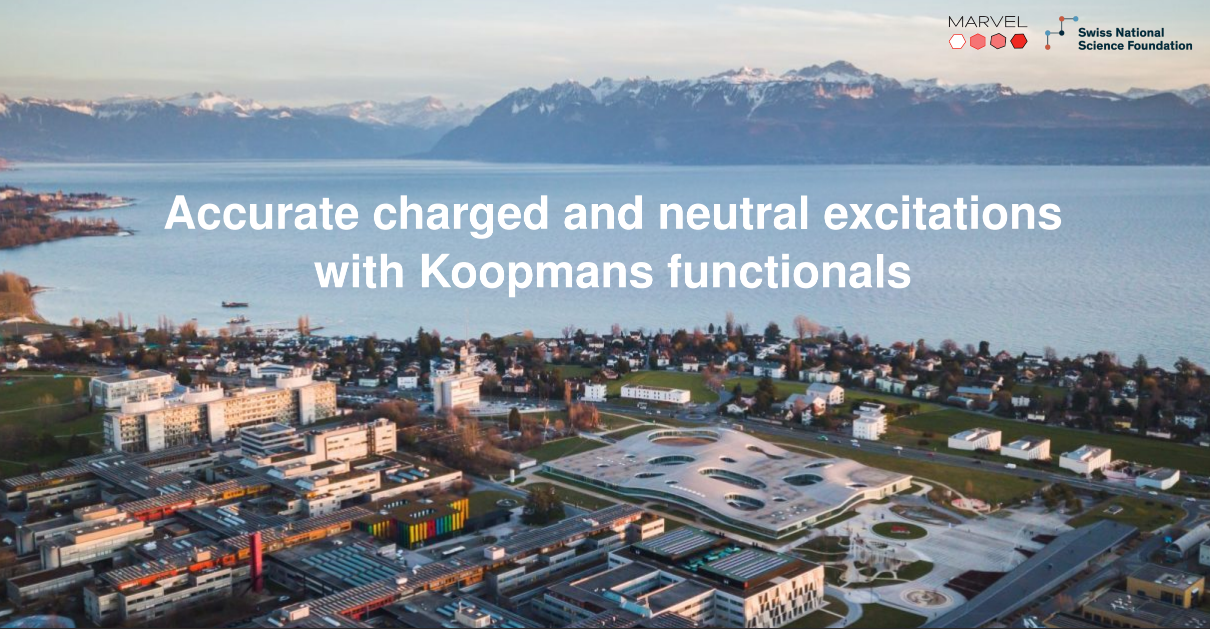


Accurate charged and neutral excitations with Koopmans functionals

MARVEL

Swiss National Science Foundation

Edward Linscott | EPFL | 9th TDDFT Workshop, Benasque | 25 Oct 2022

Take home messages

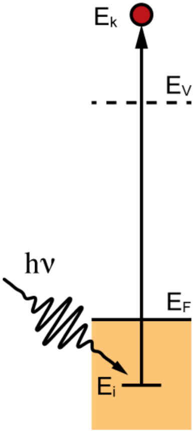
Koopmans functionals are a class of functionals that aim to reproduce spectral properties and total energies on the same footing

As a result they give band structures and orbital energies comparable to state-of-the-art GW

Koopmans can be used to replace GW when calculating neutral excitations with BSE

We have recently released `koopmans`, a package that contains everything necessary to run calculations using Koopmans functionals without expert knowledge

Goal: spectral properties (charged excitations) with a functional theory



a

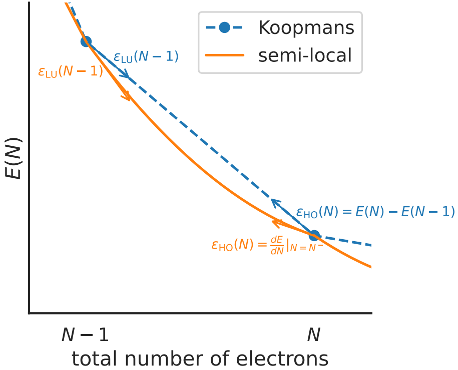
R. Costantini et al. “Exciton Dynamics in Molecular Heterojunct

Goal: spectral properties (charged excitations) with a functional theory
Core idea: for every orbital *i* their energy

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

should be...

