

Black-box, accurate, and efficient prediction of band structures with Koopmans functionals

Edward Linscott



PSI



DPG conference



21 March 2024



Accurate band structures

How can we calculate band structures accurately and efficiently?

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DFT qualitative failures

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DFT qualitative failures

GW accurate but more expensive;
diagrammatic

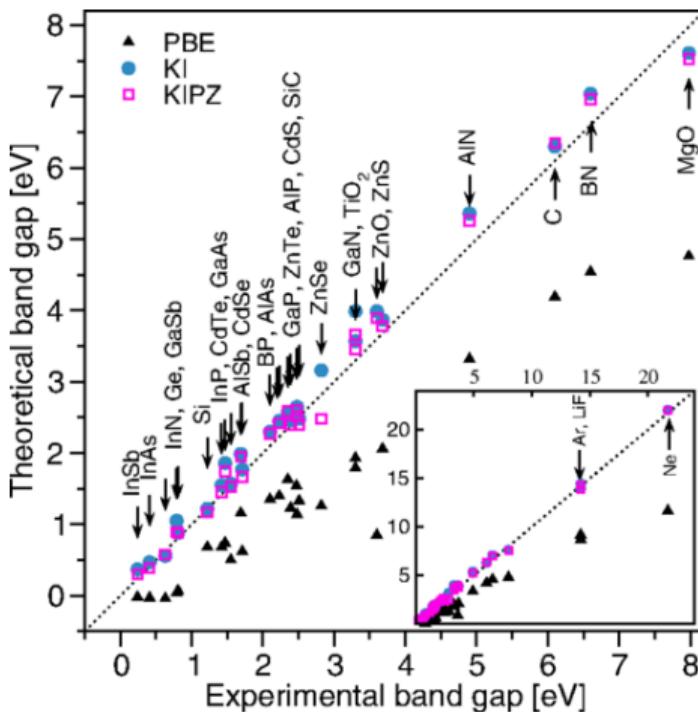
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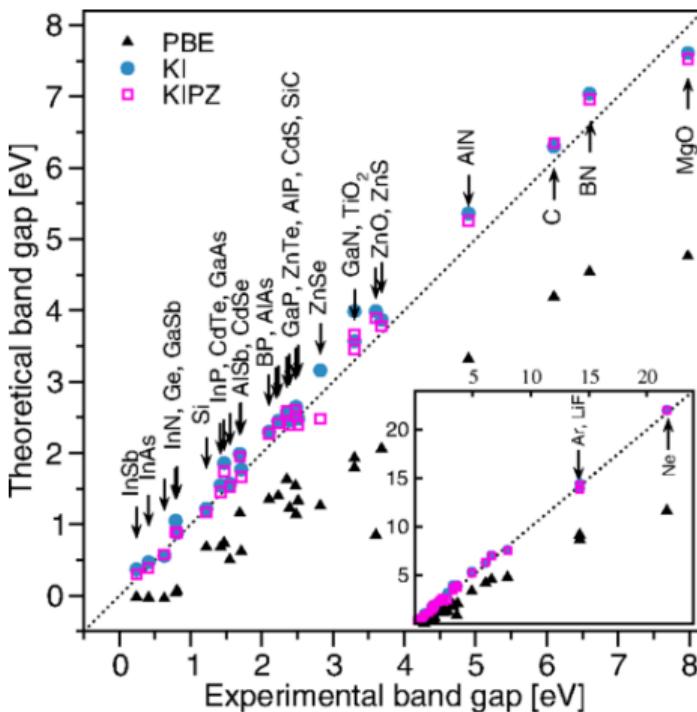
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theory

	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



$$E_{\text{Koopmans}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{DFT}[\rho] + \sum_i \alpha_i \left(- \int_0^{f_i} \varepsilon_i(f) df + f_i \eta_i \right)$$

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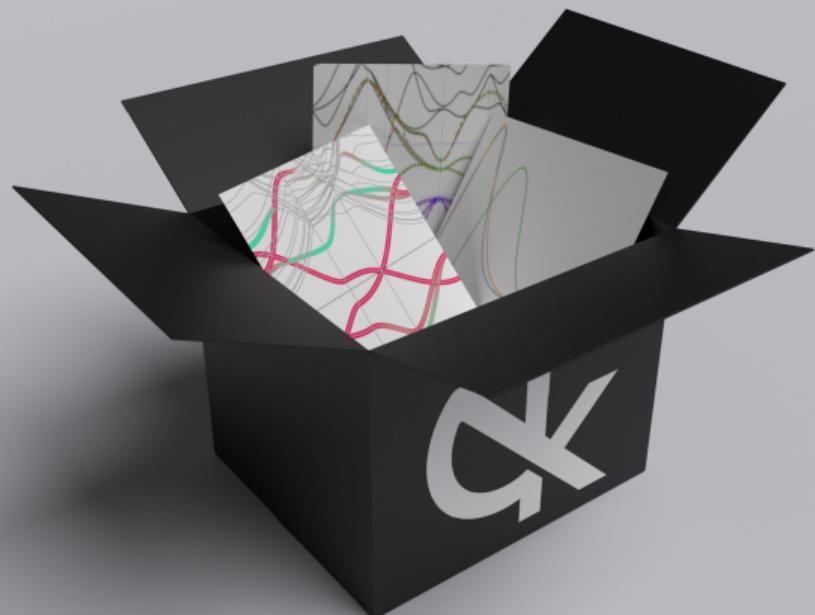
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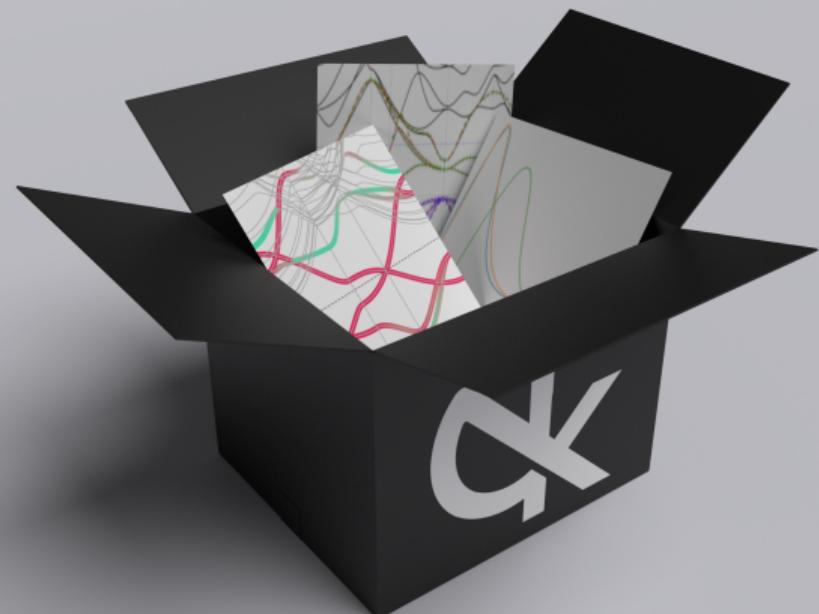
1. perform a Wannierisation
2. calculate the screening parameters $\{\alpha_i\}$
3. minimize the functional
4. diagonalize the Hamiltonian

What needs to be in the box?



For a black box, we need...

