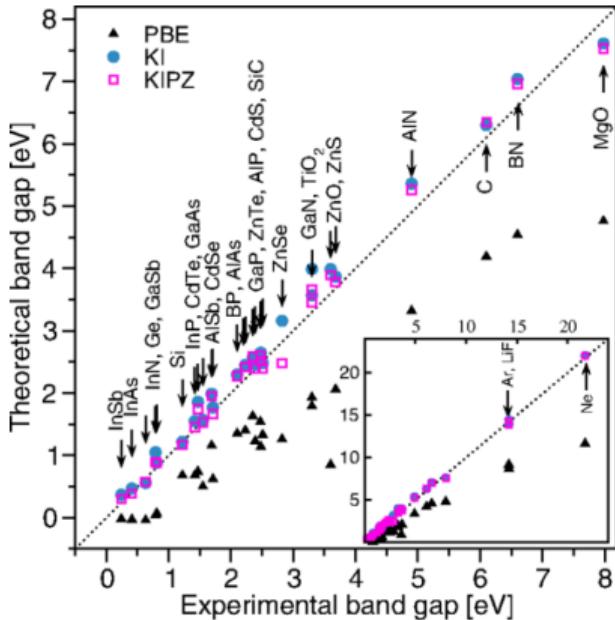


# Automating the calculation of accurate band structures with Koopmans functionals

# KOOPMANS FUNCTIONALS GIVE ACCURATE BAND STRUCTURES



Mean absolute error (eV) across prototypical semiconductors and insulators

|                  | PBE  | G <sub>0</sub> W <sub>0</sub> | KI   | KIPZ | QSGW |
|------------------|------|-------------------------------|------|------|------|
| $E_{\text{gap}}$ | 2.54 | 0.56                          | 0.27 | 0.22 | 0.18 |
| IP               | 1.09 | 0.39                          | 0.19 | 0.21 | 0.49 |

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|  | PBE   | $G_0W_0^1$ | scGW $\tilde{W}^2$ | 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 $\pm$ 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 $\pm$ 0.4   |
| $L_{1v} \rightarrow \Gamma_{25'v}$       | 6.98  | 7.18       |                    | 6.98           | 7.04     | 6.8 $\pm$ 0.2   |
| $L_{3'v} \rightarrow \Gamma_{25'v}$      | 1.19  | 1.27       |                    | 1.19           |          | 1.2 $\pm$ 0.2   |
| $\Gamma_{25'v} \rightarrow \Gamma_{15c}$ | 2.48  | 3.29       |                    | 3.17           | 3.20     | 3.35 $\pm$ 0.01 |
| $\Gamma_{25'v} \rightarrow \Gamma_{2'c}$ | 3.28  | 4.02       |                    | 3.95           | 3.95     | 4.15 $\pm$ 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 $\pm$ 0.06 |
| $\Gamma_{25'v} \rightarrow L_{3c}$       | 3.24  | 4.18       |                    | 3.91           | 3.94     | 3.9 $\pm$ 0.1   |
| MSE                                      | 0.35  | 0.02       |                    | 0.01           | 0.03     |                 |
| MAE                                      | 0.44  | 0.21       |                    | 0.14           | 0.17     |                 |

<sup>1</sup> 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;

<sup>2</sup> M. Shishkin et al. *Phys. Rev. Lett.* 99.24 (2007), 246403.

<sup>3</sup> O. Madelung. *Semiconductors*. 3rd ed. Berlin: Springer-Verlag, 2004.

# FEATURES OF KOOPMANS FUNCTIONALS

---

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

General features:

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

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

# WORKFLOWS

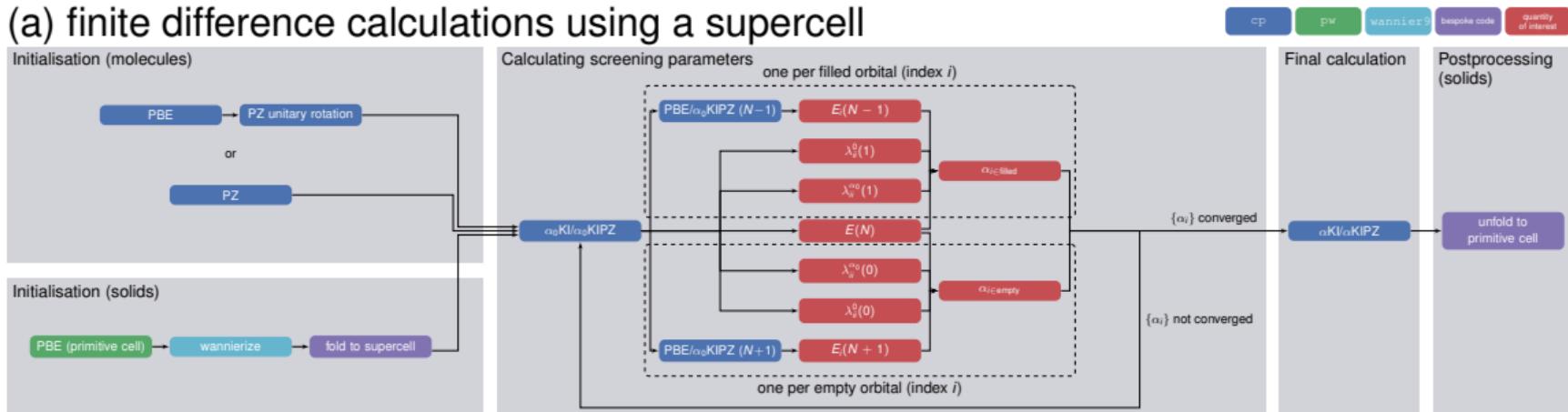
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E. B. Linscott et al. *J. Chem. Theory Comput.* (2023)



