



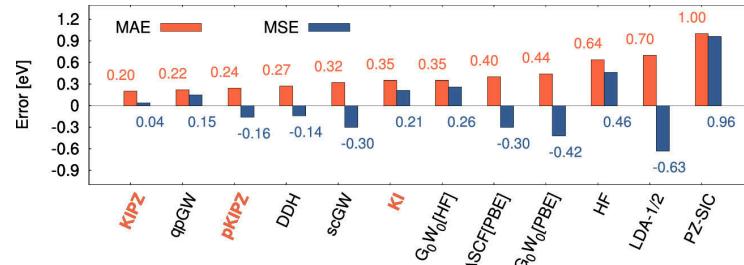
Center for Scientific Computing,
Theory and Data

Making Koopmans functionals accessible

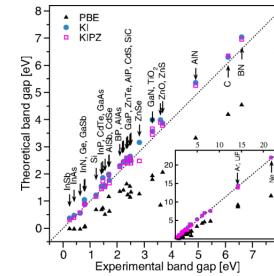
Edward Linscott

MARVEL Pillar IV Meeting, 25 June 2024

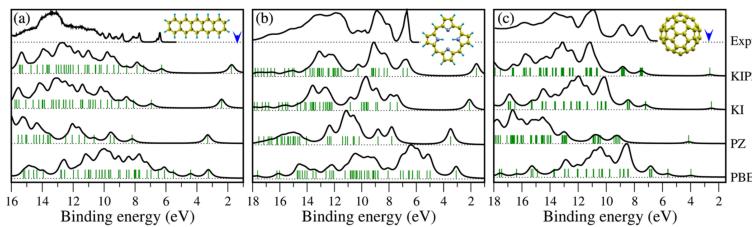
A powerful tool for computational spectroscopy



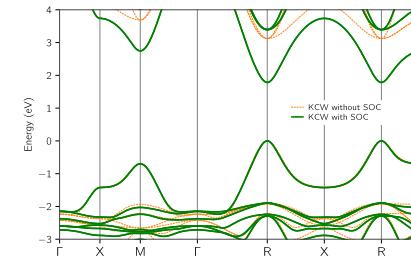
ionisation
potentials¹



band gaps²



photoemission
spectra³



spin-orbit
coupling⁴

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

²N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051–21052 (2018)

³N. L. Nguyen *et al.* *Phys. Rev. Lett.* **114**, 166405–166406 (2015)

⁴A. Marrazzo *et al.* <http://arxiv.org/abs/2402.14575> (2024) doi:10.48550/arXiv.2402.14575

Koopmans functional theory

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

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

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Powerful but complex:

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

- minimisation gives rise to localised orbitals, so we want to first Wannierise to initialise (or even define) these orbitals
- screening parameters account for orbital relaxation, should be calculated *ab initio*, and this is expensive

koopmans

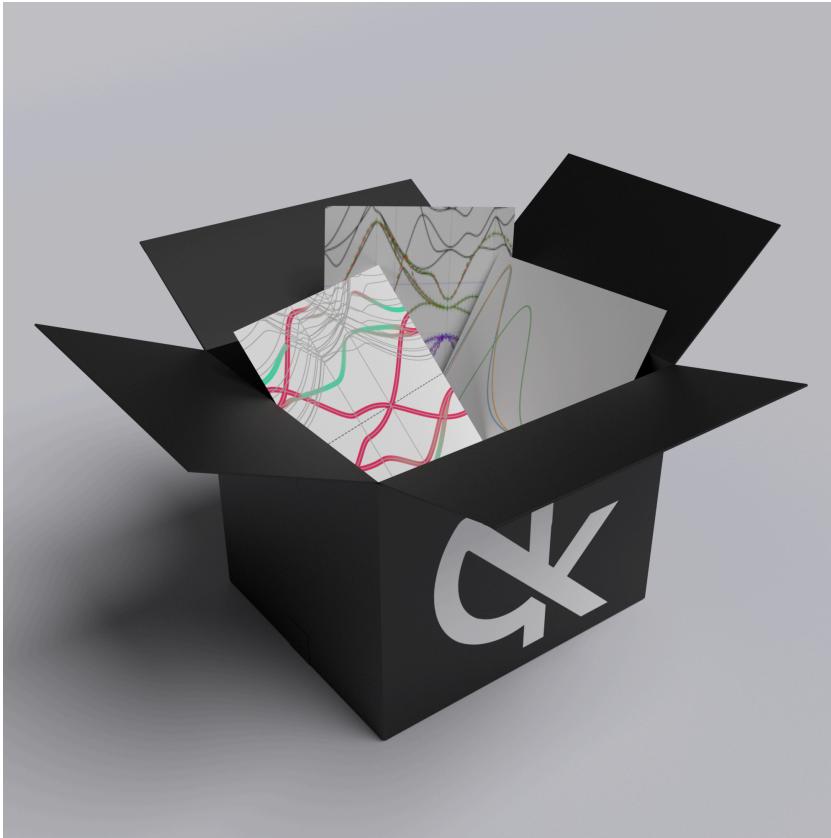
An ongoing effort to make Koopmans functional calculations straightforward for non-experts¹