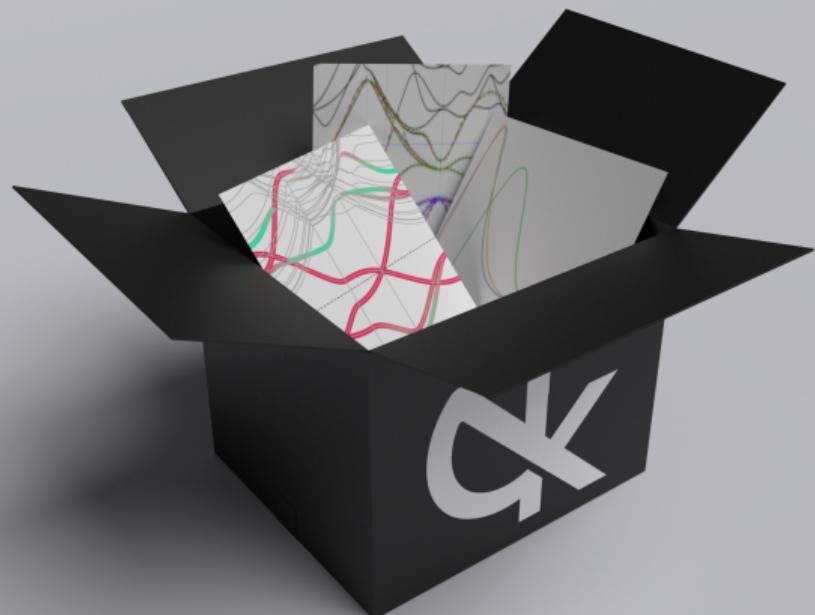
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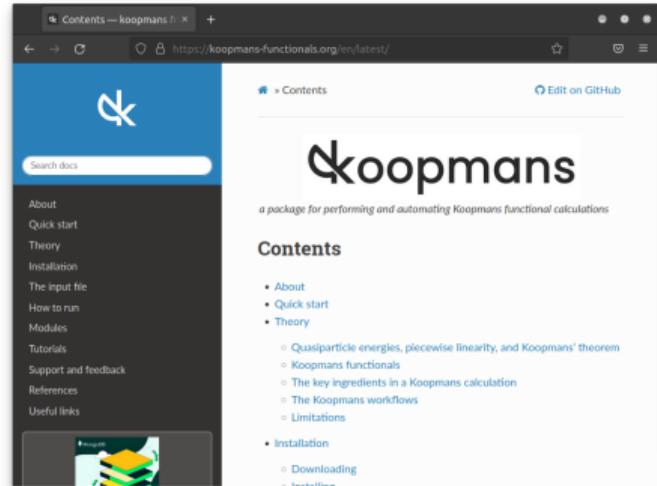
For a black box, we need...

- automated start-to-finish calculations
- minimal input required from the user

koopmans

- v1.0 released last year¹
- implementations of Koopmans functionals within Quantum ESPRESSO
- automated workflows
 - Koopmans calculations
 - Wannierisation
 - dielectric tensor
 - ...
- built on top of ASE²
- does not require expert knowledge

koopmans-functionals.org



¹ E. B. Linscott et al. *J. Chem. Theory Comput.* 19.20 (2023), 7097

² A. H. Larsen et al. *Journal of Physics: Condensed Matter* 29.27 (2017), 273002

koopmans: An Open-Source Package for Accurately and Efficiently Predicting Spectral Properties with Koopmans Functionals

Edward B. Linscott,*[△] Nicola Colonna,[△] Riccardo De Gennaro, Ngoc Linh Nguyen, Giovanni Borghi, Andrea Ferretti, Ismaila Dabo, and Nicola Marzari*



Cite This: <https://doi.org/10.1021/acs.jctc.3c00652>



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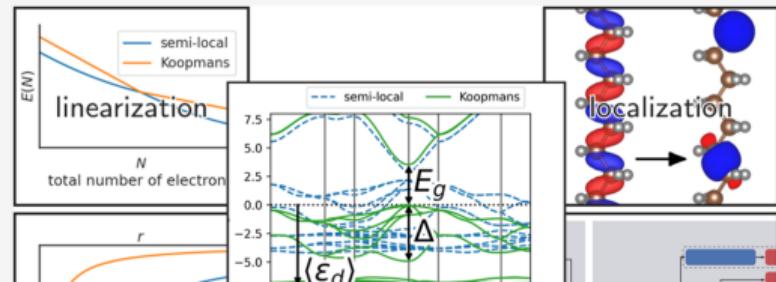
ACCESS |

Metrics & More

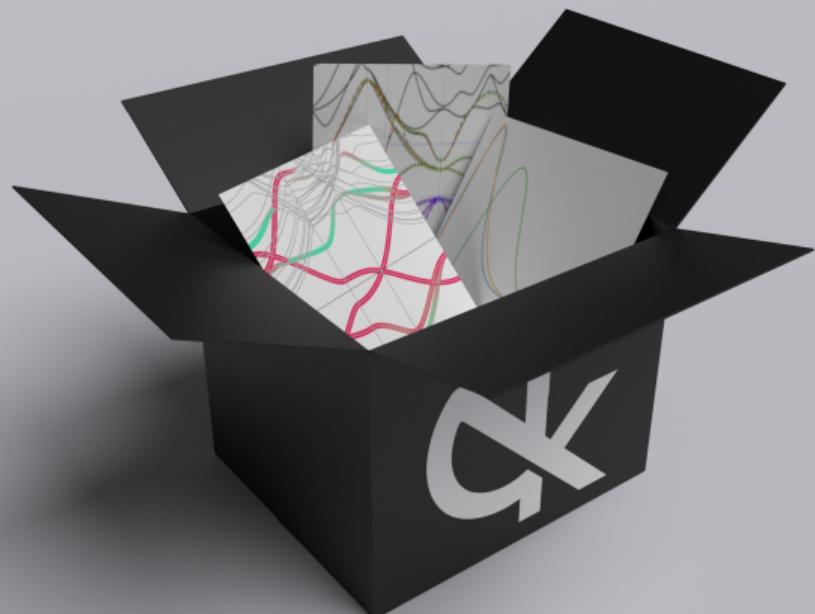
Article Recommendations

Supporting Information

ABSTRACT: Over the past decade we have developed Koopmans functionals, a computationally efficient approach for predicting spectral properties with an orbital-density-dependent functional framework. These functionals impose a generalized piecewise linearity condition to the entire electronic manifold, ensuring that orbital energies match the corresponding electron removal/addition energy differences (in contrast to semilocal DFT, where a mismatch between the two lies at the heart of the band gap



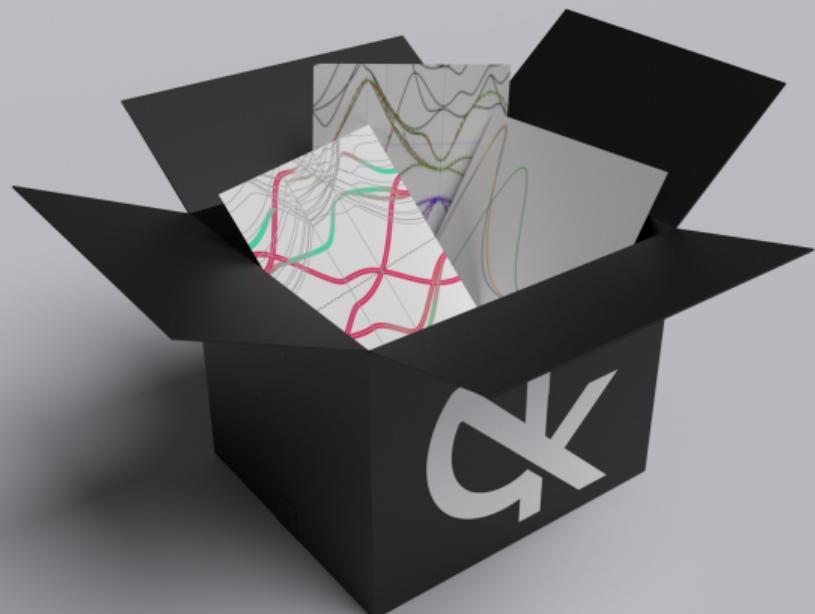
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- minimal input required from the user

