

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

Edward Linscott



PSI



DPG conference



21 March 2024



Accurate band structures

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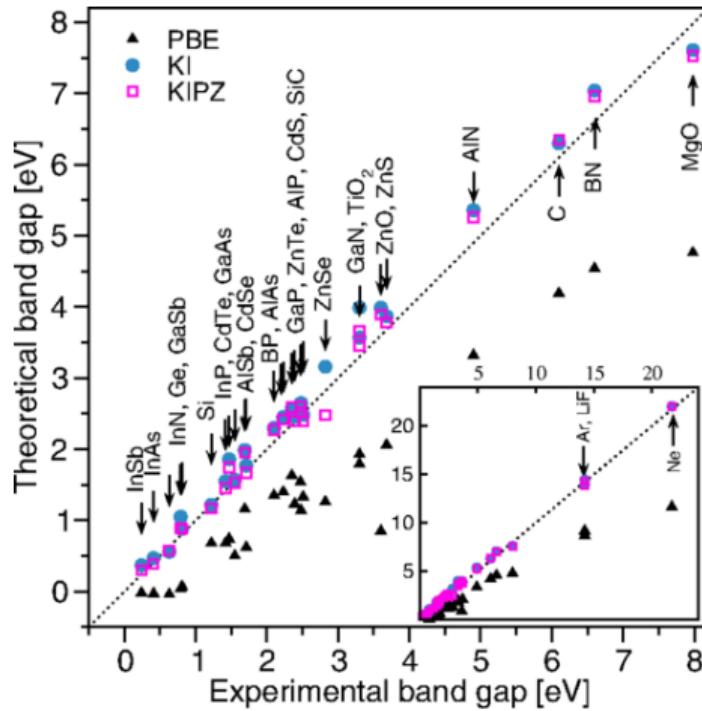
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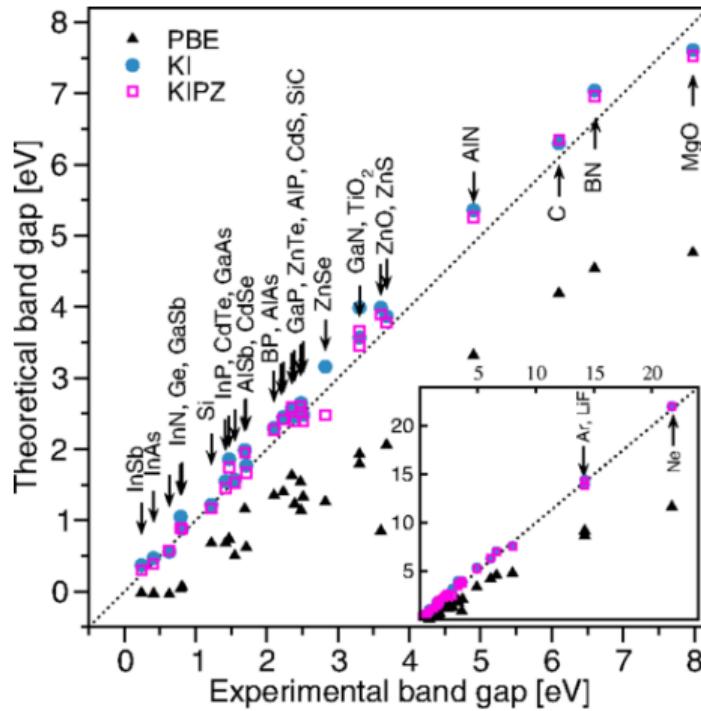
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	PBE	G_0W_0	KI	KIPZ	$QS\tilde{G}W$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49



