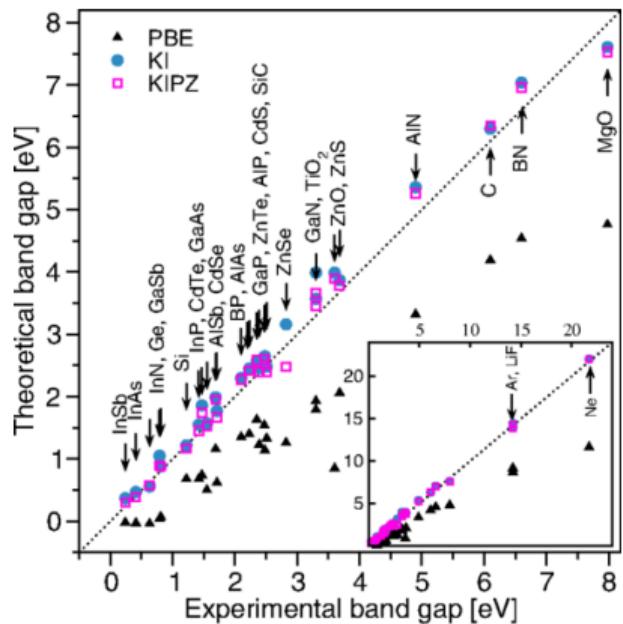


Automating the calculation of accurate band structures with Koopmans functionals

Koopmans functionals give accurate band structures



Mean absolute error (eV) across prototypical semiconductors and insulators

	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

Koopmans functionals give accurate band structures

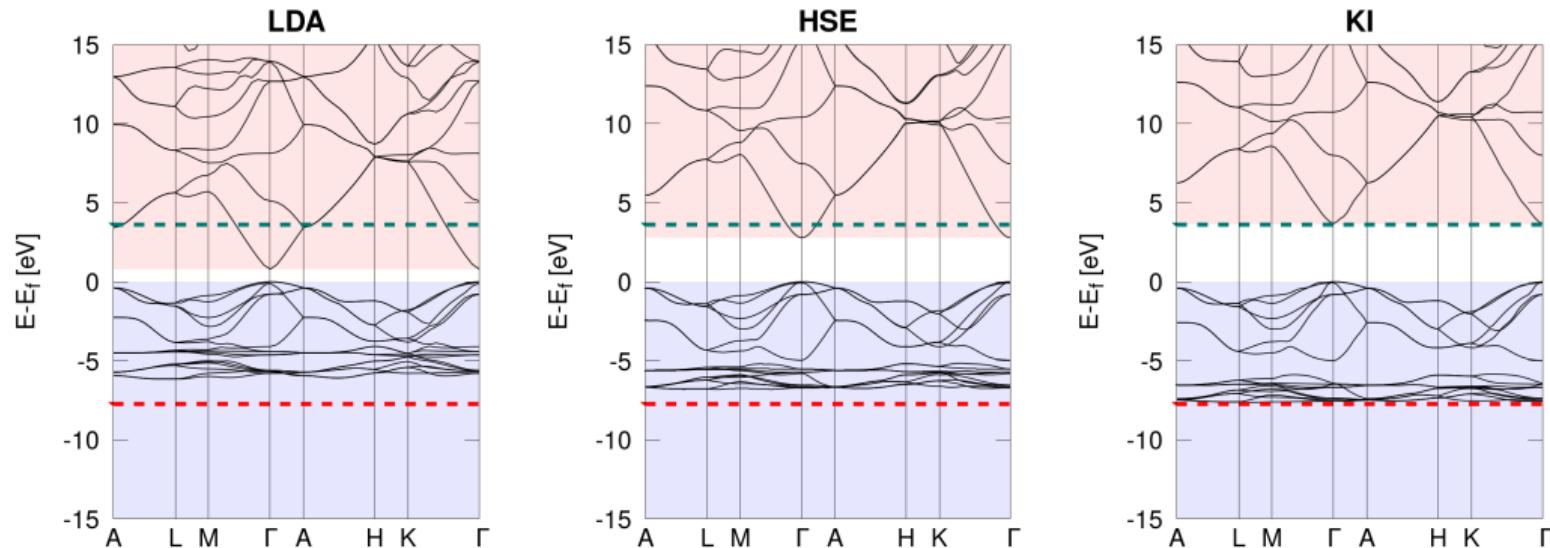
	PBE	$G_0W_0^1$	scGW 2	KI@[PBE,MLWFs]	KIPZ@PBE	exp 3
E_g	0.49	1.06	1.14	1.16	1.15	1.17
$\Gamma_{1v} \rightarrow \Gamma_{25'v}$	11.97	12.04		11.97	12.09	12.5 ± 0.6
$X_{1v} \rightarrow \Gamma_{25'v}$	7.82			7.82		7.75
$X_{4v} \rightarrow \Gamma_{25'v}$	2.85	2.99		2.85	2.86	2.90
$L_{2'v} \rightarrow \Gamma_{25'v}$	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. B* 75.23 (2007), 235102 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. Lett.* 99.24 (2007), 246403.