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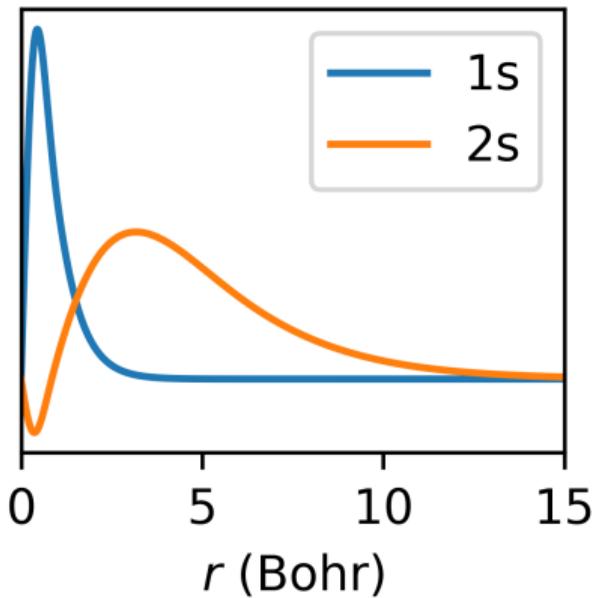
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One step still very manual: Wannierisation
Can we automate it?

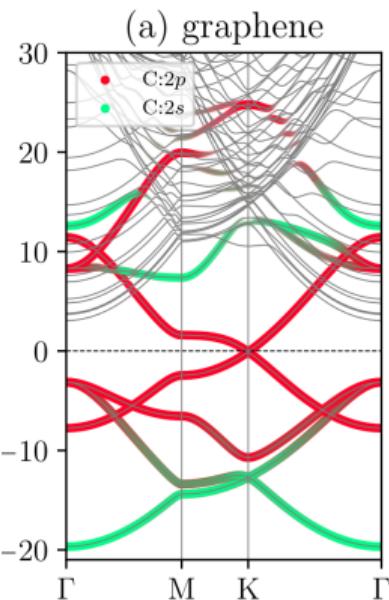
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- use PAOs found in pseudopotential files as initial guesses for Wannier functions



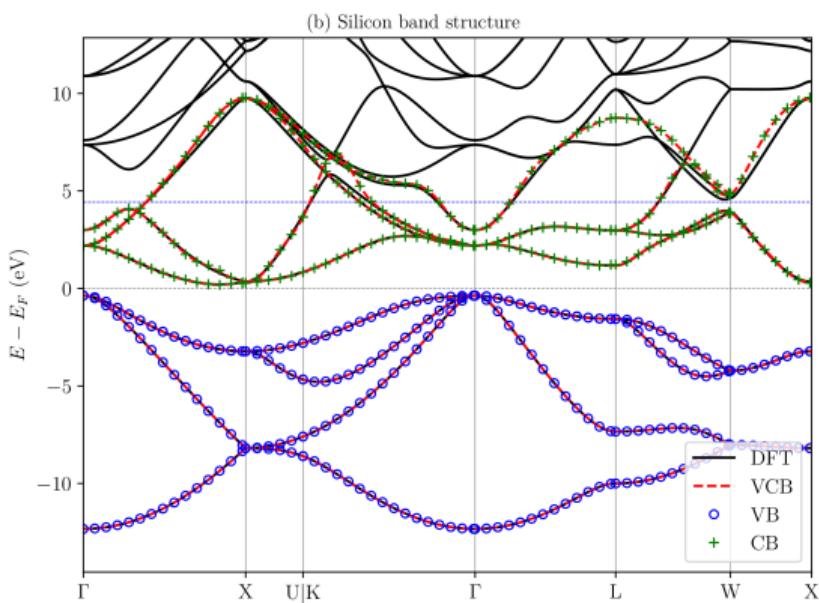
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- projectability-based disentanglement instead of energy-based disentanglement

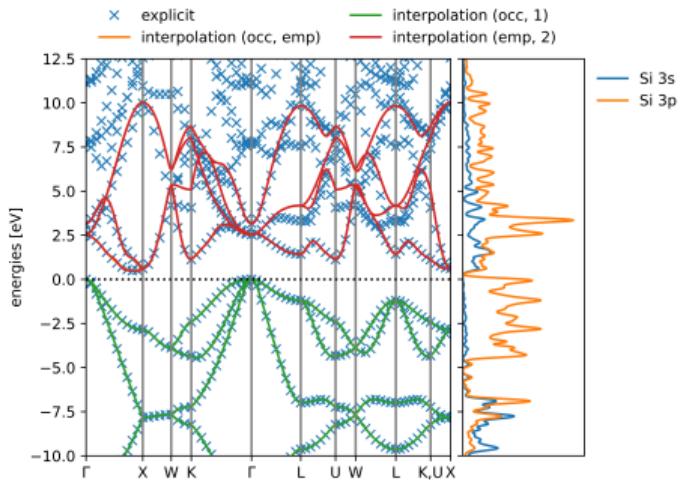


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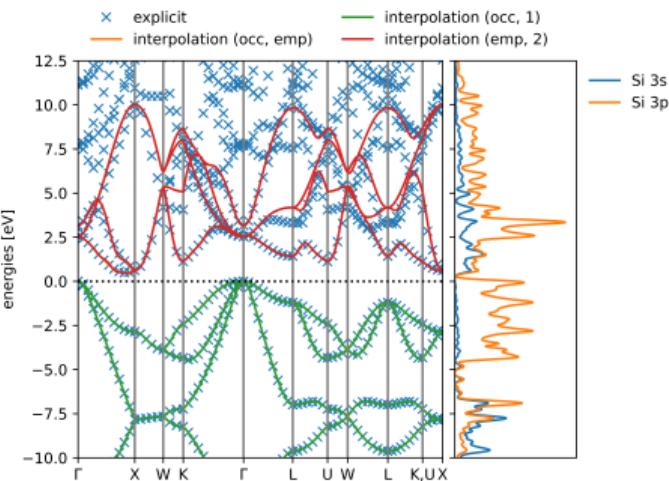
- use PAOs found in pseudopotential files as initial guesses for Wannier functions
- projectability-based disentanglement instead of energy-based disentanglement
- use a parallel transport algorithm to separate the occupied and empty manifolds



Automating Wannierisation



Automating Wannierisation



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A drawback: the number of Wannier functions is determined by the number of PAOs in the pseudopotentials

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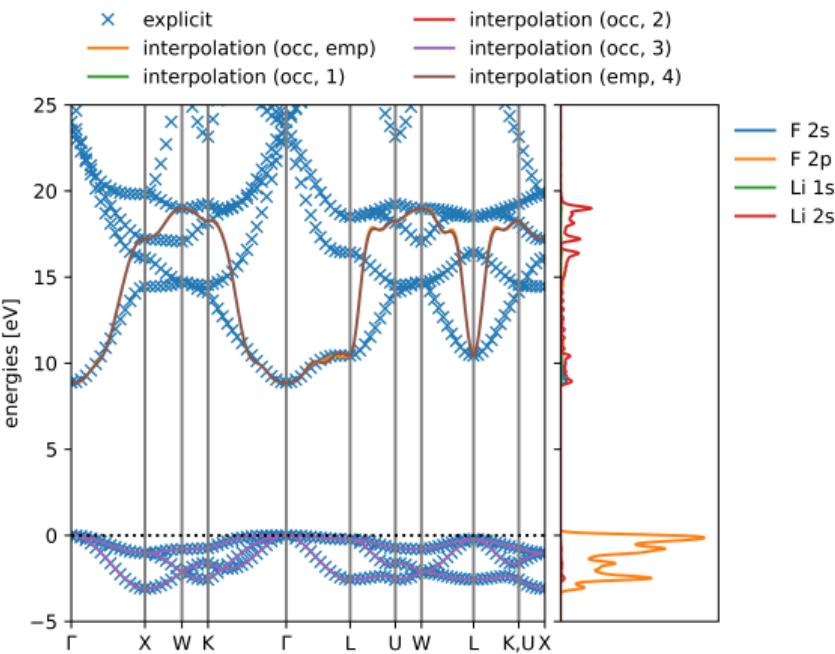
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element	configuration	PAOs
Li	$1s^2 2s^1$	1s, 2s
F	$[1s^2] 2s^2 2p^5$	2s, 2p _x , 2p _y , 2p _z