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

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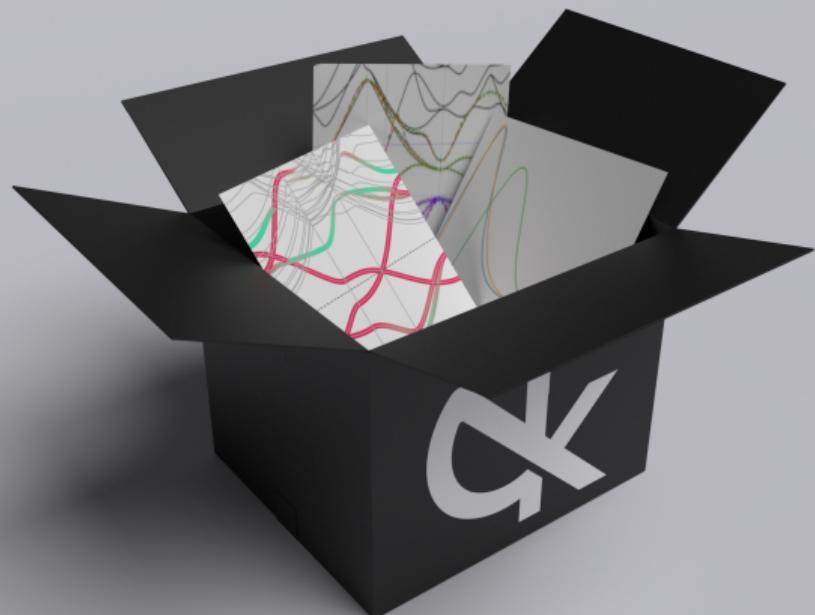
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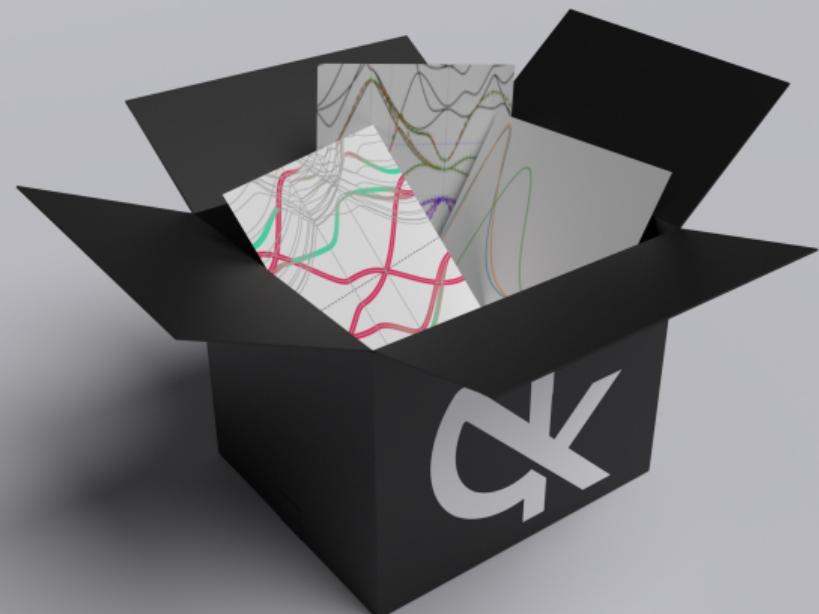
- initialize a set of variational orbitals
- calculate the screening parameters $\{\alpha_i\}$
- construct and diagonalize the Hamiltonian

What needs to be in the box?



For a black box, we need...

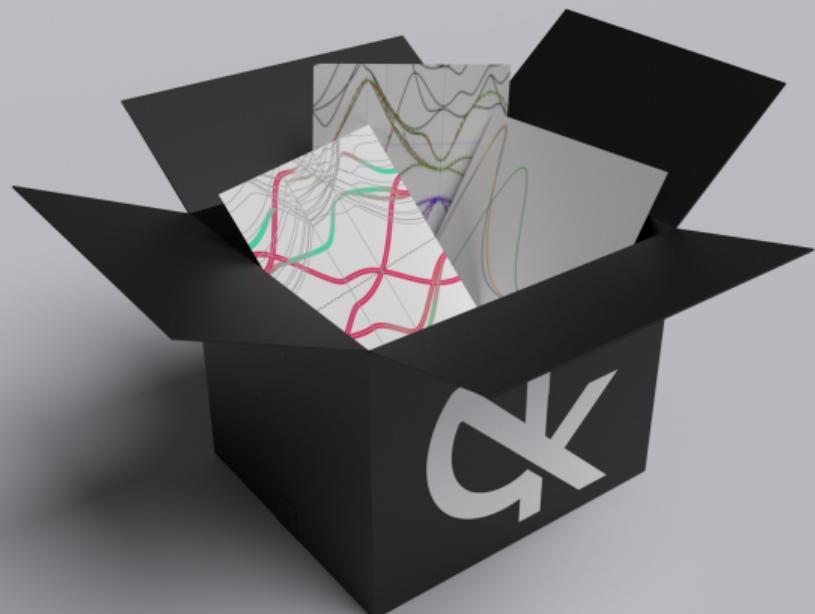
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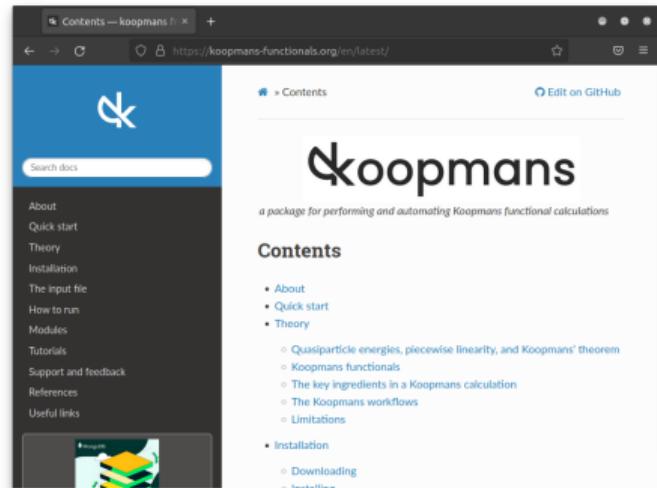
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- automated start-to-finish calculations
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koopmans