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

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

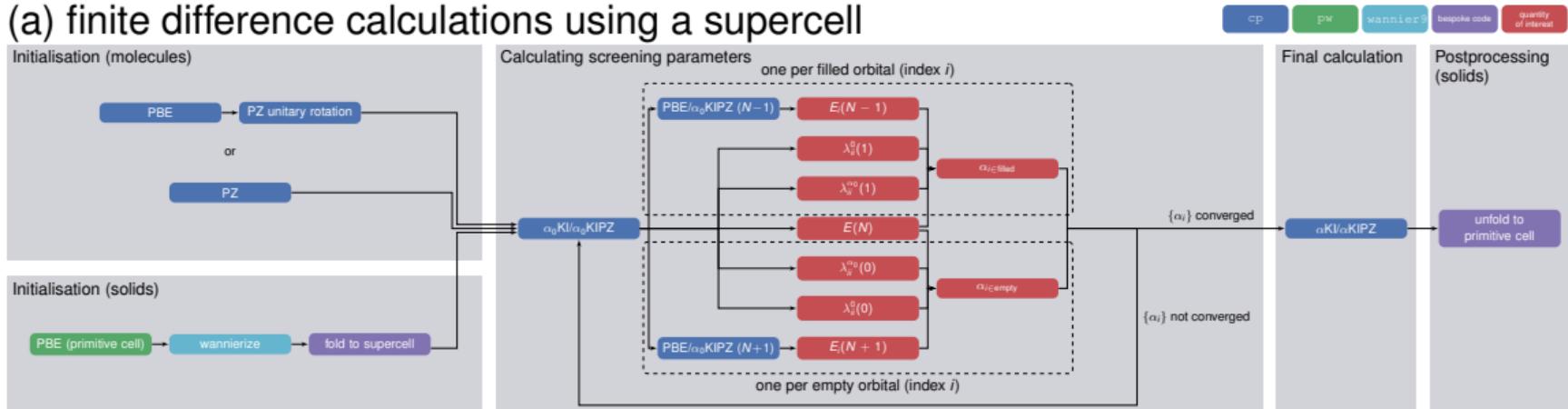
General features:

- enforces a generalized piecewise linearity condition
- depends on localization
- is orbital-density-dependent
- requires the ab initio calculation of screening parameters

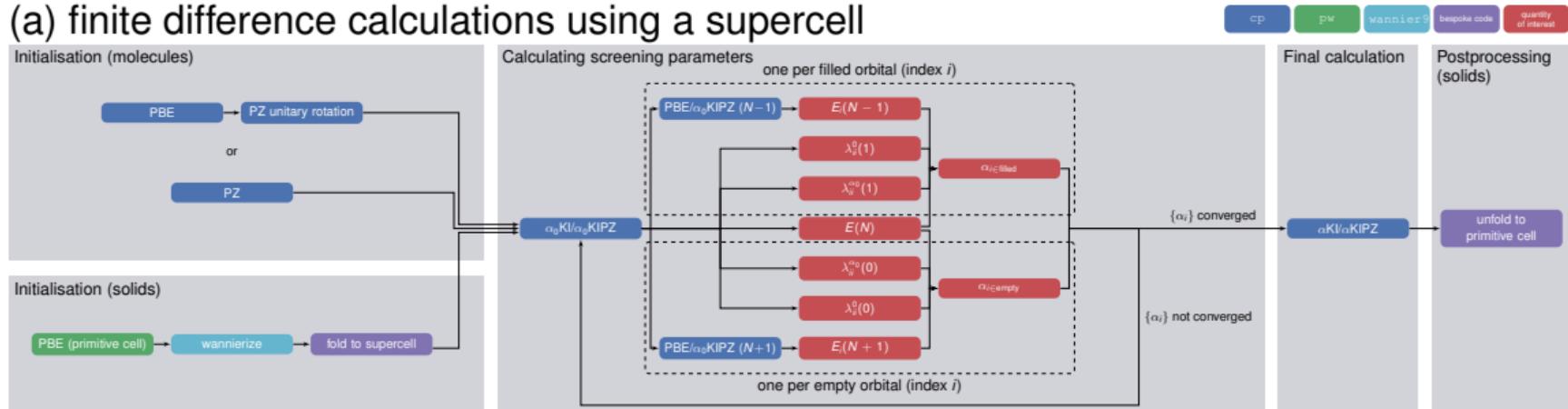
In order to evaluate this functional, one must...