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

For more details, go to koopmans-functionals.org

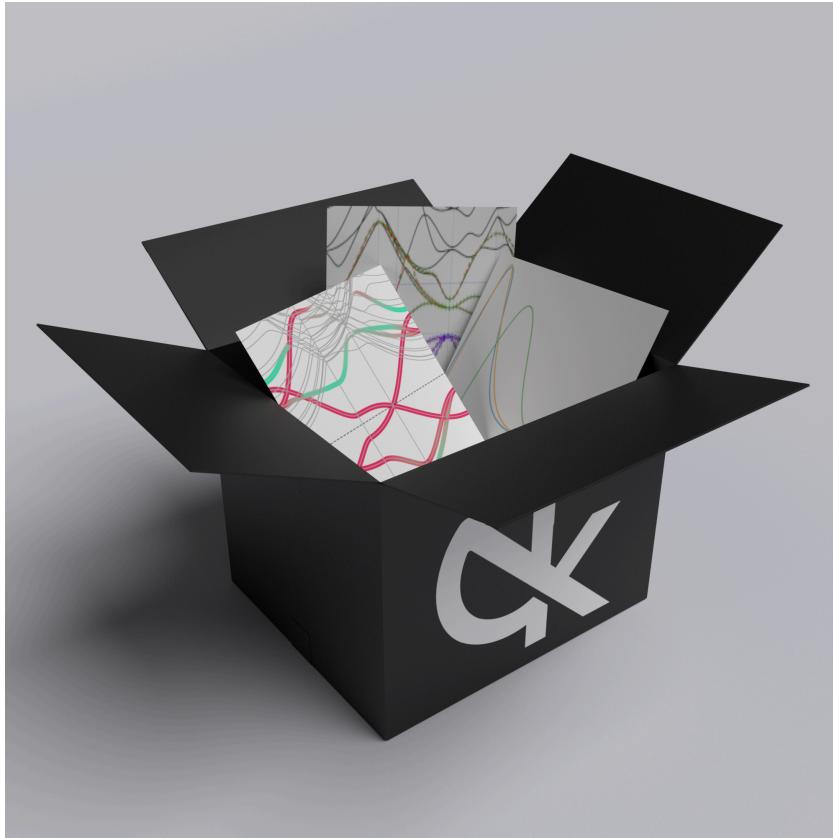
¹E. B. Linscott *et al.* *J. Chem. Theory Comput.* **19**, 7097–7111 (2023)

Making Koopmans functionals accessible



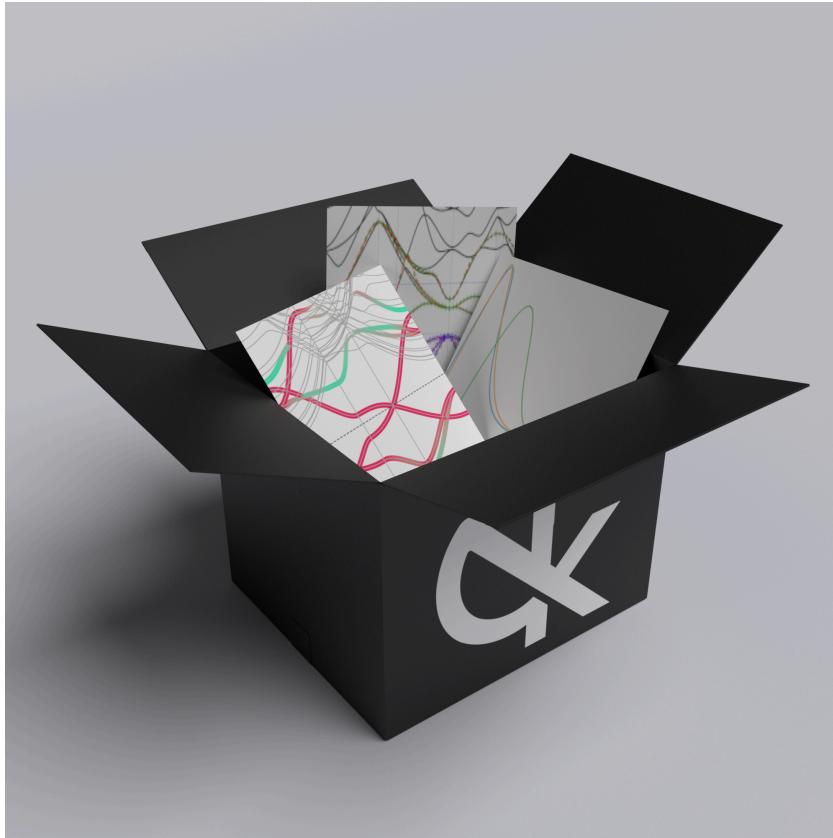
- 1.
- 2.
- 3.