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



Koopmans functionals: theory

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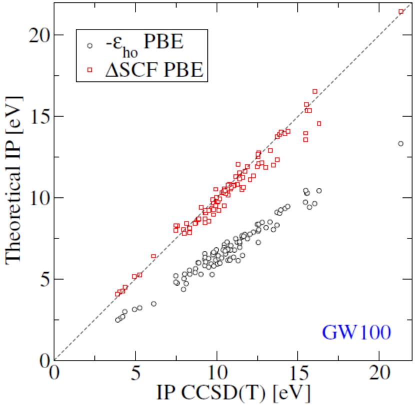
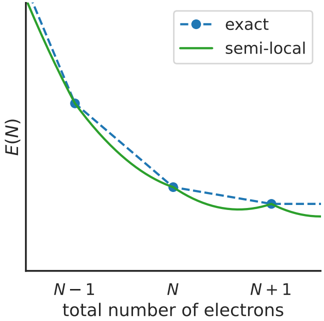


Koopmans functionals: theory

$$E_{\text{Koopmans}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{DFT}[\rho] + \sum_i \alpha_i \left(\underbrace{-\int_0^{f_i} \varepsilon_i(f) df}_{\text{removes curvature}} + \underbrace{f_i \int_0^1 \varepsilon_i(f) df}_{\text{restores linearity}} \right)$$



I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

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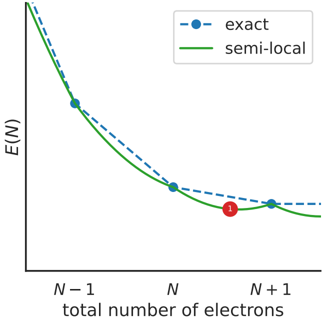

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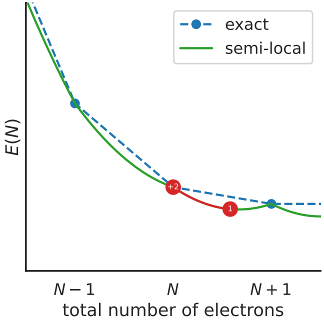

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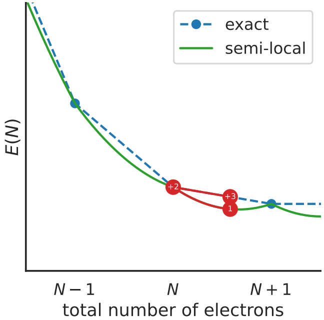

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Differences to semi-local functionals:

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

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Differences to semi-local functionals:

- screening

$$\frac{dE}{df_i} \approx \alpha_i \frac{\partial E}{\partial f_i}$$

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

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Differences to semi-local functionals:

- screening
- orbital-density dependence

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

$$\frac{dE}{df_i} \approx \alpha_i \frac{\partial E}{\partial f_i}$$

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

$$E_{\text{Koopmans}}[\rho, \{f_i\}, {\color{red}\{\alpha_i\}}] = E_{DFT}[\rho] + \sum_i {\color{red}\alpha_i} \Bigg(\underbrace{-\int_0^{f_i} \varepsilon_i(f) df}_{\text{removes curvature}} + \underbrace{f_i \int_0^1 \varepsilon_i(f) df}_{\text{restores linearity}} \Bigg)$$

Differences to semi-local functionals:

- screening
- orbital-density dependence

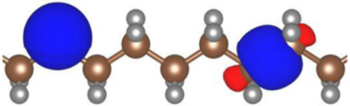
$$\frac{dE}{df_i} \approx \alpha_i \frac{\partial E}{\partial f_i} \Rightarrow \varepsilon_i^{\text{Koopmans}} = \frac{\partial E_{\text{Koopmans}}}{\partial f_i} \approx E_i(N-1) - E(N)$$

