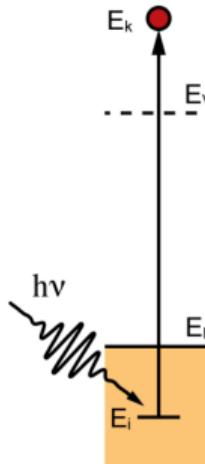




# Koopmans functionals

## a brief introduction

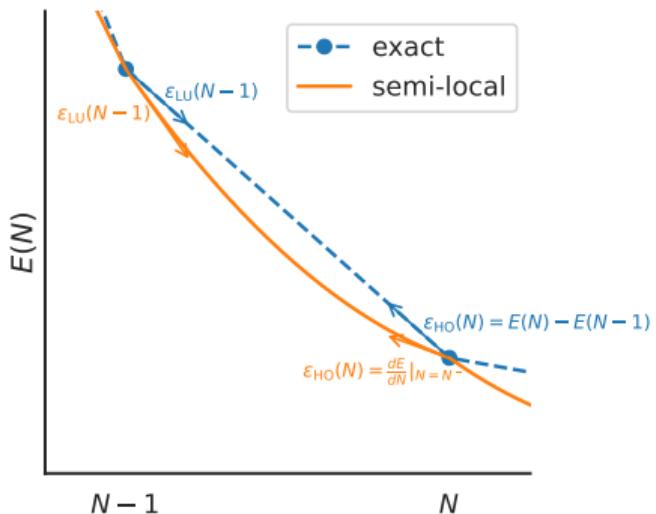
How can we calculate the energies of charged excitations? Why does DFT fail?



How can we calculate the energies of charged excitations? Why does DFT fail?

For the exact Green's function, we have poles that correspond to total energy differences

$$\varepsilon_i = \begin{cases} E(N) - E_i(N-1) & i \in \text{occ} \\ E_i(N+1) - E(N) & i \in \text{emp} \end{cases}$$

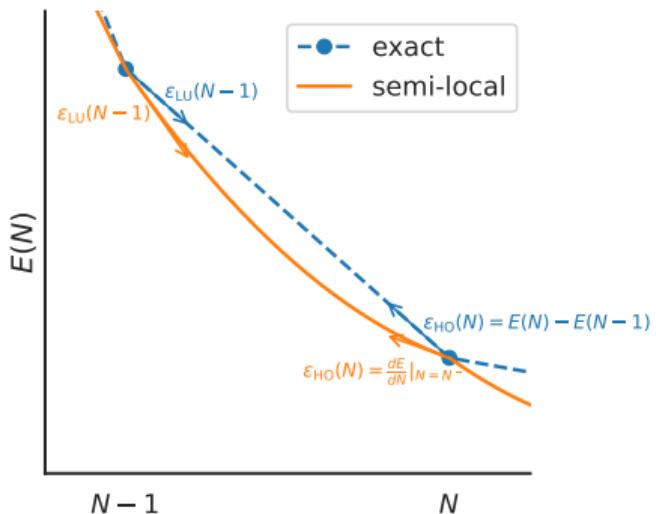


How can we calculate the energies of charged excitations? Why does DFT fail?

For the exact Green's function, we have poles that correspond to total energy differences

$$\varepsilon_i = \begin{cases} E(N) - E_i(N-1) & i \in \text{occ} \\ E_i(N+1) - E(N) & i \in \text{emp} \end{cases}$$

For DFT, this condition is *not* satisfied in general

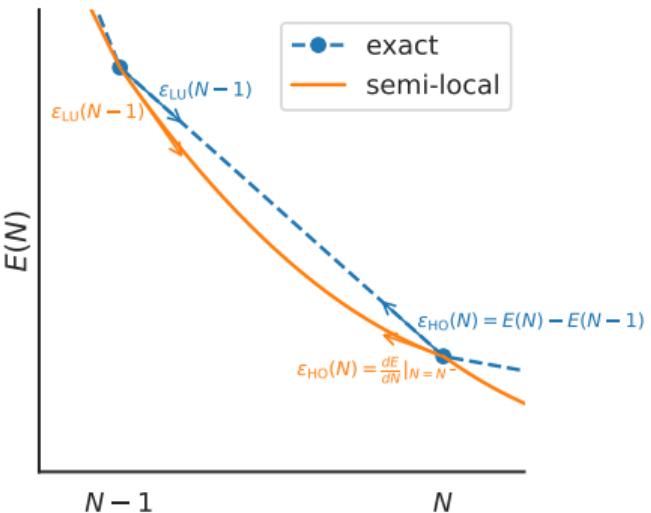


**Core idea:** for every orbital  $i$  their energy

$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

ought to be...

- independent of its own occupation  $f_i$
- equal to the corresponding total energy difference  $E_i(N - 1) - E(N)$



$$E_{\text{Kl}}[\rho, \{\rho_i\}, \{\alpha_i\}] = E_{\text{DFT}}[\rho] + \sum_i \left( \underbrace{-(E_{\text{DFT}} - E_{\text{DFT}}|_{f_i=0})}_{\text{removes erroneous curvature}} + \underbrace{f_i (E_{\text{DFT}}|_{f_i=1} - E_{\text{DFT}}|_{f_i=0})}_{\text{restores linear behaviour}} \right)$$

$$E_{\text{Kl}}[\rho, \{\rho_i\}, \{\alpha_i\}] = E_{\text{DFT}}[\rho] + \sum_i \left( \underbrace{-(E_{\text{DFT}} - E_{\text{DFT}}|_{f_i=0})}_{\text{removes erroneous curvature}} + \underbrace{f_i (E_{\text{DFT}}|_{f_i=1} - E_{\text{DFT}}|_{f_i=0})}_{\text{restores linear behaviour}} \right)$$

General features:

- a correction to DFT that ensures eigenvalues match total energy differences

$$E_{\text{KI}}[\rho, \{\rho_i\}, \{\alpha_i\}] = E_{\text{DFT}}[\rho] + \sum_i \alpha_i \left( \underbrace{E_{\text{Hxc}}[\rho - \rho_i] - E_{\text{Hxc}}[\rho]}_{\text{removes erroneous curvature}} + f_i \underbrace{(E_{\text{Hxc}}[\rho - \rho_i + n_i] - E_{\text{Hxc}}[\rho - \rho_i])}_{\text{restores linear behaviour}} \right)$$

General features:

- a correction to DFT that ensures eigenvalues match total energy differences
- to evaluate, requires the introduction of screening parameters  $\alpha_i$  (replacing  $E_{\text{DFT}}|_{f_i=f}$  with  $E_{\text{DFT}}[\rho - \rho_i + f n_i]$ )

$$E_{\text{KI}}[\rho, \{\rho_i\}, \{\alpha_i\}] = E_{\text{DFT}}[\rho] + \sum_i \alpha_i \left( \underbrace{E_{\text{Hxc}}[\rho - \rho_i] - E_{\text{Hxc}}[\rho]}_{\text{removes erroneous curvature}} \right. \\ \left. + f_i \underbrace{(E_{\text{Hxc}}[\rho - \rho_i + n_i] - E_{\text{Hxc}}[\rho - \rho_i])}_{\text{restores linear behaviour}} \right)$$

General features:

- a correction to DFT that ensures eigenvalues match total energy differences
- to evaluate, requires the introduction of screening parameters  $\alpha_i$  (replacing  $E_{\text{DFT}}|_{f_i=f}$  with  $E_{\text{DFT}}[\rho - \rho_i + f n_i]$ )
- is orbital-density-dependent