Making Koopmans functionals accessible



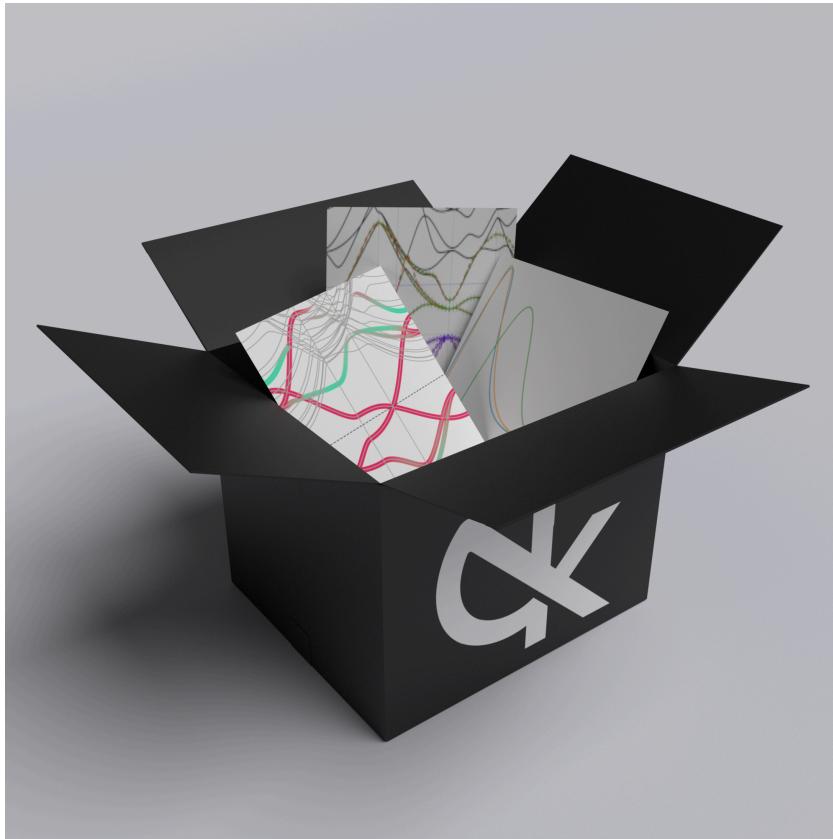
1. automated Wannerisation
- 2.
- 3.

Making Koopmans functionals accessible



1. automated Wannerisation
2. calculating the screening parameters
via machine learning
- 3.

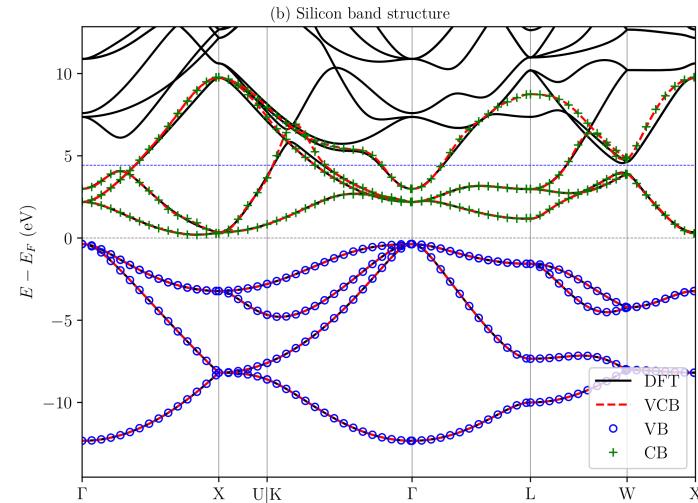
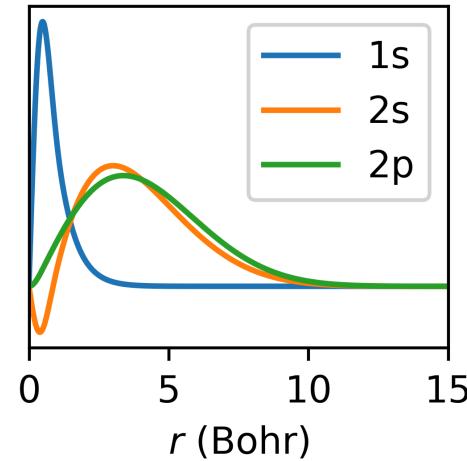
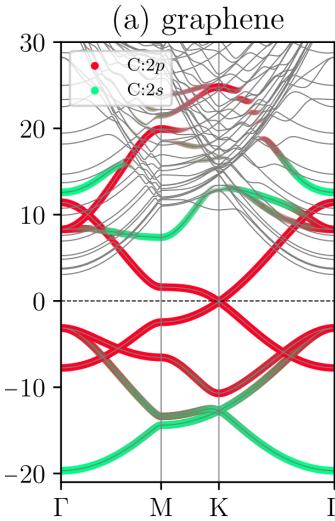
Making Koopmans functionals accessible



