



Center for Scientific Computing,  
Theory and Data

# Koopmans functionals

## Baking localised charged excitation energies into DFT

Edward Linscott

CECAM Workshop on Excited States, 7 November 2024

# Outline



Koopmans functionals: a correction to DFT tailored to improve spectral properties

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  - what do we need to do to go beyond charged excitations?
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# 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

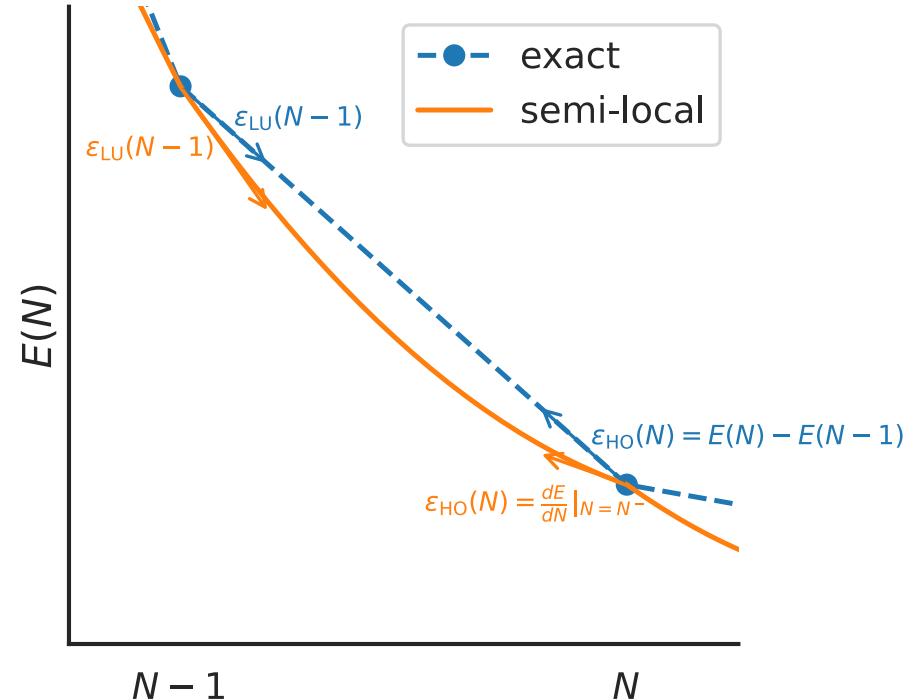
# Theory

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

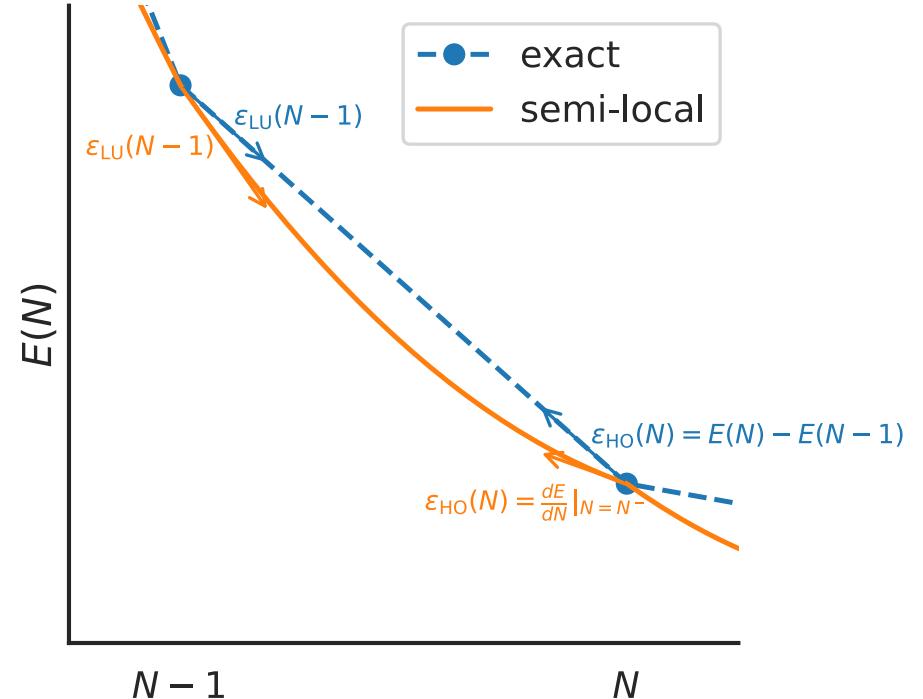
- independent of  $f_i$
- equal to  $\Delta E$  of explicit electron addition/removal

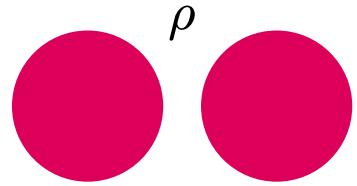


# Theory

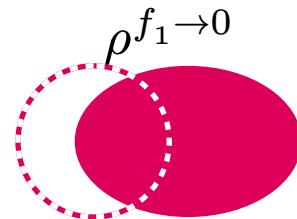
$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \left\{ - \underbrace{(E^{\text{DFT}}[\rho] - E[\rho^{f_i \rightarrow 0}])}_{\text{remove non-linear dependence}} + \underbrace{f_i(E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}])}_{\text{restore linear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

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

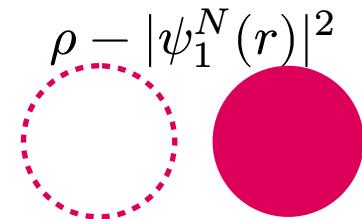




$N$ -electron solution



what we'd like to evaluate



what we can quickly  
evaluate

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

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

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>

<sup>1</sup>N. L. Nguyen *et al.* *Physical Review X* **8**, 21051–21052 (2018), R. De Gennaro *et al.* *Physical Review B* **106**, 35106–35107 (2022)

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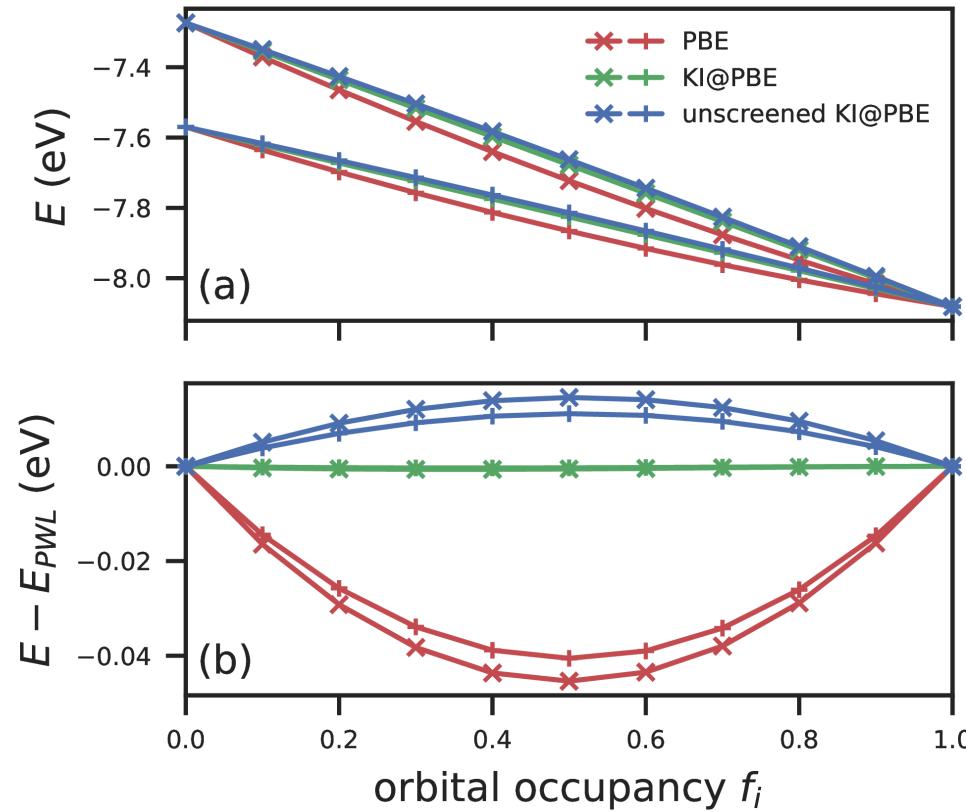
which can be efficiently computed via DFPT<sup>3</sup> ... but is still the bulk of the computational cost (can use machine-learning)

