

Koopmans functionals in practice

minimisation, screening coefficients, and more...

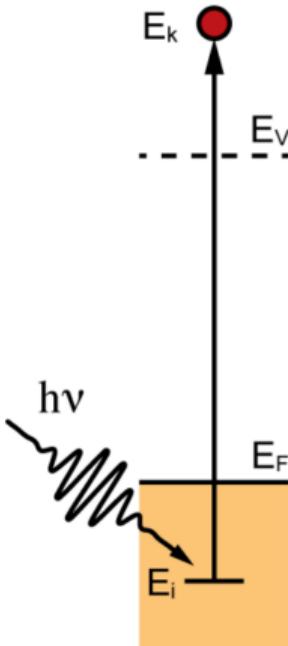
What are Koopmans functionals?

How do they differ from standard DFT?

What implications does this have for running these calculations?

What codes do we use to run these calculations?

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



Koopmans functionals: theory

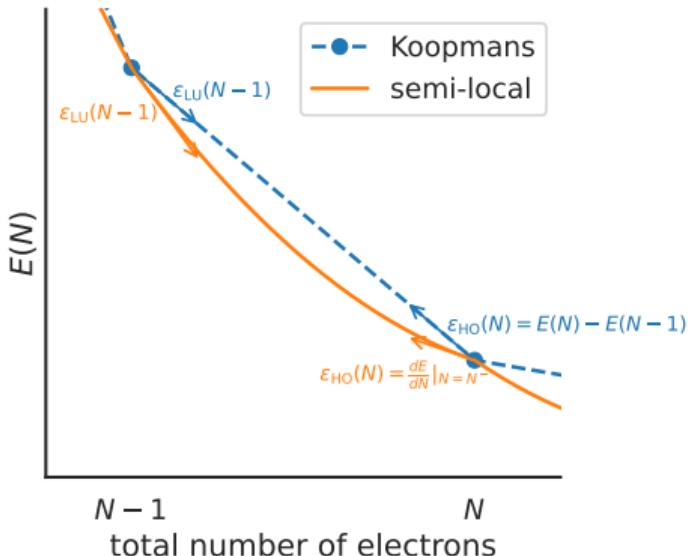
Goal: spectral properties (charged excitations) with a functional theory

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 $E(N-1) - E(N)$



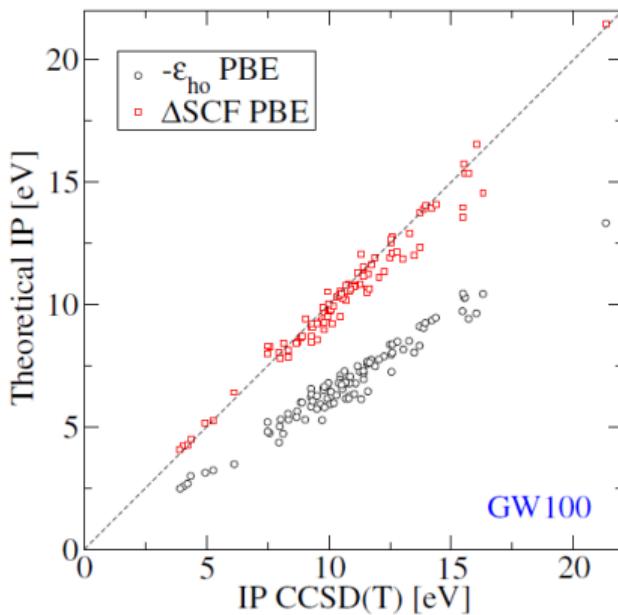
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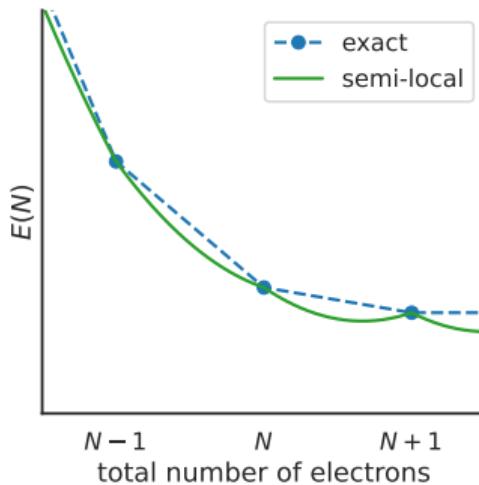
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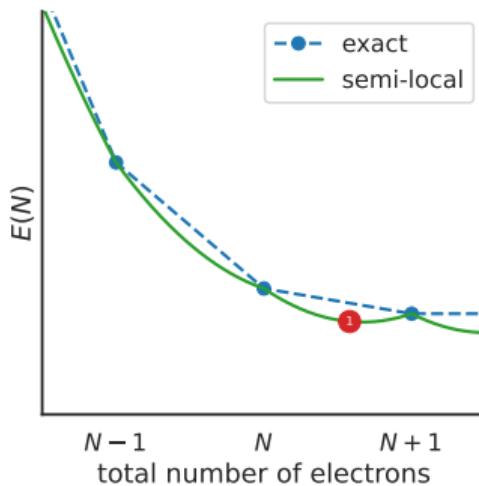
Koopmans functionals: theory