1. automated Wannerisation
2. calculating the screening parameters
via machine learning
3. integration with AiiDA

Automated Wannierisation

The key ingredients of automated Wannierisation



projectability-based
disentanglement¹

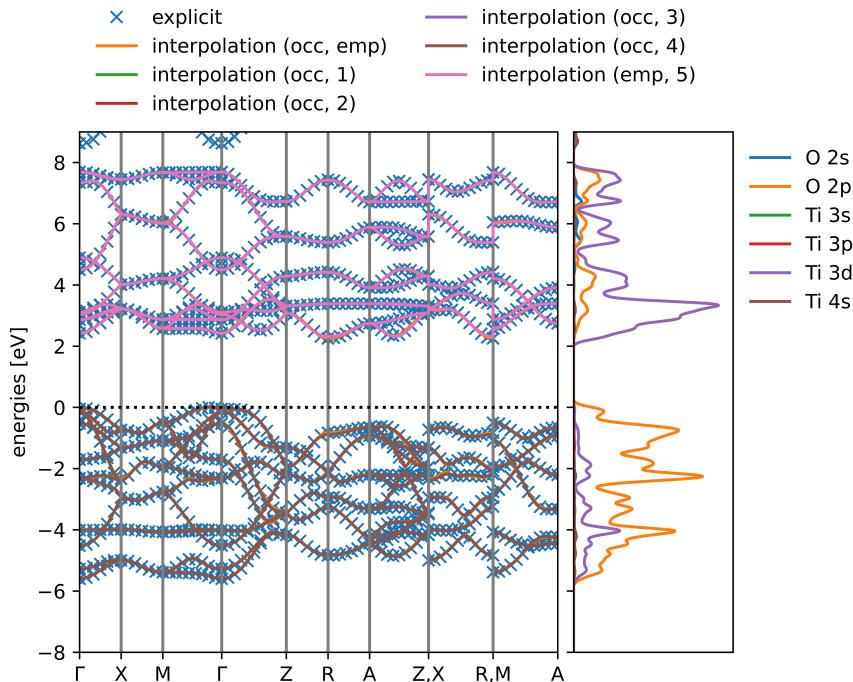
use PAOs found in
pseudopotentials

parallel transport to separate
manifolds²

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²J. Qiao *et al.* *npj Comput Mater* **9**, 206–207 (2023)