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

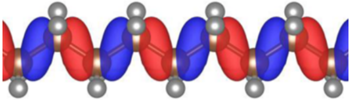
Koopmans functionals: theory

Consequences of ODD:

- a natural generalisation in the direction of spectral functional theory[1]
- variational (localised, minimising) vs canonical (delocalised, diagonalising) orbitals



(a) variational



(b) canonical

- ODD functional means that we know $\hat{H}|\varphi_i\rangle$ for variational orbitals $\{|\varphi_i\rangle\}$ but we don't know $\hat{H}$ in general
- Practically we can often use MLWFs

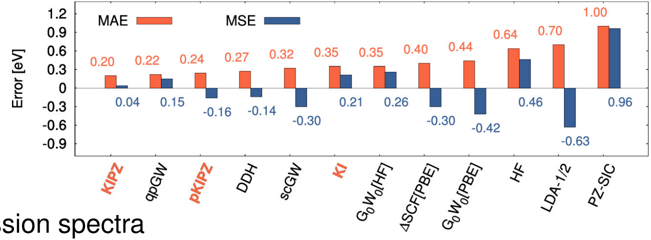
[1] A. Ferretti et al. *Phys. Rev. B* 89.19 (27, 2014), 195134.
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (23, 2018), 021051

Resonance with other efforts:

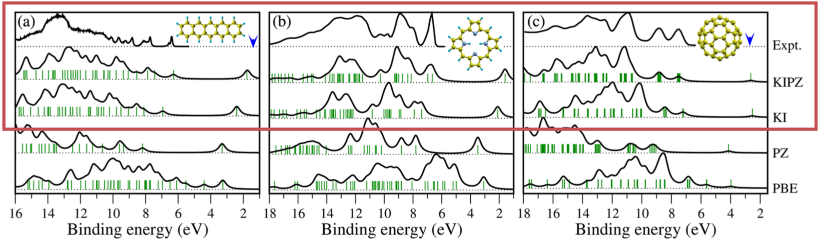
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (18, 2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (8, 2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (24, 2021), e2104556118
- Ensemble DFT of Kronik and co-workers E. Kraisler et al. *Phys. Rev. Lett.* 110.12 (19, 2013), 126403
- Koopmans-Wannier of Wang and co-workers J. Ma et al. *Sci. Rep.* 6.1 (1 26, 2016), 24924
- Dielectric-dependent hybrid functionals of Galli and co-workers J. H. Skone et al. *Phys. Rev. B* 93.23 (3, 2016), 235106
- LOSC functionals of Yang and co-workers C. Li et al. *Natl. Sci. Rev.* 5 (2018), 203

Koopmans functionals: results for molecules

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

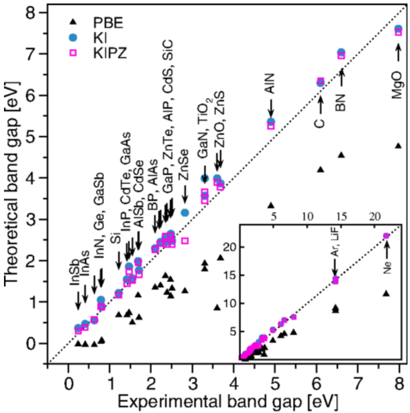


Ultraviolet photoemission spectra



N. Colonna et al. *J. Chem. Theory Comput.* 14.5 (8, 2018), 2549; N. L. Nguyen et al. *Phys. Rev. Lett.* 114.16 (24, 2015), 166405