Orbital density dependence:

$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[n_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - n_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) n_i(\mathbf{r}')$$

# Koopmans functionals: theory

Orbital density dependence:

$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[n_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - n_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) n_i(\mathbf{r}')$$

How to solve: initialise with MLWFs, then minimize with CG

# Koopmans functionals: theory

Orbital density dependence:

$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[n_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - n_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) n_i(\mathbf{r}')$$

How to solve: initialise with MLWFs, then minimize with CG

outer loop:  $\varphi_i^{(n+1)} = \varphi_i^{(n)} + \Delta_i$

Orbital density dependence:

$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[n_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - n_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) n_i(\mathbf{r}')$$

How to solve: initialise with MLWFs, then minimize with CG

outer loop:  $\varphi_i^{(n+1)} = \varphi_i^{(n)} + \Delta_i$

inner loop:  $\varphi_i^{(n+1)} = \sum_j U_{ij} \varphi_j^{(n)}$

# Koopmans functionals: theory

Orbital density dependence:

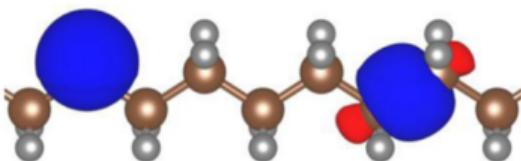
$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[n_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - n_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) n_i(\mathbf{r}')$$

How to solve: initialise with MLWFs, then minimize with CG

outer loop:  $\varphi_i^{(n+1)} = \varphi_i^{(n)} + \Delta_i$

inner loop:  $\varphi_i^{(n+1)} = \sum_j U_{ij} \varphi_j^{(n)}$

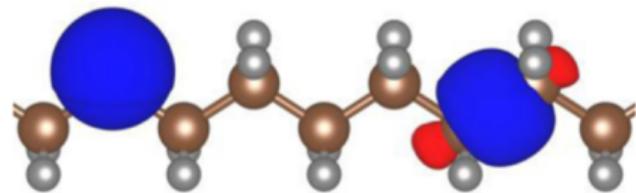
Leads to "variational" orbitals  $\varphi_i$



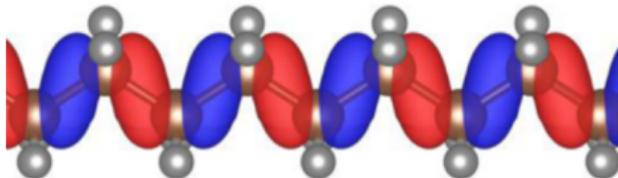
But these don't diagonalise the Hamiltonian...

# Koopmans functionals: theory

Two sets of orbitals:



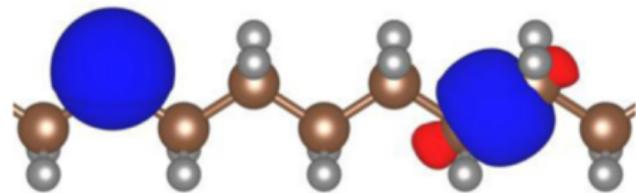
(a) "variational"  $\varphi_i$  (localised, minimising)



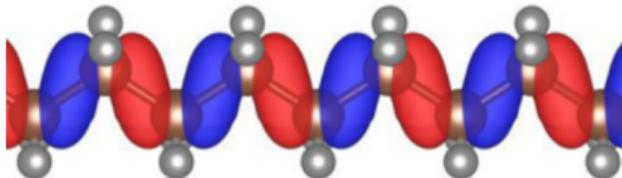
(b) "canonical"  $\psi_i$  (delocalised, diagonalising)

# Koopmans functionals: theory

Two sets of orbitals:



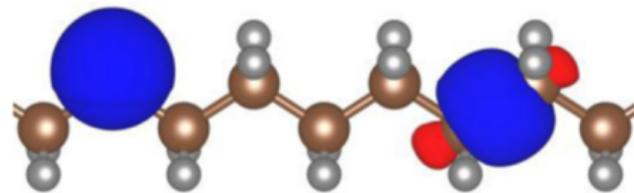
(a) "variational"  $\varphi_i$  (localised, minimising)



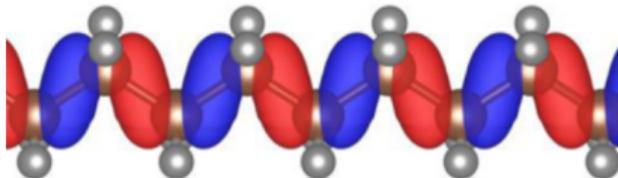
(b) "canonical"  $\psi_i$  (delocalised, diagonalising)

$$\hat{H}|\psi_i\rangle = \hat{h}^{\text{DFT}}|\psi_i\rangle + \sum_j U_{ij}v_j^{\text{KL}}|\varphi_j\rangle$$

Two sets of orbitals:



(a) "variational"  $\varphi_i$  (localised, minimising)

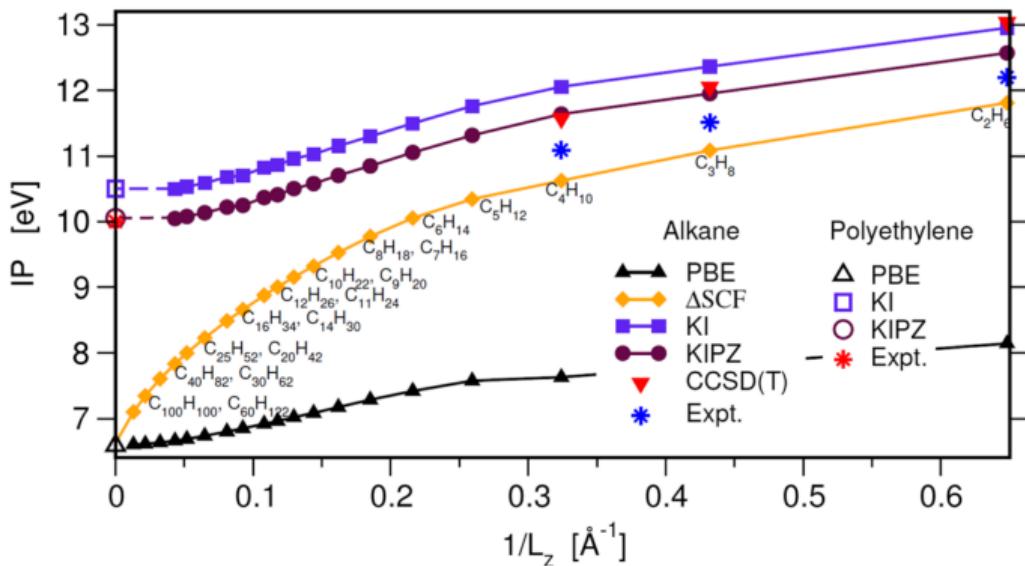


(b) "canonical"  $\psi_i$  (delocalised, diagonalising)