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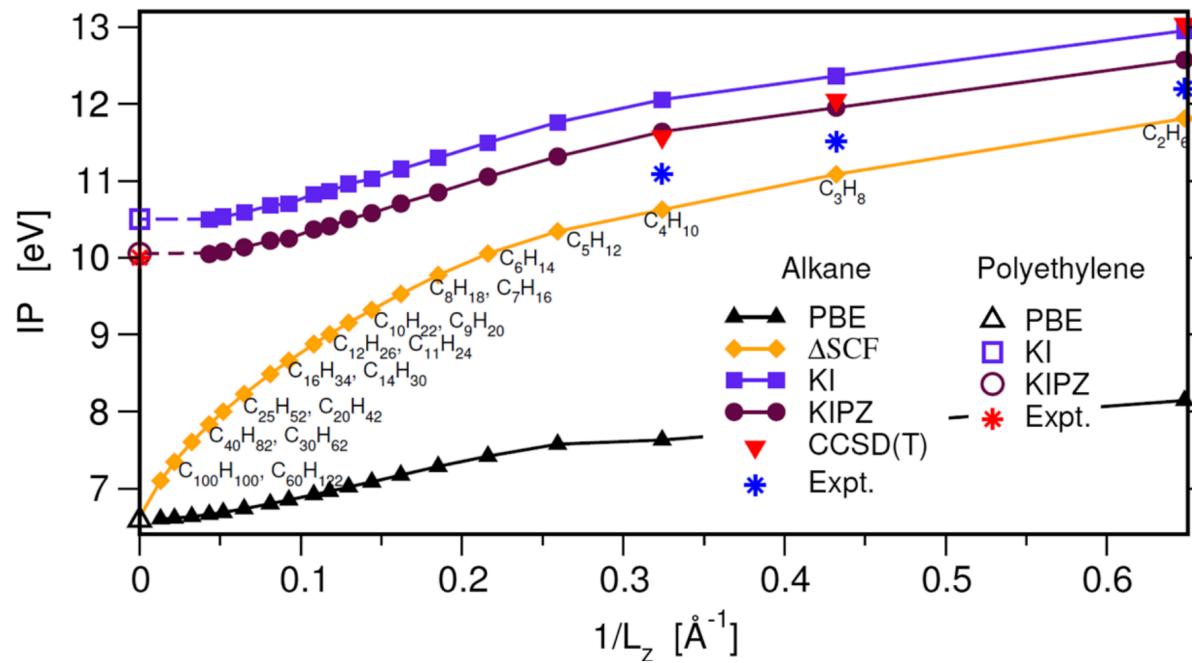
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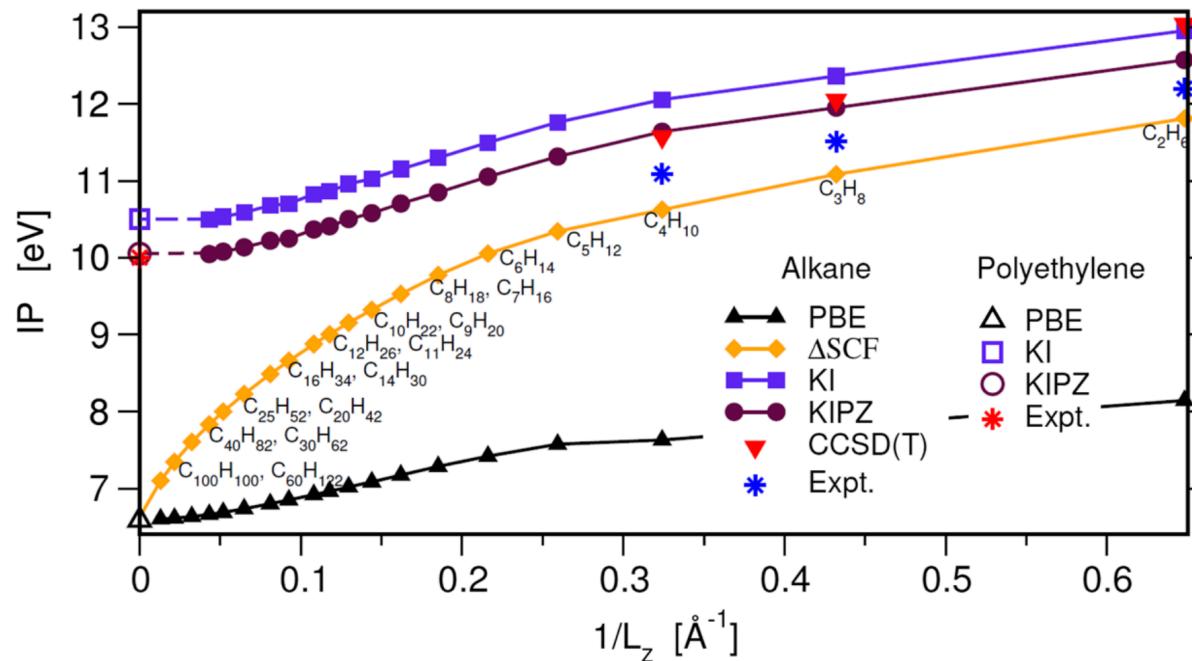


# Issues with extended systems



<sup>1</sup>N. L. Nguyen *et al.* *Physical Review X* **8**, 21051–21052 (2018)

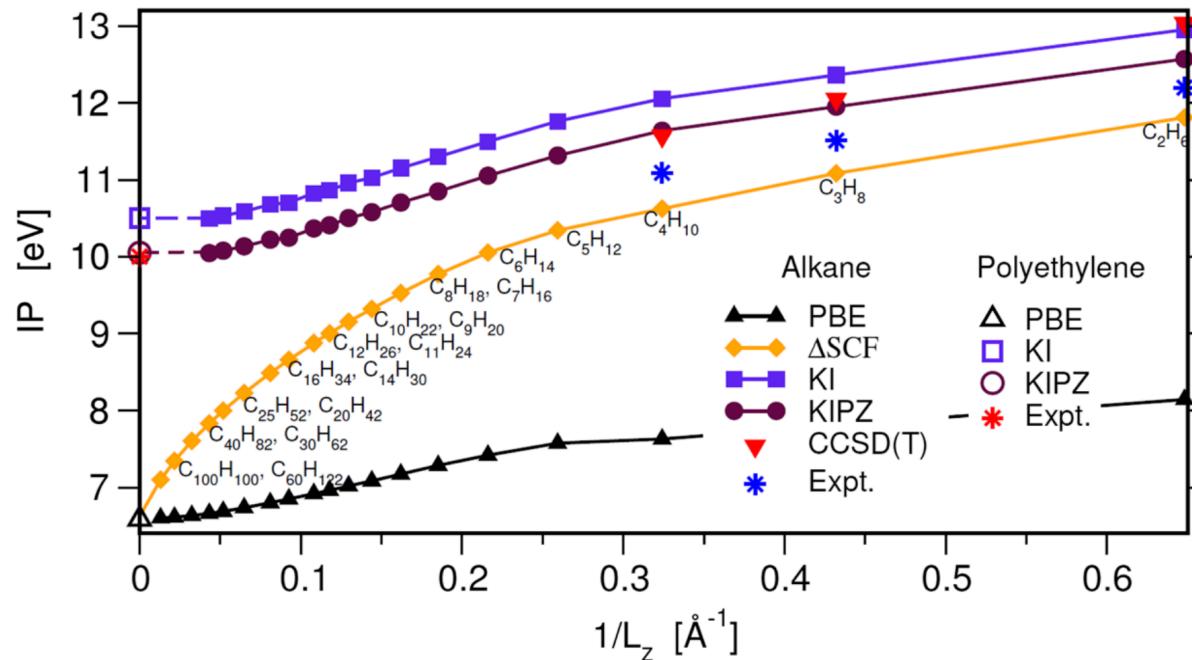
# Issues with extended systems



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

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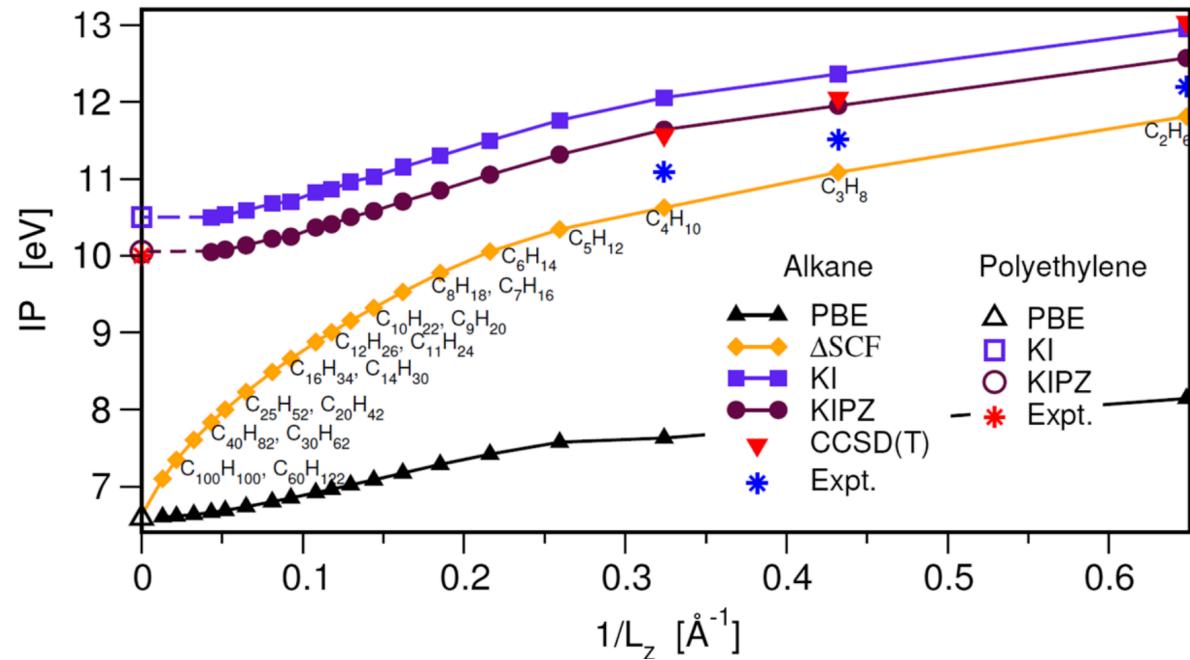
# Issues with extended systems