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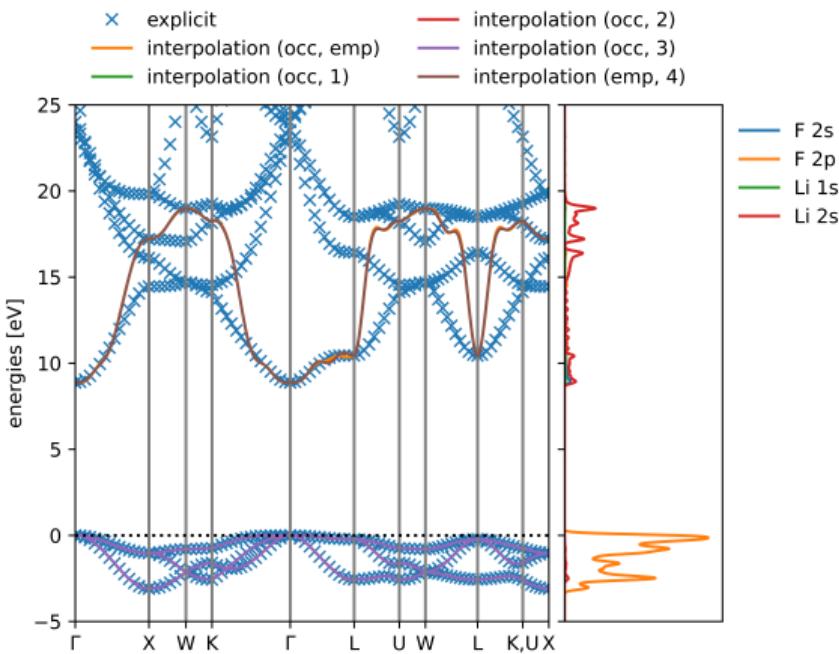


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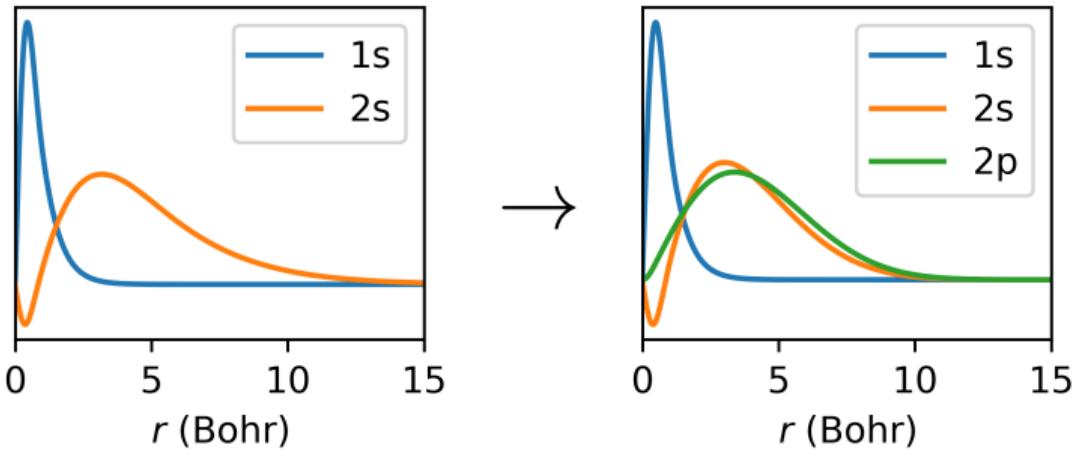
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If we want a better representation of the conduction bands, we're gonna need a bigger boat more PAOs...



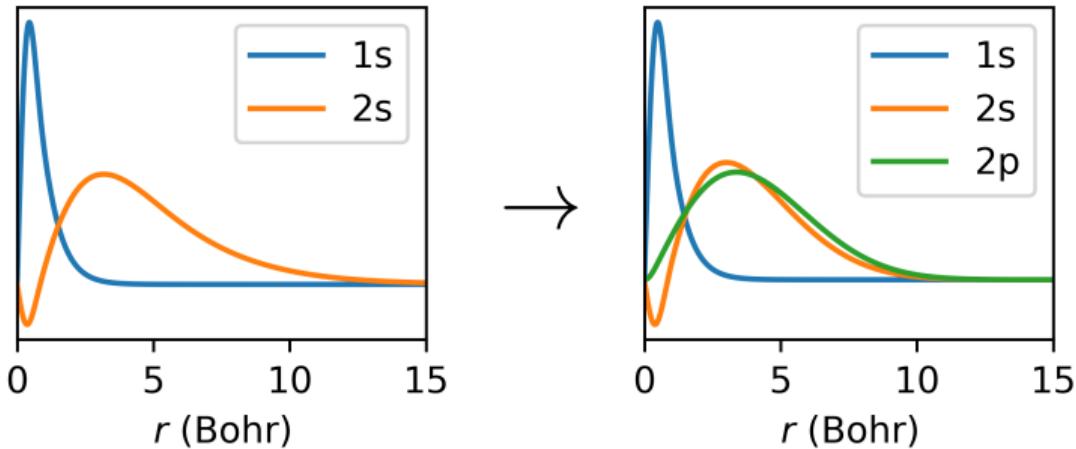
Automating Wannierisation



For cases such as LiF:

- re-solve the radial Schrödinger equation for higher subshells

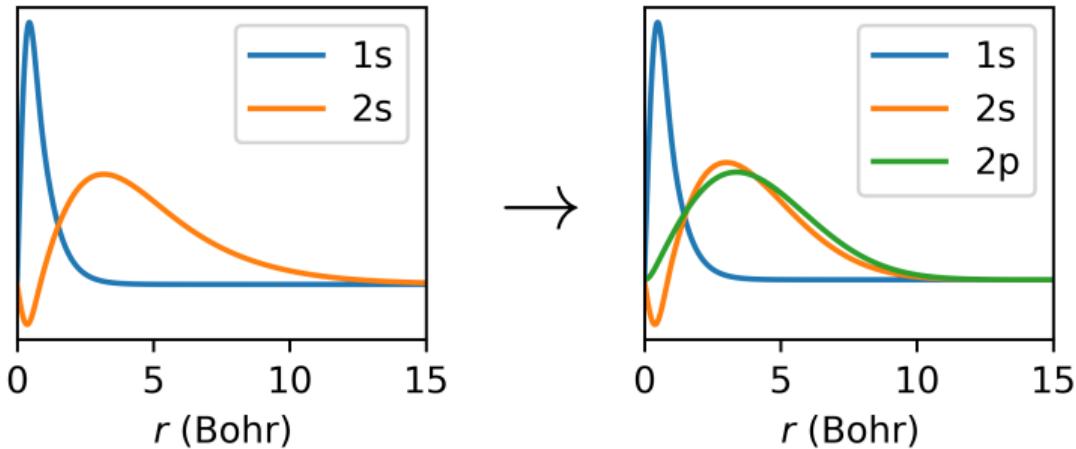
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For cases such as LiF:

- re-solve the radial Schrödinger equation for higher subshells
- apply a confining potential while doing so