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

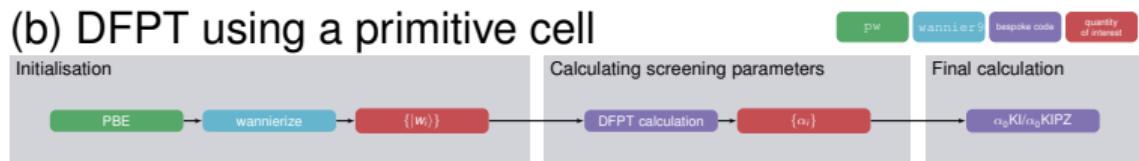
(a) finite difference calculations using a supercell



(a) finite difference calculations using a supercell



(b) DFPT using a primitive cell



Complicated workflows mean that...

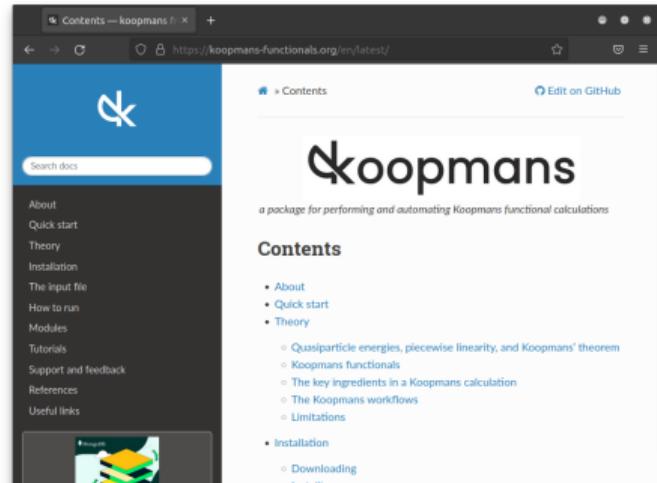
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- v1.0 released earlier this year¹
- implementations of Koopmans functionals within Quantum ESPRESSO
- automated workflows
 - start-to-finish Koopmans calculations
 - Wannierisation
 - dielectric tensor
 - convergence tests
 - ...
- built on top of ASE²
- does not require expert knowledge

koopmans-functionals.org



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

² A. H. Larsen et al. *J. Phys. Condens. 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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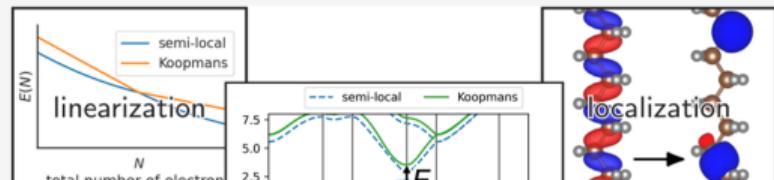
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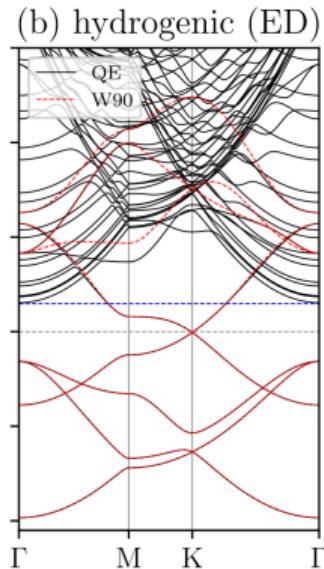
Supporting Information

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



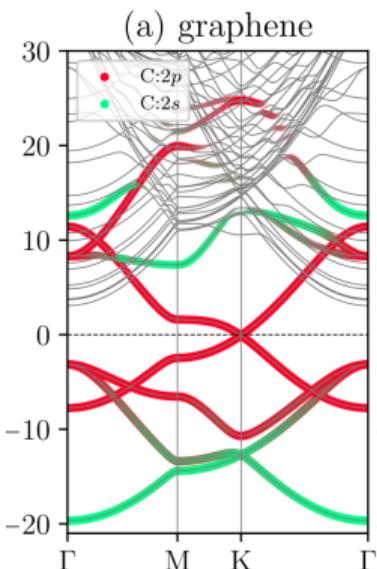
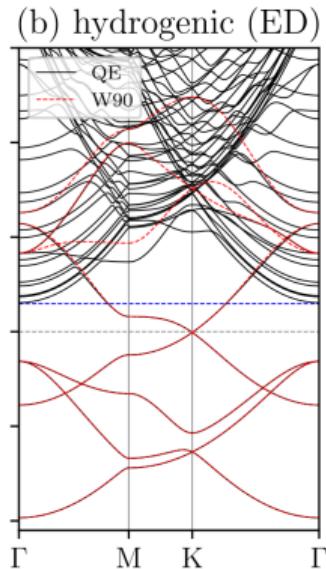
One remaining manual step: Wannierization. Can we automate this?