- v1.0 released last year¹
- implementations of Koopmans functionals within Quantum ESPRESSO
- automated workflows
 - Koopmans calculations
 - Wannierization
 - 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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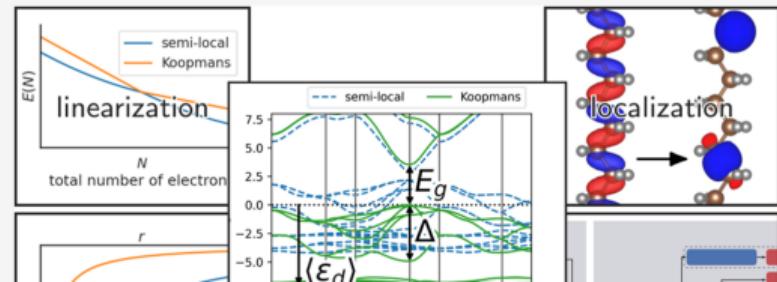
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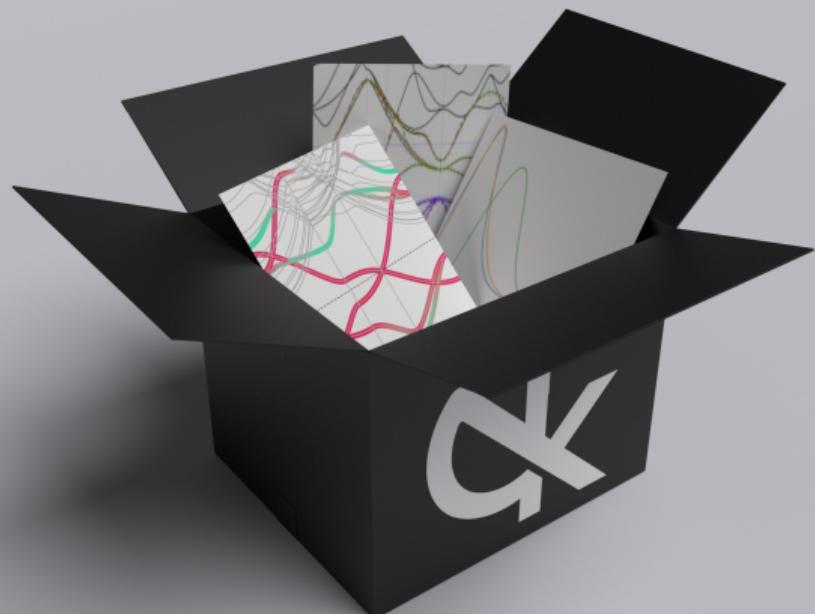
Article Recommendations

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



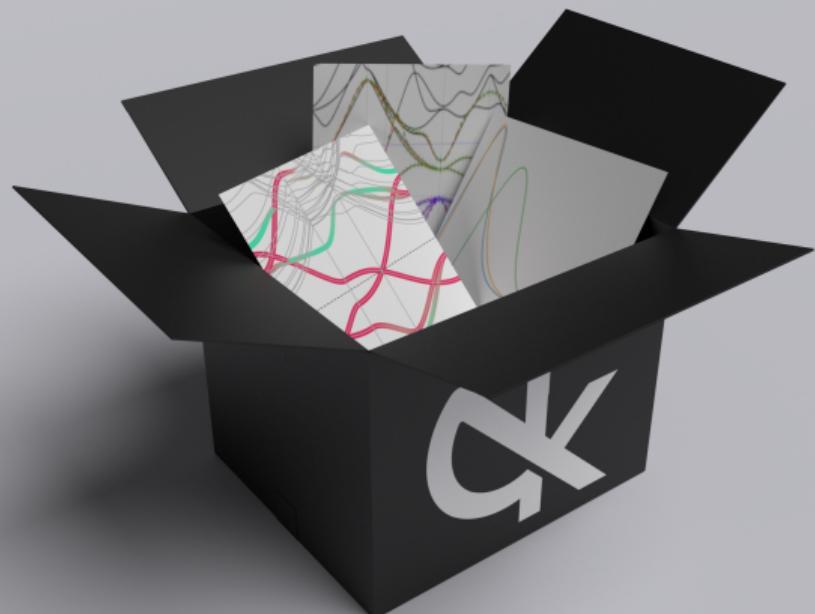
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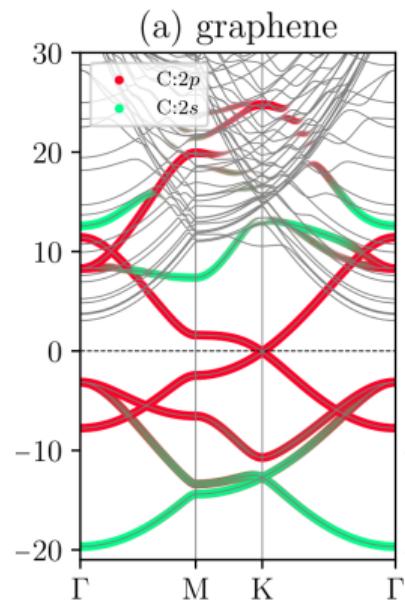
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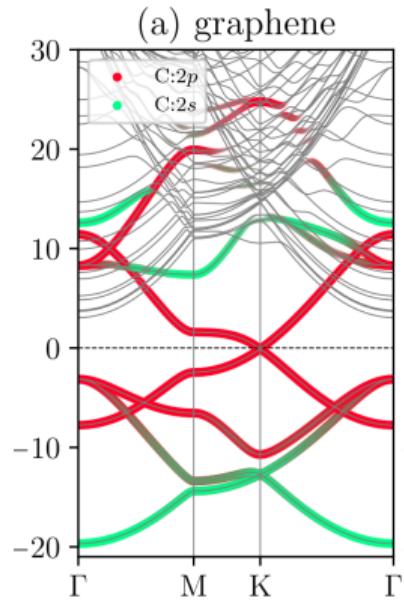