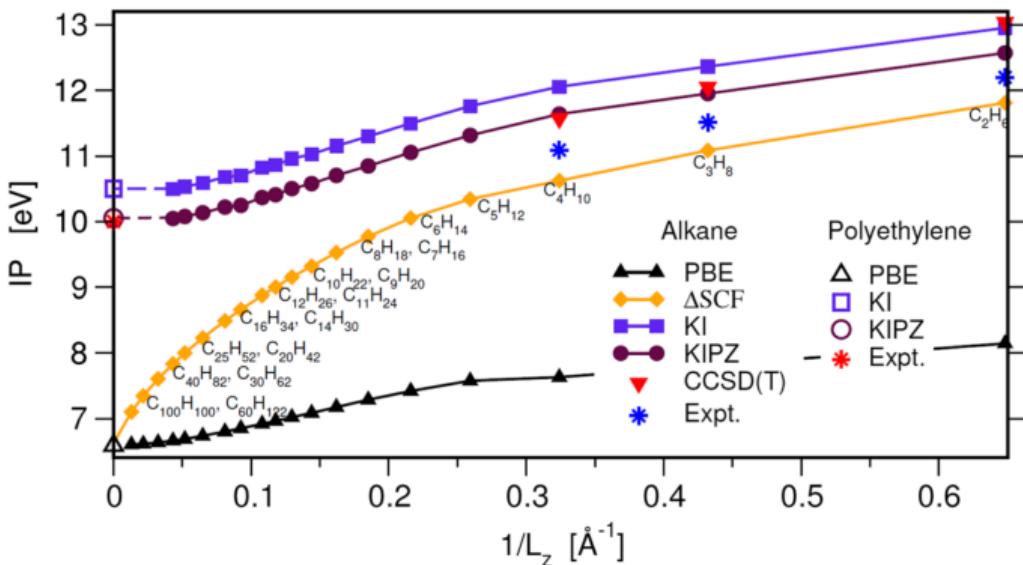
$$\hat{H}|\psi_i\rangle = \hat{h}^{\text{DFT}}|\psi_i\rangle + \sum_j U_{ij}v_j^{\text{KL}}|\varphi_j\rangle$$

N.B. we know  $\hat{H}|\varphi_i\rangle$  for variational orbitals  $\{|\varphi_i\rangle\}$  but we don't know  $\hat{H}$  in general

# Koopmans functionals: the bulk limit

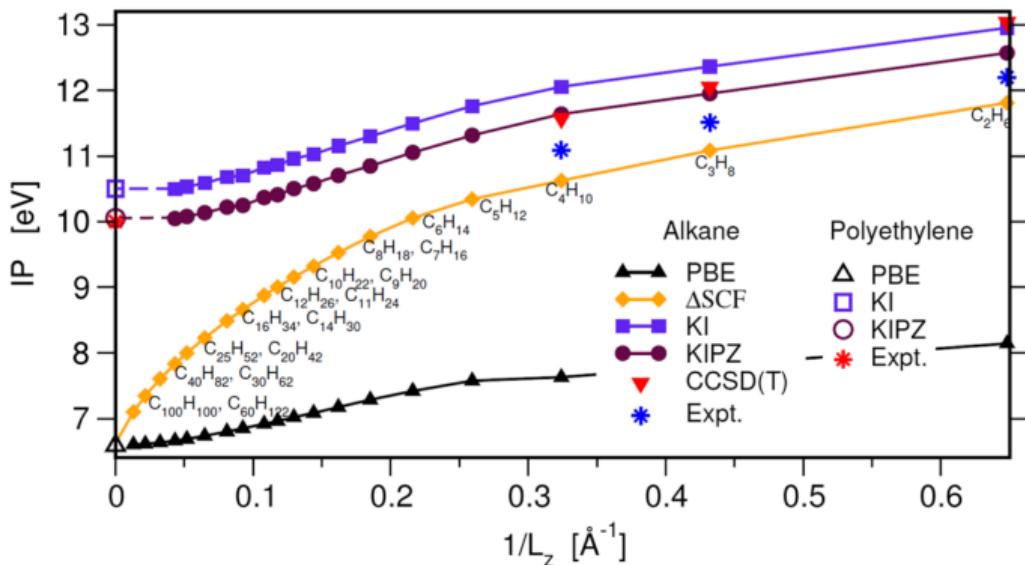


# Koopmans functionals: the bulk limit



In the bulk limit for one cell  $\Delta E_{\text{one cell}} = E(N - \delta N) - E(N)$

# Koopmans functionals: the bulk limit



In the bulk limit for one cell  $\Delta E_{\text{one cell}} = E(N - \delta N) - E(N)$

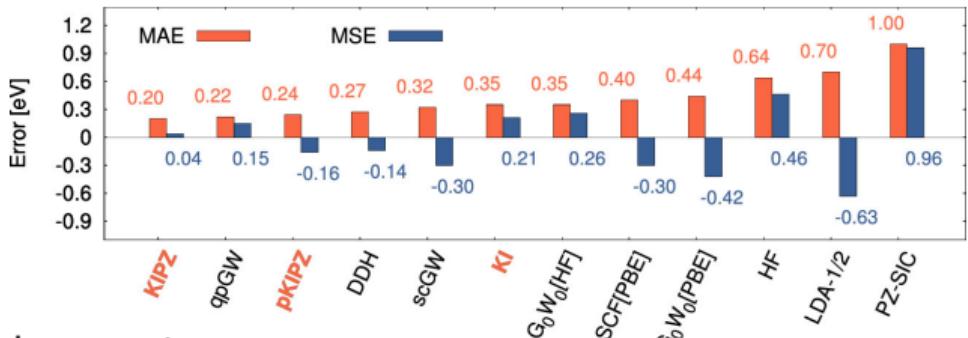
Across all the cells  $\Delta E_{\text{all cells}} = \frac{1}{\delta N} (E(N - \delta N) - E(N)) = -\frac{dE}{dN} = -\varepsilon_{\text{HO}}$

Resonance with other efforts:

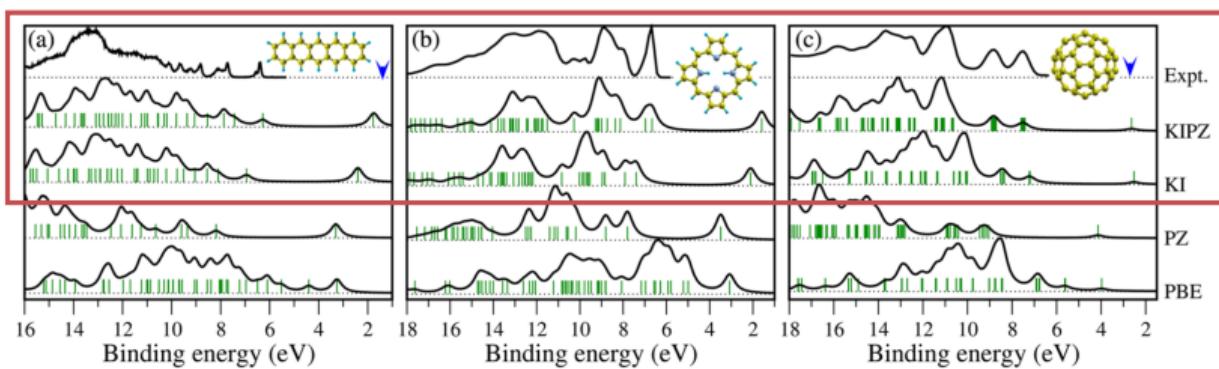
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021), e2104556118
- Ensemble DFT of Kronik and co-workers E. Kraisler et al. *Phys. Rev. Lett.* 110.12 (2013), 126403
- Koopmans-Wannier of Wang and co-workers J. Ma et al. *Sci. Rep.* 6.1 (2016), 24924
- Dielectric-dependent hybrid functionals of Galli and co-workers J. H. Skone et al. *Phys. Rev. B* 93.23 (2016), 235106
- LOSC functionals of Yang and co-workers C. Li et al. *Natl. Sci. Rev.* 5 (2018), 203