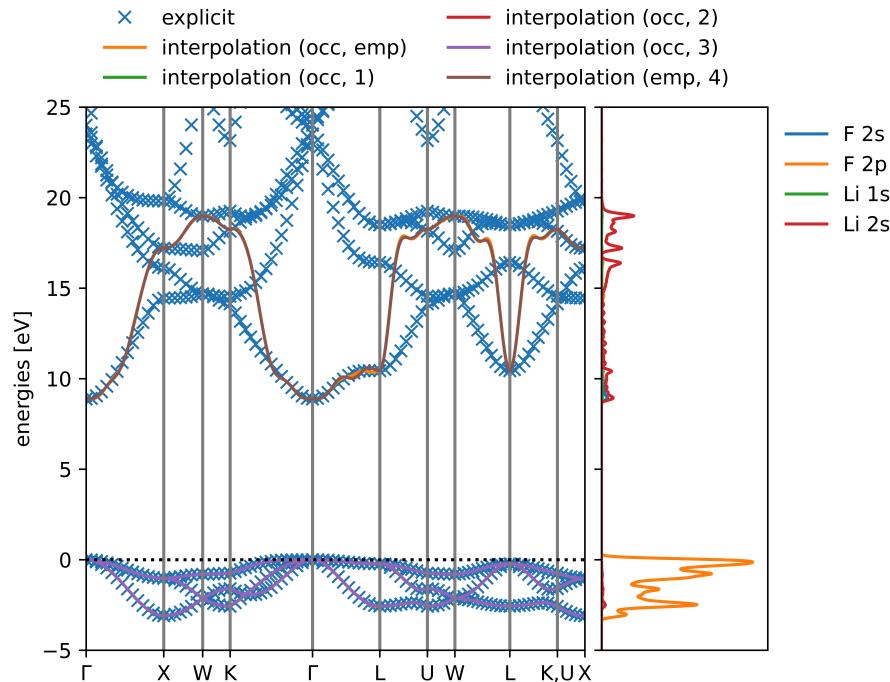
Example 1: TiO₂



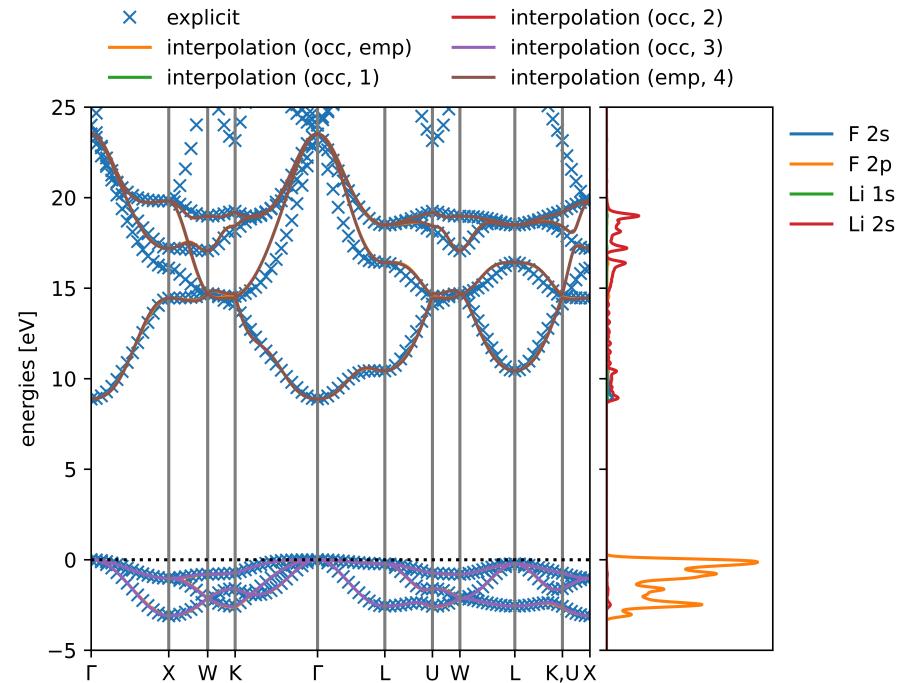
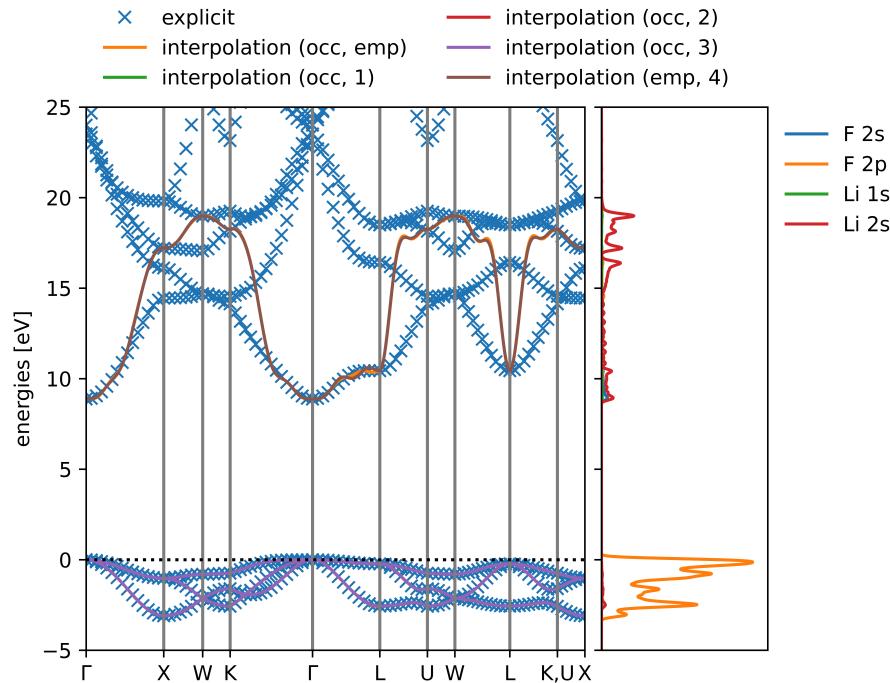
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      "celldms": {"1": 8.675923, "3": 0.645248},
      "periodic": true},
    "atomic_positions": {
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        ["O", 0.1814, 0.8186, 0.5],
        ["O", 0.8186, 0.1814, 0.5],
        ["O", 0.3186, 0.3186, 0.0],
        ["O", 0.6814, 0.6814, 0.0]
      ],
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    "kpoints": {"grid": [3, 3, 4]},
    "calculator_parameters": {
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```

Example 2: LiF



Example 2: LiF



Electronic screening via machine learning

Electronic screening via machine learning



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

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

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051–21052 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106–35107 (2022)

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Electronic screening via machine learning