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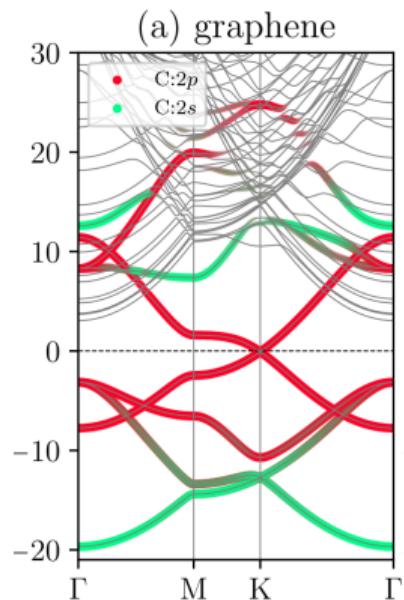


Can we automate the Wannierization?



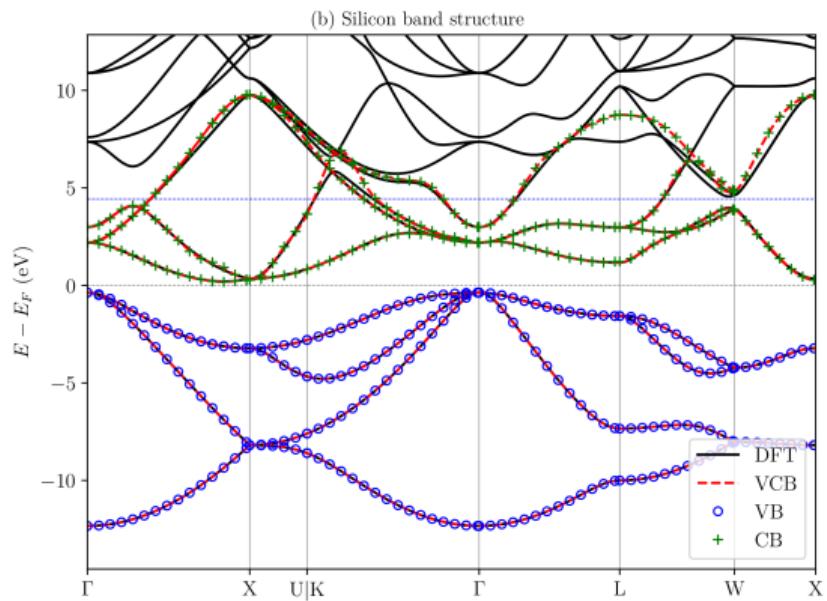
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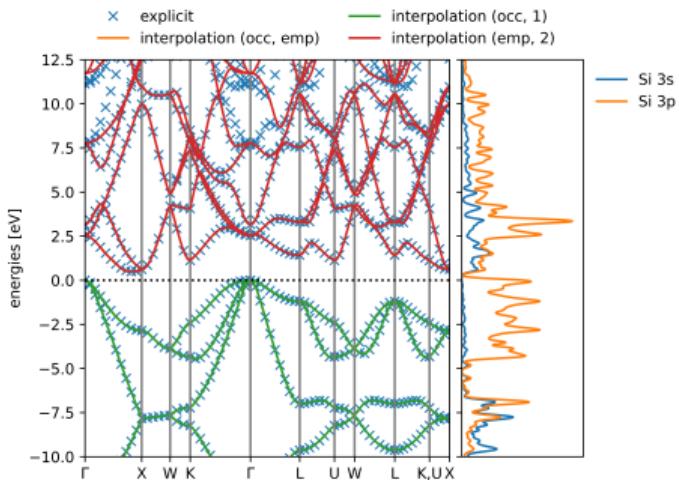
- PAOs from the pseudopotentials as the initial guess for the projectors
- projectability-based disentanglement instead of energy-based disentanglement
- a parallel transport algorithm is used to separate the occupied and empty manifolds