# Koopmans functionals: results for molecules

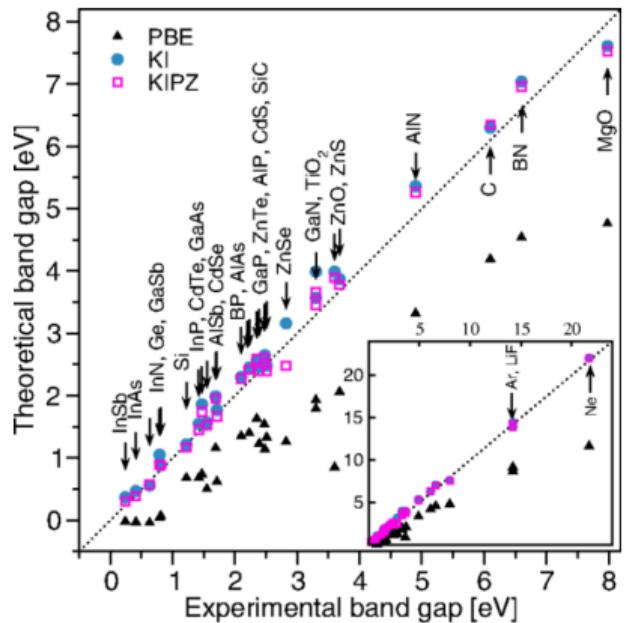
Ionization potentials for the GW100 set cf. CCSD(T)



Ultraviolet photoemission spectra



# Koopmans functionals: results for solids



Mean absolute error (eV) across prototypical semiconductors and insulators

|                  | PBE  | $G_0W_0$ | KI   | KIPZ | $QSG\tilde{W}$ |
|------------------|------|----------|------|------|----------------|
| $E_{\text{gap}}$ | 2.54 | 0.56     | 0.27 | 0.22 | 0.18           |
| IP               | 1.09 | 0.39     | 0.19 | 0.21 | 0.49           |

# Koopmans functionals: results for solids

|  | PBE   | $G_0W_0^1$ | scGW <sup>2</sup> | KI@[PBE,MLWFs] | KIPZ@PBE | exp <sup>3</sup> |
|--|-------|------------|-------------------|----------------|----------|------------------|
| $E_g$                                    | 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     |                  |

<sup>1</sup> 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;

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

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



- restricted to systems with a non-zero band gap

- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit

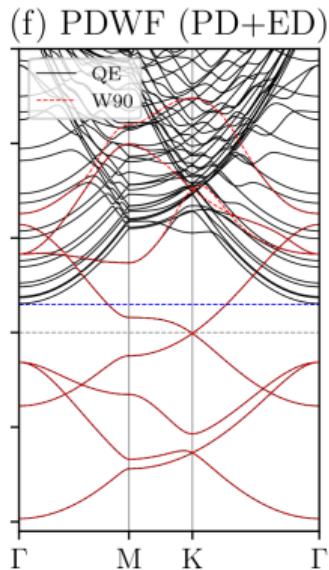
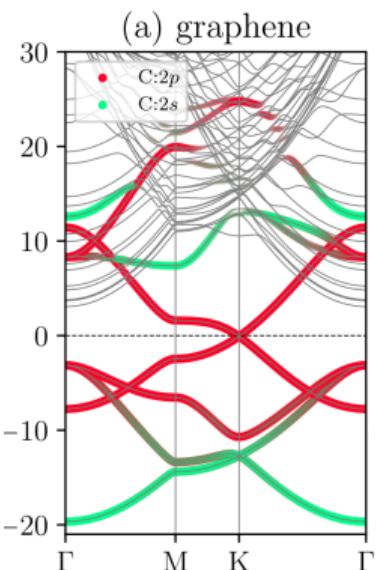
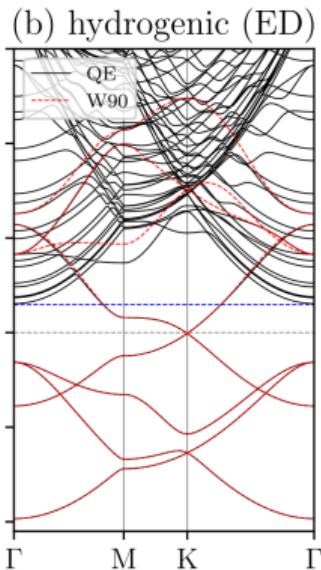
- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit
- can potentially break the crystal point group symmetry

The general workflow:

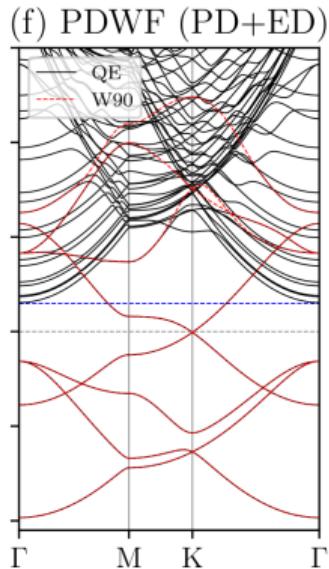
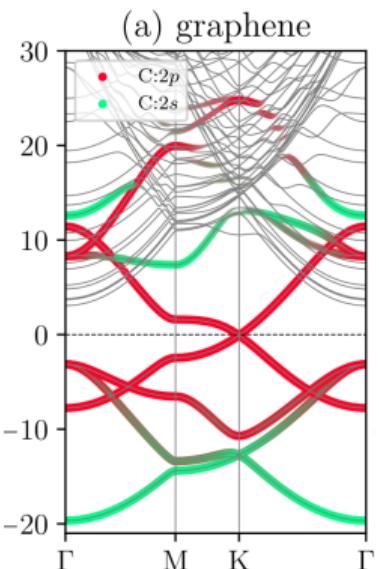
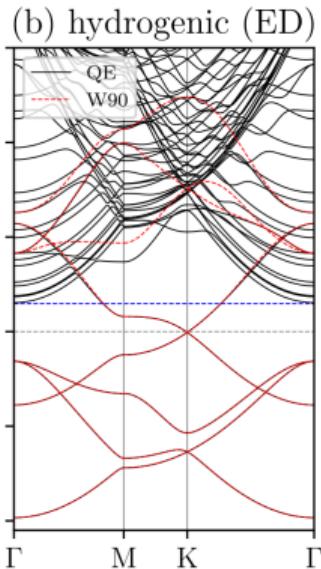
- initialize a set of variational orbitals
- calculate the screening parameters  $\{\alpha_i\}$
- construct and diagonalize the Hamiltonian

Recent advances make some of these steps a lot easier...