Koopmans functionals: results for solids

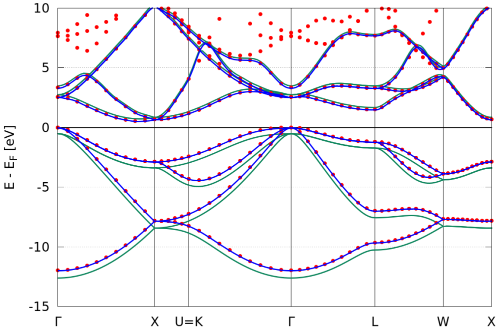


Mean absolute error (eV) across prototypical semiconductors and insulators

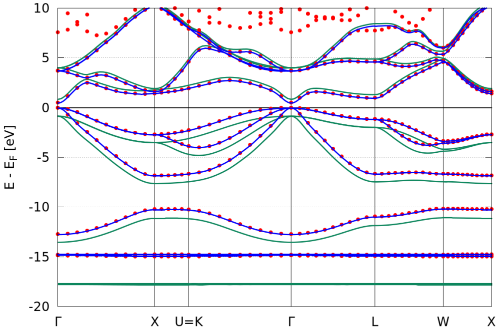
	PBE	G_0W_0	**KI**	**KIPZ**	QSG$\tilde{W}$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (23, 2018), 021051

Koopmans functionals: results for solids



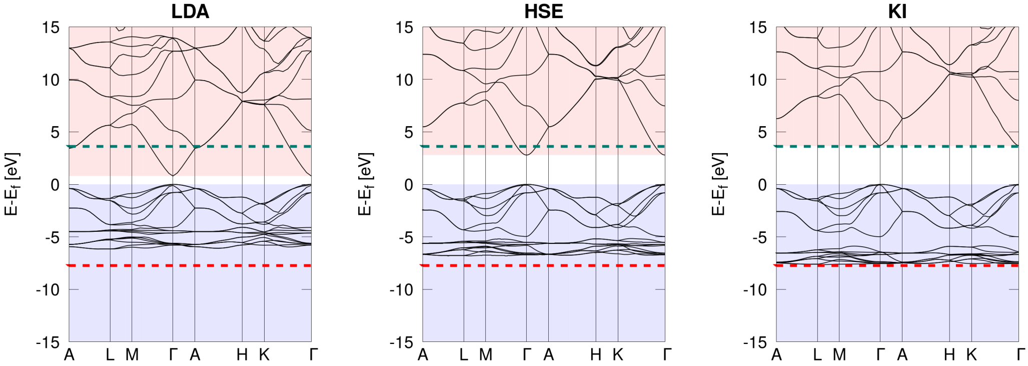
(a) Si, KIPZ



(b) GaAs, KI

		PBE	QSG$\tilde{W}$	**KI**	**pKIPZ**	**KIPZ**	exp
Si	E_{gap}	0.55	1.24	1.18	1.17	1.19	1.17
GaAs	E_{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	$\mathrm{sc}G\tilde{W}$	**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.* (4, 2022)

Koopmans functionals: the workflows

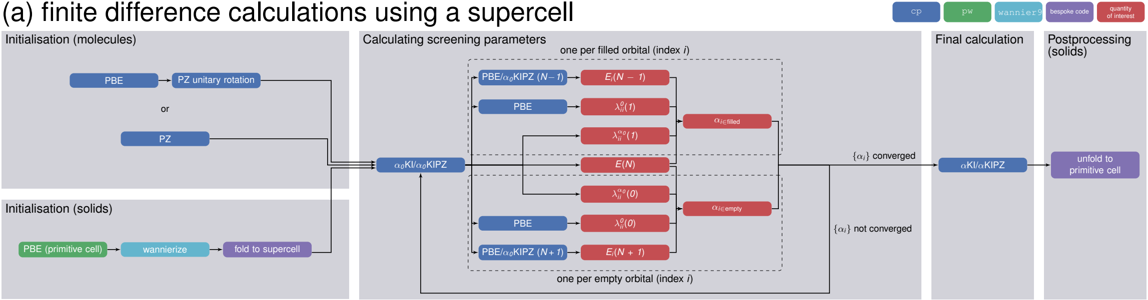
Screening coefficients $\{\alpha_i\}$ must be determined first, via...

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106; N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022);
Y. Schubert. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". ETH Zürich, 2022

Koopmans functionals: the workflows

Screening coefficients $\{\alpha_i\}$ must be determined first, via...