One remaining manual step: Wannierization. Can we automate this?



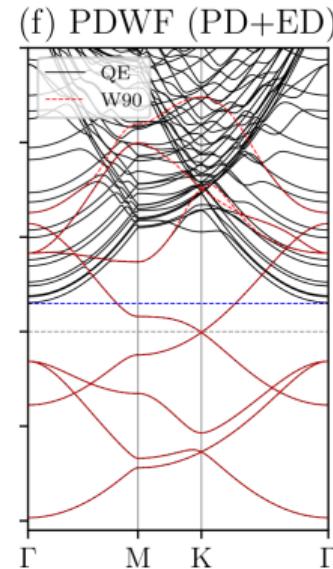
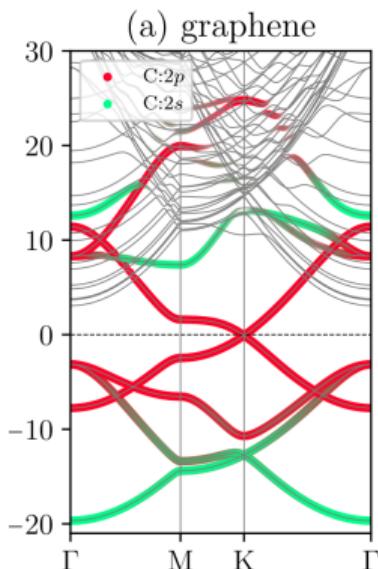
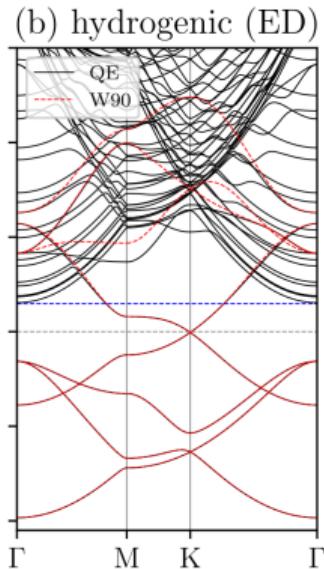
Automating Wannierization

One remaining manual step: Wannierization. Can we automate this?



Automating Wannierization

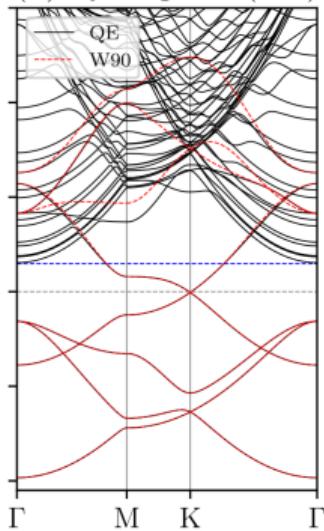
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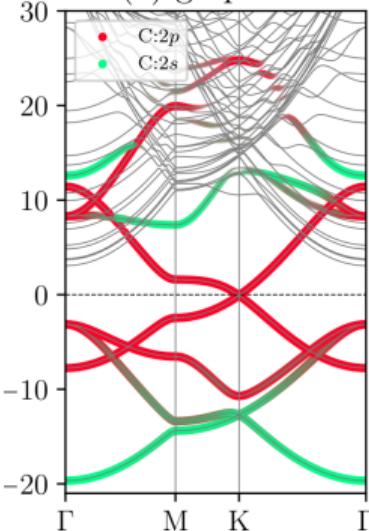
Automating Wannierization

One remaining manual step: Wannierization. Can we automate this?

