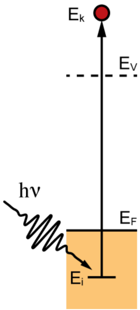
# Koopmans functionals
## a brief introduction

Edward Linscott | PSI | 24 April 2024 | Swiss National Science Foundation MARVEL

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



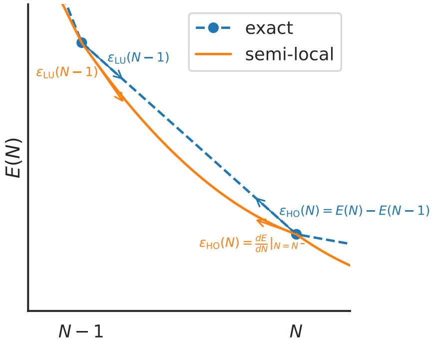

R. Costantini et al. “Exciton Dynamics in Molecular Heterojunctions”. PhD thesis. Universita degli Studi di Trieste, 2020

# Koopmans functionals: theory

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

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

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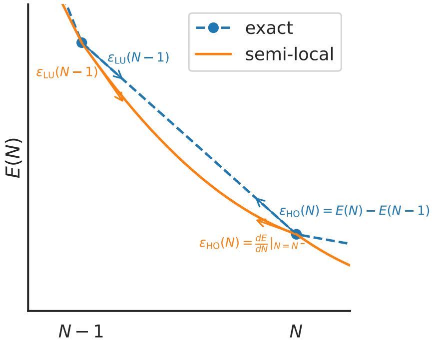
For DFT, this condition is *not* satisfied in general

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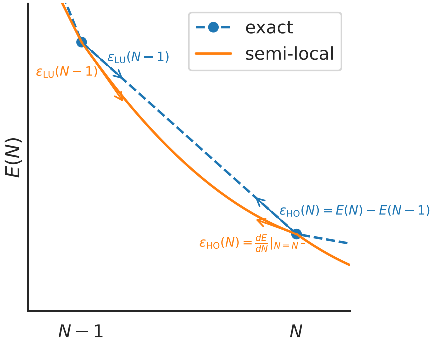
**Core idea:** for every orbital $i$ their energy

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

ought to be...

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

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# Koopmans functionals: theory

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

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General features:

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

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

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General features:

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- to evaluate, requires the introduction of screening parameters $\alpha_i$ (replacing $E_{\mathrm{DFT}}|_{f_i=f}$ with $E_{\mathrm{DFT}}[\rho - \rho_i + fn_i]$)
- is orbital-density-dependent

Consequences of ODD:

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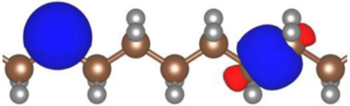
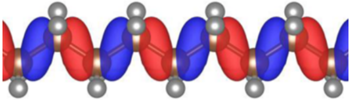
- variational (localized, minimizing) vs canonical (delocalized, diagonalizing) orbitals



(a) variational



(b) canonical

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

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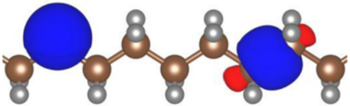
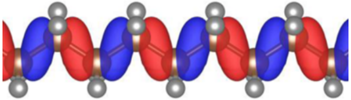


(a) variational



(b) canonical

- Practically we can often use MLWFs

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

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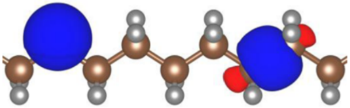
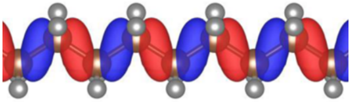


(a) variational

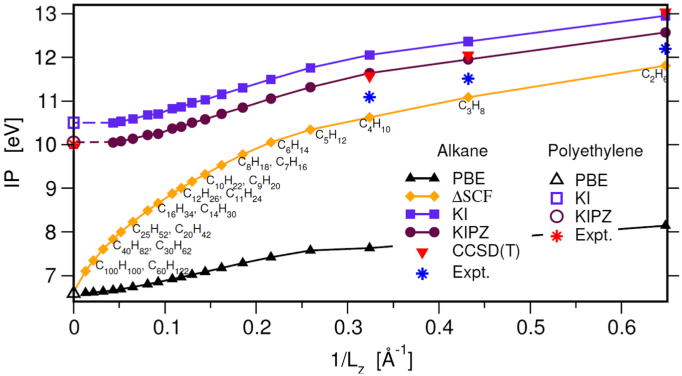


(b) canonical

- Practically we can often use MLWFs
- localized variational orbitals naturally allow us to treat bulk systems