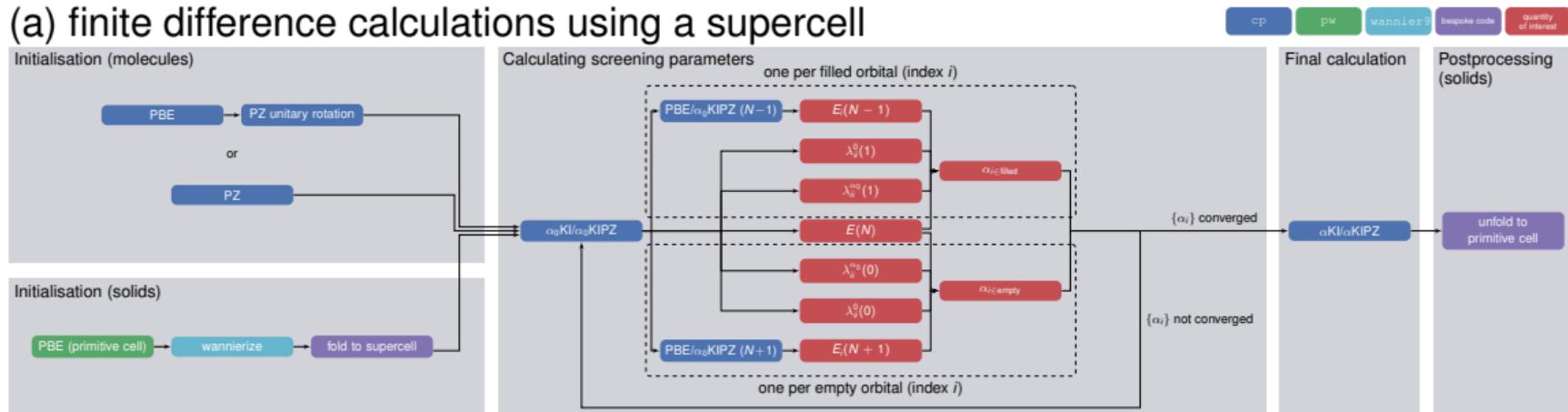
# WORKFLOWS

## (a) finite difference calculations using a supercell

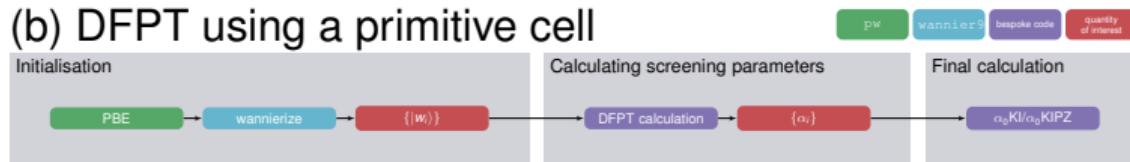


# WORKFLOWS

## (a) finite difference calculations using a supercell



## (b) DFPT using a primitive cell



# WORKFLOWS

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Complicated workflows mean that...

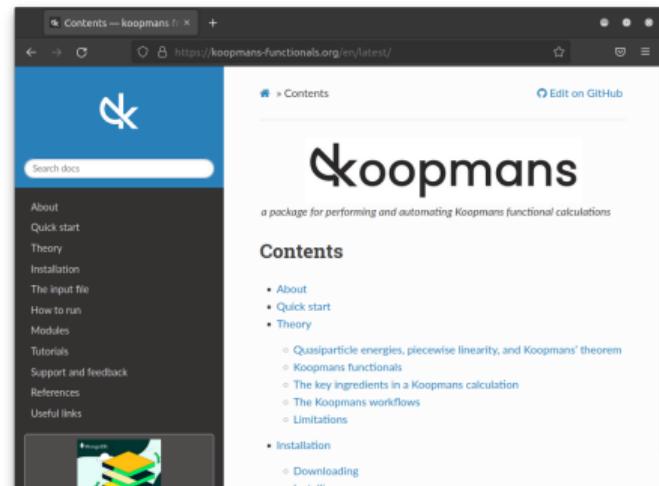
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