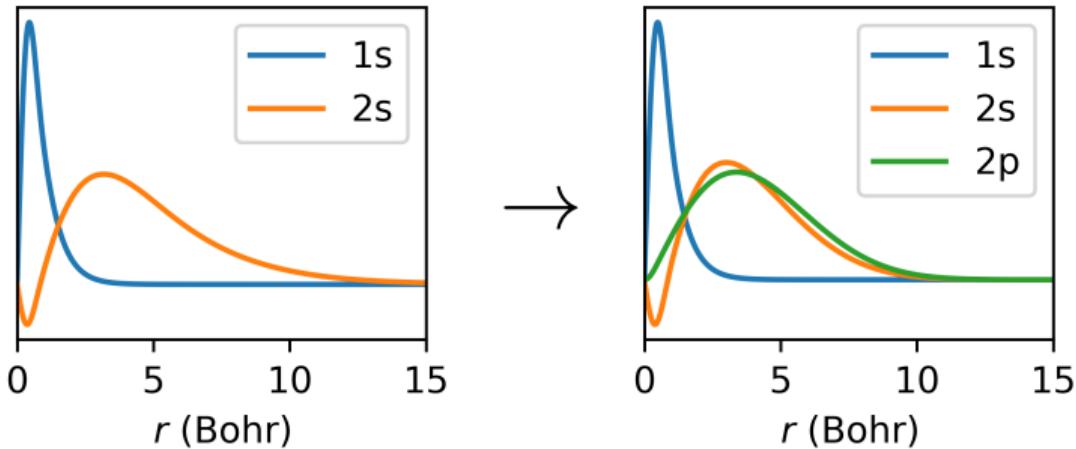
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For cases such as LiF:

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- optimize the confining potential to maximise projectability

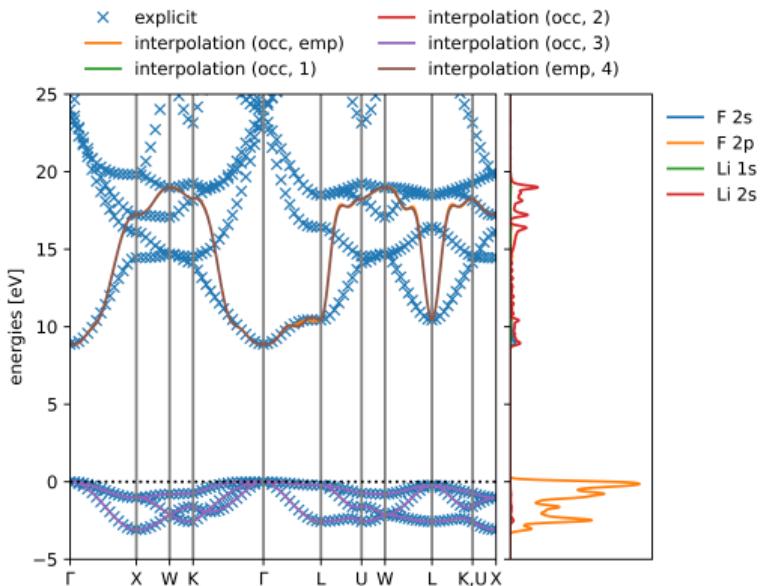
Automating Wannierisation



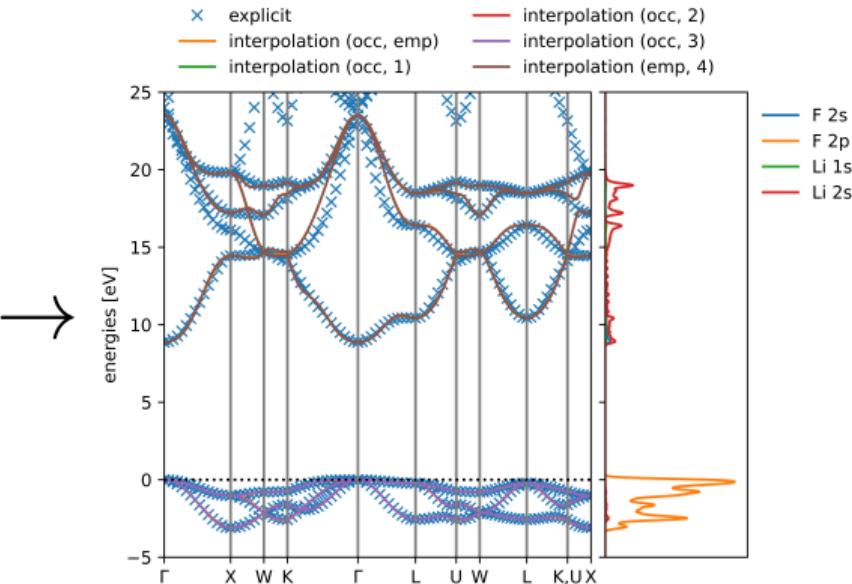
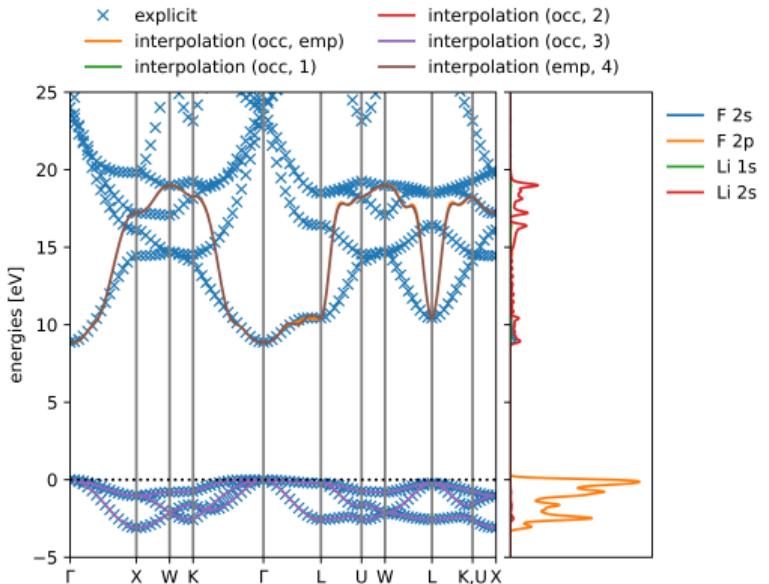
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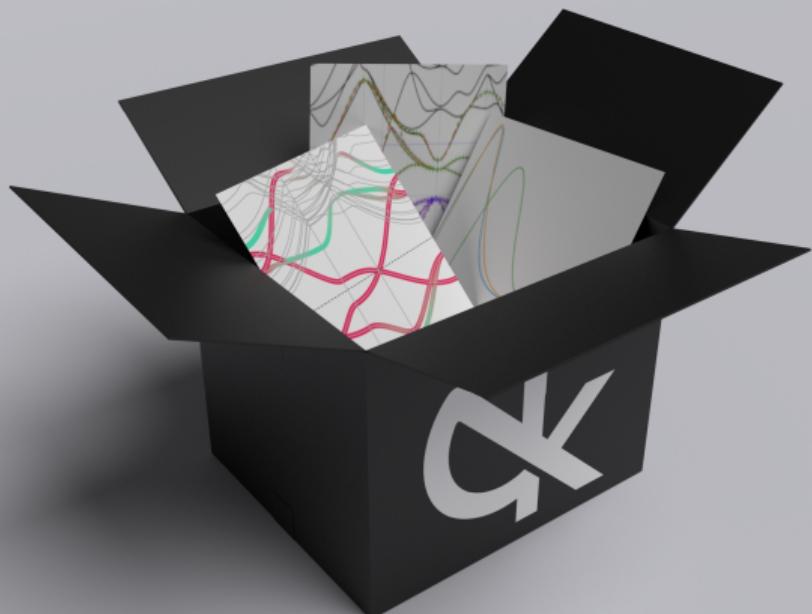
- re-solve the radial Schrödinger equation for higher subshells
- apply a confining potential while doing so
- optimize the confining potential to maximise projectability
- N.B. only once per pseudopotential