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>

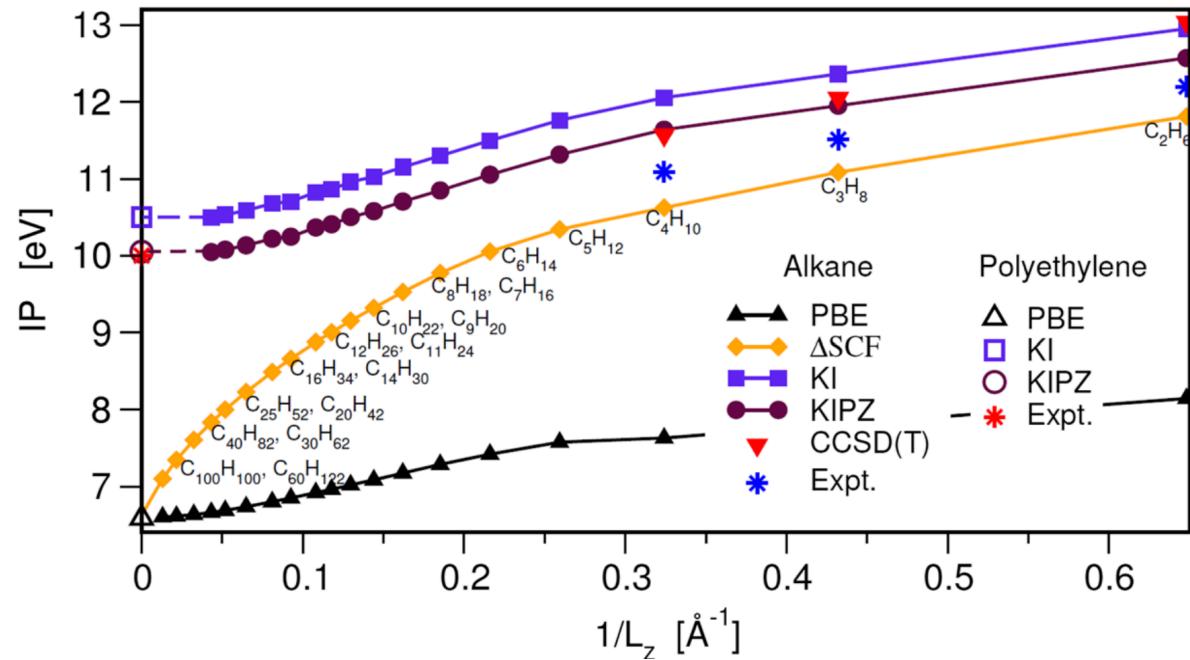
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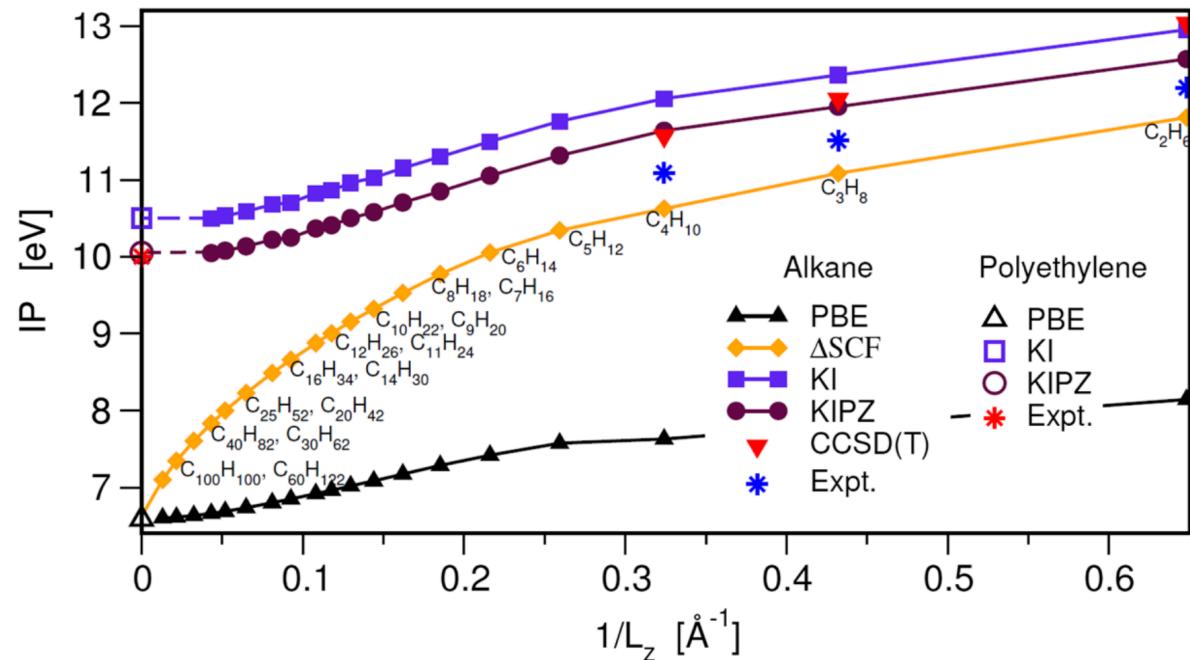
Two options:

# 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

- minimisation gives rise to localised orbitals, so we want to first Wannierise to initialise (or even define) these orbitals
- 
- 
- 

<sup>1</sup>N. Marzari *et al.* *Reviews of Modern Physics* **84**, 1419–1475 (2012)

<sup>2</sup>A. Ferretti *et al.* *Physical Review B* **89**, 195134–195135 (2014)

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- we know  $\hat{H}|\varphi_i\rangle$  but we don't know  $\hat{H}$
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- we know  $\hat{H}|\varphi_i\rangle$  but we don't know  $\hat{H}$
- we can use MLWFs<sup>1</sup>
- a natural generalisation in the direction of spectral functional theory<sup>2</sup>

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## A brief summary

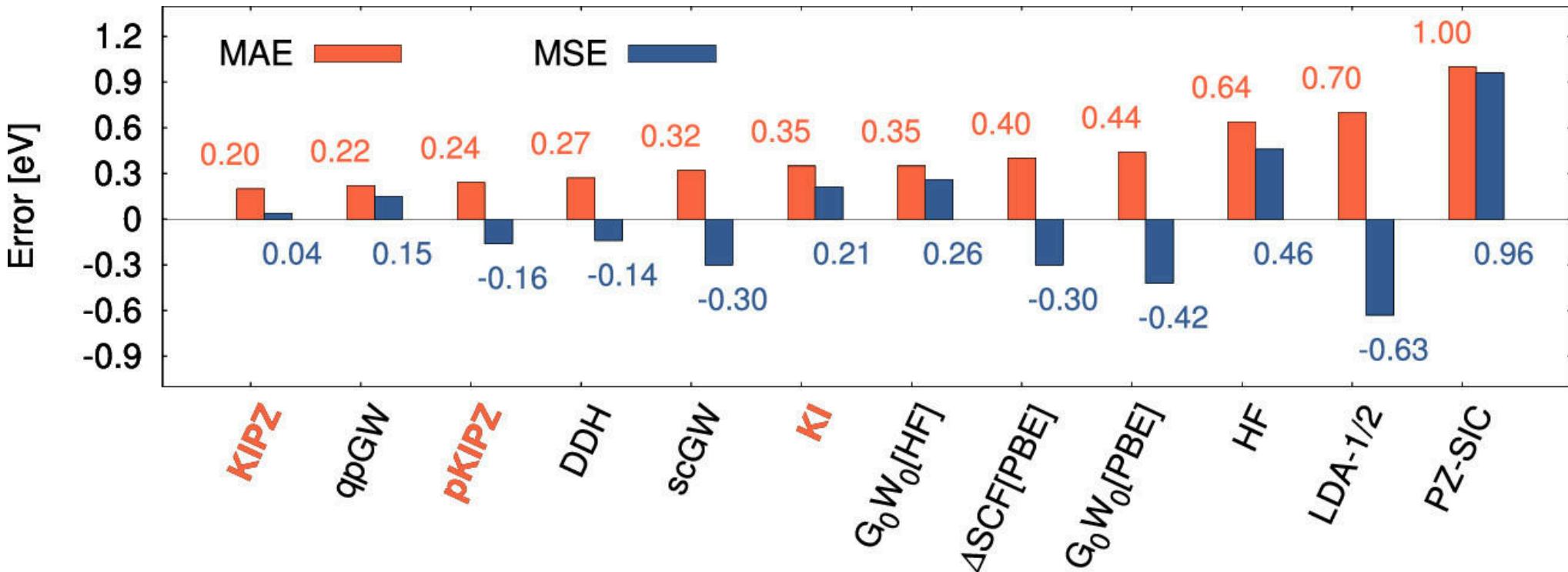
$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}[\rho - \rho_i]}) \right. \\ \left. + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

- an orbital-by-orbital correction to DFT
- localised charge excitations baked into derivatives
- total energy unchanged!
- screening parameters
- orbital-density-dependence

# Results

# Molecular systems

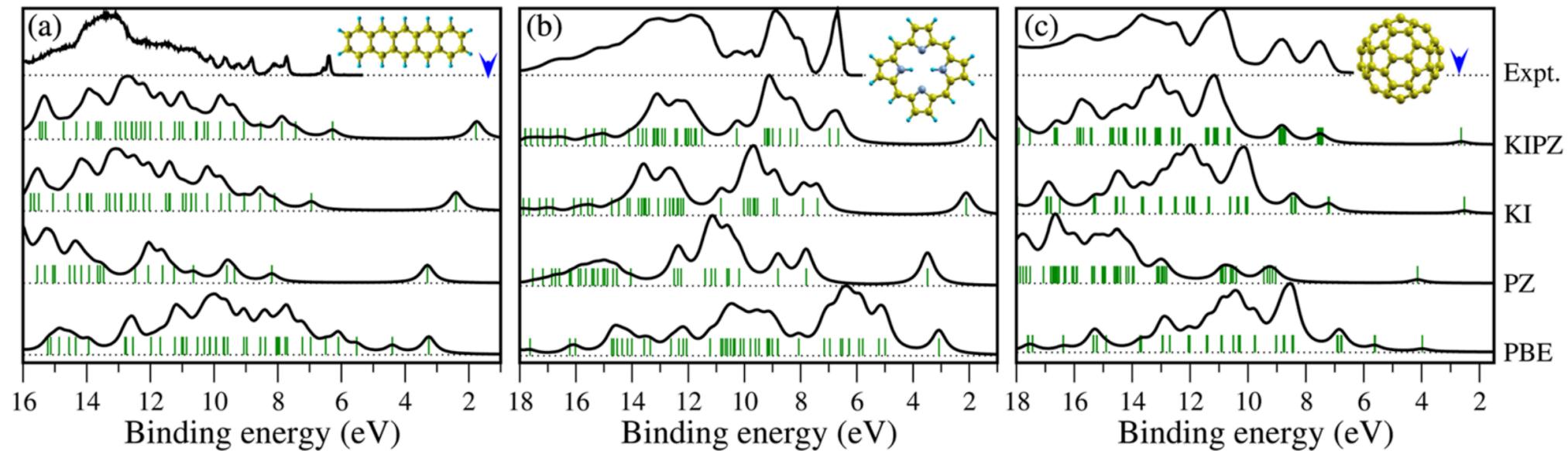
## Ionisation potentials<sup>1</sup>



<sup>1</sup>N. Colonna et al. *Journal of Chemical Theory and Computation* **15**, 1905–1914 (2019)

# Molecular systems

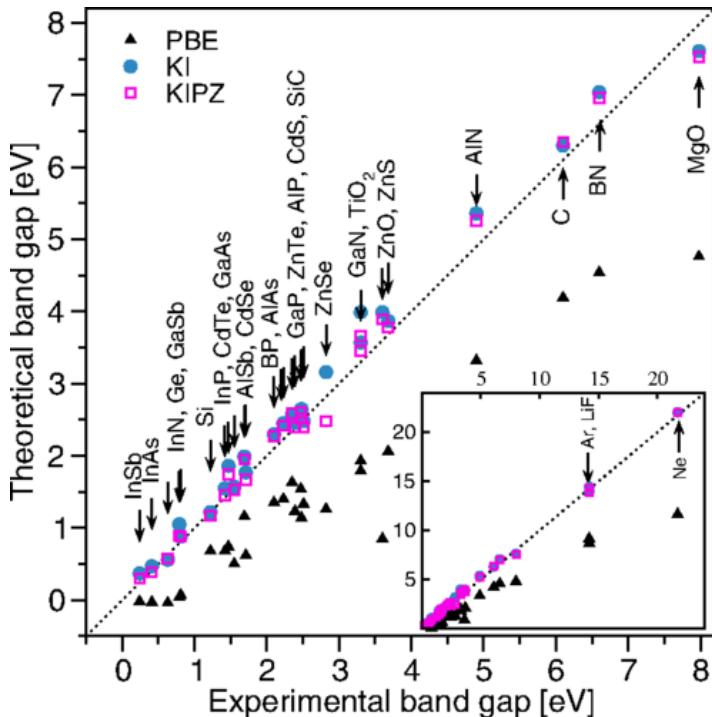
## UV photoemission spectra<sup>2</sup>



<sup>2</sup>N. L. Nguyen et al. *Physical Review Letters* **114**, 166405–166406 (2015)