(a) finite difference calculations using a supercell



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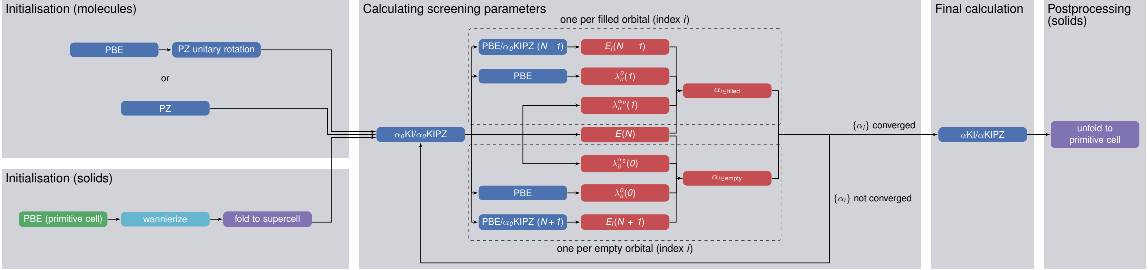
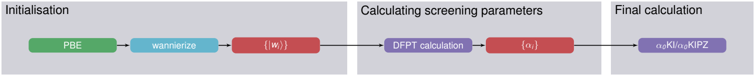


(b) DFPT using a primitive cell



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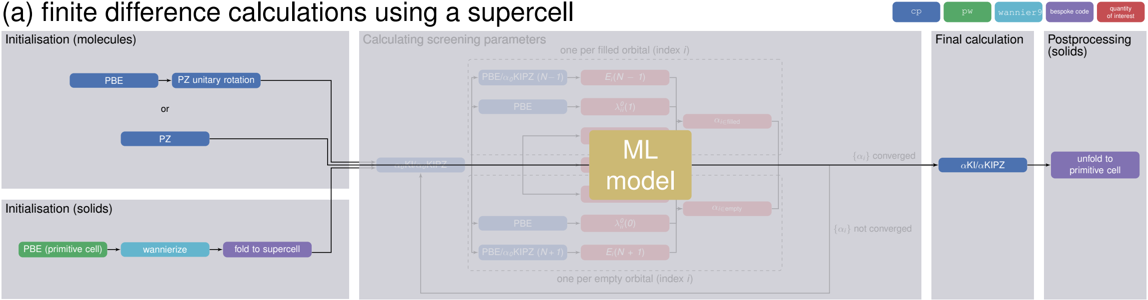

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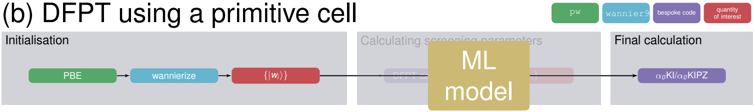
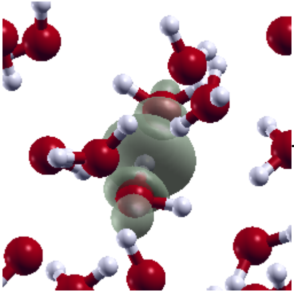


(c) via machine learning (resulting band gaps within $\sim$ 0.02 eV of explicit approach)

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106; N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022);
Y. Schubert. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". ETH Zürich, 2022

Learning the screening parameters



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

Y. Schubert. “Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations”. ETH Zürich, 2022

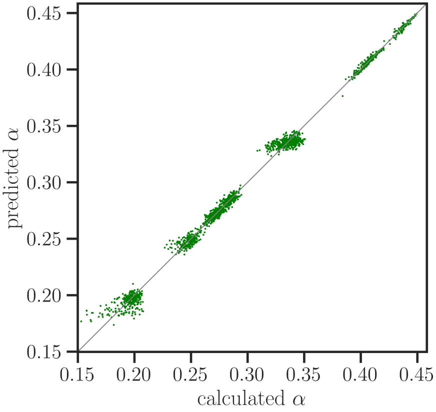
Details of the power spectrum

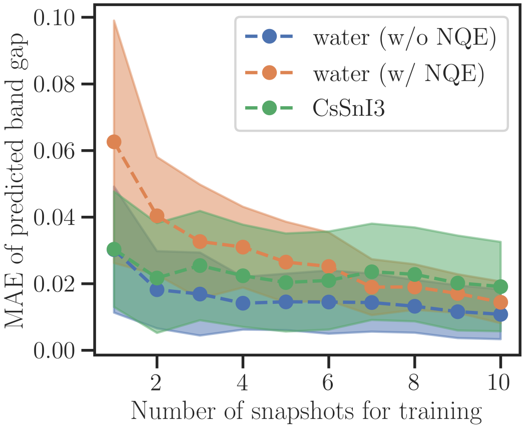
$$c^i_{nlm,k=\text{orbital}} = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) \rho^i(\mathbf{r} - \mathbf{R}^i)$$