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

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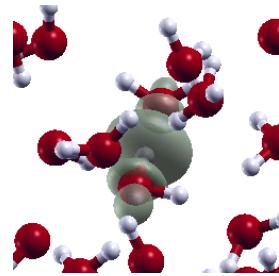
$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of 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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The machine-learning framework



power spectrum decomposition



$$\begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix}$$

ridge regression

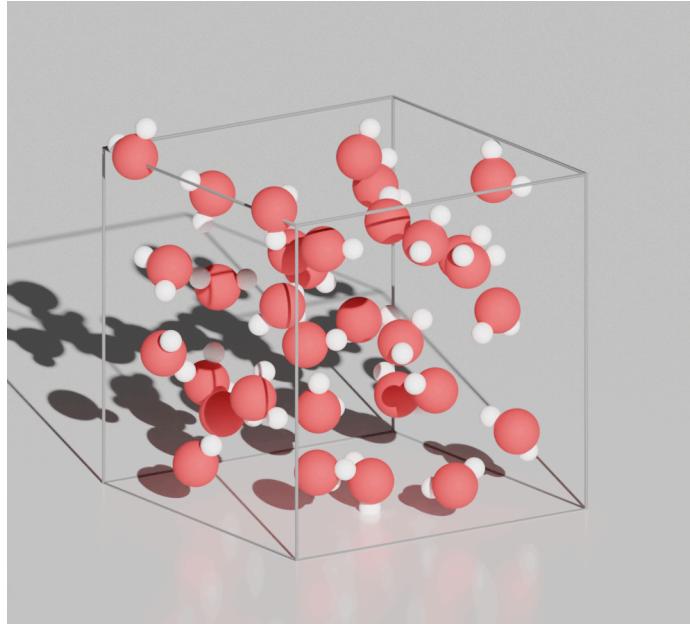
$$\alpha_i$$

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

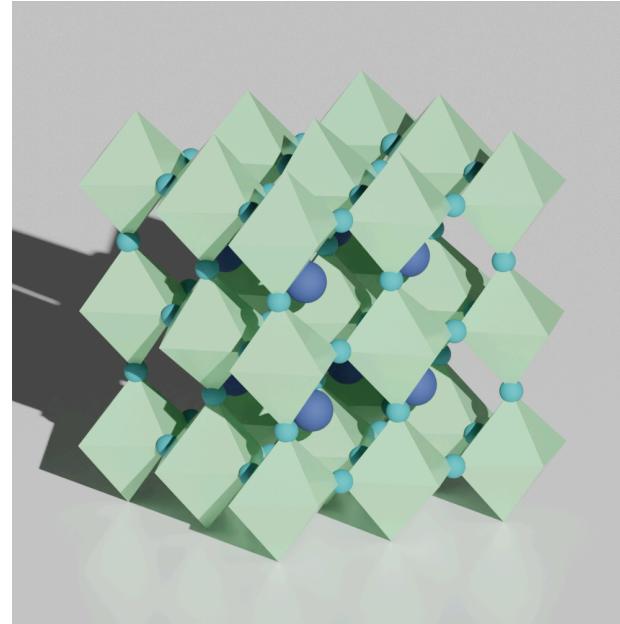
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

Two test systems



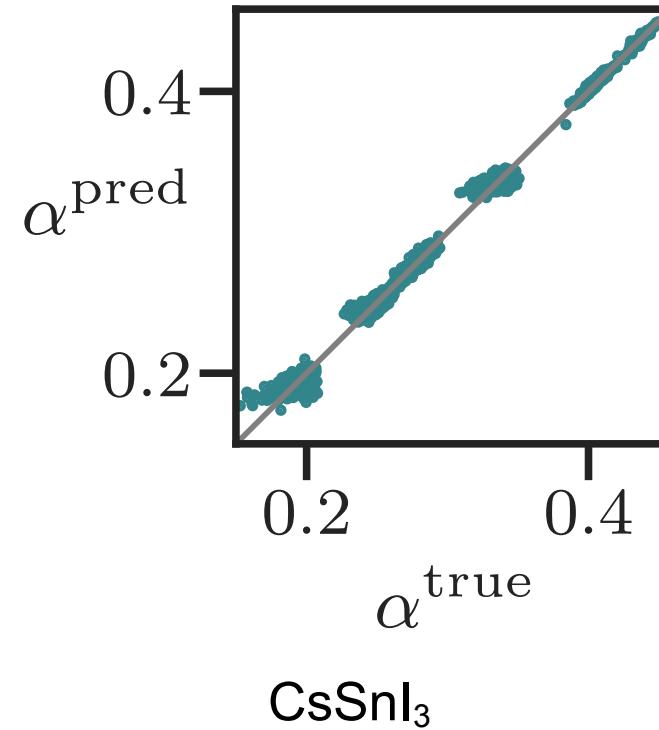
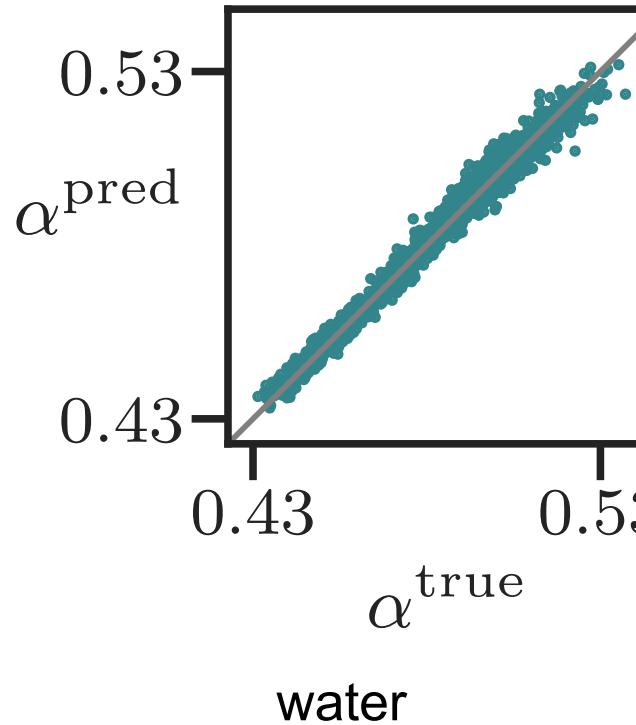
water