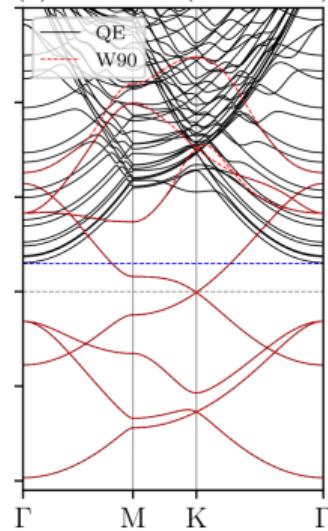
(b) hydrogenic (ED)



(a) graphene

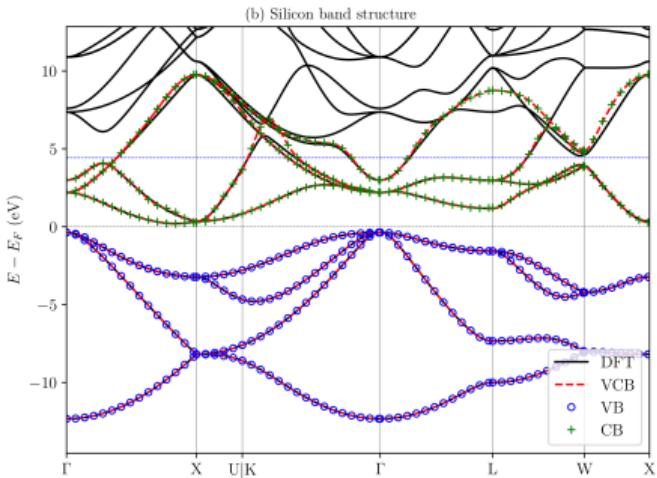


(f) PDWF (PD+ED)

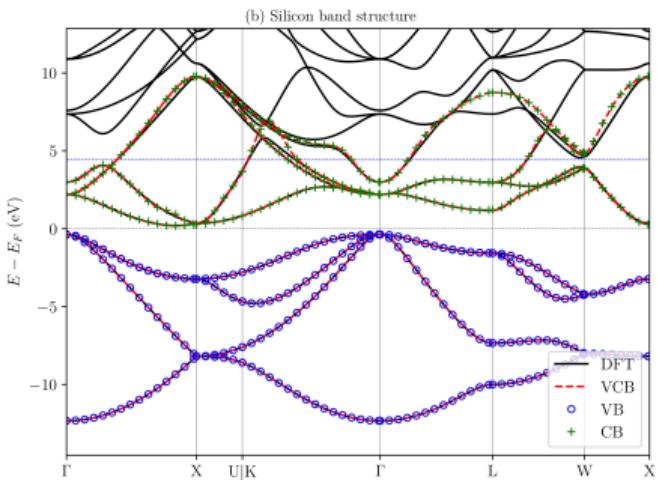


Demonstrated on >20,000 materials → black-box Wannierization

We separate target manifolds via parallel transport to obtain separate occupied and empty manifolds

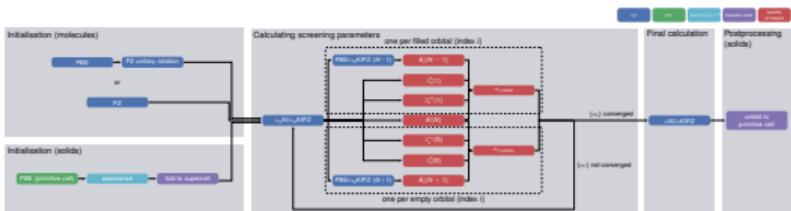
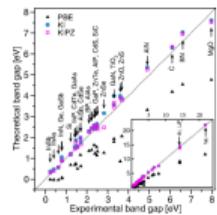
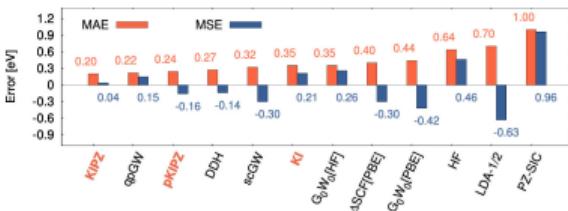


We separate target manifolds via parallel transport to obtain separate occupied and empty manifolds



All of the above is supported by koopmans, but more details to be resolved... watch this space!

Take home messages



- Koopmans functionals can give orbital energies and band structures with comparable accuracy to state-of-the-art GW
- the release of koopmans means non-experts can now use Koopmans functionals in their own research
- work is ongoing to automate the Wannierization bottleneck

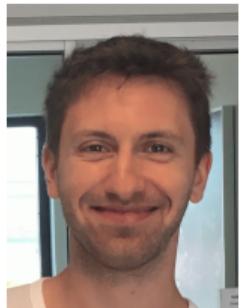
Acknowledgements



Nicola Marzari



Nicola Colonna



Riccardo De Gennaro



Yannick Schubert



**Swiss National
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NATIONAL CENTRE OF COMPETENCE IN RESEARCH

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

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