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

# Koopmans functionals: the bulk limit

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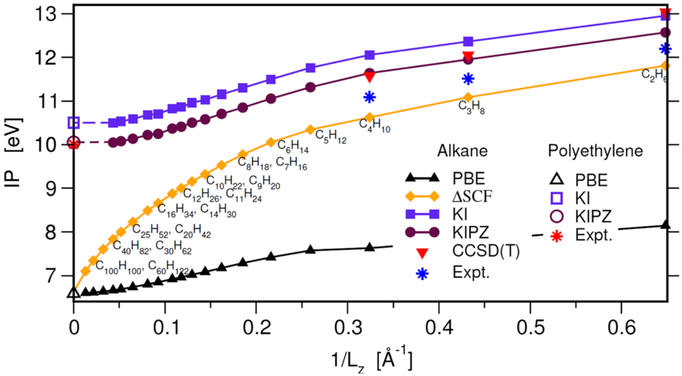
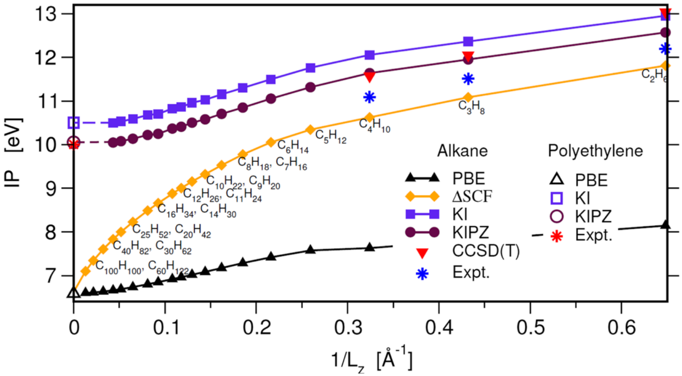



In the bulk limit for one cell $\Delta E_{\text{one cell}} = E(N - \delta N) - E(N)$

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051




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

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

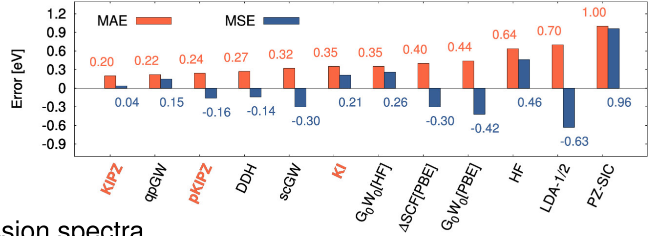
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

# Koopmans functionals: theory

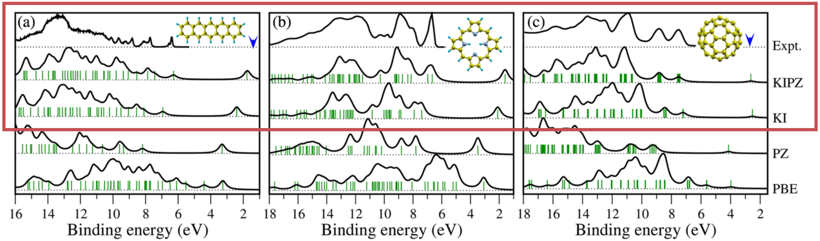
Resonance with other efforts:

- 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

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

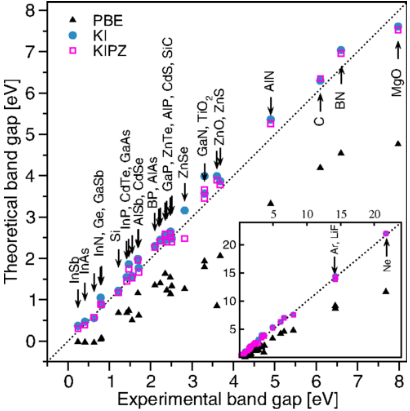



Ultraviolet photoemission spectra





N. Colonna et al. *J. Chem. Theory Comput.* 14.5 (2018), 2549; N. L. Nguyen et al. *Phys. Rev. Lett.* 114.16 (2015), 166405




Mean absolute error (eV) across prototypical semiconductors and insulators

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

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

| | PBE | $G_0W_0$[1] | sc$G\tilde{W}$[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 ±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.