# Recent improvements: easier Wannierization



# Recent improvements: easier Wannierization

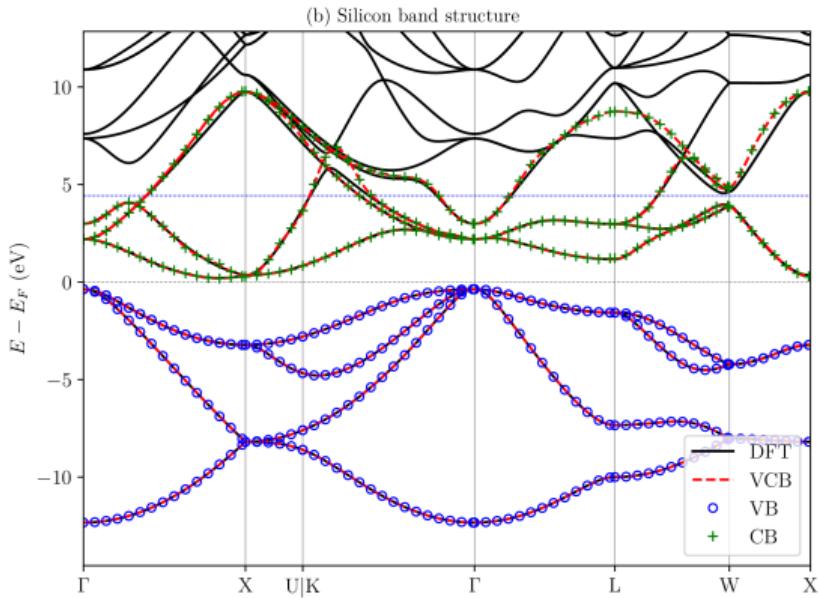


Demonstrated on >20,000 materials → black-box Wannierization!

Separation of target manifolds via parallel transport to obtain separate occupied and empty manifolds

# Recent improvements: easier Wannierization

Separation of target manifolds via parallel transport to obtain separate occupied and empty manifolds



Original formulation requires explicit charged defect calculations in a supercell

$$\alpha_i^{n+1} = \alpha_i^n \frac{\Delta E_i^{\text{Koopmans}} - \lambda_{ii}(0, 1)}{\lambda_{ii}(\alpha_i^n, 1) - \lambda_{ii}(0, 1)}, \quad \Delta E_i^{\text{Koopmans}} = E^{\text{Koopmans}}(N) - E_i^{\text{Koopmans}}(N-1)$$

<sup>1</sup> N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.

<sup>2</sup> N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435.

Original formulation requires explicit charged defect calculations in a supercell

$$\alpha_i^{n+1} = \alpha_i^n \frac{\Delta E_i^{\text{Koopmans}} - \lambda_{ii}(0, 1)}{\lambda_{ii}(\alpha_i^n, 1) - \lambda_{ii}(0, 1)}, \quad \Delta E_i^{\text{Koopmans}} = E^{\text{Koopmans}}(N) - E_i^{\text{Koopmans}}(N-1)$$

Now reformulated in terms of DFPT<sup>1</sup>...

$$\alpha_i = 1 + \frac{\langle v_{\text{pert}}^i | \Delta^i n \rangle}{\langle n_i | v_{\text{pert}}^i \rangle}.$$

<sup>1</sup> N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.

<sup>2</sup> N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435.

Original formulation requires explicit charged defect calculations in a supercell

$$\alpha_i^{n+1} = \alpha_i^n \frac{\Delta E_i^{\text{Koopmans}} - \lambda_{ii}(0, 1)}{\lambda_{ii}(\alpha_i^n, 1) - \lambda_{ii}(0, 1)}, \quad \Delta E_i^{\text{Koopmans}} = E^{\text{Koopmans}}(N) - E_i^{\text{Koopmans}}(N-1)$$

Now reformulated in terms of DFPT<sup>1</sup>...

$$\alpha_i = 1 + \frac{\langle v_{\text{pert}}^i | \Delta^i n \rangle}{\langle n_i | v_{\text{pert}}^i \rangle}.$$

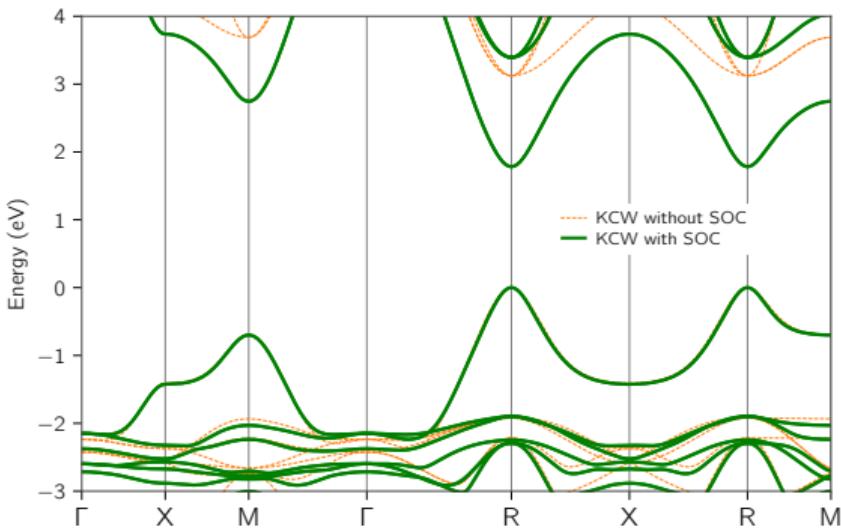
... in reciprocal space<sup>2</sup>

$$\alpha_{0i} = 1 + \frac{\sum_{\mathbf{q}} \langle v_{\text{pert}, \mathbf{q}}^{0i} | \Delta_{\mathbf{q}}^{0i} n \rangle}{\sum_{\mathbf{q}} \langle n_{\mathbf{q}}^{0i} | v_{\text{pert}, \mathbf{q}}^{0i} \rangle}.$$

<sup>1</sup> N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.

<sup>2</sup> N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435.

# Recent improvements: spin-orbit coupling



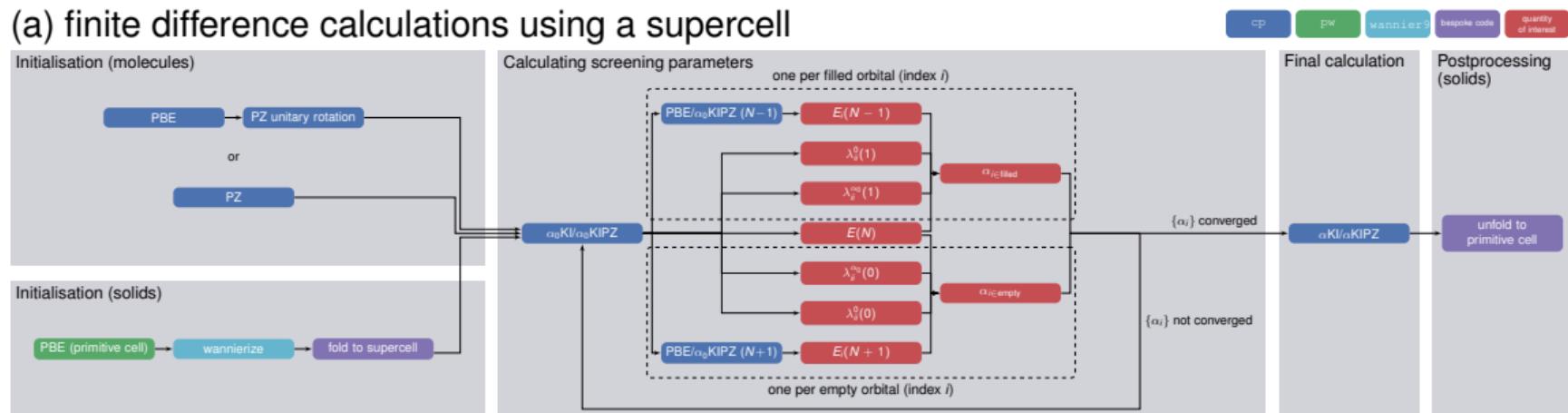
| CsPbBr <sub>3</sub> | LDA  | HSE  | G <sub>0</sub> W <sub>0</sub> | KI   | QSGW | exp  |
|---------------------|------|------|-------------------------------|------|------|------|
| without SOC         | 1.40 | 2.09 | 2.56                          | 3.12 | 3.15 |      |
| with SOC            | 0.18 | 0.78 | 0.94                          | 1.78 | 1.53 | 1.85 |

We have complicated workflows, with either...