$$-\underbrace{\int_0^{f_i} \varepsilon_i(f) df}_{\text{removes curvature}} + f_i \underbrace{\int_0^1 \varepsilon_i(f) df}_{\text{restores linearity}}$$



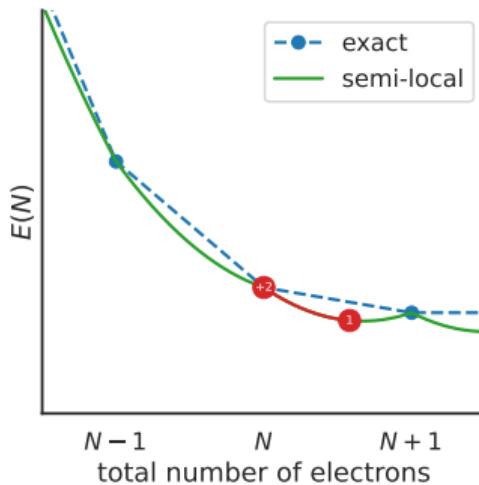
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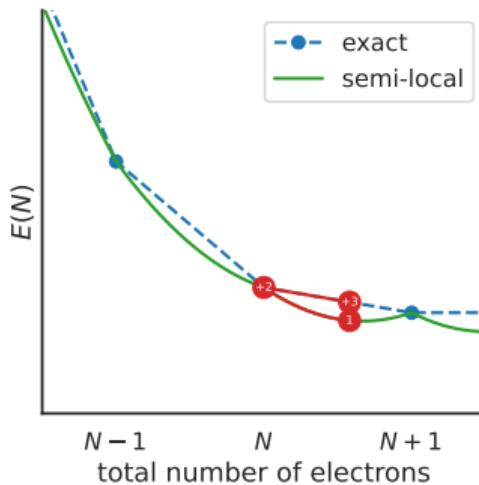
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$$E_{\text{Koopmans}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{DFT}[\rho] + \sum_i \alpha_i \left(-\underbrace{\int_0^{f_i} \varepsilon_i(f) df}_{\text{removes curvature}} + f_i \underbrace{\int_0^1 \varepsilon_i(f) df}_{\text{restores linearity}} \right)$$

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Differences to semi-local functionals:

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Differences to semi-local functionals:

- orbital-density dependence

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Differences to semi-local functionals:

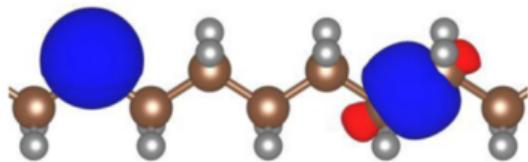
- orbital-density dependence
- screening

Discuss here why we have orbital-density-dependence

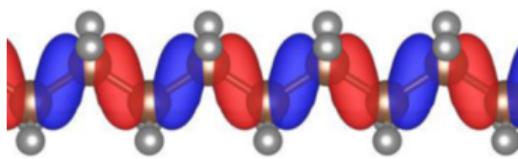
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$$v_i^{\text{KI}}/\alpha_i = -E_H[\mathbf{n}_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - \mathbf{n}_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) \mathbf{n}_i(\mathbf{r}')$$

variational (localised, minimising) vs canonical (delocalised, diagonalising) orbitals



(a) variational



(b) canonical

Discuss here other consequences of ODD:

- 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

¹ A. Ferretti et al. *Phys. Rev. B* 89.19 (27, 2014), 195134.

