



Center for Scientific Computing,
Theory and Data

Koopmans functionals

Baking knowledge of localized charged excitations into DFT

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CECAM Workshop on Excited States, 7 November 2024

Outline



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

- Theory
 - what physical conditions motivate these functionals?
 - what key approximations underpins them?
- Results
 - what sort of accuracy can these functionals achieve?
- Extensions
 - where can we employ machine learning to speed up these calculations?
 - what do we need to do to go beyond charged excitations?
 - how can we make these calculations accessible?
- Open questions
 - what don't we understand?

Koopmans functional basics



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*

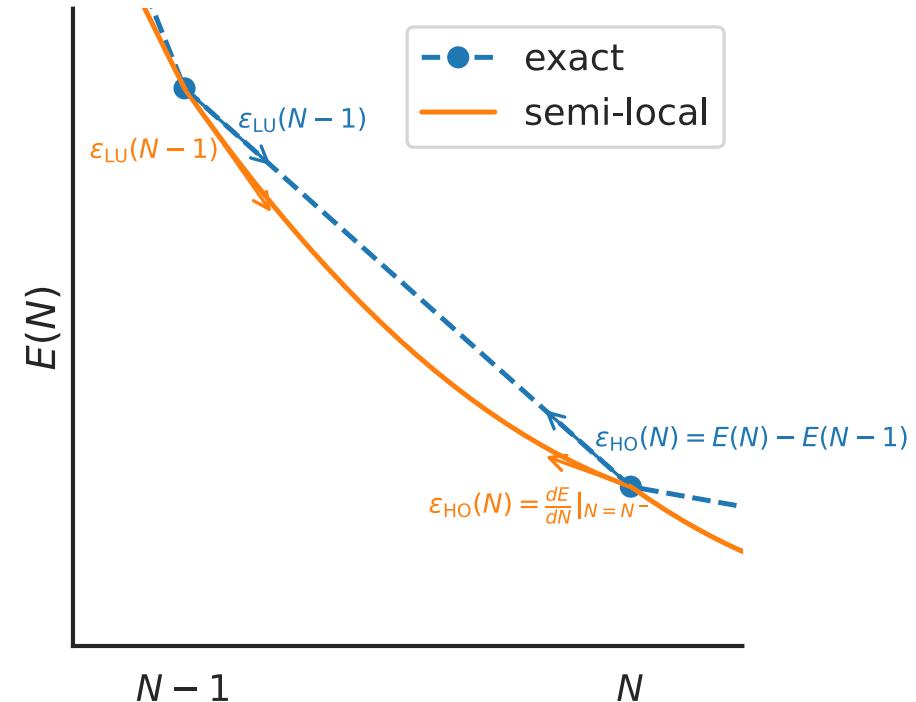
Core idea: impose this condition to
DFT to improve its description of
spectral properties

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

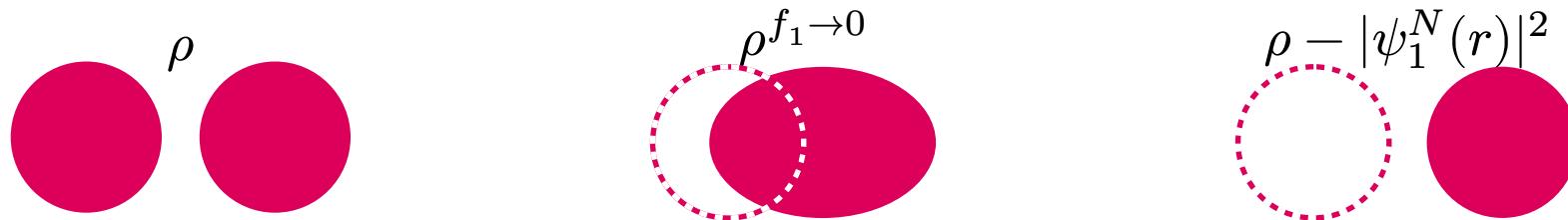


Koopmans functional theory



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

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



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

But what exactly are these energy differences? And how do we compute them?

Ingredient 1: screening

$E[\rho^{f_i \rightarrow f}]$ is the energy of the $N - f_i + f$ -electron problem with orbital i 's occupation changed from f_i to f – cannot directly evaluate

Instead evaluate in a frozen-orbital picture:

$$\rho^{f_i \rightarrow f}(\mathbf{r}) \approx \rho(\mathbf{r}) + (f - f_i) |\varphi_i^N(\mathbf{r})|^2$$

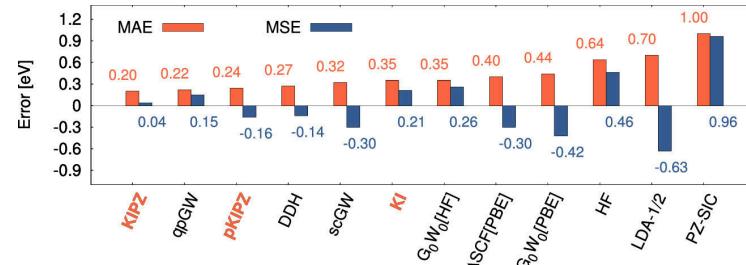
very easy to evaluate – but not at all accurate! Correct this *post hoc* via a screening parameter i.e.