N. Q. Su et al. *J. Phys. Chem. Lett.* 11.4 (2020), 1528

- restricted to systems with a non-zero band gap

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# Koopmans functionals: caveats

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

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

N. Q. Su et al. *J. Phys. Chem. Lett.* 11.4 (2020), 1528

# Recent improvements

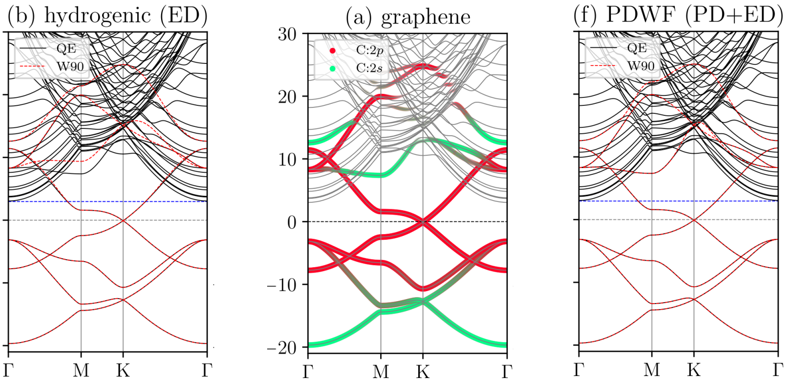


The general workflow:

- 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




J. Qiao et al. *npj Comput Mater* 9 (2023), 208

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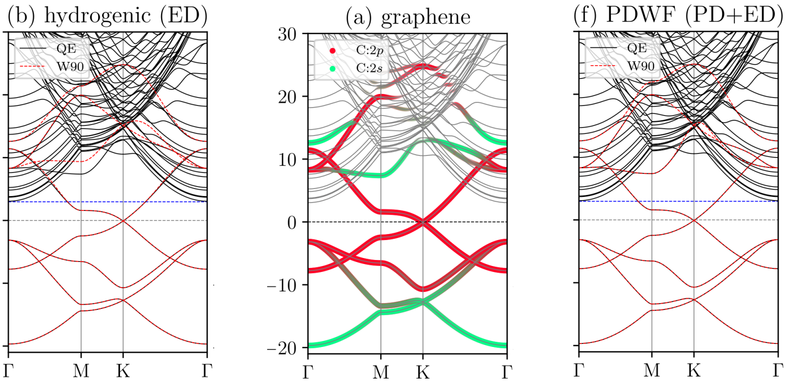


Demonstrated on >20,000 materials → black-box Wannierization!

J. Qiao et al. *npj Comput Mater* 9 (2023), 208

# Recent improvements: easier Wannierization

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

J. Qiao et al. *npj Comput Mater* 9 (2023), 206

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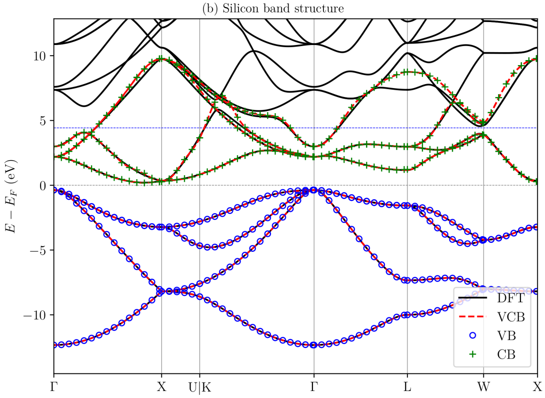


J. Qiao et al. *npj Comput Mater* 9 (2023), 206

Original formulation requires explicit charged defect calculations in a supercell

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

[1] N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.
[2] N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435.

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Now reformulated in terms of DFPT[1]...

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

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... in reciprocal space[2]

$$\alpha_{\mathbf{0}i} = 1 + \frac{\sum_{\mathbf{q}} \langle v^{\mathbf{0}i}_{\text{pert},\mathbf{q}} | \Delta^{\mathbf{0}i}_{\mathbf{q}} n \rangle}{\sum_{\mathbf{q}} \langle n^{\mathbf{0}i}_{\mathbf{q}} | v^{\mathbf{0}i}_{\text{pert},\mathbf{q}} \rangle}.$$