# Recent improvements: automated workflows

We have complicated workflows, with either...

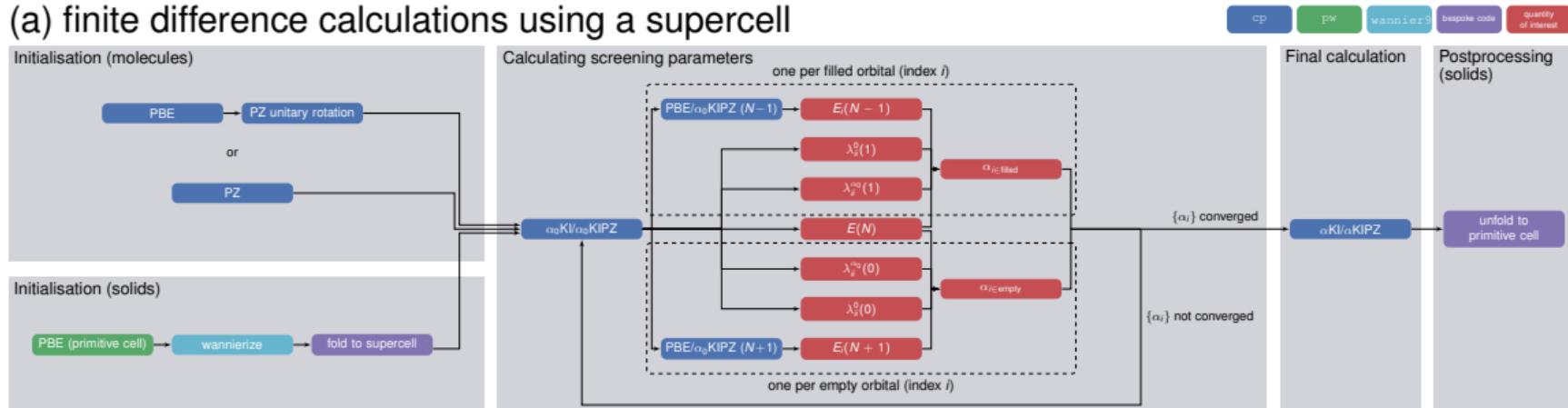
## (a) finite difference calculations using a supercell



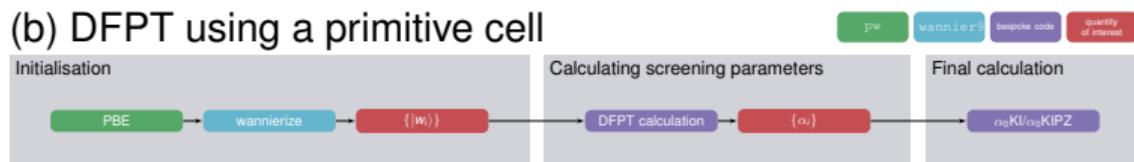
# Recent improvements: automated workflows

We have complicated workflows, with either...

## (a) finite difference calculations using a supercell



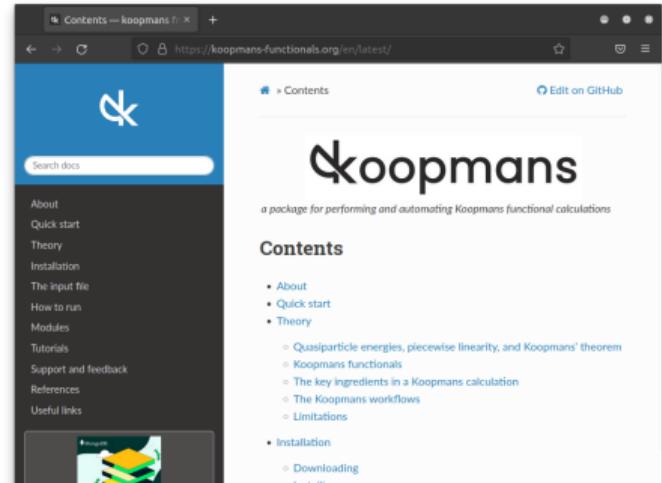
## (b) DFPT using a primitive cell



# koopmans

- v1.0 released last year<sup>1</sup>
- implementations of Koopmans functionals within Quantum ESPRESSO
- automated workflows
  - start-to-finish Koopmans calculations
  - Wannierization
  - dielectric tensor
  - convergence tests
  - ...
- built on top of ASE<sup>2</sup>
- does not require expert knowledge

[koopmans-functionals.org](https://koopmans-functionals.org)



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

<sup>2</sup> A. H. Larsen et al. *J. Phys. Condens. Matter* 29.27 (2017), 273002

# koopmans: the input file

```
{  
  "workflow": {  
    "task": "singlepoint",  
    "functional": "ki",  
    "method": "dscf",  
    "init_orbitals": "mlwfs"  
  },  
  "atoms": {  
    "atomic_positions": {  
      "units": "crystal",  
      "positions": [[{"Si": 0.00, 0.00, 0.00},  
                    {"Si": 0.25, 0.25, 0.25}]]  
    },  
    "cell_parameters": {  
      "periodic": true,  
      "ibrav": 2,  
      "celldm(1)": 10.262  
    }  
  },  
  "k_points": {
```

```
    "grid": [8, 8, 8],  
    "path": "LGXKG"  
  },  
  "calculator_parameters": {  
    "ecutwfc": 60.0  
  }  
}
```

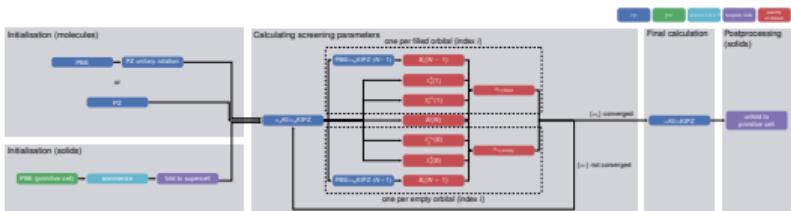
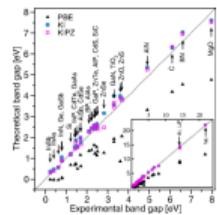
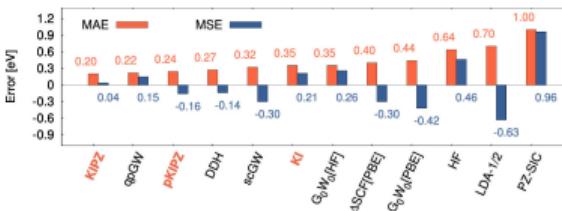
```
from ase.build import bulk
from koopmans.kpoints import Kpoints
from koopmans.workflows import SinglepointWorkflow

# Use ASE to create bulk silicon
atoms = bulk('Si')

# Create the workflow
workflow = SinglepointWorkflow(atoms = atoms,
    ecutwfc = 40.0,
    kpoints = Kpoints(grid=[8, 8, 8], path='LGXKG', cell=atoms.cell),
    calculator_parameters = {'pw': {'nbnd': 10}})

# Run the workflow
workflow.run()
```