Automating Wannierisation



Automating Wannierisation



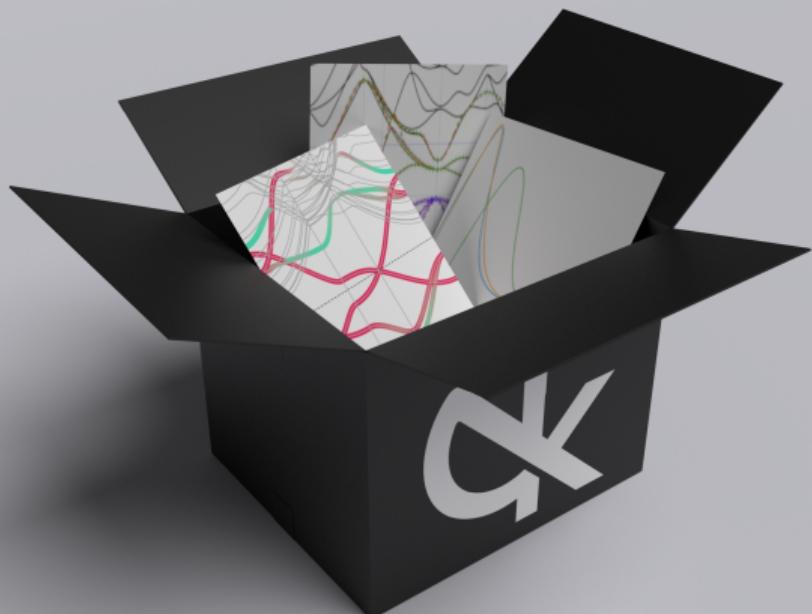


Koopmans functionals can accurately and efficiently predict the band structure of materials

To make these calculations black box, we have...

- automated start-to-finish calculations

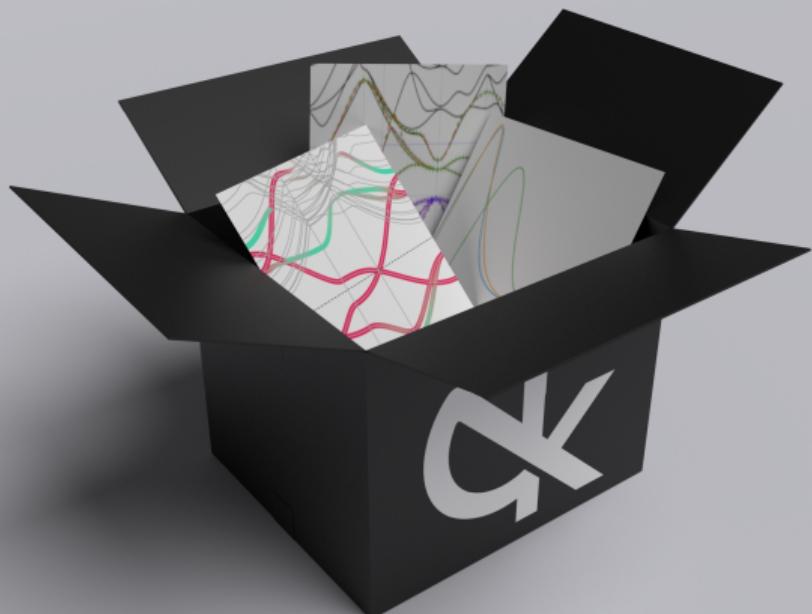
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Koopmans functionals can accurately and efficiently predict the band structure of materials

To make these calculations black box, we have...

- automated start-to-finish calculations *with the koopmans package*
- minimal input required from the user *enabled via automated Wannierisation*

Acknowledgements



Nicola Marzari



Nicola Colonna



Junfeng Qiao



**Swiss National
Science Foundation**

MARVEL
The logo for MARVEL consists of four red hexagons arranged in a horizontal row, with the second and third hexagons partially overlapping.

NATIONAL CENTRE OF COMPETENCE IN RESEARCH

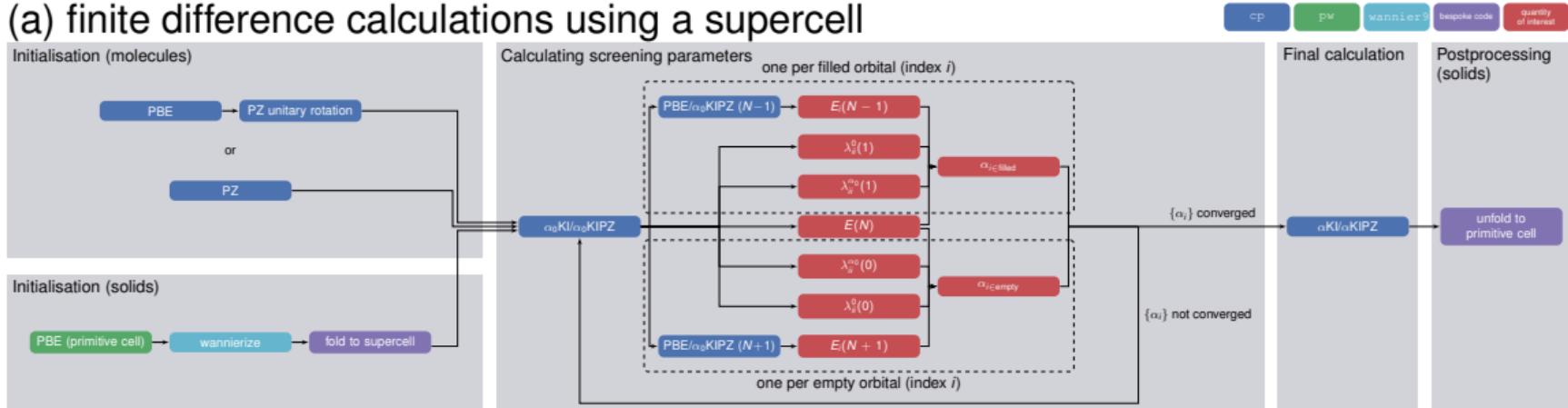
Want to find out more? Go to koopmans-functionals.org