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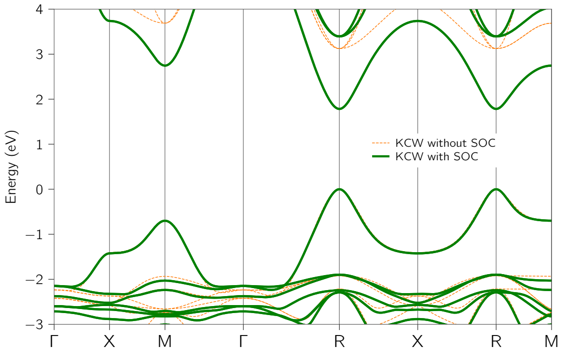



| $CsPbBr_3$ | LDA | HSE | $G_0W_0$ | **KI** | $QSG\tilde{W}$ | exp |
|---|---|---|---|---|---|---|
| without SOC | 1.40 | 2.09 | 2.56 | 3.12 | 3.15 | 1.85 |
| with SOC | 0.18 | 0.78 | 0.94 | 1.78 | 1.53 | |

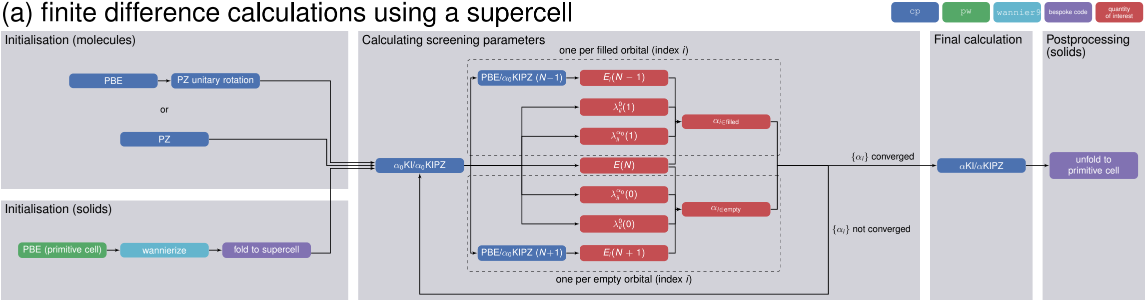
A. Marrazzo et al. *Spin-Dependent Interactions in Orbital-Density-Dependent Functionals: Non-Collinear Koopmans Spectral Functionals*. 2024

We have complicated workflows, with either...

# Recent improvements: automated workflows

We have complicated workflows, with either...

(a) finite difference calculations using a supercell




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

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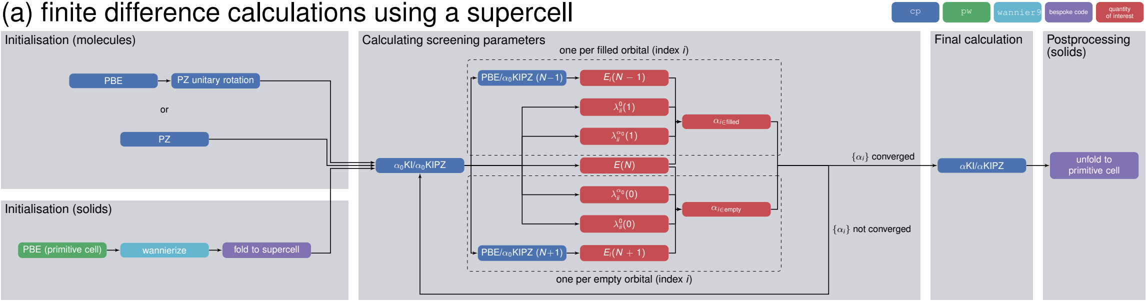
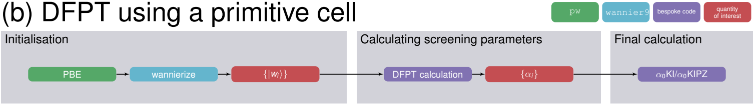
## (a) finite difference calculations using a supercell



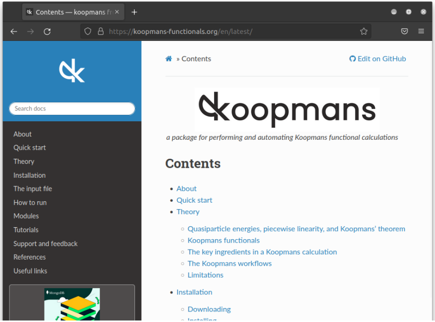

## (b) DFPT using a primitive cell



# koopmans

- v1.0 released last year[1]
- implementations of Koopmans functionals within Quantum ESPRESSO
- automated workflows
  - start-to-finish Koopmans calculations
  - Wannierization
  - dielectric tensor
  - convergence tests
  - ...
- built on top of ASE[2]
- 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. *J. Phys. Condens. Matter* 29.27 (2017), 273002