CsSnI₃

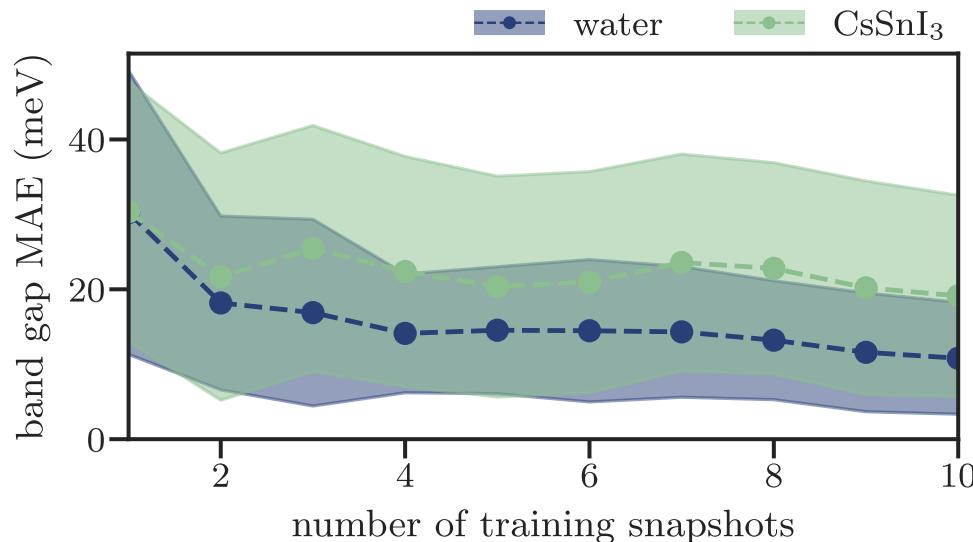
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Results: screening parameters

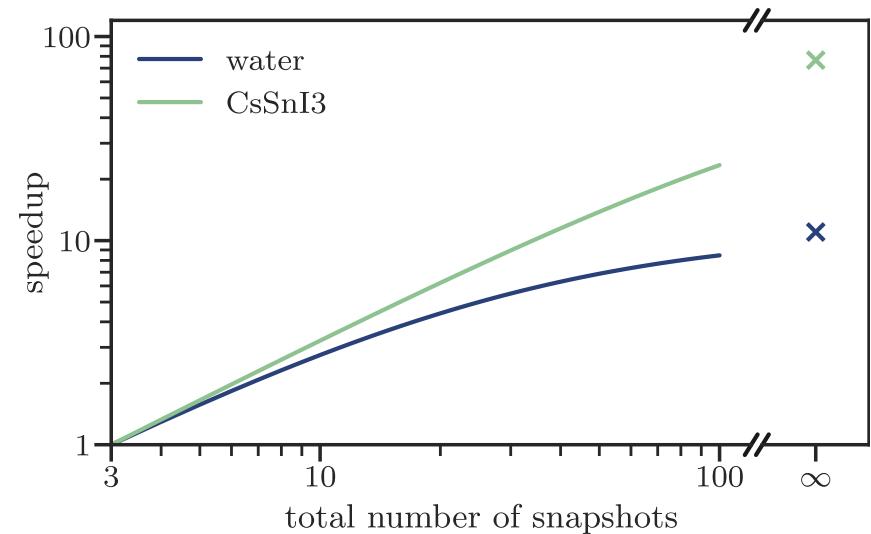


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Results: balancing accuracy and speedup



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 $\mathcal{O}(100)$

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

Integration with AiiDA

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Work has begun to interface koopmans with AiiDA, which would allow for...