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SPARE SLIDES

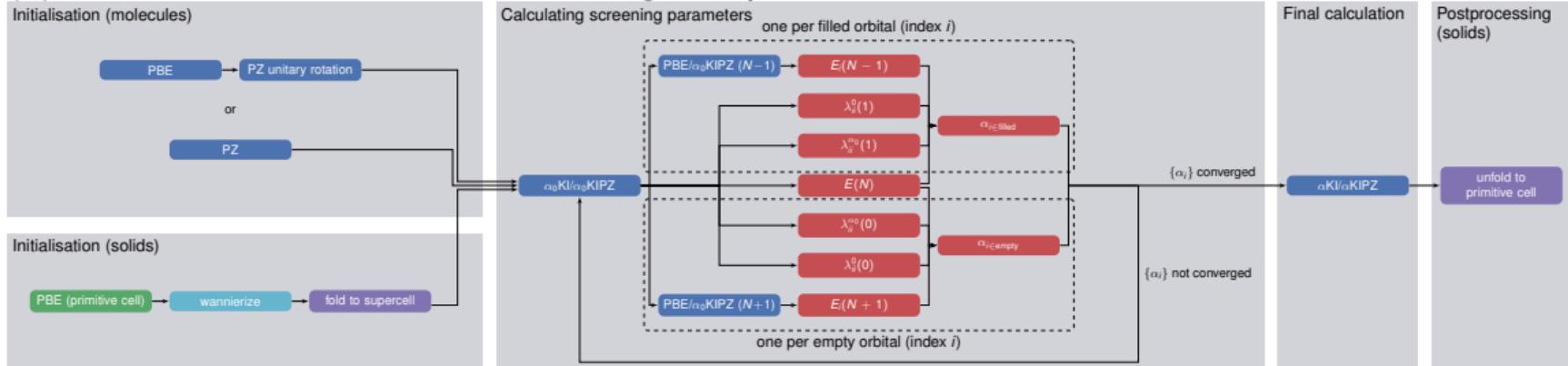
Workflows

(a) finite difference calculations using a supercell



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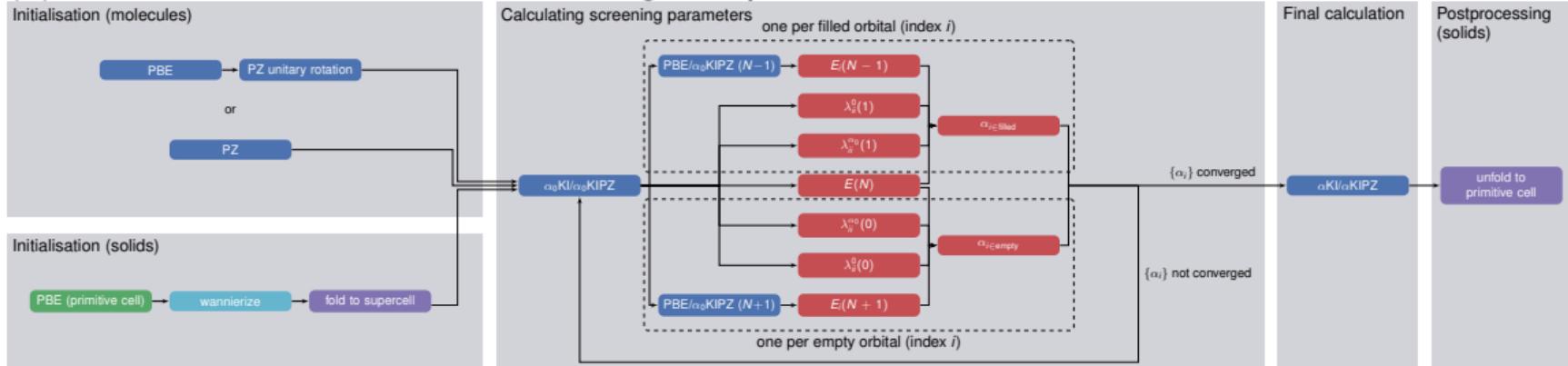


(b) DFPT using a primitive cell



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(b) DFPT using a primitive cell



All implemented in Koopmans

Accurate band structures

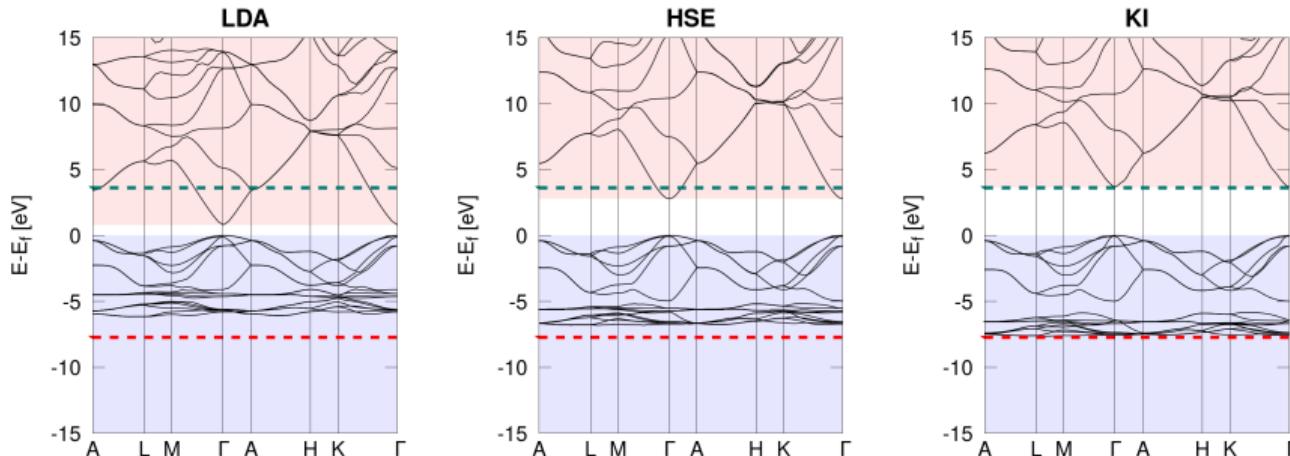
	PBE	$G_0W_0^1$	scGW ²	KI@[PBE,MLWFs]	KIPZ@PBE	exp ³
E_g	0.49	1.06	1.14	1.16	1.15	1.17
$\Gamma_{1v} \rightarrow \Gamma_{25'v}$	11.97	12.04		11.97	12.09	12.5 ± 0.6
$X_{1v} \rightarrow \Gamma_{25'v}$	7.82			7.82		7.75
$X_{4v} \rightarrow \Gamma_{25'v}$	2.85	2.99		2.85	2.86	2.90
$L_{2'v} \rightarrow \Gamma_{25'v}$	9.63	9.79		9.63	9.74	9.3 ± 0.4
$L_{1v} \rightarrow \Gamma_{25'v}$	6.98	7.18		6.98	7.04	6.8 ± 0.2
$L_{3'v} \rightarrow \Gamma_{25'v}$	1.19	1.27		1.19		1.2 ± 0.2
$\Gamma_{25'v} \rightarrow \Gamma_{15c}$	2.48	3.29		3.17	3.20	3.35 ± 0.01
$\Gamma_{25'v} \rightarrow \Gamma_{2'c}$	3.28	4.02		3.95	3.95	4.15 ± 0.05
$\Gamma_{25'v} \rightarrow X_{1c}$	0.62	1.38		1.28	1.31	1.13
$\Gamma_{25'v} \rightarrow L_{1c}$	1.45	2.21		2.12	2.13	2.04 ± 0.06
$\Gamma_{25'v} \rightarrow L_{3c}$	3.24	4.18		3.91	3.94	3.9 ± 0.1
MSE	0.35	0.02		0.01	0.03	
MAE	0.44	0.21		0.14	0.17	

¹ M. Shishkin et al. *Phys. Rev. Lett.* 99.24 (2007), 246403 for E_g and M. S. Hybertsen et al. *Phys. Rev. B* 34.8 (1986), 5390 for the transitions;

² M. Shishkin et al. *Phys. Rev. B* 75.23 (2007), 235102.

³ O. Madelung. *Semiconductors*. 3rd ed. Berlin: Springer-Verlag, 2004.