# Extended systems

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

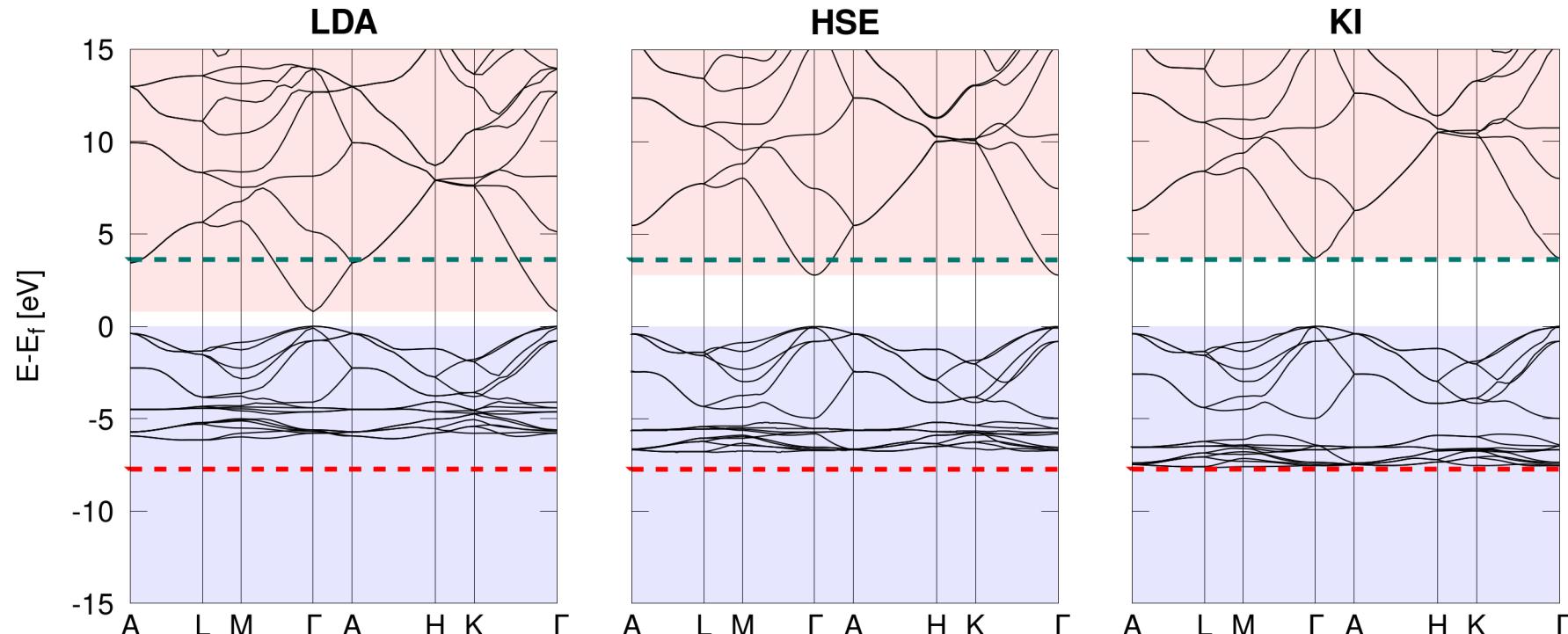


	PBE	$G_0W_0$	KI	KIPZ	$QS\tilde{G}W$
$E_{\text{gap}}$	2.54	0.56	<b>0.27</b>	<b>0.22</b>	0.18
IP	1.09	0.39	<b>0.19</b>	<b>0.21</b>	0.49

<sup>1</sup>N. L. Nguyen et al. *Physical Review X* **8**, 21051–21052 (2018)

# Extended systems

$\text{ZnO}^1$



<sup>1</sup>N. Colonna et al. *Journal of Chemical Theory and Computation* **18**, 5435–5448 (2022)

# Extended systems



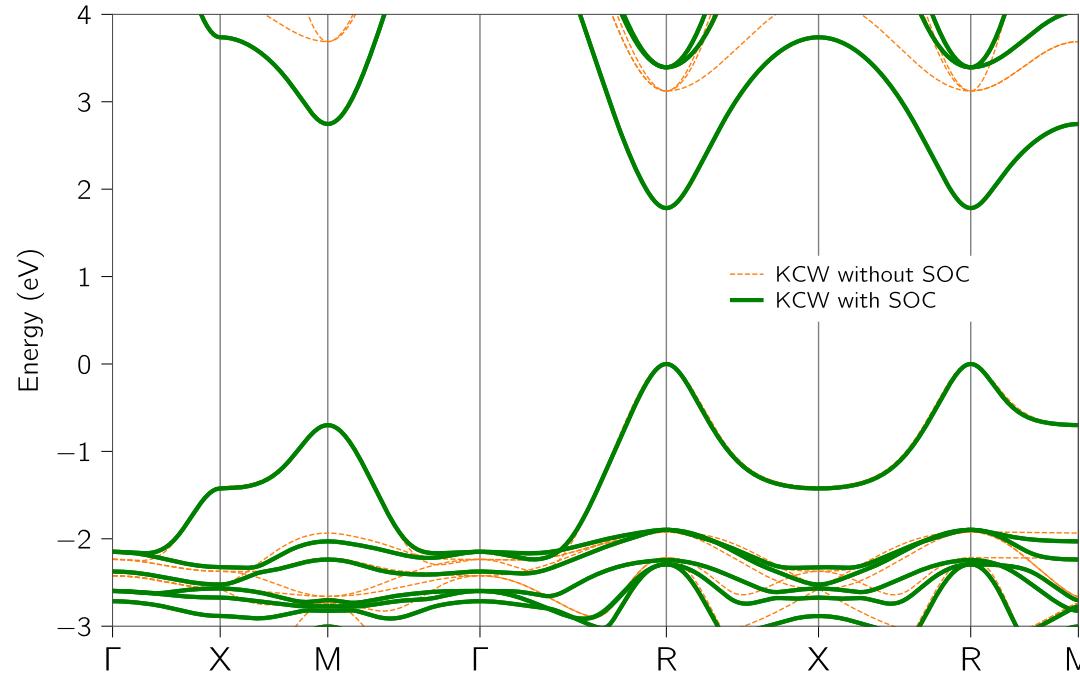
## ZnO<sup>1</sup>

	LDA	HSE	GW <sub>0</sub>	scG $\tilde{W}$	KI	exp
$E_{\text{gap}}$	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.* *Journal of Chemical Theory and Computation* **18**, 5435–5448 (2022)

# Extended systems

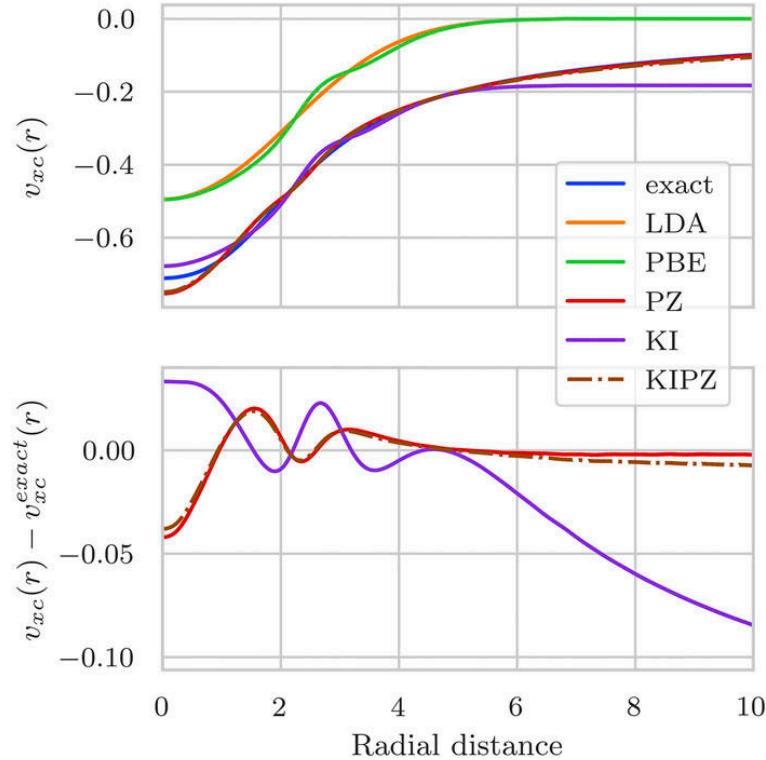
## Spin-orbit coupling<sup>1</sup>



<sup>1</sup>A. Marrazzo *et al.* (2024) doi:10.48550/arXiv.2402.14575

# Model systems

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



<sup>1</sup>Y. Schubert et al. *The Journal of Chemical Physics* **158**, 144113–144114 (2023)

# Caveats

## Limitations

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

# Resonance with other efforts



- Wannier transition state method of Anisimov and 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.* *Physical Review B* **72**, 75125–75126 (2005)

<sup>2</sup>L. Kronik *et al.* *Journal of Chemical Theory and Computation* **8**, 1515–1531 (2012), D. Wing *et al.* *Proceedings of the National Academy of Sciences* **118**, e2104556118 (2021)

<sup>3</sup>E. Kraisler *et al.* *Physical Review Letters* **110**, 126403–126404 (2013)

<sup>4</sup>J. Ma *et al.* *Scientific Reports* **6**, 24924–24925 (2016)

<sup>5</sup>J. H. Skone *et al.* *Physical Review B* **93**, 235106–235107 (2016)

<sup>6</sup>C. Li *et al.* *National Science Review* **5**, 203–215 (2018)