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- Practically we can often use MLWFs

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- Practically we can often use MLWFs
- a natural generalisation in the direction of spectral functional theory¹

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Discuss here screening, how to determine these ab initio

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

Discuss here screening, how to determine these ab initio

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

Slides on importance of localisation

Koopmans functionals: comparing

	DFT+ <i>U</i>	Koopmans
designed to correct SIE, as defined by...	erroneous global curvature in total energies	dependence of ε_i on $f_i \forall i$
by construction...	corrects local curvature in total energies	removes dependence of ε_i on f_i and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
correction applied to...	selected subspaces only (e.g. <i>3d</i> orbitals)	the entire system
orbitals defined by...	Hubbard projectors (atom-centred, frozen, incomplete)	
corrective parameters are...	$\{U^I\}$, defined with respect to charge-neutral excitations (if using LR)	

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Koopmans functionals: comparing

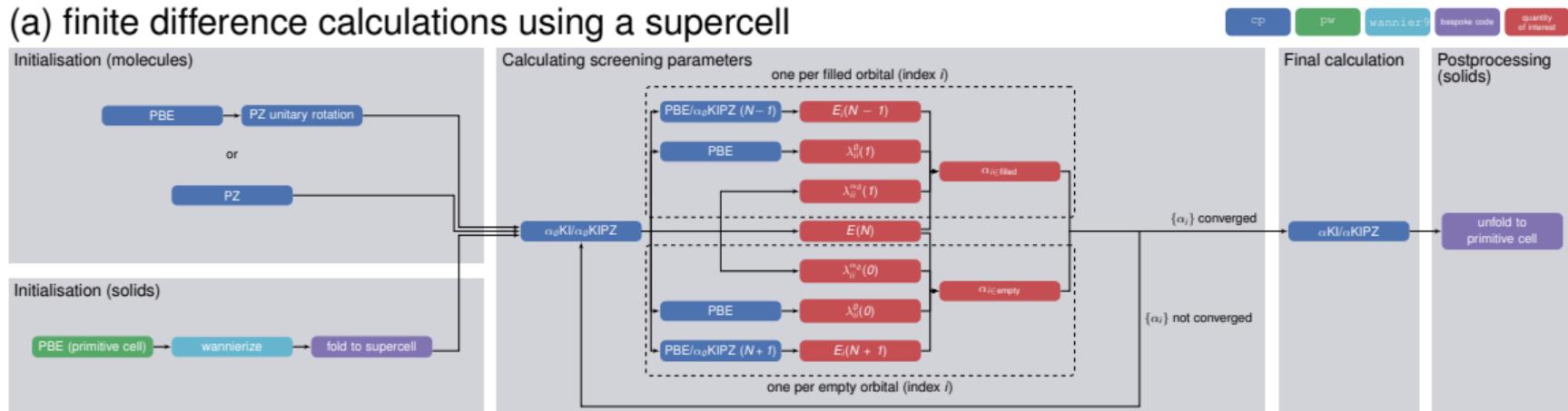
	DFT+ <i>U</i>	Koopmans
designed to correct SIE, as defined by...	erroneous global curvature in total energies	dependence of ε_i on $f_i \forall i$ (canonical orbitals)
by construction...	corrects local curvature in total energies	removes dependence of ε_i on f_i and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$ (variational orbitals)
correction applied to...	selected subspaces only (e.g. <i>3d</i> orbitals)	the entire system
orbitals defined by...	Hubbard projectors (atom-centred, frozen, incomplete)	variational (minimising) orbitals
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Screening coefficients $\{\alpha_i\}$ must be determined first, via...

