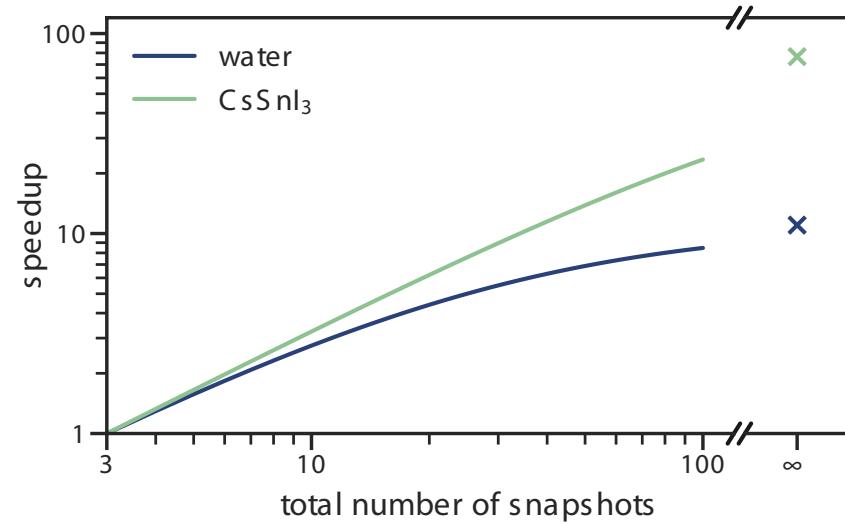


¹Y. Schubert et al. npj Comput Mater **10**, 1–12 (2024)

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 $\mathcal{O}(100)$

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

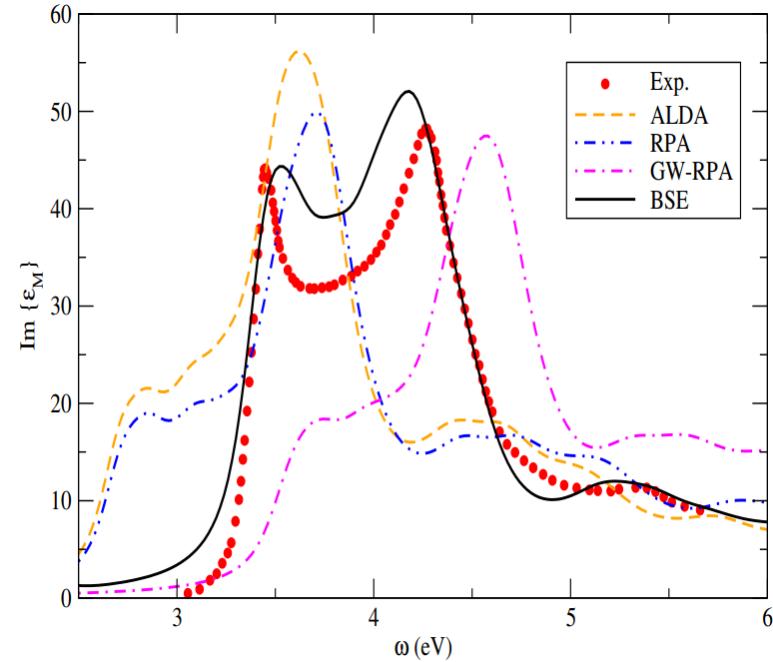
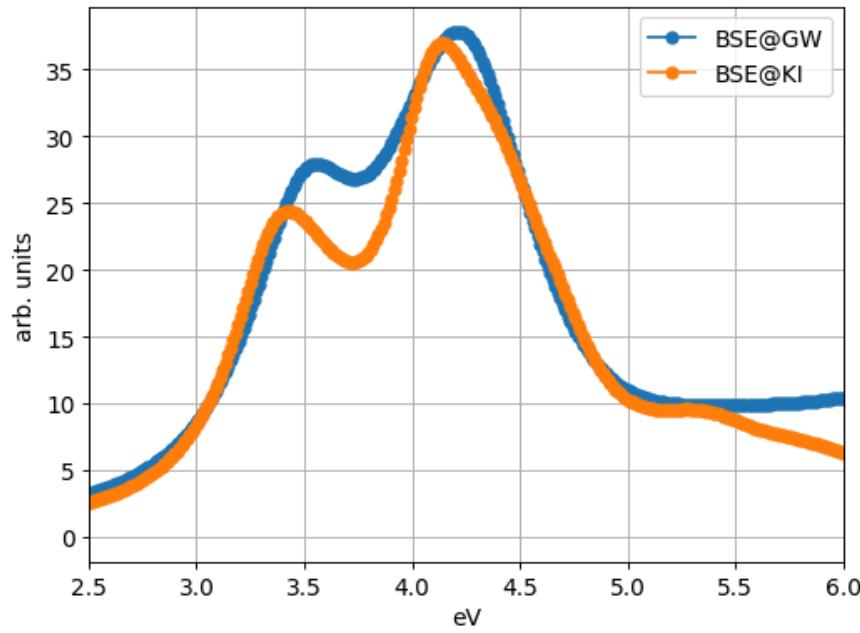