# Electronic screening via machine learning

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

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

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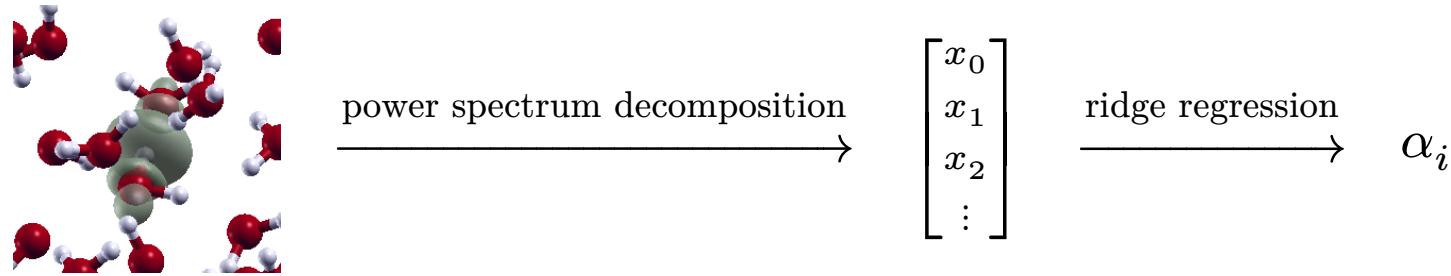
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- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital
- must be computed *ab initio* via  $\Delta\text{SCF}$ <sup>1</sup> or DFPT<sup>2</sup>
- corresponds to the vast majority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

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# The machine-learning framework

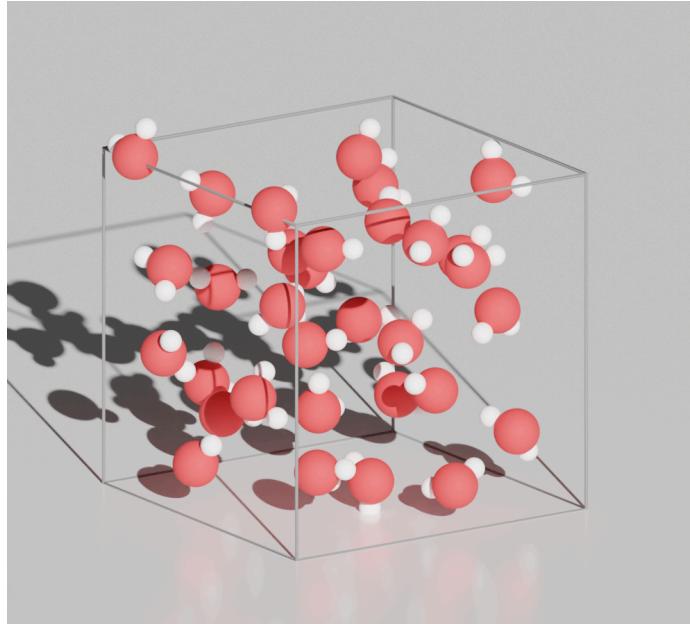


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

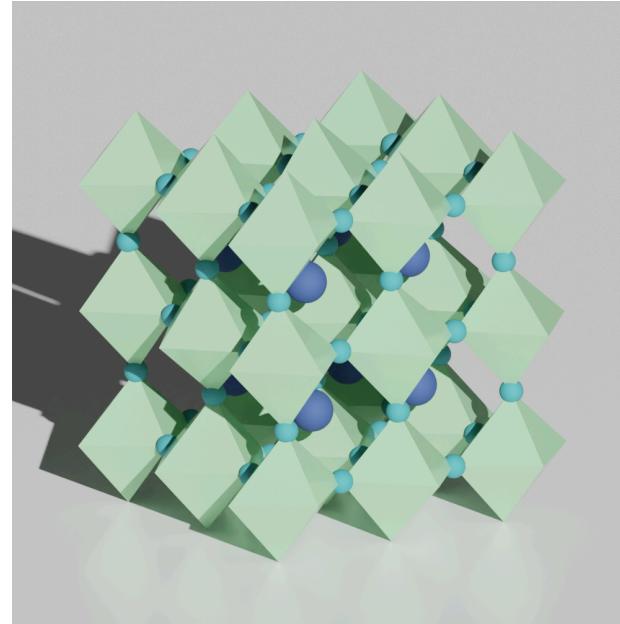
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

<sup>1</sup>Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

## Two test systems



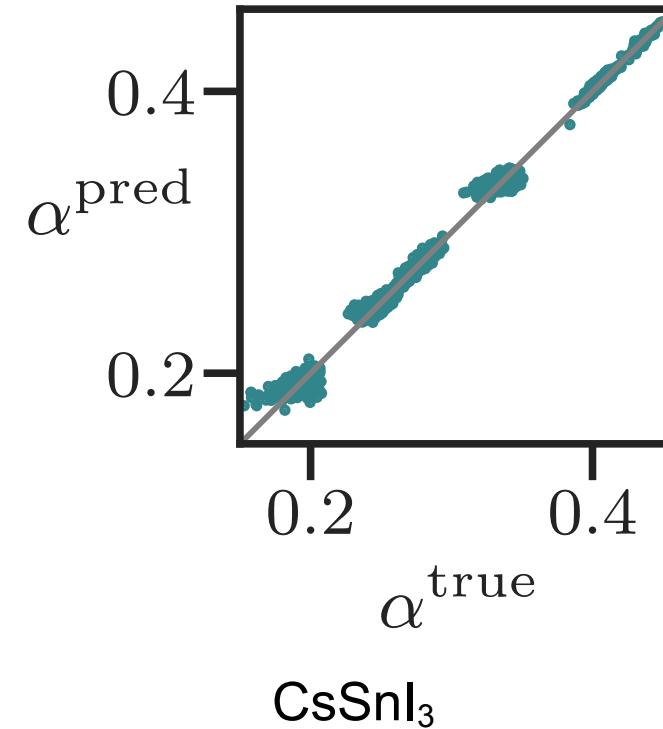
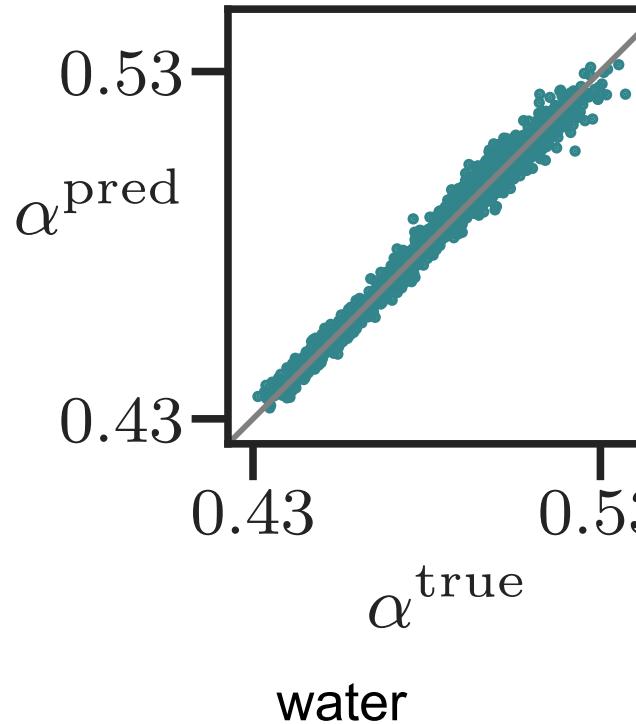
water



CsSnI<sub>3</sub>

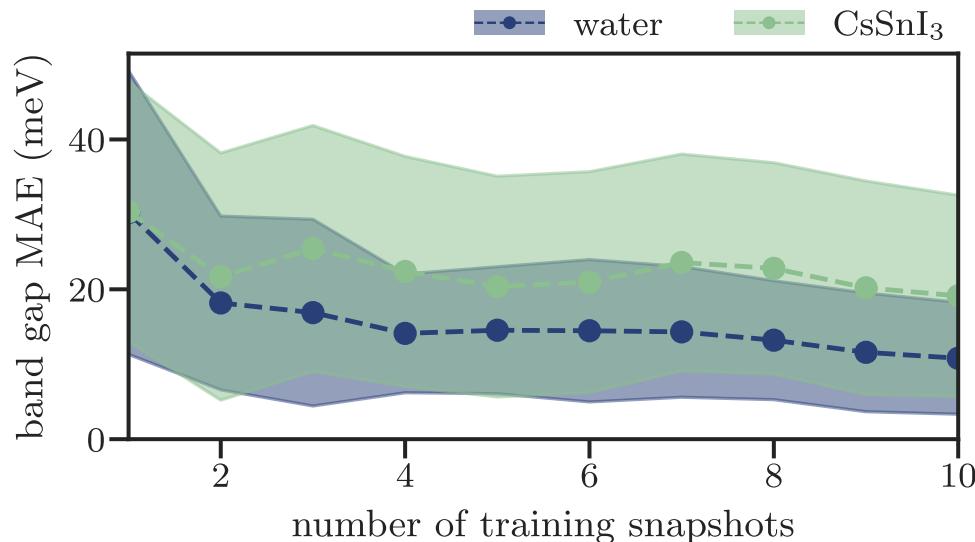
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## Results: screening parameters

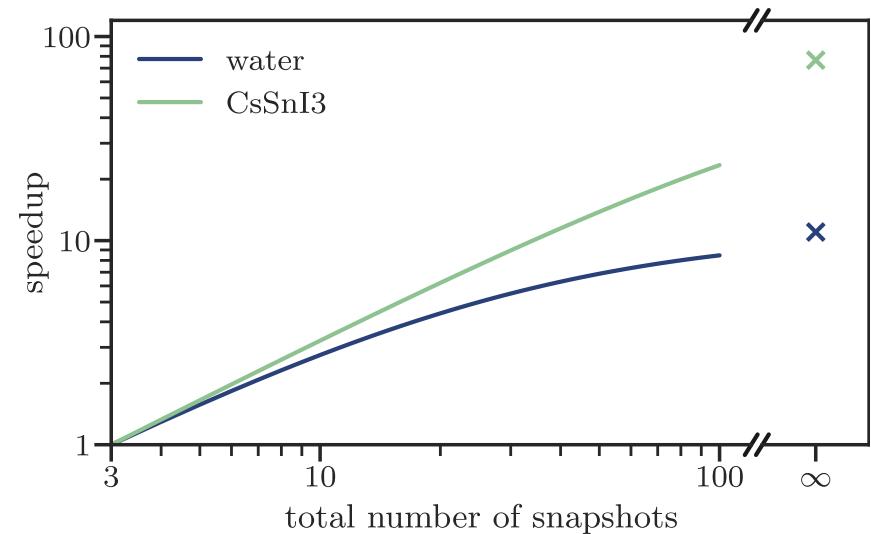


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# Results: balancing accuracy and speedup