$$E[\rho^{f_i \rightarrow f}] \approx \alpha_i E[\rho + (f - f_i) |\varphi_i^N(\mathbf{r})|^2]$$

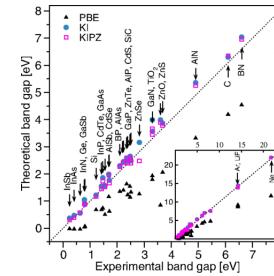
- minimisation gives rise to localised orbitals, so we want to first Wannierise to initialise (or even define) these orbitals
-

- 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

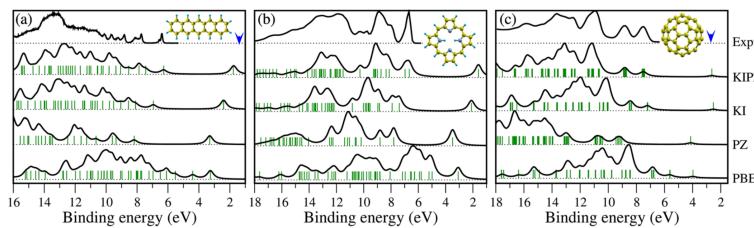
A powerful tool for computational spectroscopy



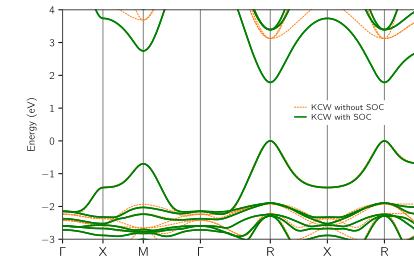
ionisation
potentials¹



band gaps²



photoemission
spectra³



spin-orbit
coupling⁴

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

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

³N. L. Nguyen *et al.* *Physical Review Letters* **114**, 166405–166406 (2015)

⁴A. Marrazzo *et al.* (2024) doi:10.48550/arXiv.2402.14575

koopmans

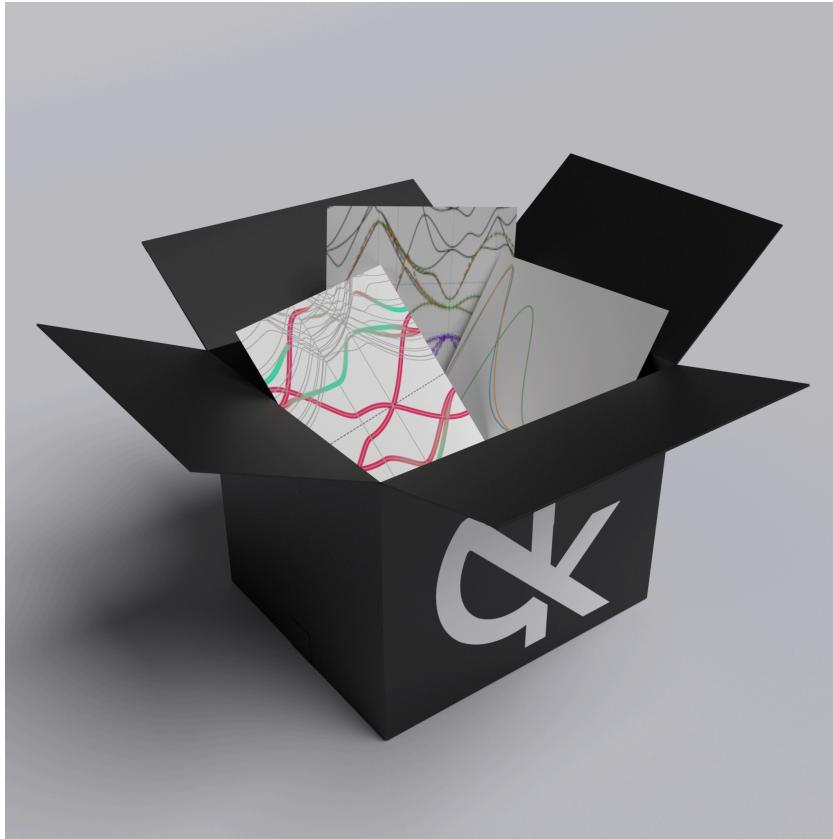
An ongoing effort to make Koopmans functional calculations straightforward for non-experts¹