g_{nl} = orthonormalised radial Gaussian basis functions
Y_{lm} = spherical harmonics

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

Learning the screening parameters





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

How can we make these calculations easier?

`kcw.x` (DFPT implementation) is distributed in Quantum ESPRESSO v7.1 onwards

But complex workflows mean that...

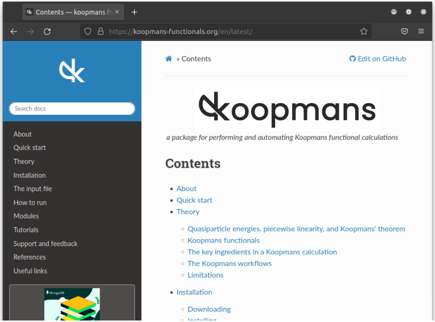
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- beta version released earlier this year[1]
- implementations of Koopmans functionals
- automated workflows
  - start-to-finish Koopmans calculations
  - Wannierisation
  - dielectric tensor
  - convergence tests
  - ...
- built on top of ASE[2]
- does not require expert knowledge

koopmans-functionals.org



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[1] Linscott et al., in prep

[2] A. H. Larsen et al. *J. Phys. Condens. Matter* 29.27 (12, 2017), 273002

koopmans: the input file

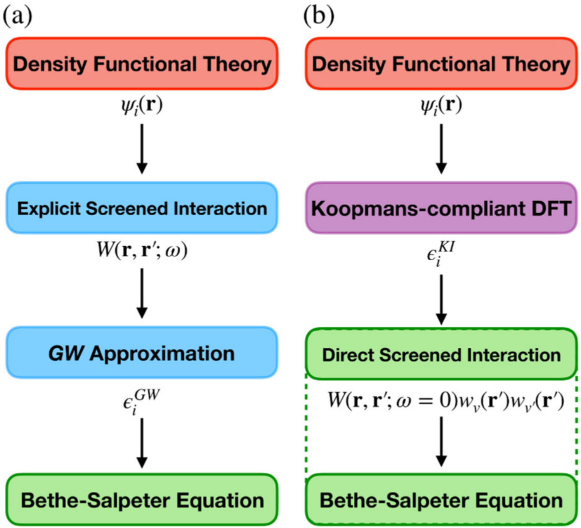

```json
{
  "workflow": {
    "task": "singlepoint",
    "functional": "ki",
    "method": "dscf",
    "init_orbitals": "mlwfs",
    "alpha_guess": 0.1
  },
  "atoms": {
    "atomic_positions": {
      "units": "crystal",
      "positions": [["Si", 0.00, 0.00, 0.00],
                    ["Si", 0.25, 0.25, 0.25]]
    },
    "cell_parameters": {
      "periodic": true,
      "ibrav": 2,
      "celldm(1)": 10.262
    }
  },
```

```json
  "k_points": {
    "grid": [8, 8, 8],
    "path": "LGXKG"
  },
  "calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
      "projections": [
          [{"fsite": [0.125, 0.125, 0.125],
            "ang_mtm": "sp3"}],
          [{"fsite": [0.125, 0.125, 0.125],
            "ang_mtm": "sp3"}]
      ],
      "dis_froz_max": 11.5,
      "dis_win_max": 17.0
    }
  }
}
```