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

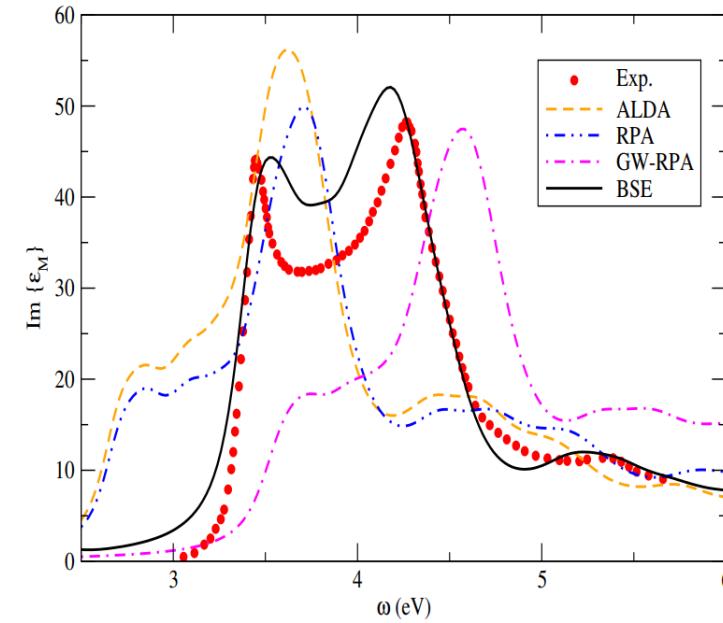
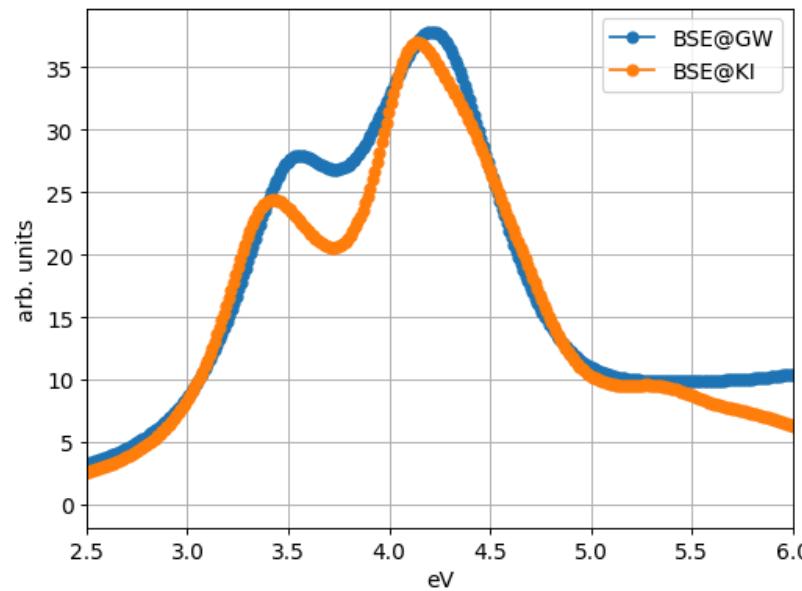


speedup of  $\mathcal{O}(10)$  to  $\mathcal{O}(100)$

<sup>1</sup>Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

# Going beyond single-particle excitations (preliminary)

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.* *Physical Review B* **36**, 4821–4830 (1987), F. Sottile. (2003).

# Making Koopmans functionals accessible

# koopmans

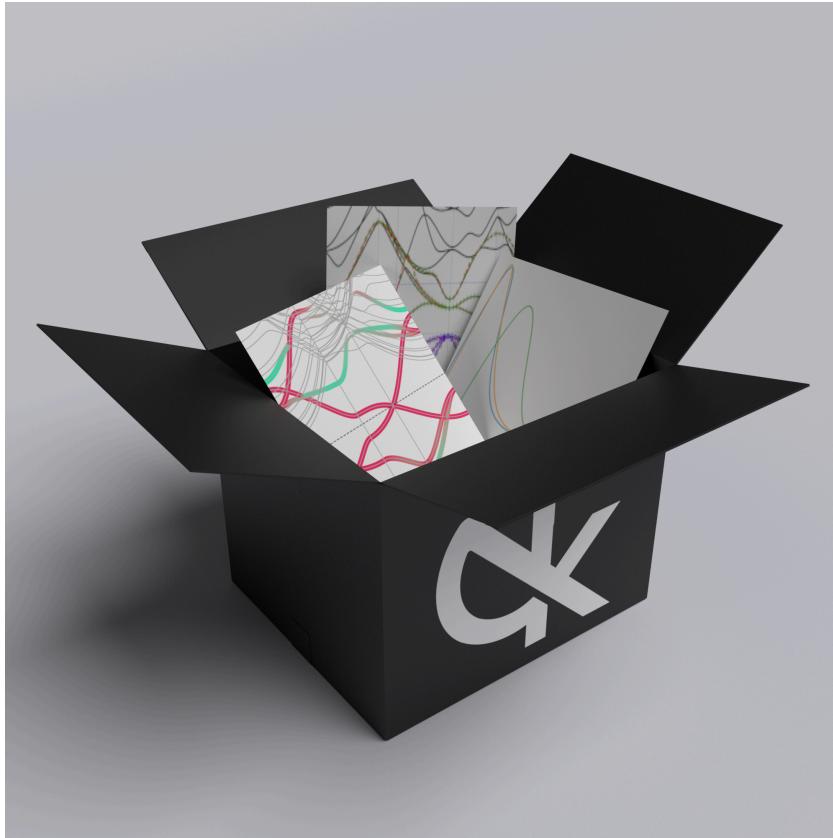
An ongoing effort to make Koopmans functional calculations straightforward for non-experts<sup>1</sup>

- easy installation
- automated workflows
- minimal input required of the user

For more details, go to [koopmans-functionals.org](https://koopmans-functionals.org)

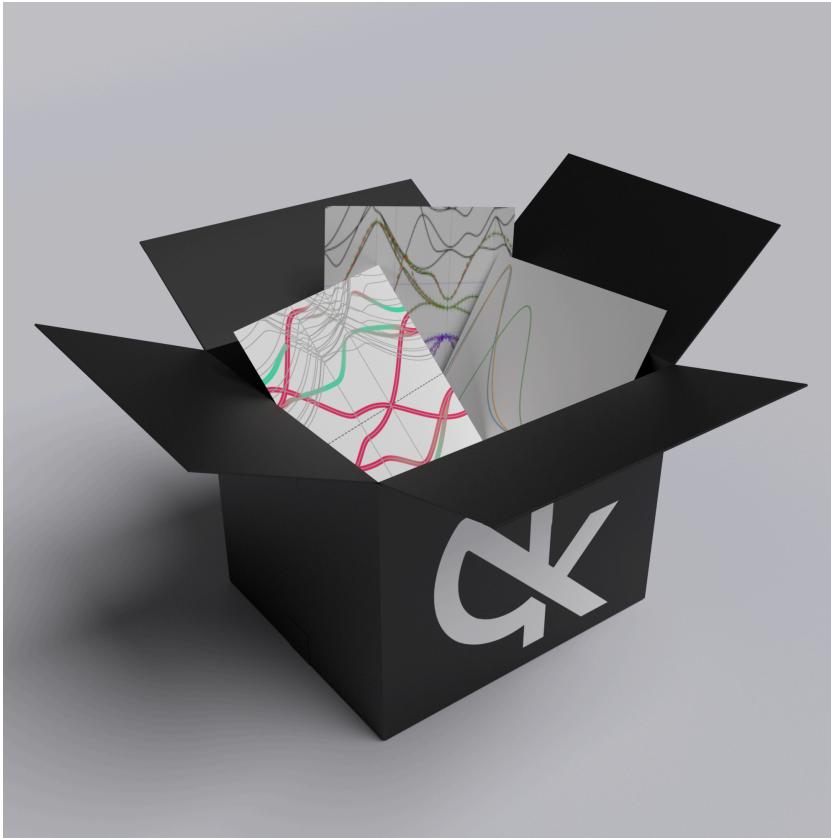
<sup>1</sup>E. B. Linscott *et al.* *Journal of Chemical Theory and Computation* **19**, 7097–7111 (2023)

# Making Koopmans functionals accessible



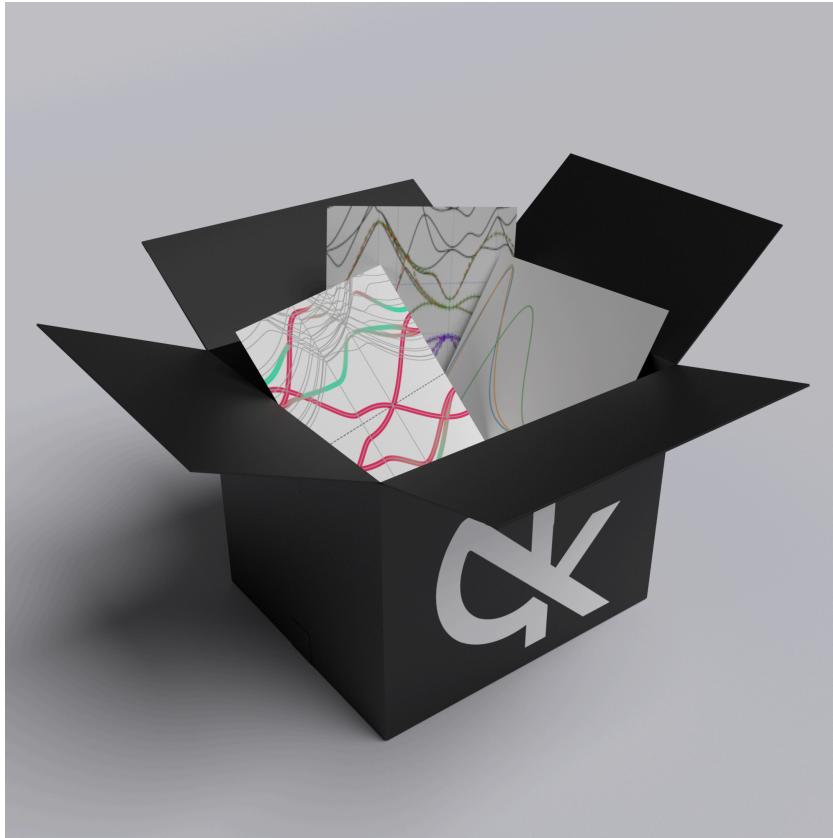
- 1.
- 2.

# Making Koopmans functionals accessible



1. automated Wannerisation
- 2.