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

For more details, go to koopmans-functionals.org

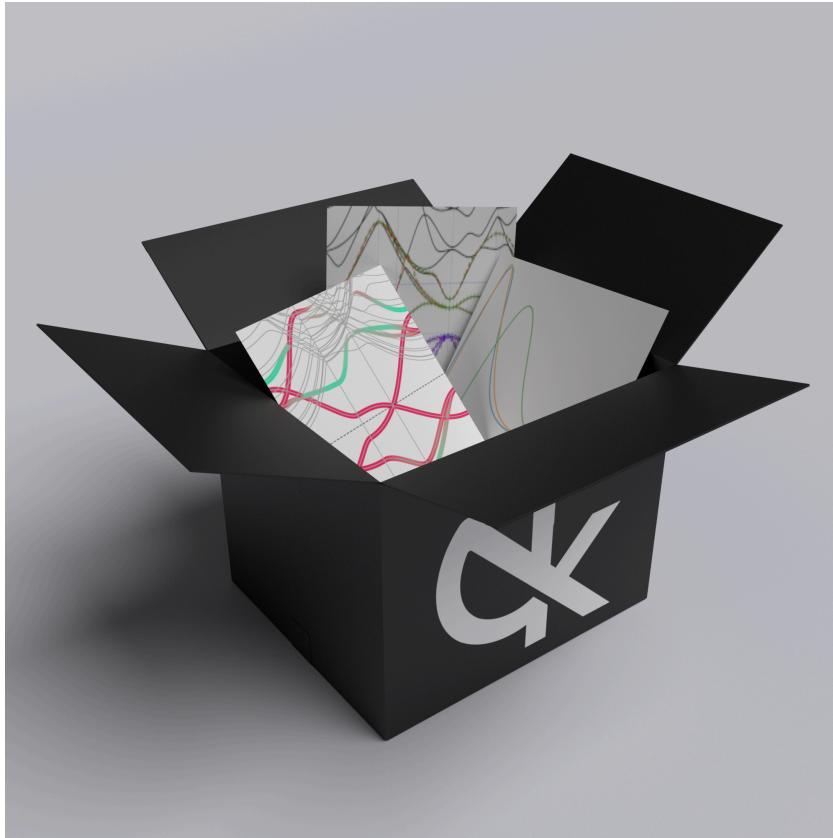
¹E. B. Linscott *et al.* *Journal of Chemical Theory and Computation* **19**, 7097–7111 (2023)

Making Koopmans functionals accessible



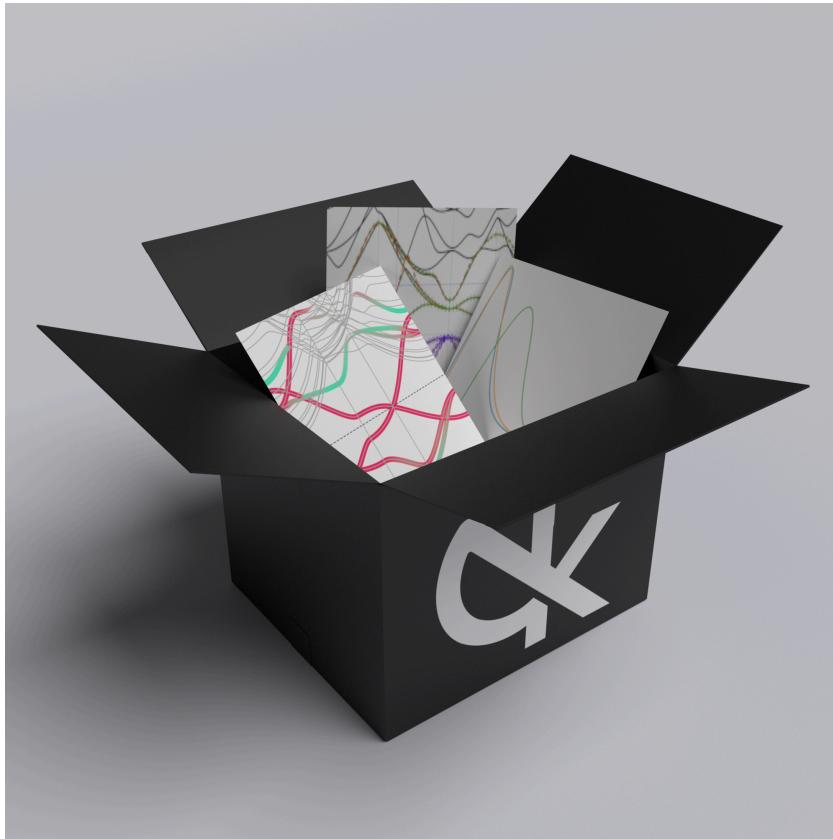
- 1.
- 2.
- 3.