Automating Wannierization

```
{  
  "workflow": {  
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  "atoms": {  
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      "celldms": {"1": 10.2622}},  
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element	electronic configuration	PAOs	number of PAOs
Li	$1s^2 2s^1$	$1s, 2s$	2
F	$[1s^2] 2s^2 2p^5$	$2s, 2p_x, 2p_y, 2p_z$	4

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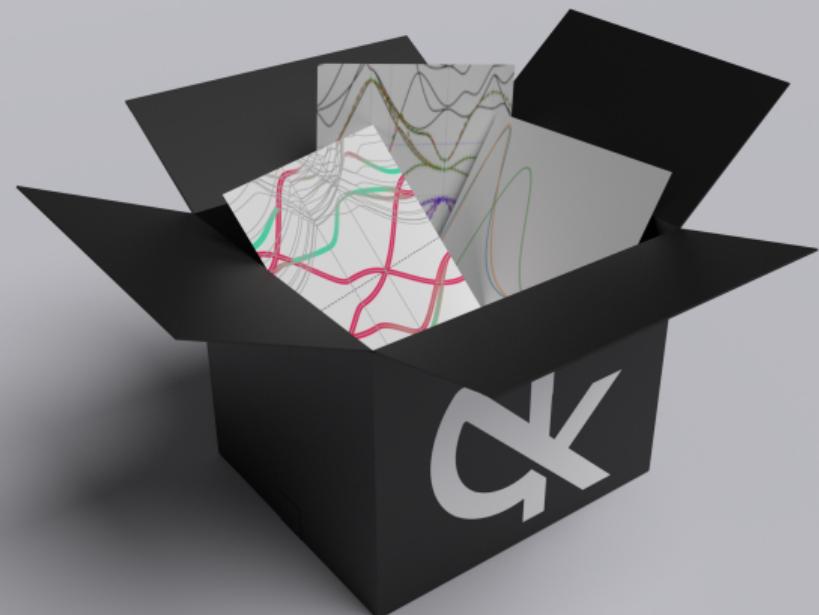
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If we want more Wannier functions, we're gonna need a bigger boat more PAOs...

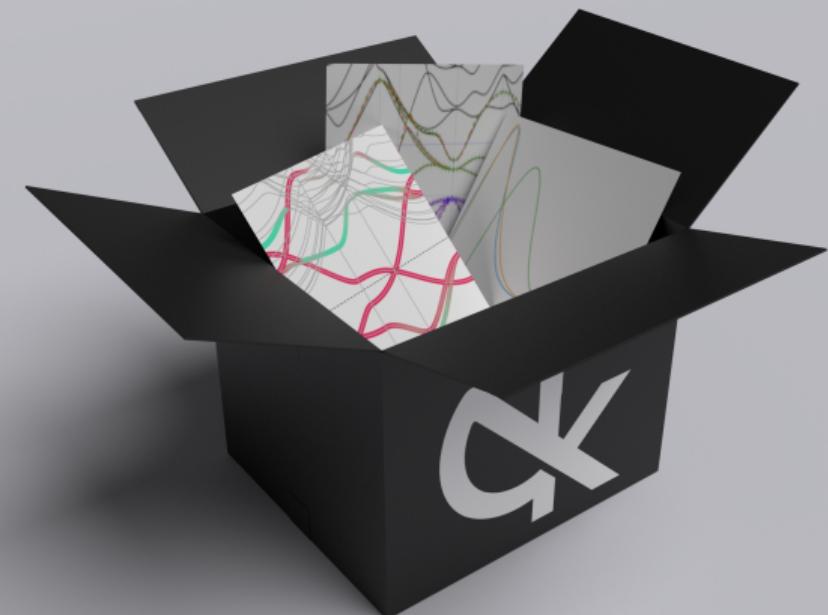
For cases such as LiF, we...