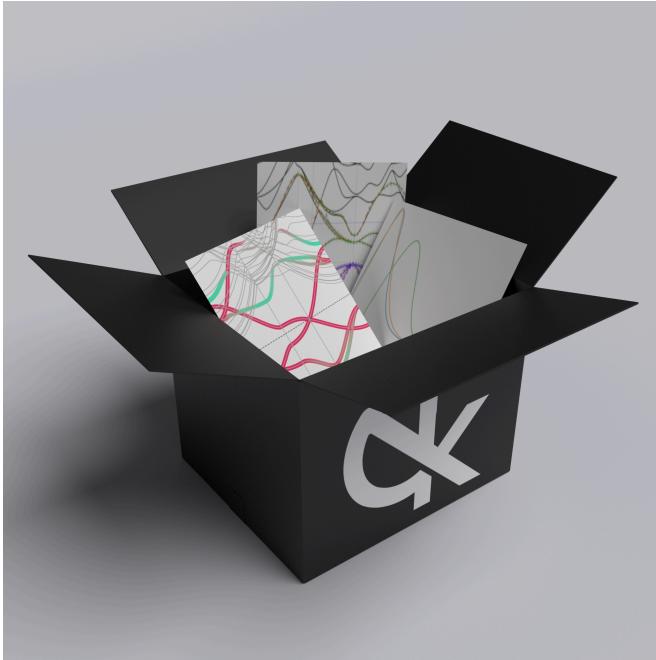
# Making Koopmans functionals accessible



1. automated Wannerisation
2. integration with AiiDA

# Summary

# Summary



Koopmans functionals are

- a powerful tool for computational spectroscopy, and
- are increasingly user-friendly:
  - Wannierisation is more black-box<sup>1</sup>
  - machine learning can be used to calculate the screening parameters<sup>2</sup>
  - parallel and remote execution with AiiDA is on the horizon
  - GUI development is also underway (up next!)

<sup>1</sup>J. Qiao *et al.* *npj Computational Materials* **9**, 208–209 (2023), J. Qiao *et al.* *npj Computational Materials* **9**, 206–207 (2023)

<sup>2</sup>Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

## Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (i.e. the subspace with respect to which we enforce PWL?)
- are off-diagonal corrections appropriate? What form should they take?
- how to extend to metallic systems?
- can we provide a formal basis for the Koopmans correction?
  - GKS
  - spectral functional theory<sup>1</sup>
  - ensemble DFT
  - RDMFT

<sup>1</sup>A. Ferretti *et al.* *Physical Review B* **89**, 195134–195135 (2014)

# Acknowledgements



Nicola Marzari



Nicola Colonna



Junfeng Qiao



Yannick Schubert

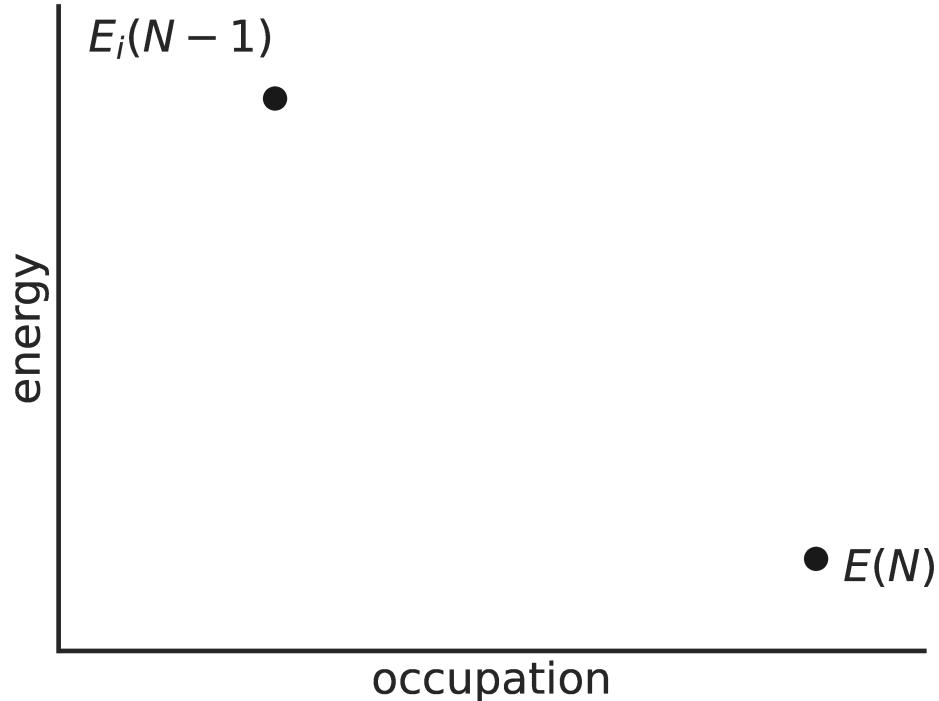


Miki Bonacci

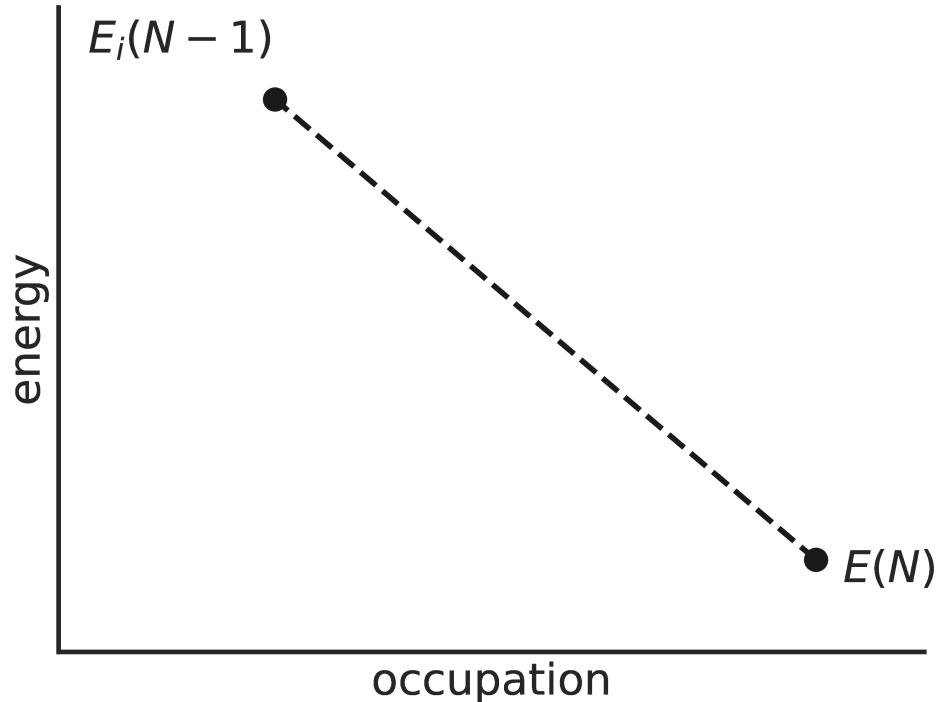


# Spare slides

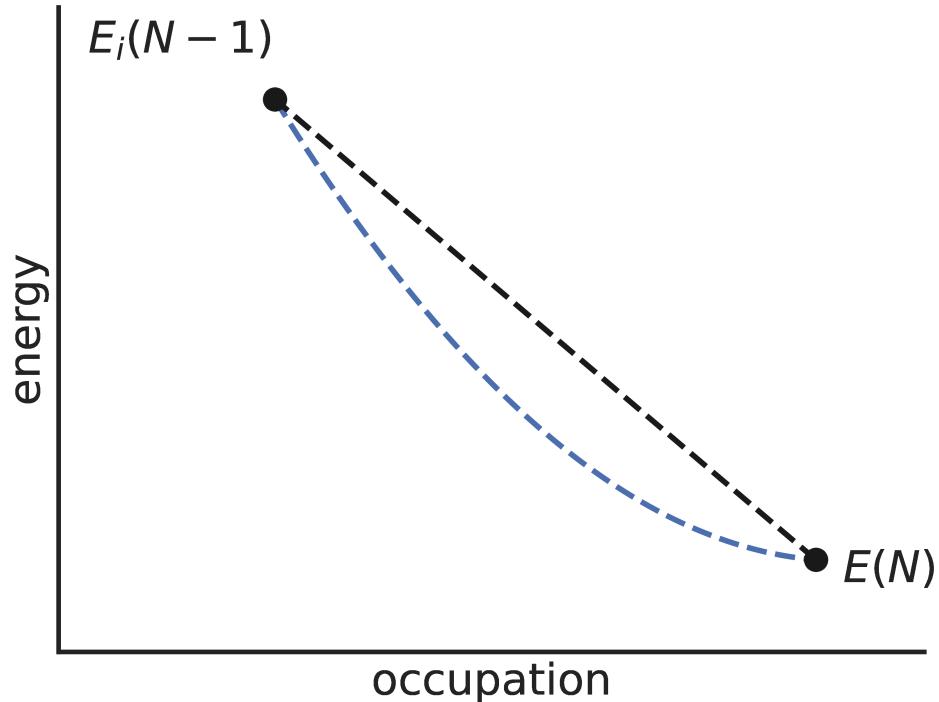
# Calculating screening parameters via SCF



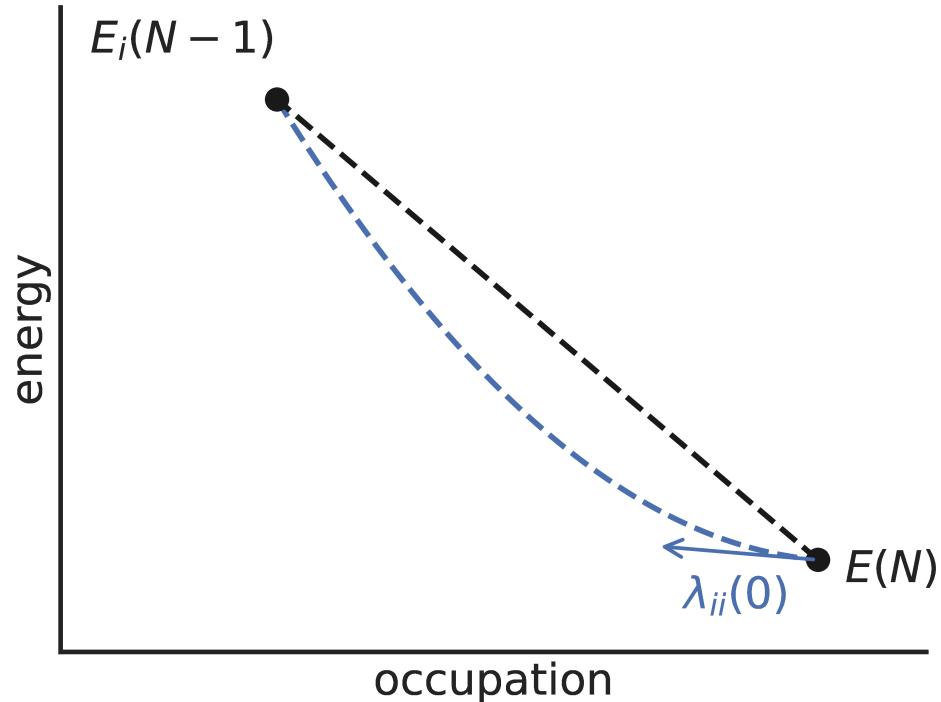
# Calculating screening parameters via SCF