# koopmans

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

koopmans-functionals.org



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

Edward B. Linscott,\*<sup>△</sup> Nicola Colonna,<sup>△</sup> 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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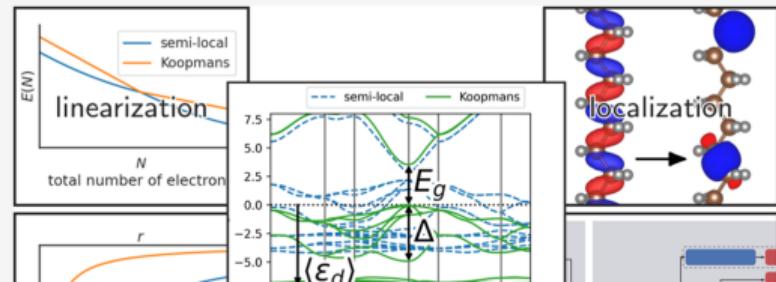
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**ABSTRACT:** Over the past decade we have developed Koopmans functionals, a computationally efficient approach for predicting spectral properties with an orbital-density-dependent functional framework. These functionals impose a generalized piecewise 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



# AUTOMATING WANNIERIZATION

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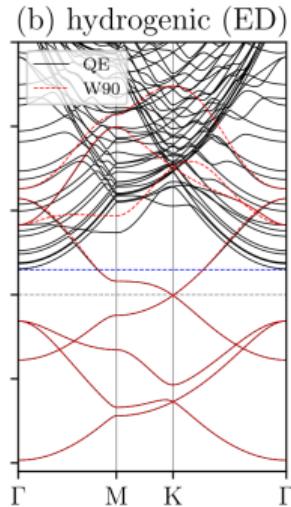
One remaining manual step: Wannierization. Can we automate this?

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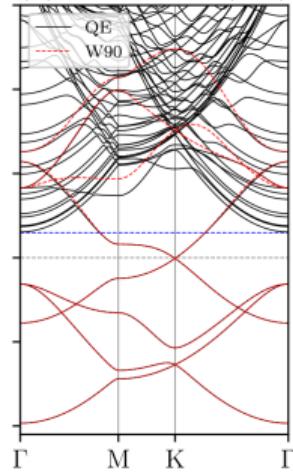


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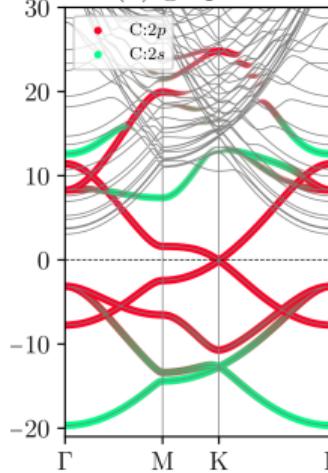
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(b) hydrogenic (ED)



(a) graphene

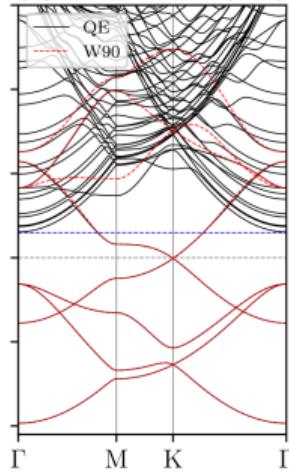


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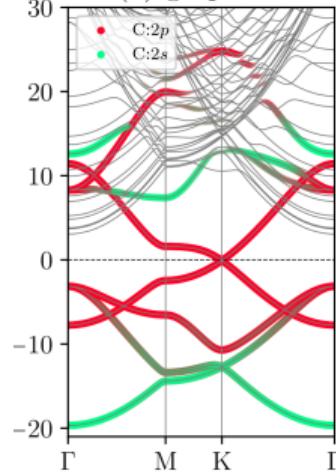
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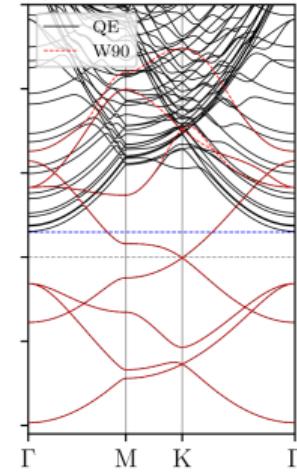
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(f) PDWF (PD+ED)