Koopmans functionals: the workflows

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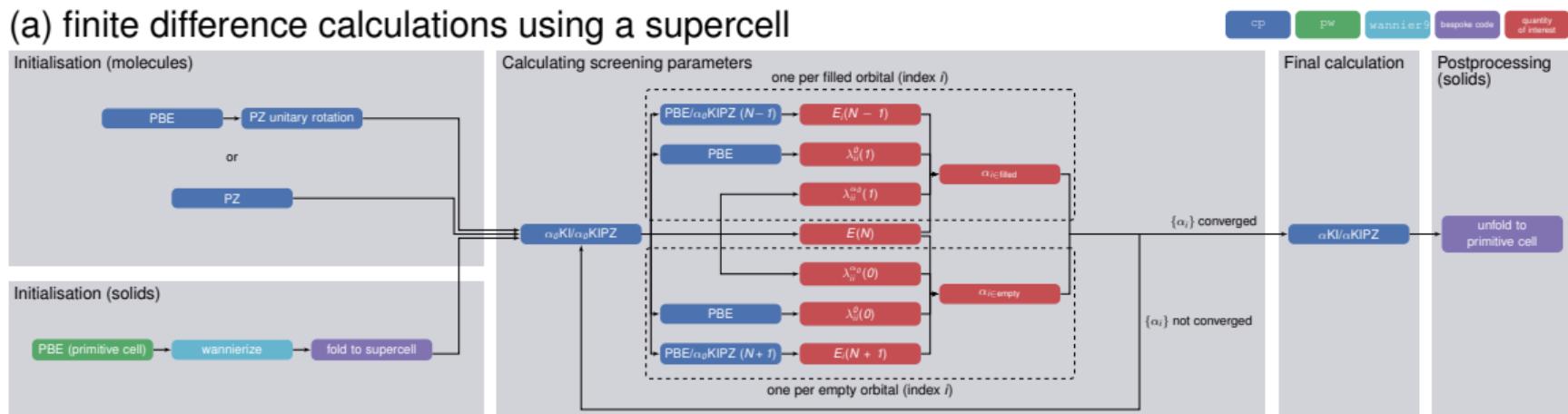
(a) finite difference calculations using a supercell



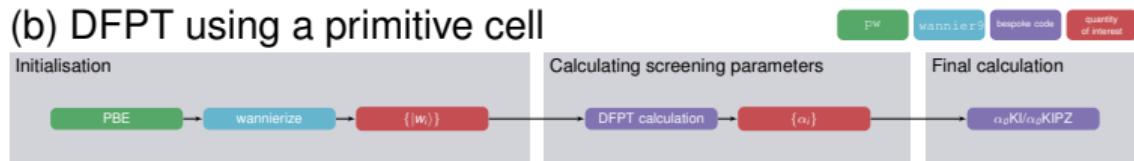
Koopmans functionals: the workflows

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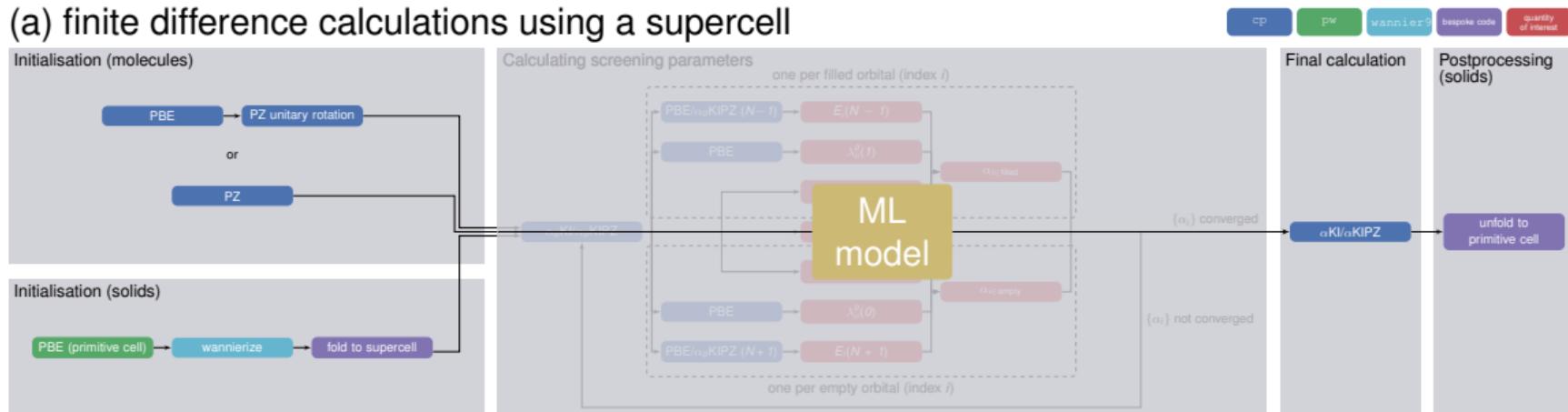
(b) DFPT using a primitive cell