Making Koopmans functionals accessible



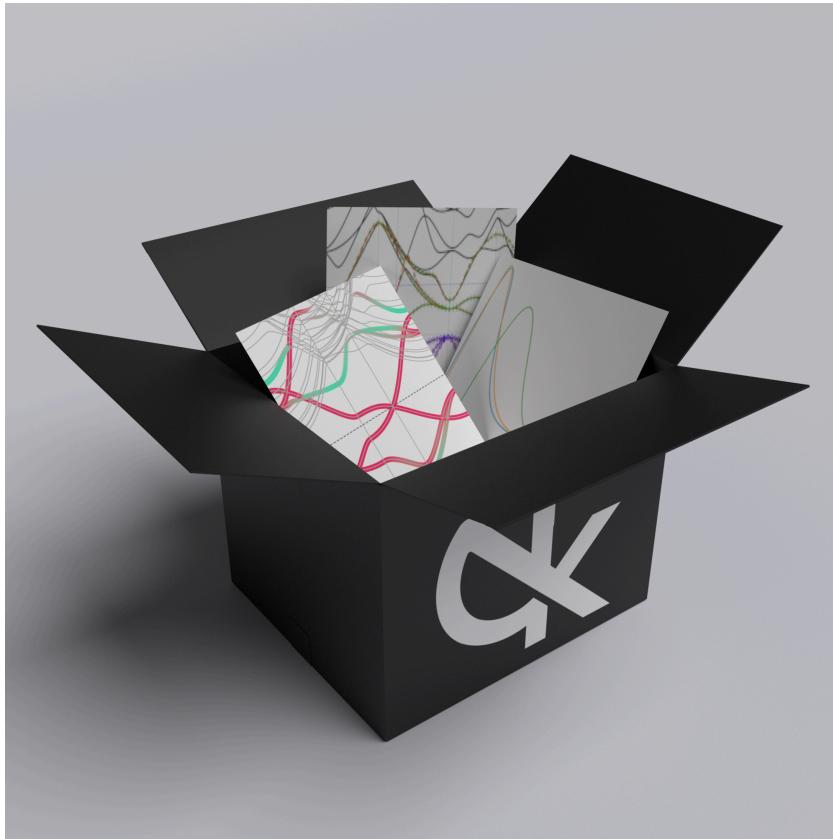
1. automated Wannerisation
- 2.
- 3.

Making Koopmans functionals accessible



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

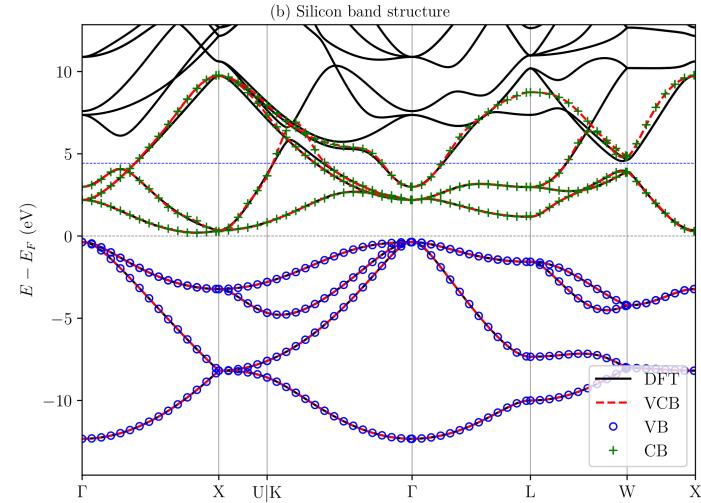
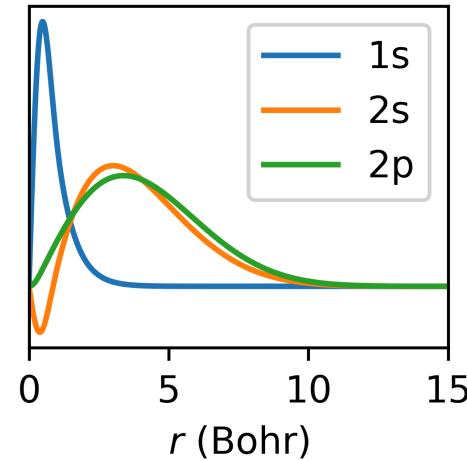
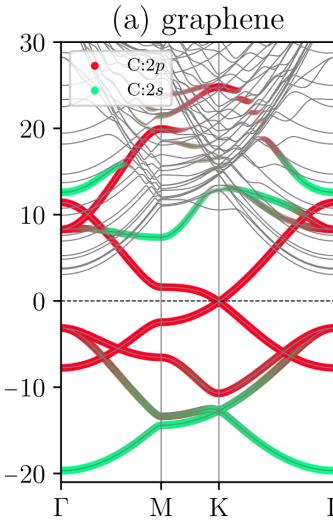
Making Koopmans functionals accessible