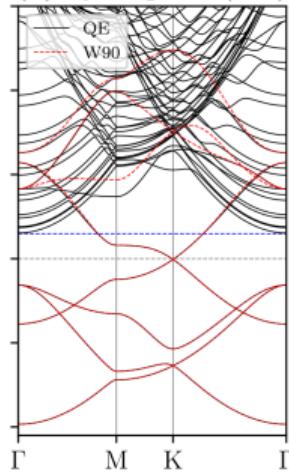


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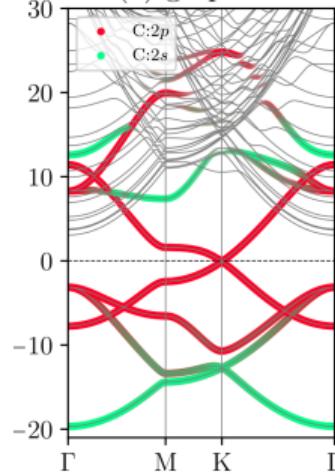
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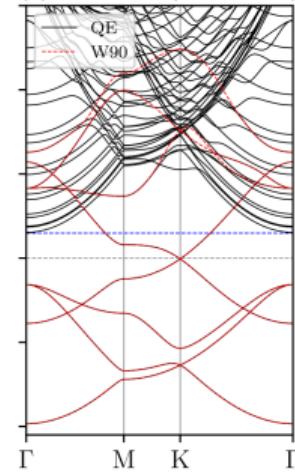
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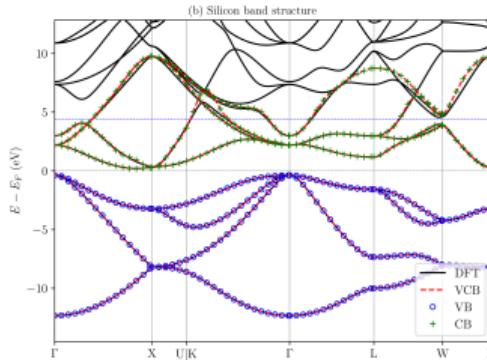


Demonstrated on >20,000 materials → black-box Wannierization

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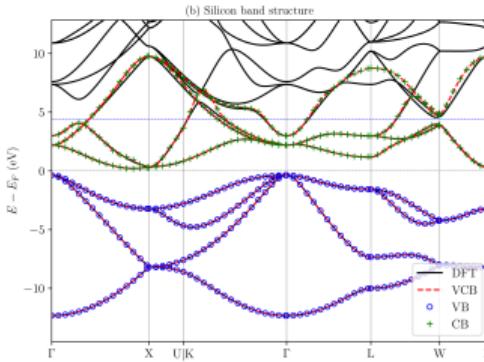
We separate target manifolds via parallel transport to obtain separate occupied and empty manifolds



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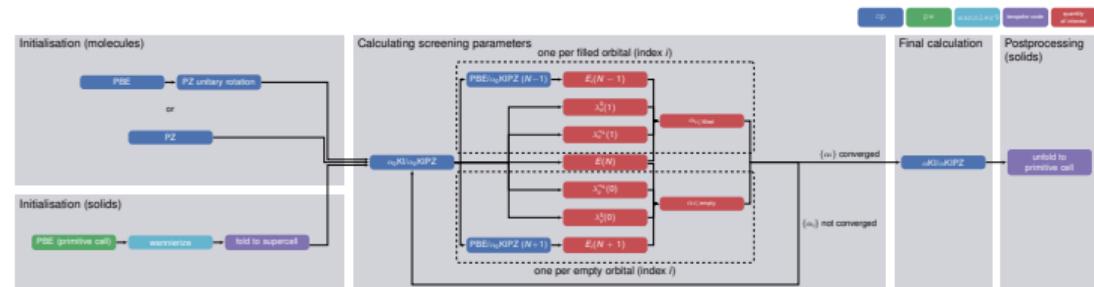
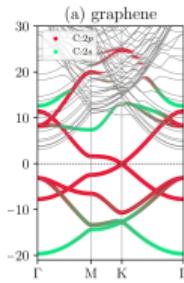
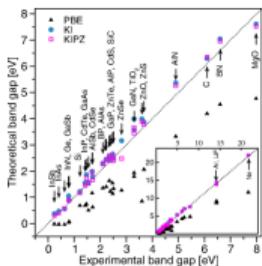
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All of the above is being integrated into koopmans, but more details to be resolved... watch this space!

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# TAKE HOME MESSAGES



- Koopmans functionals yield 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

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Nicola Marzari



Nicola Colonna



Riccardo De Gennaro



Yannick Schubert



**Swiss National  
Science Foundation**

**MARVEL**  
NATIONAL CENTRE OF COMPETENCE IN RESEARCH



Want to find out more? Go to [koopmans-functionals.org](http://koopmans-functionals.org)

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