# Take home messages



- Koopmans functionals are a class of functionals that treat spectral properties on the same footing as total energy differences (via GPWL)
- they can give orbital energies and band structures with comparable accuracy to state-of-the-art GW
- the koopmans package simplifies running these calculations

# Acknowledgements



Nicola Marzari



Nicola Colonna



**Swiss National  
Science Foundation**

**MARVEL**



NATIONAL CENTRE OF COMPETENCE IN RESEARCH

find out more at [koopmans-functionals.org](http://koopmans-functionals.org)

follow  [@elinscott](https://twitter.com/elinscott) for updates

slides at [github/elinscott-talks/prendergast\\_meeting\\_apr\\_2024](https://github.com/elinscott-talks/prendergast_meeting_apr_2024)

# SPARE SLIDES

## Recap from earlier

Key idea: construct a functional such that the *variational* orbital energies

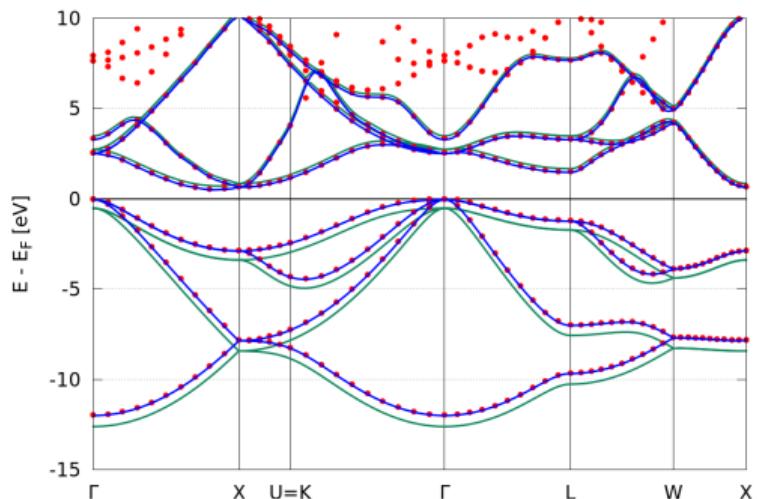
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

are...

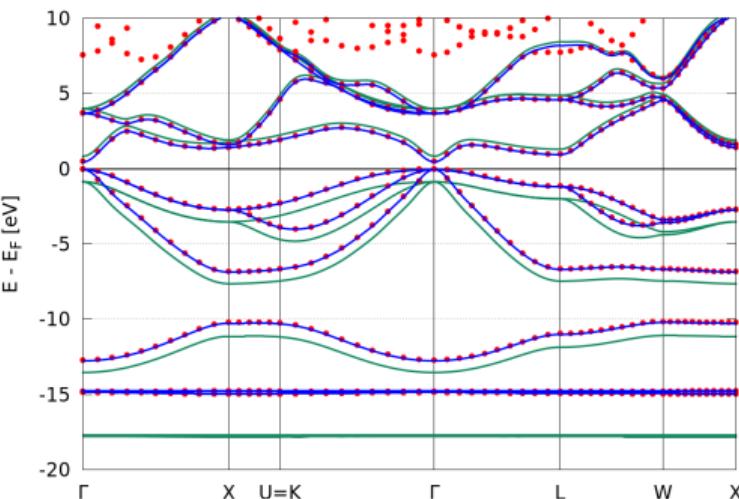
- independent of the corresponding occupancies  $f_i$
- equal to the corresponding total energy difference  $E_i(N - 1) - E(N)$

zero band gap  $\rightarrow$  occupancy matrix for variational orbitals is off-diagonal