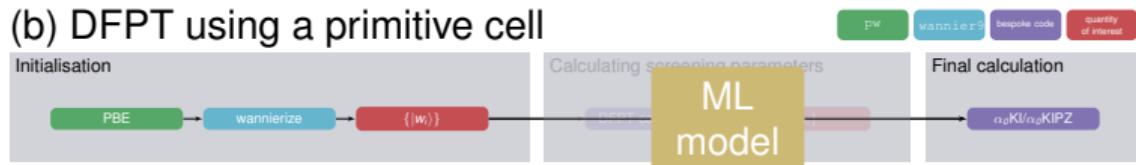
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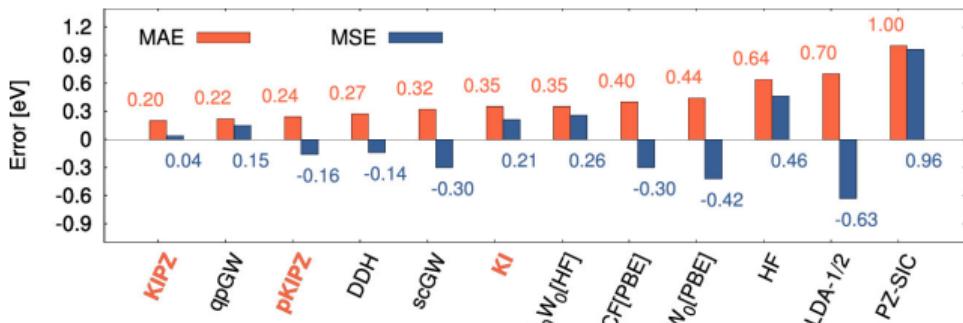
(c) via machine learning

Resonance with other efforts:

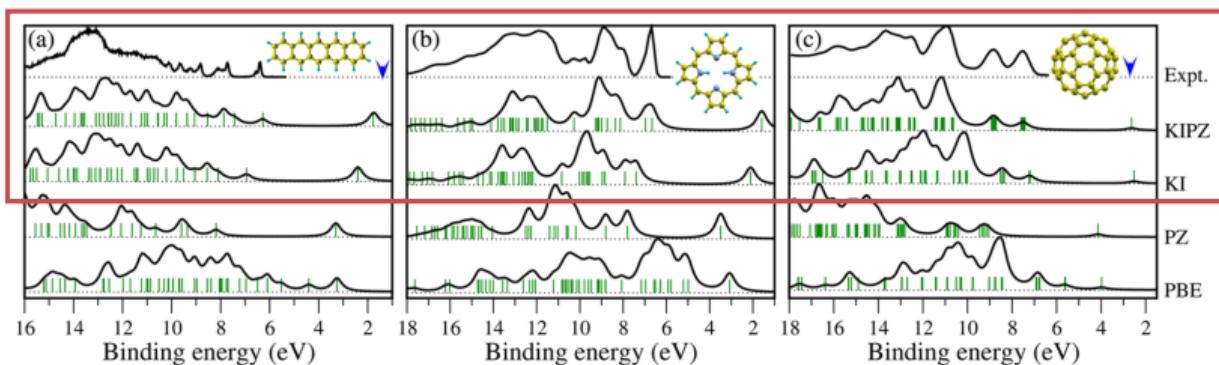
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (18, 2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others (refer back to Leeor's talk on Wednesday) L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (8, 2012), 1515; 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

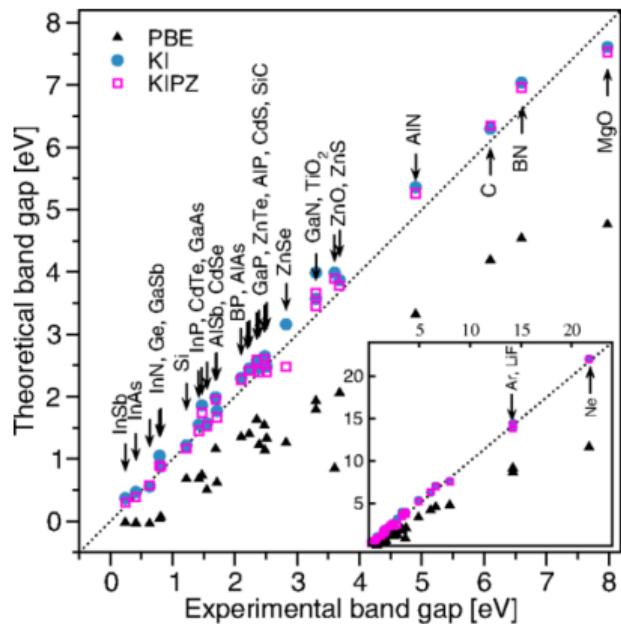
Ionisation potentials = $E(N - 1) - E(N)$? $= -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