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

Automated Wannierisation

The key ingredients of automated Wannierisation



projectability-based
disentanglement¹

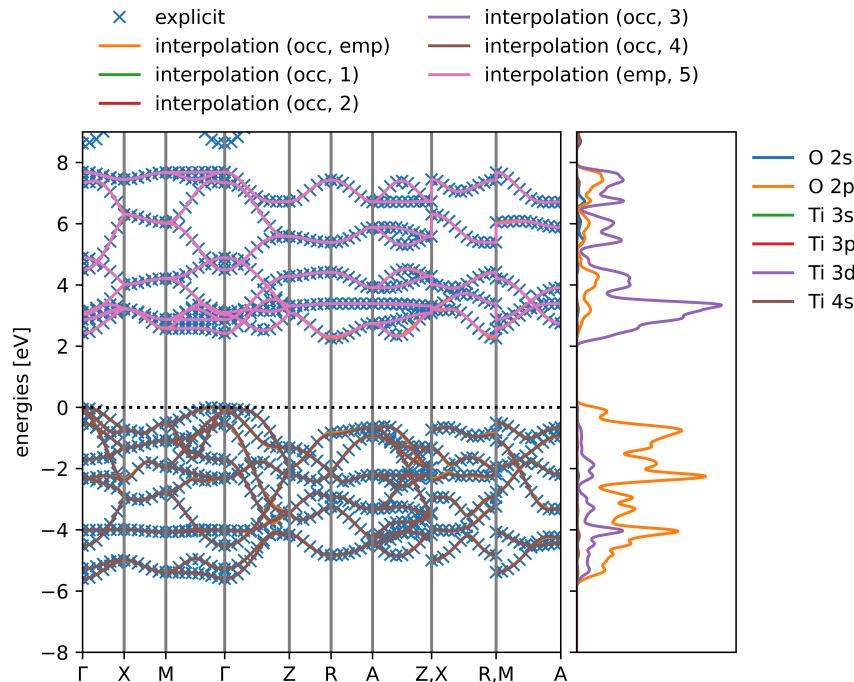
use PAOs found in
pseudopotentials

parallel transport to separate
manifolds²

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

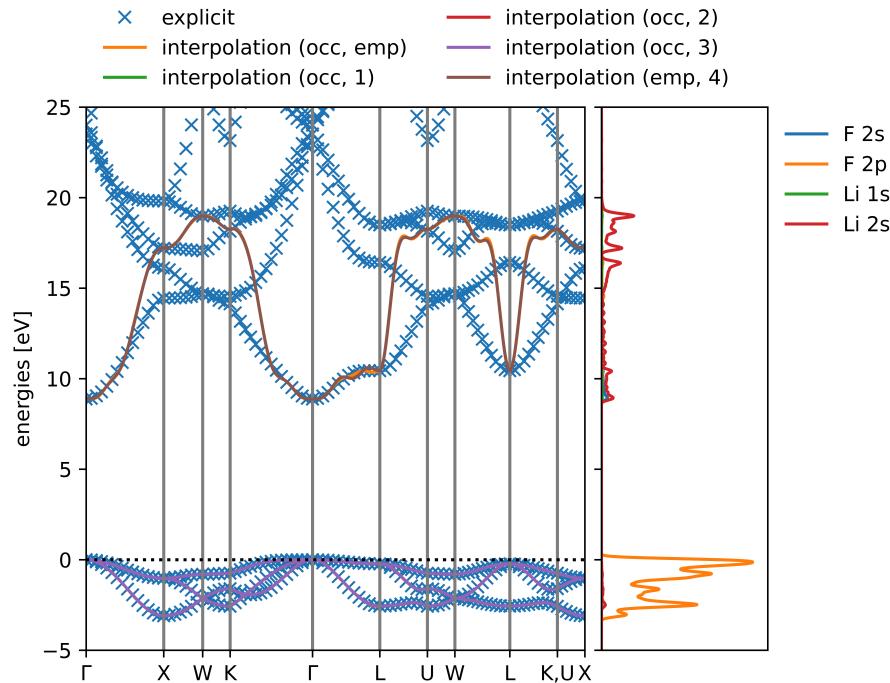
Example 1: TiO₂



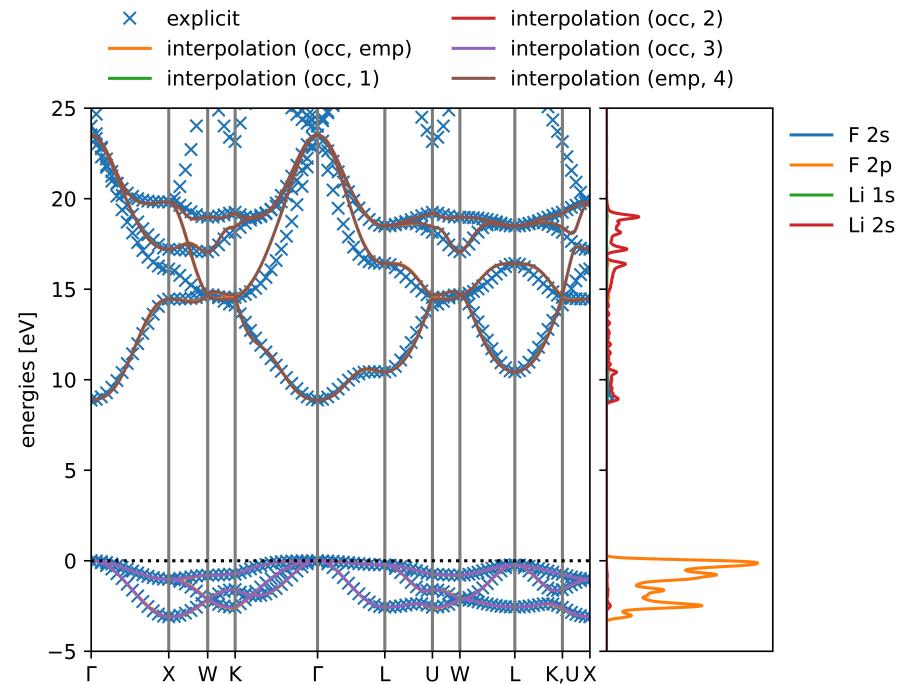
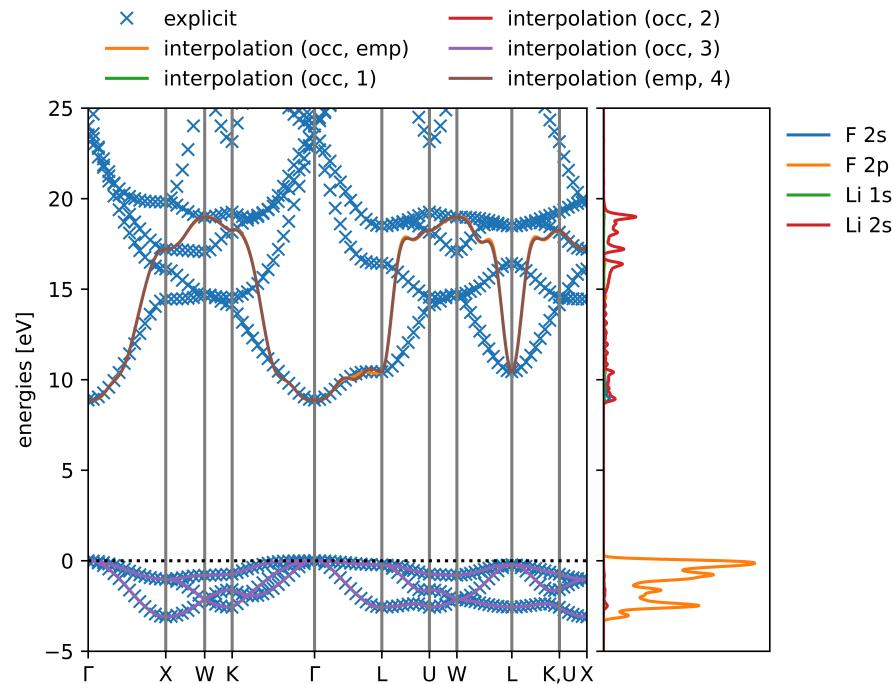
```
{
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    "init_orbitals": "mlwfs",
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  "atoms": {
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      "celldms": {"1": 8.675923, "3": 0.645248},
      "periodic": true},
    "atomic_positions": {
      "positions": [
        ["Ti", 0.5, 0.5, 0.5],
        ["Ti", 0.0, 0.0, 0.0],
        ["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]
      ],
      "units": "crystal"}},
    "kpoints": {"grid": [3, 3, 4]},
    "calculator_parameters": {
      "w90": {"auto_projections": true}}}
}
```