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- remote execution
-
-
-

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- parallel execution
-
-

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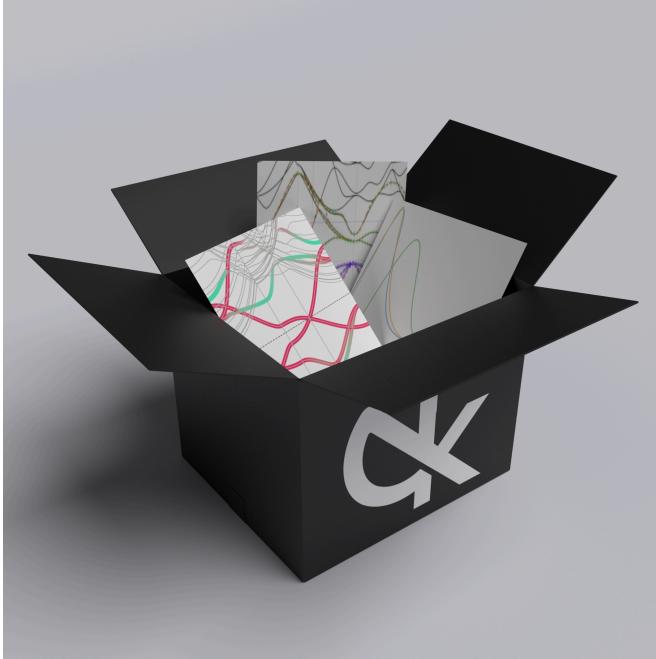
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Watch this space!

Summary

Summary



Koopmans functionals are

- a powerful tool for computational spectroscopy, and
- are increasingly user-friendly:
 - Wannierisation is more black-box¹
 - machine learning can be used to calculate the screening parameters²
 - parallel and remote execution with AiiDA is on the horizon
 - GUI development is also underway (up next!)

¹J. Qiao *et al.* *npj Comput Mater* **9**, 208–209 (2023), J. Qiao *et al.* *npj Comput Mater* **9**, 206–207 (2023)

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

Acknowledgements



Nicola Marzari



Nicola Colonna



Junfeng Qiao



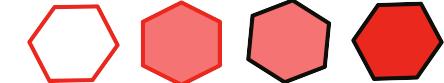
Yannick
Schubert



Miki Bonacci



**Swiss National
Science Foundation**

MARVEL


Spare slides

Koopmans functional basics

How do we calculate the energies of charged excitations? And why does DFT fail?

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

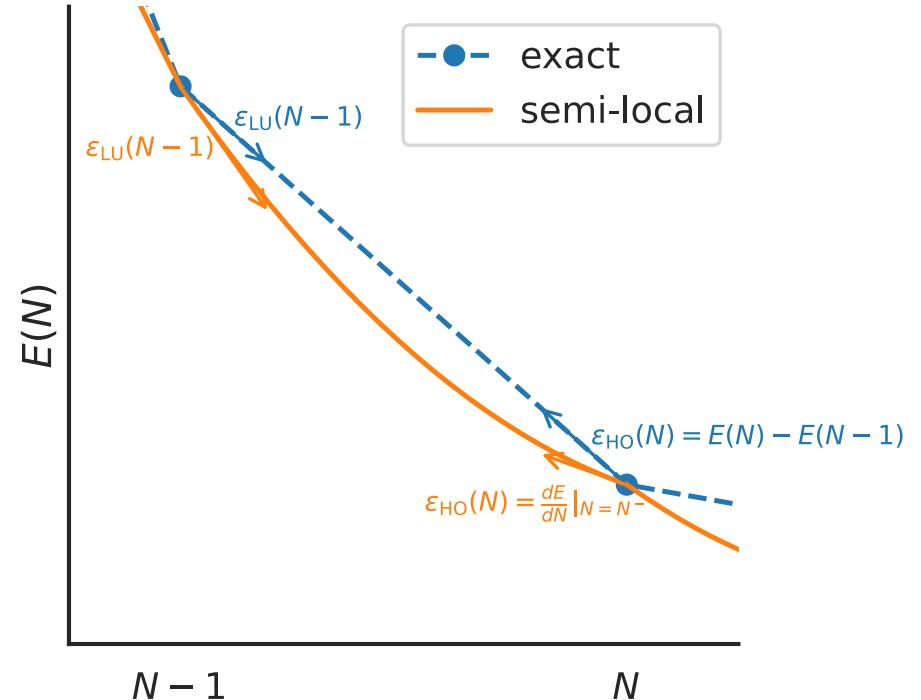
Spare slides

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



References



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- N. L. Nguyen *et al.* Koopmans-Compliant Spectral Functionals for Extended Systems. *Phys. Rev. X* **8**, 21051–21052 (2018)
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- N. Colonna *et al.* Koopmans Spectral Functionals in Periodic Boundary Conditions. *J. Chem. Theory Comput.* **18**, 5435–5448 (2022)

References



Y. Schubert *et al.* Predicting Electronic Screening for Fast Koopmans Spectral Functional Calculations. <http://arxiv.org/abs/2406.15205> (2024)