koopmans is scriptable

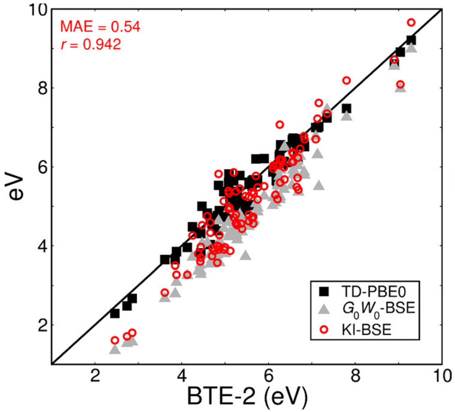

```python
from ase.build import bulk
from koopmans.kpoints import Kpoints
from koopmans.projections import ProjectionBlocks
from koopmans.workflows import SinglepointWorkflow

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

# Define the projections for the Wannierization (same for filled and empty manifold)
si_proj = [{'fsite': [0.25, 0.25, 0.25], 'ang_mtm': 'sp3'}]
si_projs = ProjectionBlocks.from_list([si_proj, si_proj], atoms=atoms)

# Create the workflow
workflow = SinglepointWorkflow(atoms = atoms,
        projections = si_projs,
        ecutwfc = 40.0,
        kpoints = Kpoints(grid=[8, 8, 8], path='LGXKG', cell=atoms.cell),
        calculator_parameters = {'pw': {'nbnd': 10},
        'w90': {'dis_froz_max': 10.6, 'dis_win_max': 16.9}})

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

Neutral excitations with Koopmans



J. D. Elliott et al. *J. Chem. Theory Comput.* 15.6 (11, 2019), 3710

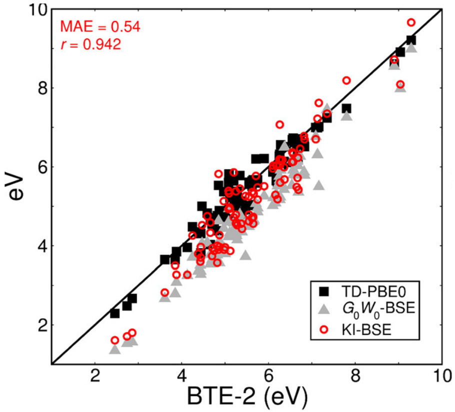
Neutral excitations with Koopmans



Thiel's set	**KI-BSE**	G_0W_0-BSE		TDDFT	
	PBE	PBE	B3LYP	PBE	B3LYP
MAE (eV)	0.54	0.83	0.46	0.55	0.27

J. D. Elliott et al. *J. Chem. Theory Comput.* 15.6 (11, 2019), 3710
N. L. Nguyen et al. *Phys. Rev. Lett.* 122.23 (14, 2019), 237402

Neutral excitations with Koopmans



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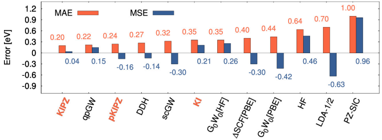
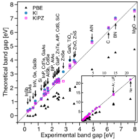
	PBE	PBE	B3LYP	PBE	B3LYP
MAE (eV)	0.54	0.83	0.46	0.55	0.27

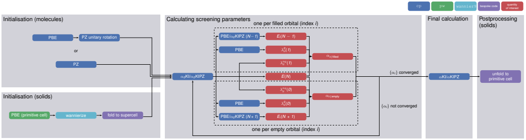
Based on RPA $\rightarrow$ room for improvement with finite-field approaches

J. D. Elliott et al. *J. Chem. Theory Comput.* 15.6 (11, 2019), 3710
N. L. Nguyen et al. *Phys. Rev. Lett.* 122.23 (14, 2019), 237402

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 release of `koopmans` means you don't need expert knowledge to run Koopmans functional calculations
- Koopmans can replace GW when calculating neutral excitations with BSE

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MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

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

Free online school Nov 9-11 2022 *Advanced Quantum ESPRESSO tutorial: Hubbard and Koopmans functionals from linear response*. Too late to register but it will be recorded!

Follow @ed_linscott for updates | Slides available at github/elinscott

SPARE SLIDES

Koopmans functionals: off-diagonal occupancies

Edward Linscott
EPFL

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