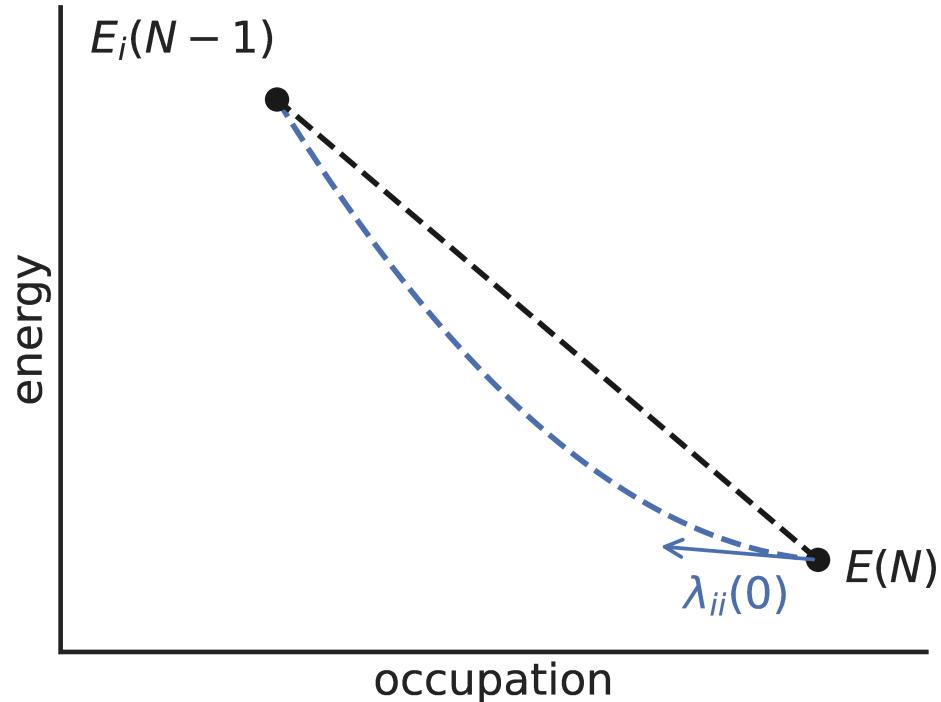
# Calculating screening parameters via SCF



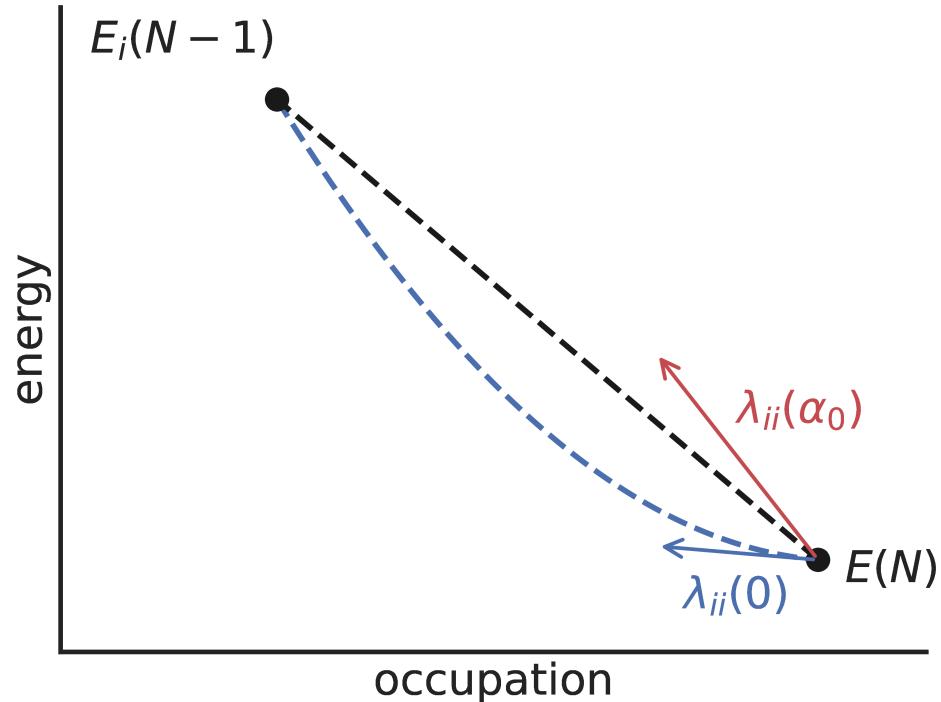
# Calculating screening parameters via SCF



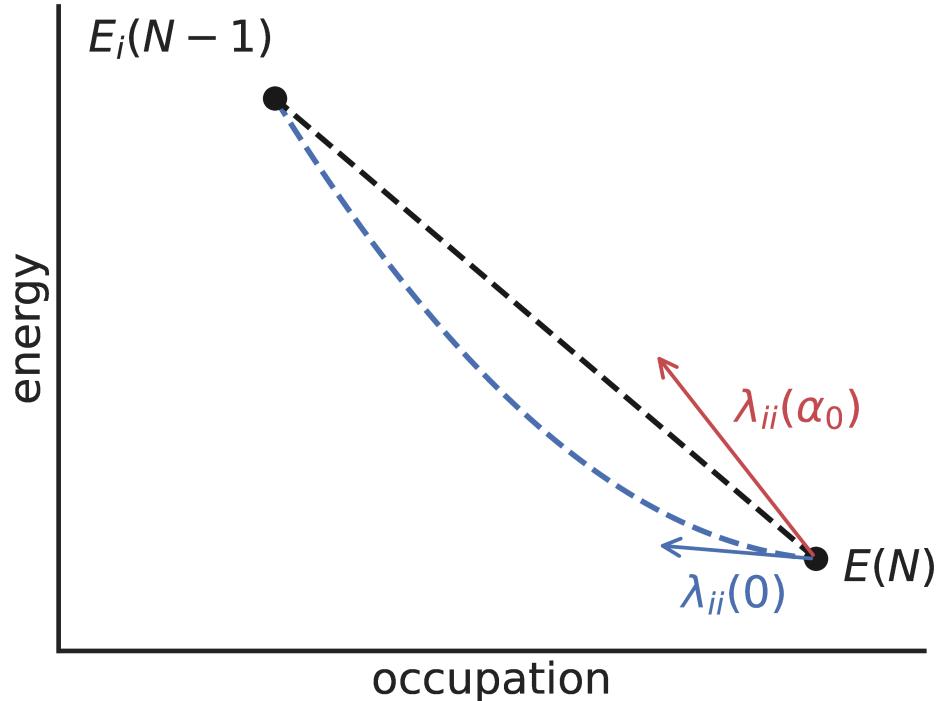
# Calculating screening parameters via SCF



# Calculating screening parameters via SCF



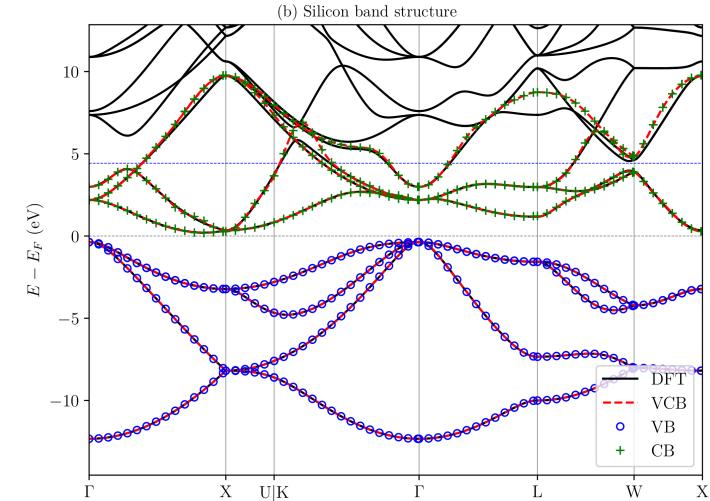
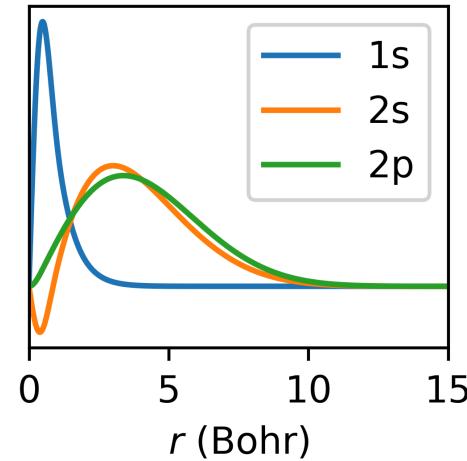
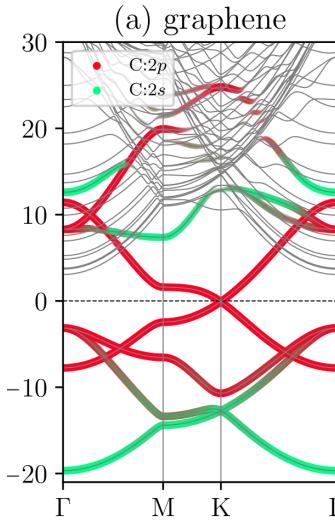
# Calculating screening parameters via SCF



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

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

# The key ingredients of automated Wannierisation



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 Computational Materials* **9**, 208–209 (2023)

<sup>2</sup>J. Qiao *et al.* *npj Computational Materials* **9**, 206–207 (2023)

## Connections with approximate self-energies<sup>3</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

## Connections with approximate self-energies<sup>2</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

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

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-energies<sup>2</sup>



Screened exchange plus Coulomb hole (COHSEX)

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

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

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

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

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

## Connections with approximate self-energies<sup>2</sup>

Static  $\text{GW}\Gamma_{\text{xc}}$  — local (DFT-based) vertex corrections<sup>2</sup>

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

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

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

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>2</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)

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