Example 2: LiF



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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.* *Physical Review X* **8**, 21051–21052 (2018), R. De Gennaro *et al.* *Physical Review B* **106**, 35106–35107 (2022)

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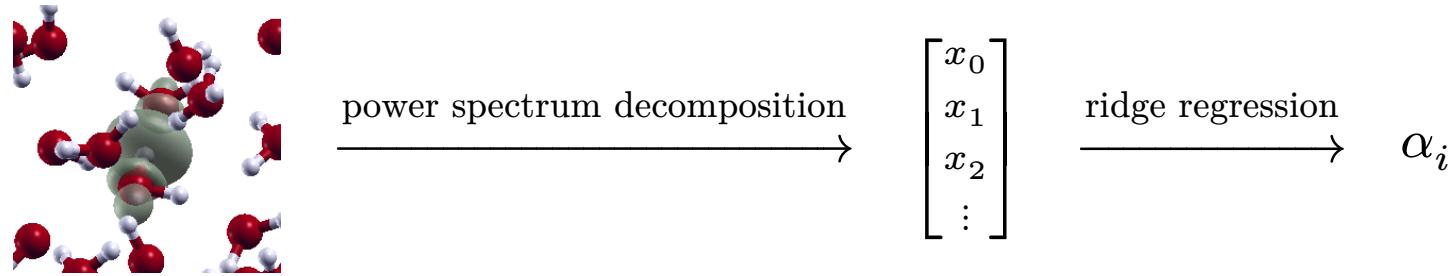
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- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital
- must be computed *ab initio* via ΔSCF ¹ or DFPT²
- corresponds to the vast majority of the computational cost of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

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The machine-learning framework