Going beyond single-particle excitations



Preliminary results

The idea: solve the BSE, skipping GW and instead using Koopmans eigenvalues¹



N.B. using DFT response

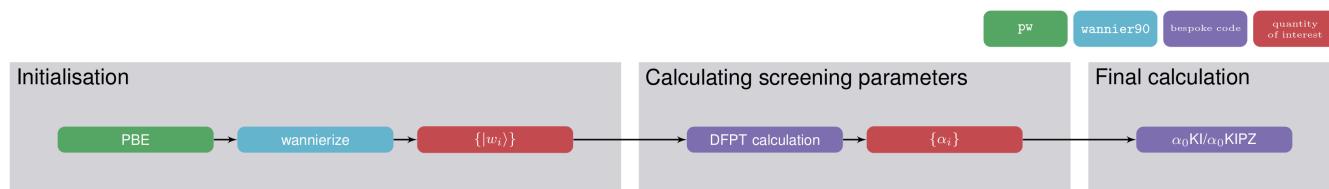
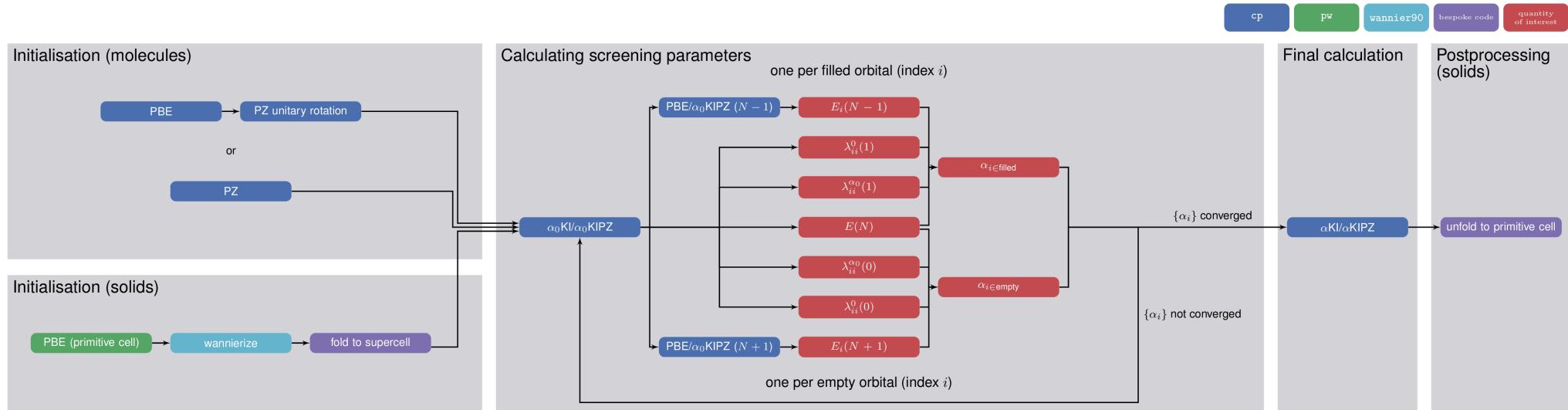
¹P. Lautenschlager et al. Phys. Rev. B **36**, 4821–4830 (1987), F. Sottile. (École Polytechnique, 2003).



Miscellaneous



The general workflows



Connections with approximate self-energies¹

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-energies¹

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-energies¹

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 approximate self-energies¹

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-energies¹

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

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

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

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

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

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

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