Ultraviolet photoemission spectra



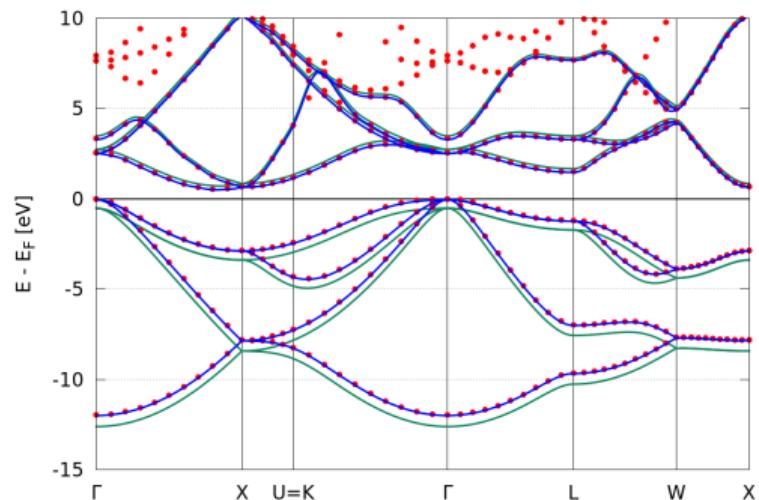
Koopmans functionals: results for solids



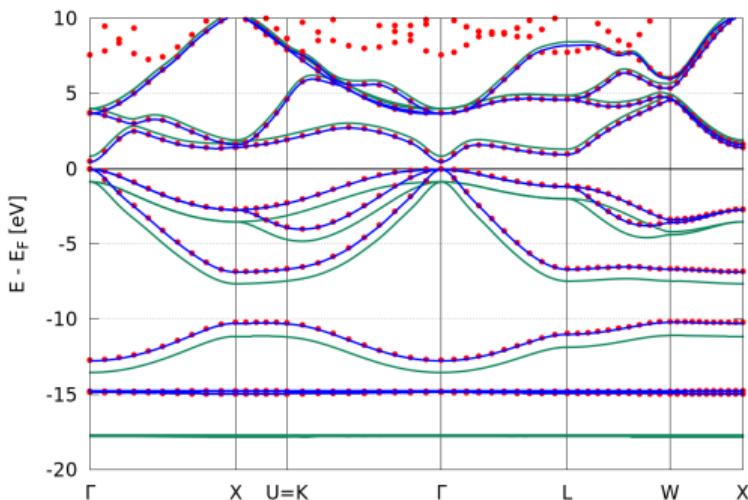
Mean absolute error (eV) across prototypical semiconductors and insulators

	PBE	G ₀ W ₀	KI	KIPZ	QSGW̃
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: results for solids