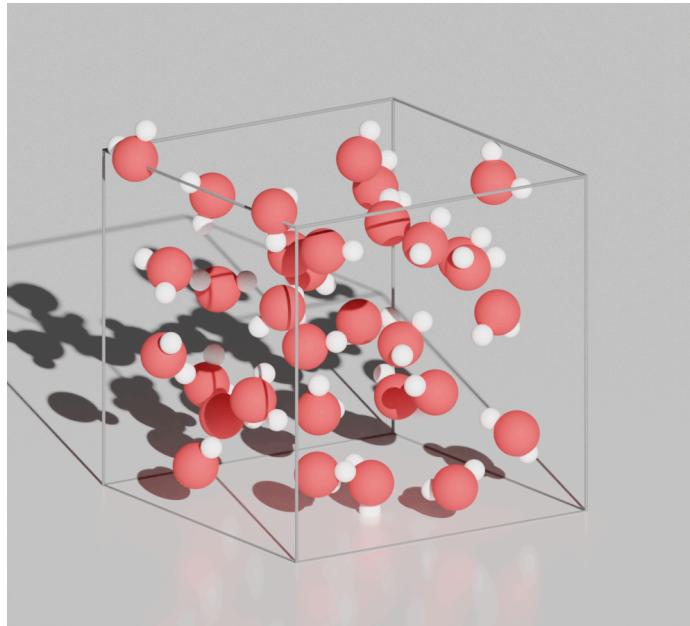


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

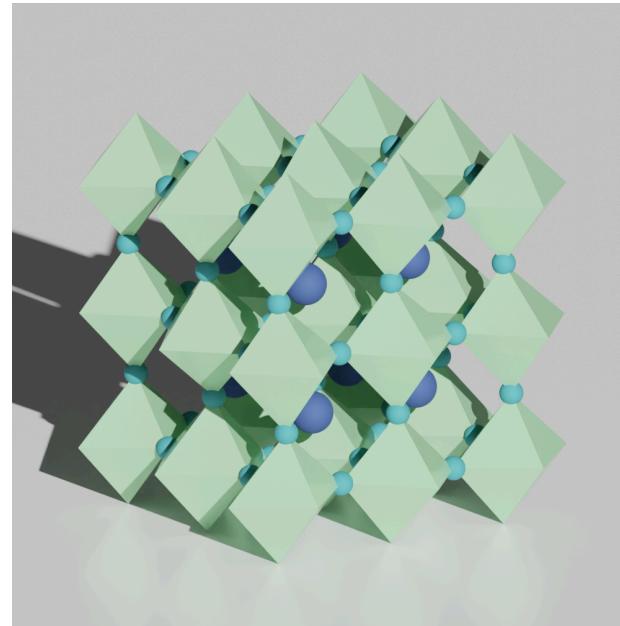
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

Two test systems



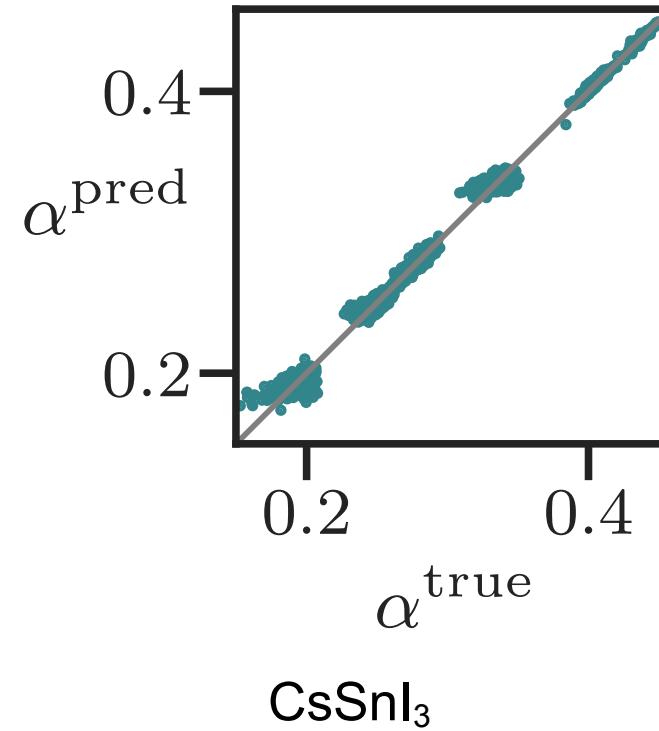
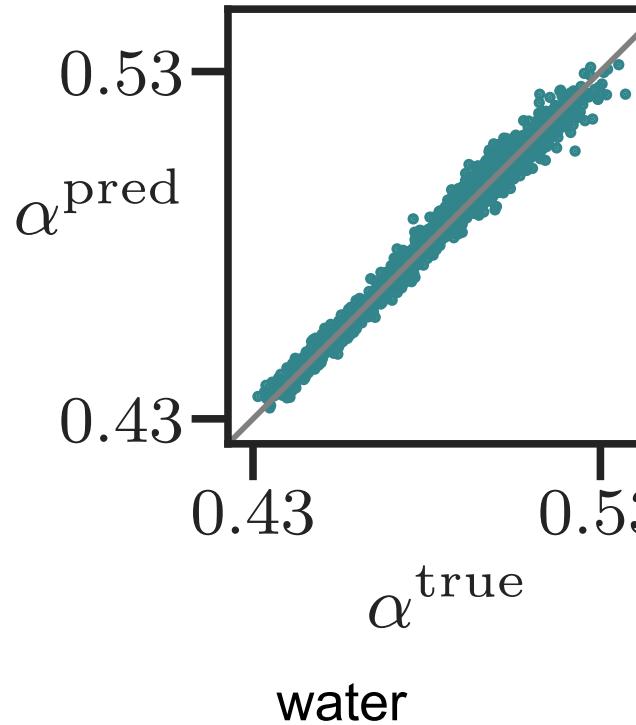
water