re-solve the radial Schrödinger equation for additional pseudoatomic orbitals. A fictitious
confining potential is required to localise the empty
Note that this does not add complexity to the user as it only needs to be performed once
per pseudopotential

Take home messages



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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

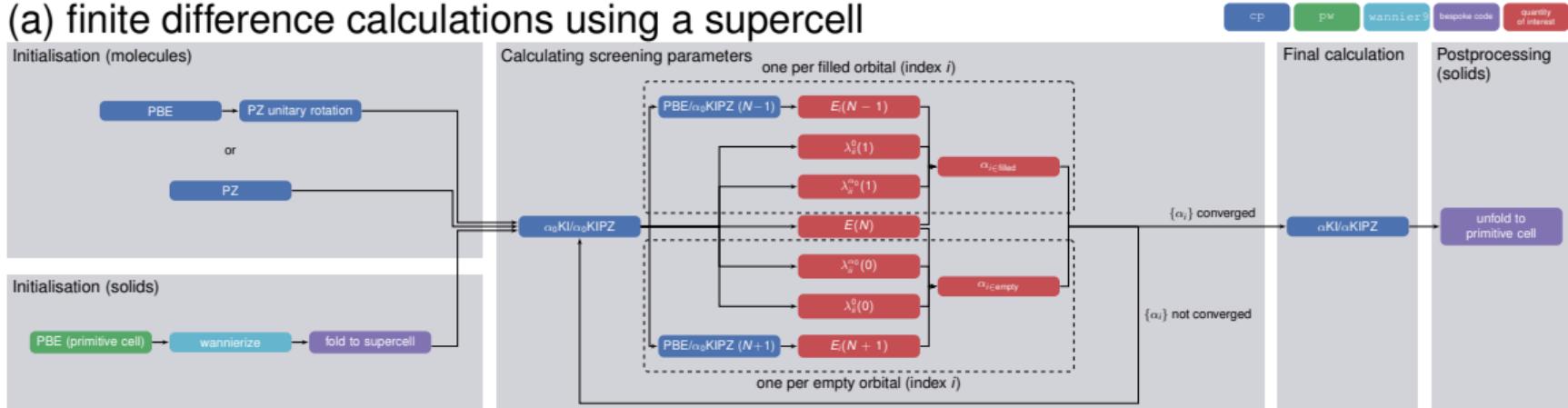
Want to find out more? Go to koopmans-functionals.org

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SPARE SLIDES

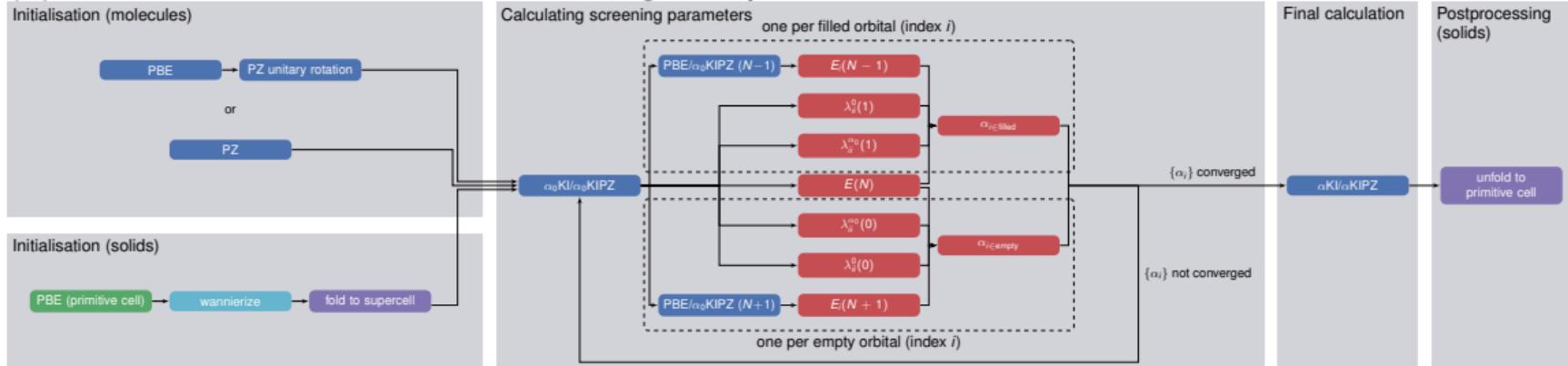
Workflows

(a) finite difference calculations using a supercell



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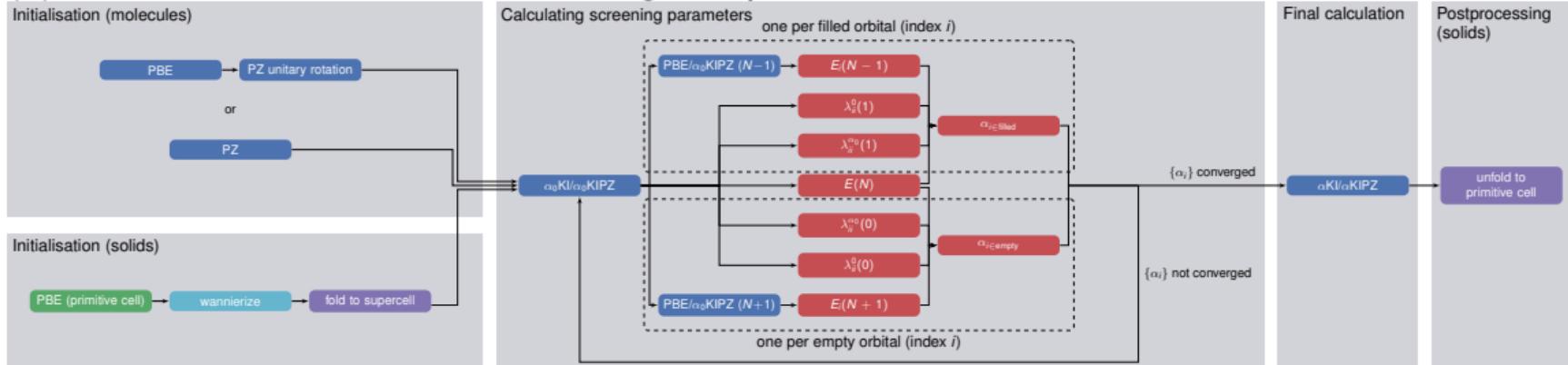