# koopmans: the input file



```json
{
  "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
  }
}
```

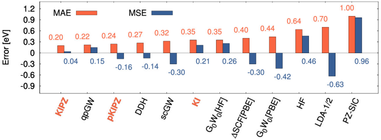
# koopmans is scriptable

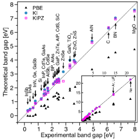


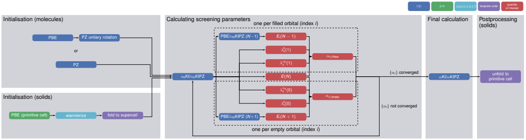
```python
from ase.build import bulk
from koopmans.kpoints import Kpoints
from koopmans.workflows import SinglepointWorkflow

# 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

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

Follow @ed_linscott for updates | Slides available at
**`github/elinscott-talks/prendergast`**$_{m}eeting_{a}pr_{2}024$

# SPARE SLIDES

# Koopmans functionals: off-diagonal occupancies

## Recap from earlier

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

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

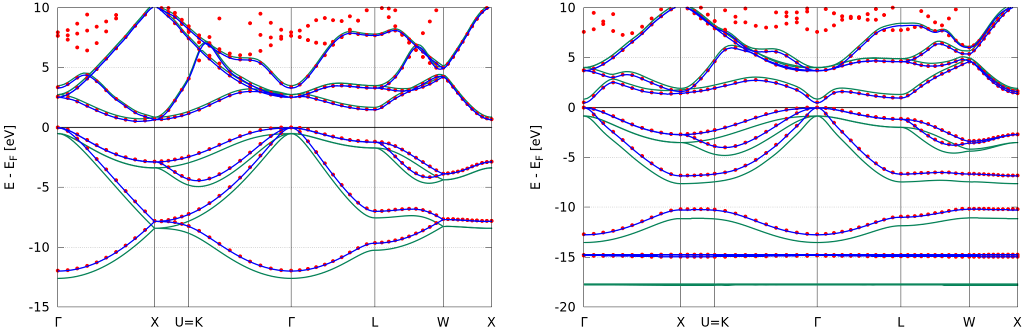
are...

- 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

Edward Linscott
PSI



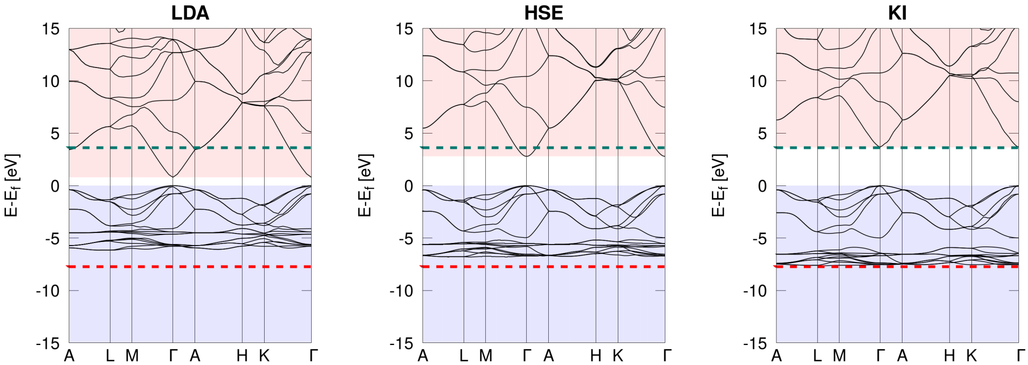

(a) Si, KIPZ

(b) GaAs, KI

| | | PBE | QSGW̃ | **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 |

R. De Gennaro. “Spectral Properties of Extended Systems from Koopmans-compliant Functionals”. PhD thesis.

# Koopmans functionals: results for solids




| 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 |