# Koopmans functionals: results for solids



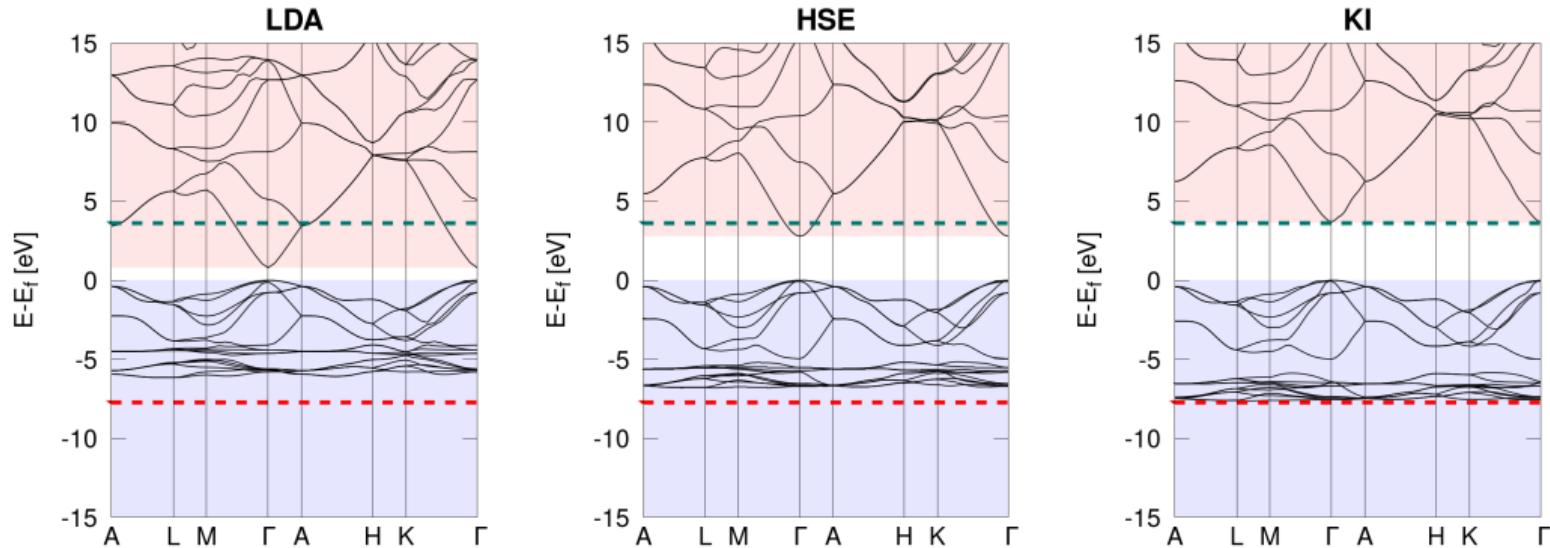
(a) Si, KIPZ



(b) GaAs, KI

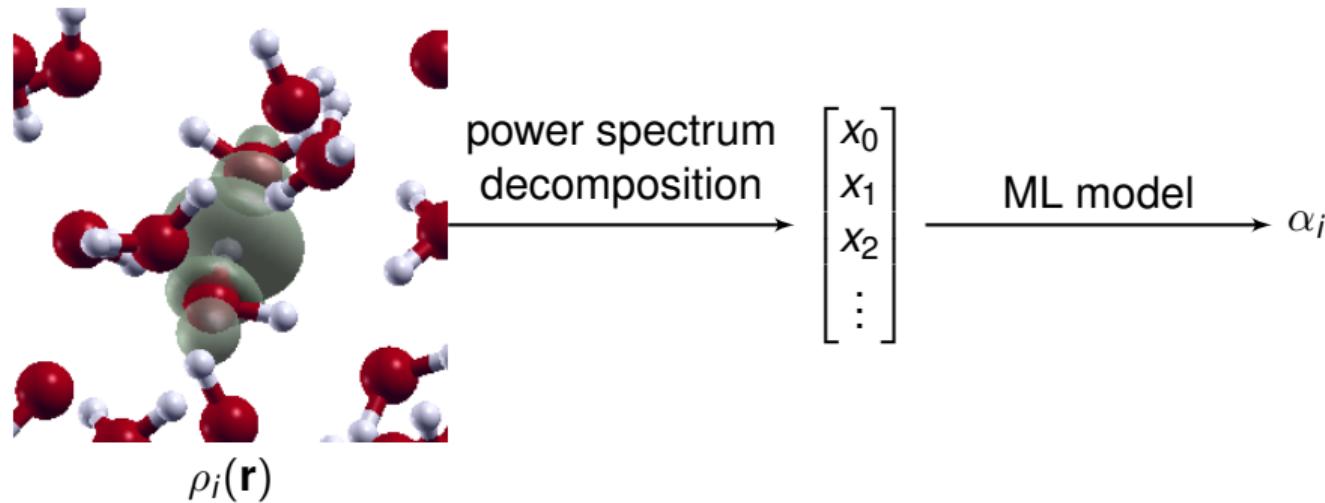
|      |                                 | PBE  | QSGW | KI   | pKIPZ | KIPZ | exp  |
|------|---------------------------------|------|------|------|-------|------|------|
| Si   | $E_{\text{gap}}$                | 0.55 | 1.24 | 1.18 | 1.17  | 1.19 | 1.17 |
| GaAs | $E_{\text{gap}}$                | 0.50 | 1.61 | 1.53 | 1.49  | 1.50 | 1.52 |
|      | $\langle \varepsilon_d \rangle$ | 14.9 | 17.6 | 16.9 |       | 17.7 | 18.9 |

# Koopmans functionals: results for solids



| ZnO                                  | LDA  | HSE  | $GW_0$ | $scG\tilde{W}$ | KI   | exp       |
|--------------------------------------|------|------|--------|----------------|------|-----------|
| $E_{\text{gap}}$ (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 |

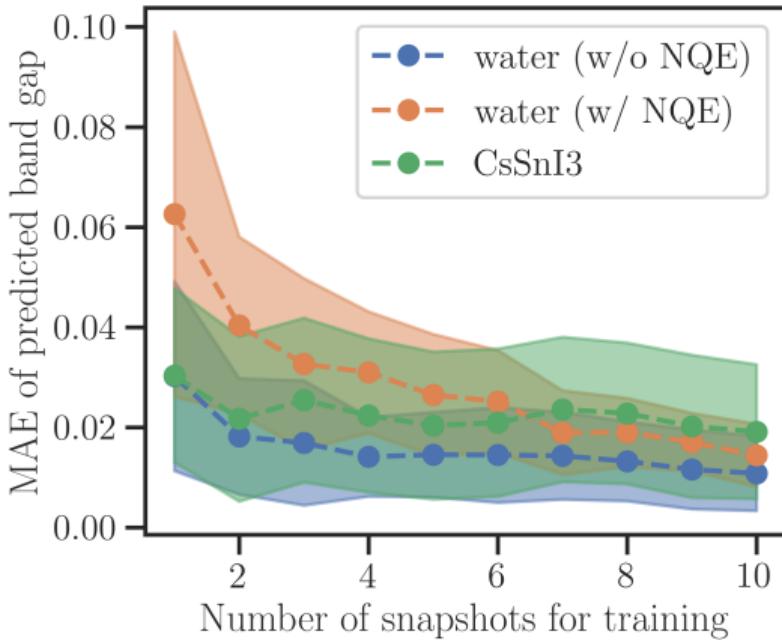
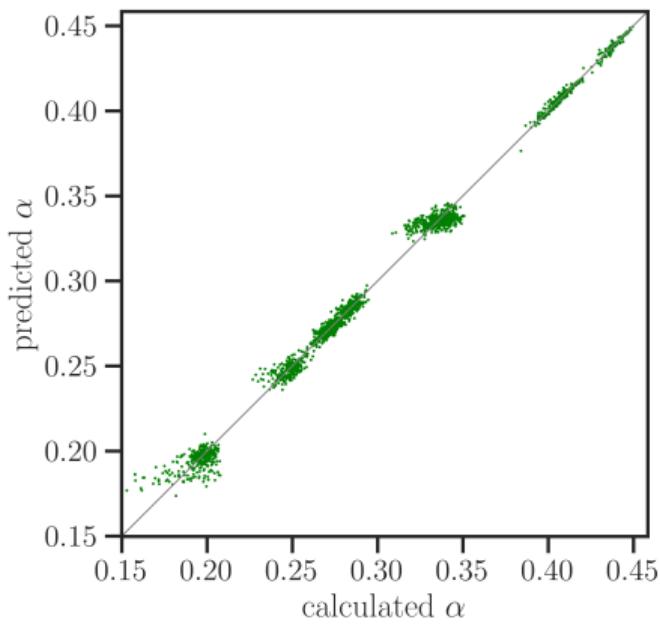
# Accelerating improvements: screening via ML



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

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

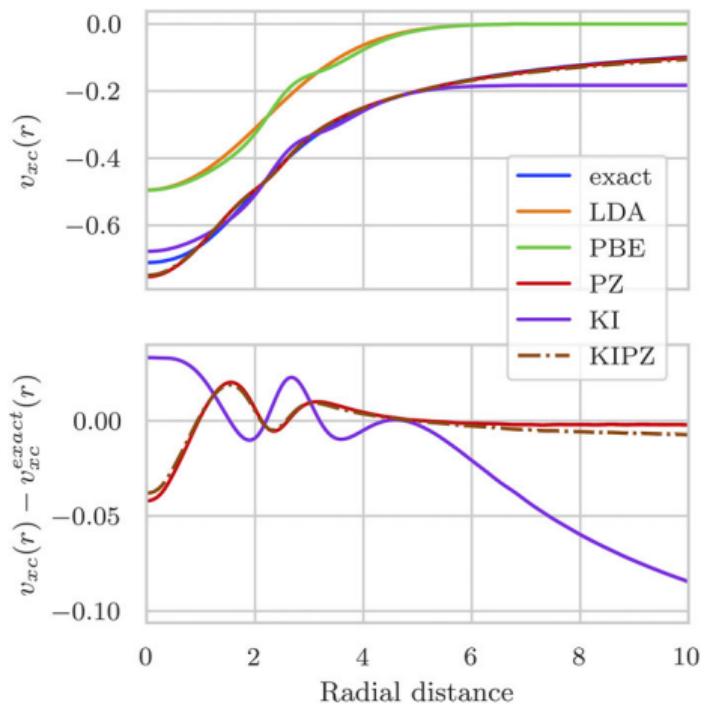
# Recent improvements: screening via ML



loss of accuracy of the band gap of  $\sim 0.02$  eV  
(cf. when calculating screening parameters *ab initio*)  
speedup of 70 $\times$

# Koopmans functionals: results for toy systems

Hooke's atom (two electrons in a harmonic confining potential)



# Koopmans functionals: results for toy systems

Hooke's atom (two electrons in a harmonic confining potential)