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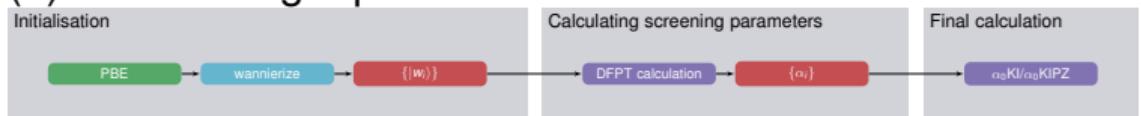


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All implemented in Koopmans

Accurate band structures

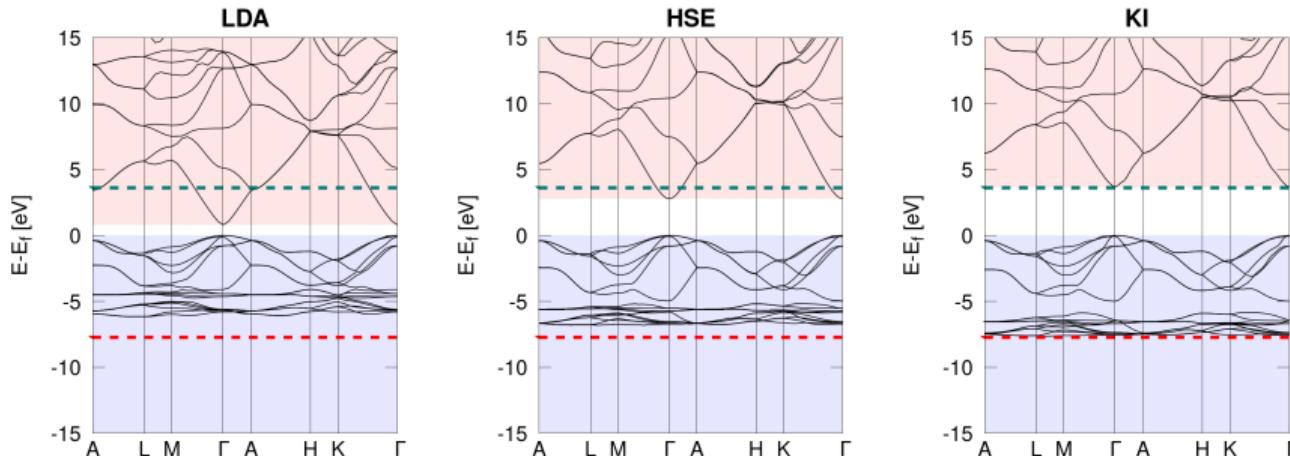
	PBE	$G_0W_0^1$	scGW ²	KI@[PBE,MLWFs]	KIPZ@PBE	exp ³
E_g	0.49	1.06	1.14	1.16	1.15	1.17
$\Gamma_{1v} \rightarrow \Gamma_{25'v}$	11.97	12.04		11.97	12.09	12.5 ± 0.6
$X_{1v} \rightarrow \Gamma_{25'v}$	7.82			7.82		7.75
$X_{4v} \rightarrow \Gamma_{25'v}$	2.85	2.99		2.85	2.86	2.90
$L_{2'v} \rightarrow \Gamma_{25'v}$	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.

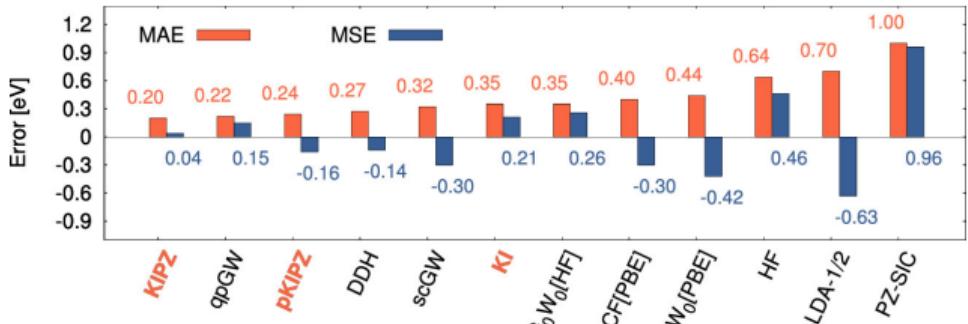