CsSnI₃

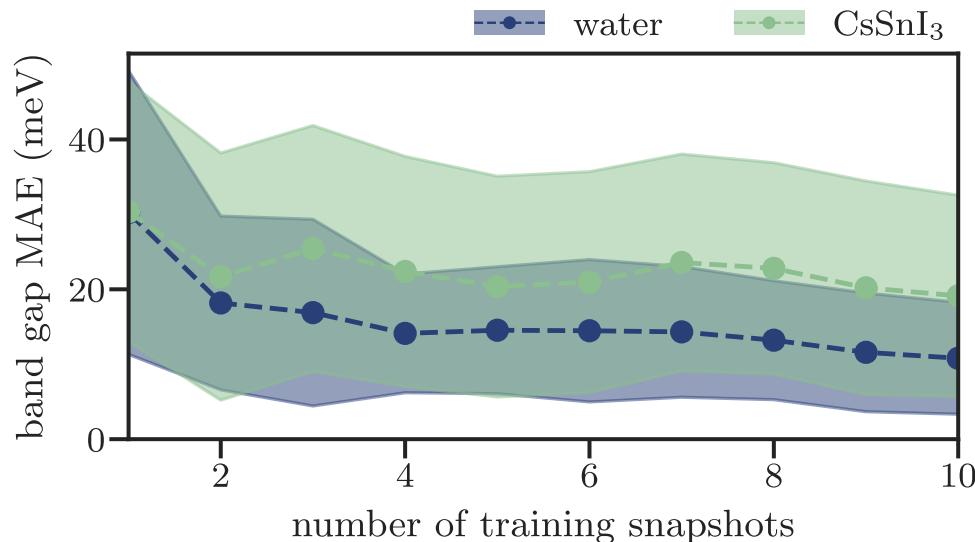
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Results: screening parameters

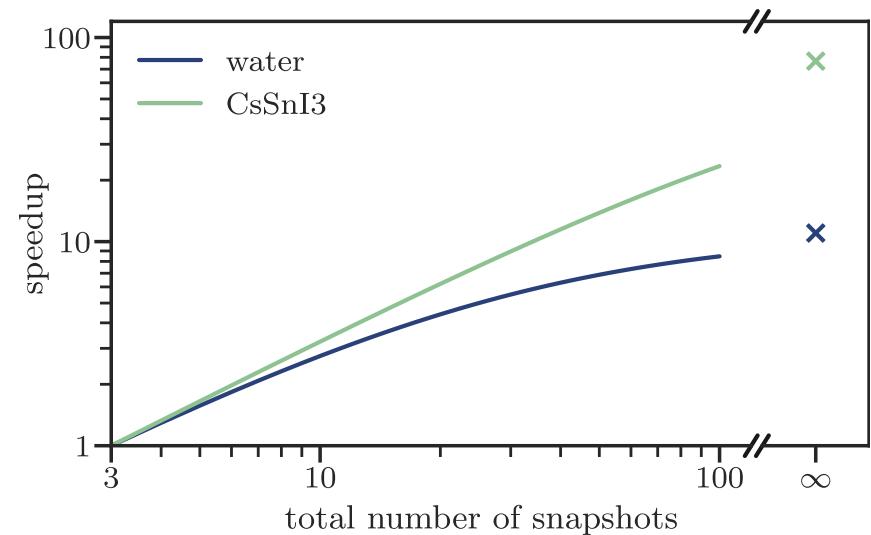


¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

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.* <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...

Integration with AiiDA



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- remote execution
-
-
-

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- remote execution
- parallel execution
-
-

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- making use of AiiDA's workflows
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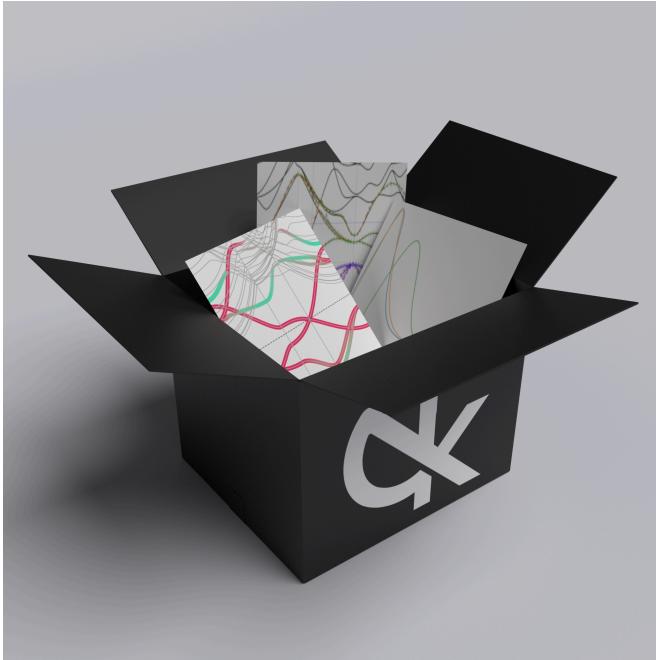
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Watch this space!

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 Computational Materials* **9**, 208–209 (2023), J. Qiao *et al.* *npj Computational Materials* **9**, 206–207 (2023)

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

Acknowledgements



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Nicola Colonna



Junfeng Qiao



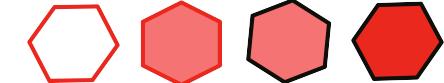
Yannick
Schubert



Miki Bonacci



**Swiss National
Science Foundation**

MARVEL


Spare slides

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