N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435

# Accelerating improvements: screening via ML

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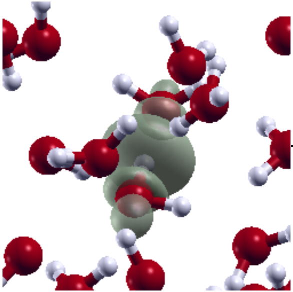

$\rho_i(\mathbf{r})$

$$\rho_i(\mathbf{r}) \xrightarrow{\text{power spectrum decomposition}} \begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix} \xrightarrow{\text{ML model}} \alpha_i$$

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

$$p^i_{n_1 n_2 l,k_1 k_2} = \pi\sqrt{\frac{8}{2l+1}}\sum_m c^{i*}_{n_1 lm,k_1} c^i_{n_2 lm,k_2}$$

Y. Schubert et al. *Testing Koopmans Spectral Functionals on the Analytically-Solvable Hooke's Atom*. 2022

# Recent improvements: screening via ML

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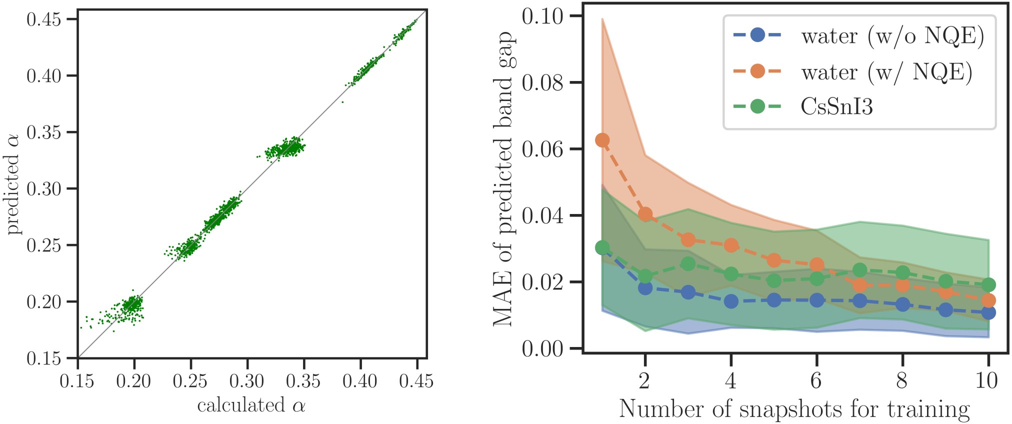
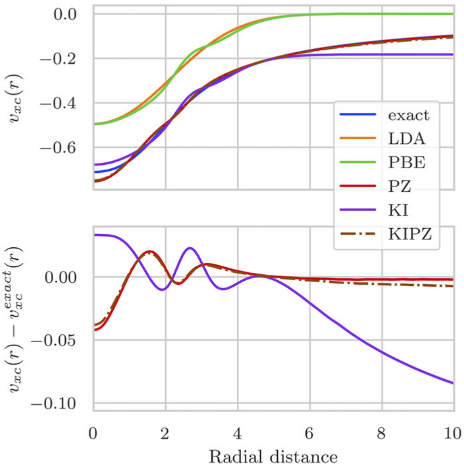



loss of accuracy of the band gap of $\sim$ 0.02 eV
(cf. when calculating screening parameters *ab initio*)
speedup of 70$\times$

# Koopmans functionals: results for toy systems



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

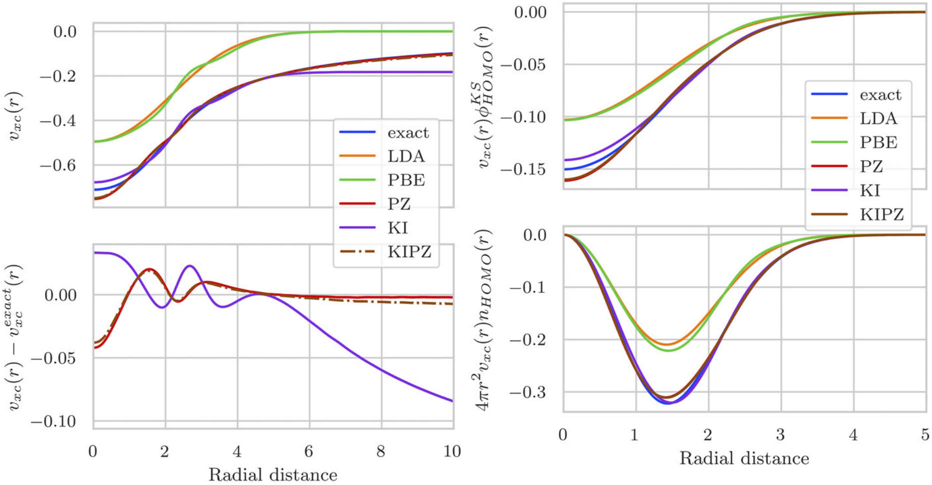



Y. Schubert et al. *J. Chem. Phys.* 158.14 (2023), 144113

# Koopmans functionals: results for toy systems



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




Y. Schubert et al. *J. Chem. Phys.* 158.14 (2023), 144113