Koopmans functionals give accurate band structures



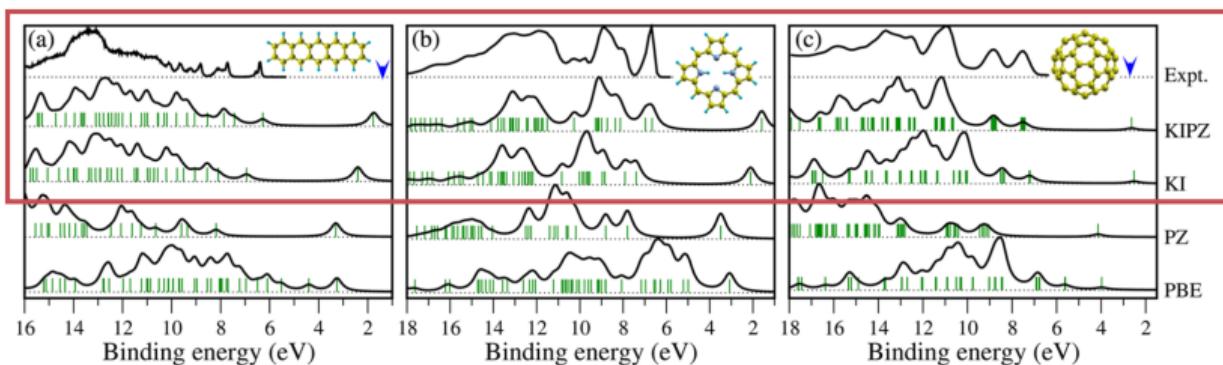
ZnO	LDA	HSE	GW_0	$scG\tilde{W}$	KI	exp
E_{gap} (eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle \varepsilon_d \rangle$ (eV)	-5.1	-6.1	-6.4	-6.7	-6.9	-7.5/-8.0

Koopmans functionals: results for molecules

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

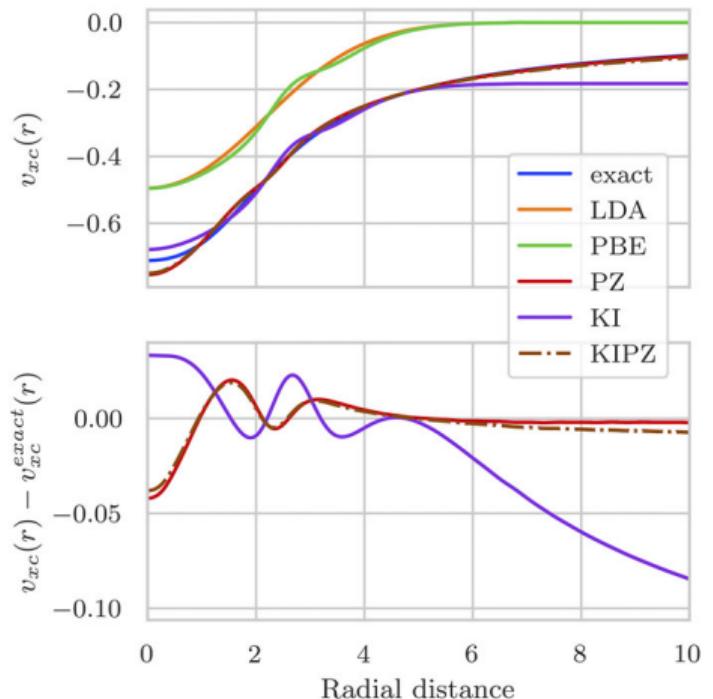


Ultraviolet photoemission spectra



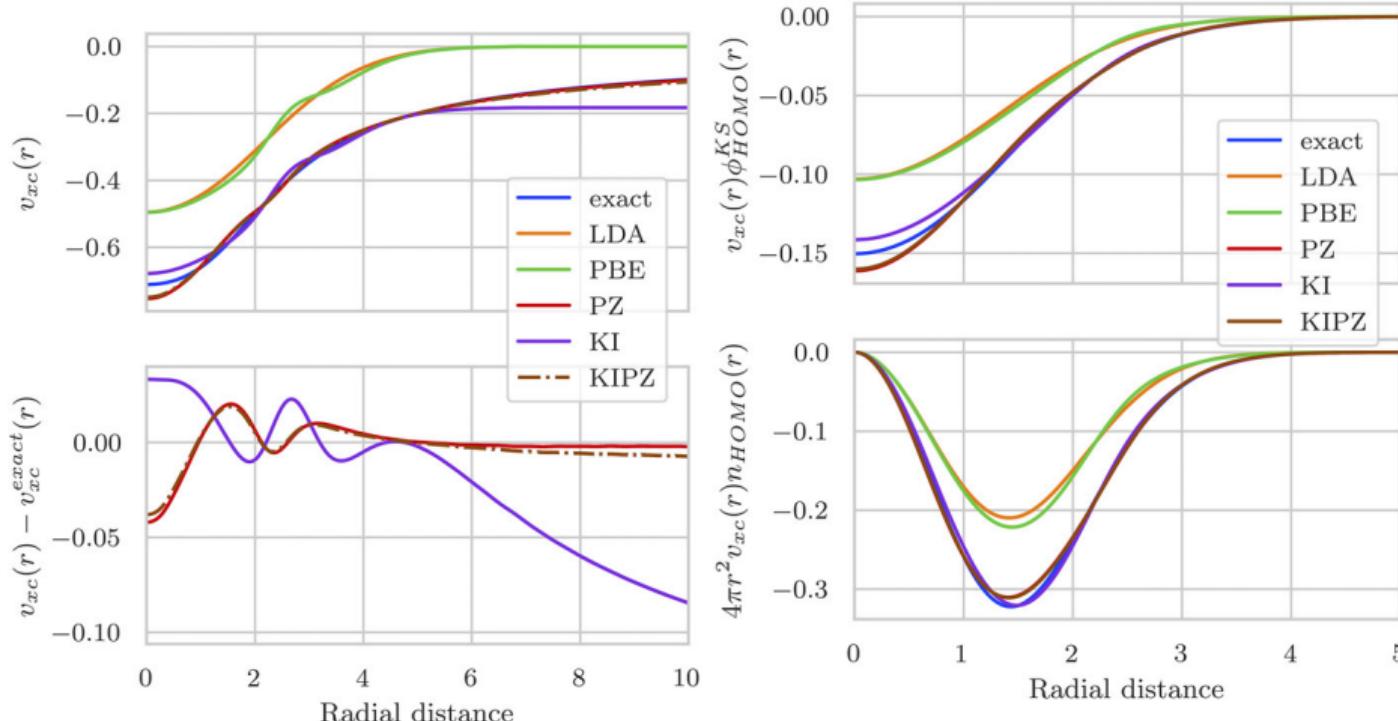
Koopmans functionals: results for toy systems

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



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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 $p_{m\mathbf{k}}$.