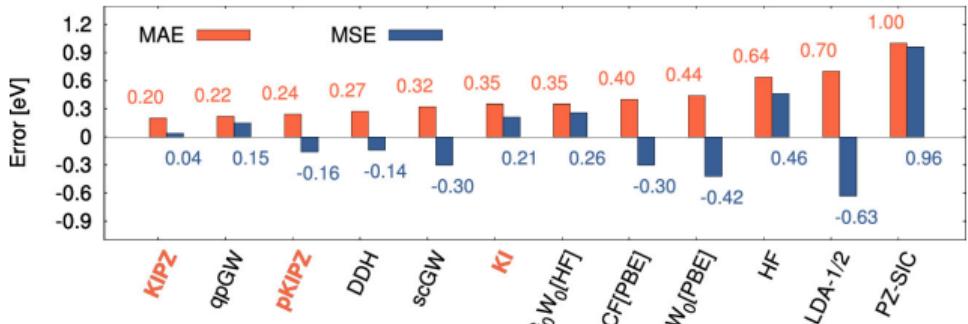
Koopmans functionals give accurate band structures



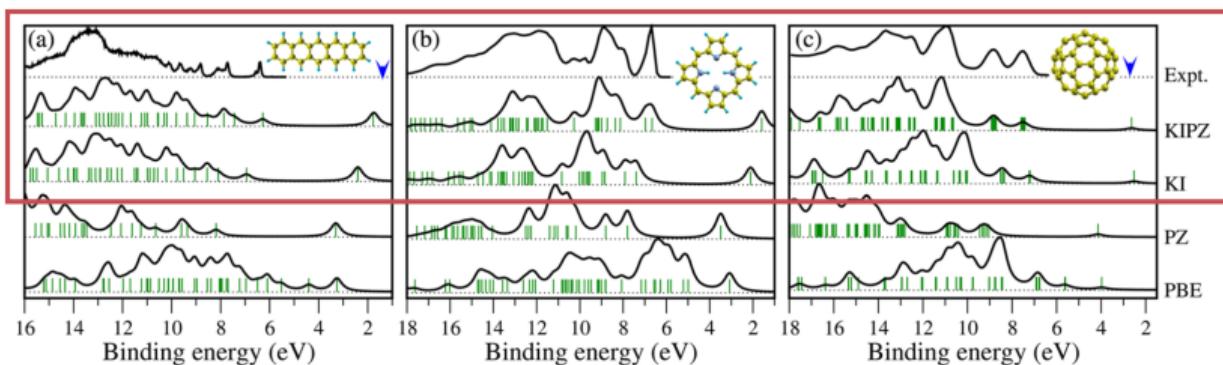
ZnO	LDA	HSE	GW_0	$scG\tilde{W}$	KI	exp
E_{gap} (eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle \varepsilon_d \rangle$ (eV)	-5.1	-6.1	-6.4	-6.7	-6.9	-7.5/-8.0

Koopmans functionals: results for molecules

Ionisation potentials = $E(N - 1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)

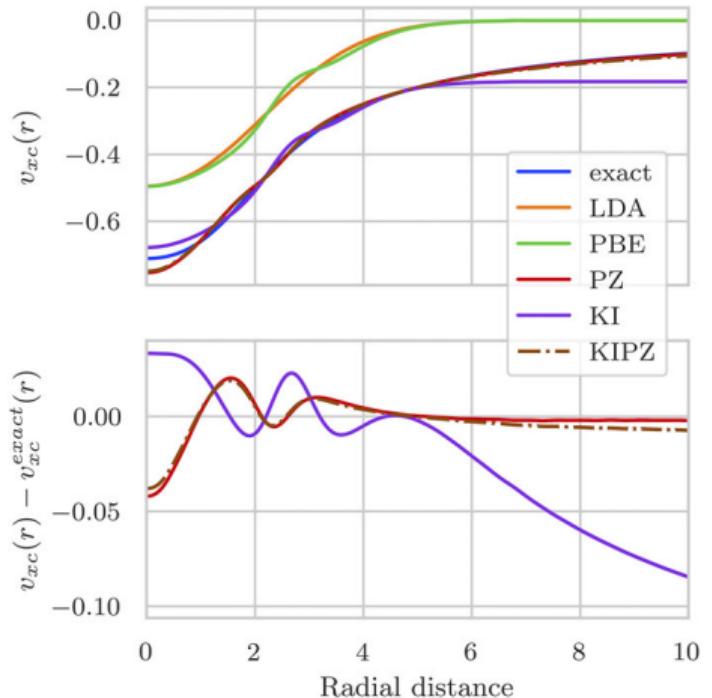


Ultraviolet photoemission spectra



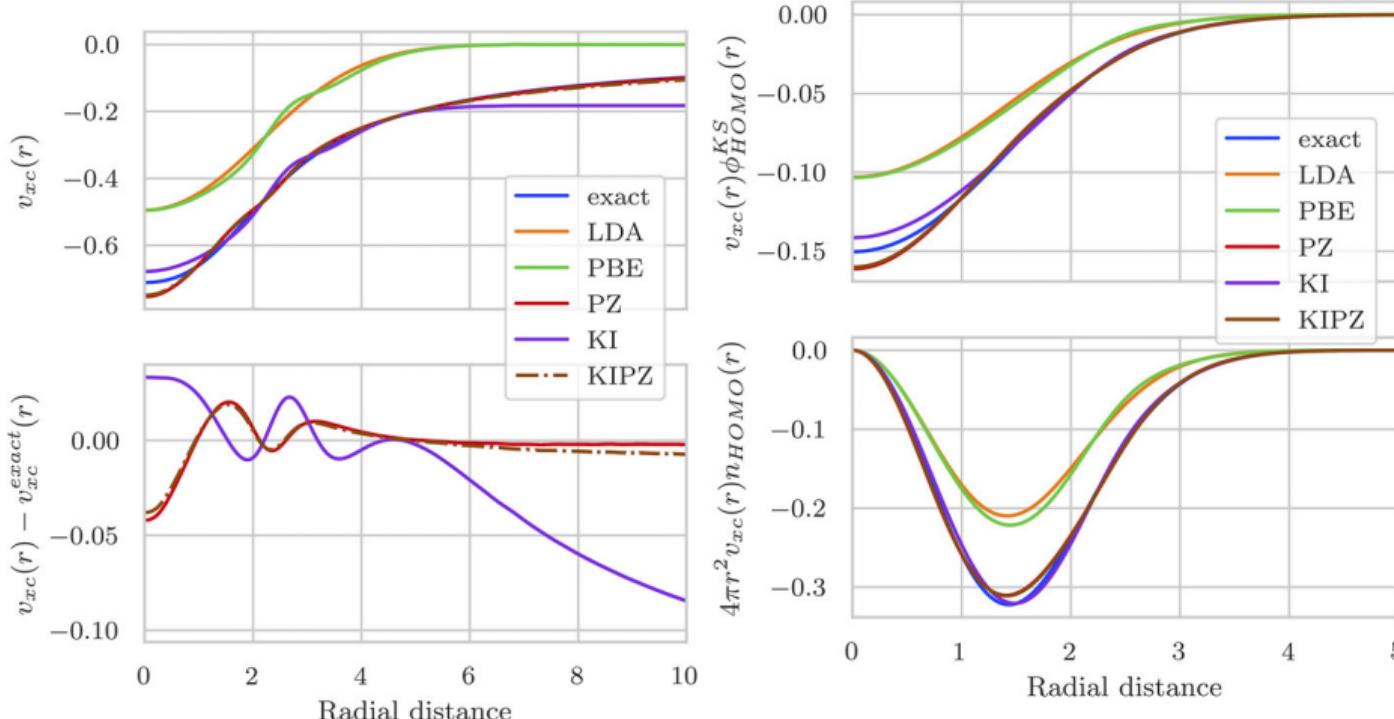
Koopmans functionals: results for toy systems

For Hooke's atom (two electrons in a harmonic confining potential with Coulombic repulsion)



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For Hooke's atom (two electrons in a harmonic confining potential with Coulombic repulsion)



The projectability is

$$p_{m\mathbf{k}} = \sum_n |\langle \varphi_n | \psi_{m\mathbf{k}} \rangle|^2$$

We want a set of projectors such that...

- they should have a large overlap with some Kohn-Sham states and a small overlap with all the others
- they should lie within the span of the Kohn-Sham states

We can meet these criteria if we maximise the functional

$$F[\{\varphi_n\}] = \frac{1}{N_{\mathbf{k}} N_w} \sum_{\mathbf{k}} \sum_{m \in S_{\mathbf{k}}} p_{m\mathbf{k}}$$

where $S_{\mathbf{k}}$ corresponds to the N_w -largest values of $p_{m\mathbf{k}}$.

Bayesian optimisation