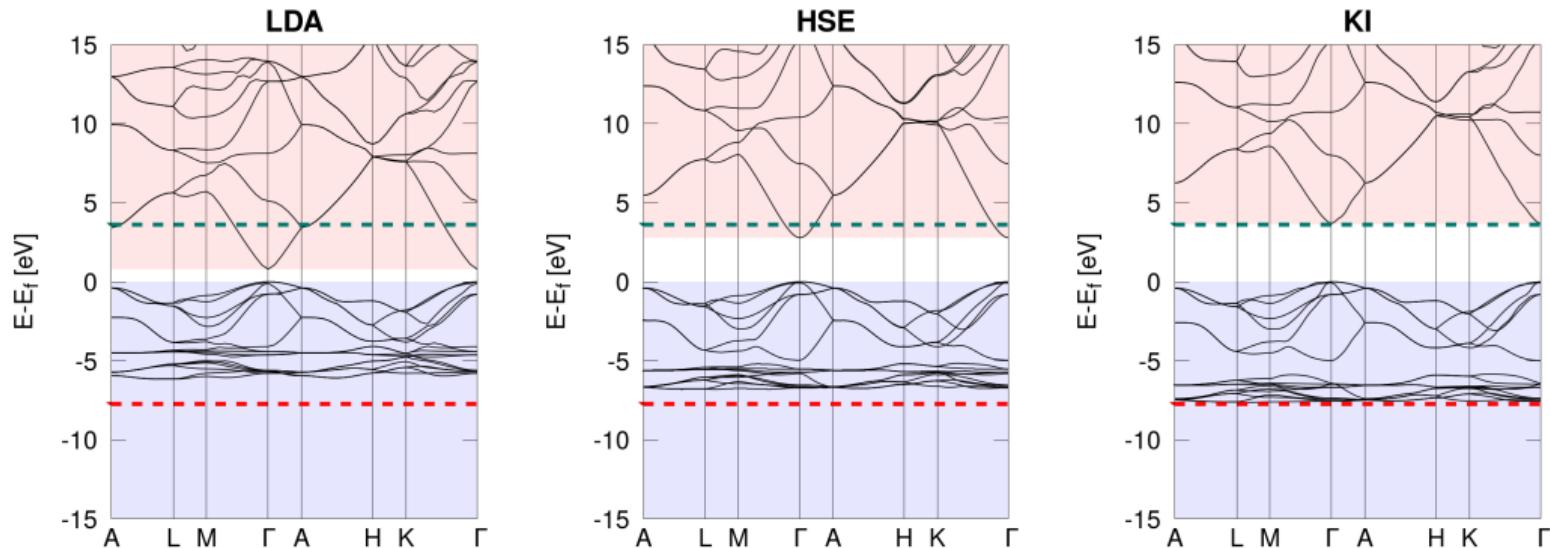
(a) Si, KIPZ



(b) GaAs, KI

		PBE	QSGW	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	$scG\tilde{W}$	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

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

But complex workflows mean that...

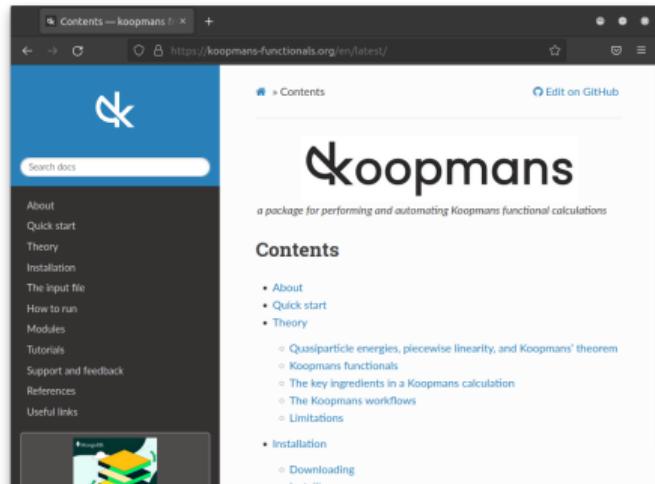
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- beta version released earlier this year¹
- implementations of Koopmans functionals
- 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



¹Linscott et al., in prep

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

koopmans: the input file

```
{  
    "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  
        }  
    },  
}
```

```
"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

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

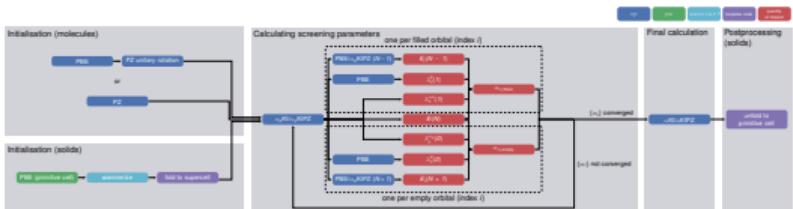
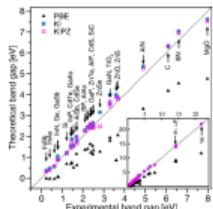
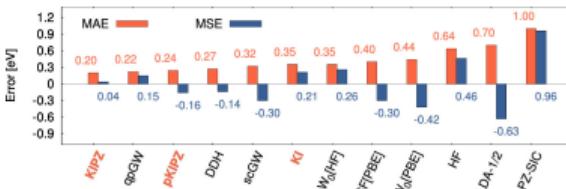
# Use ASE to create bulk silicon
atoms = bulk('Si')

# 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()
```

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

Acknowledgements



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

Follow [@ed_linscott](https://twitter.com/ed_linscott) for updates | Slides available at [github/elinscott](https://github.com/elinscott)

SPARE SLIDES

Recap from earlier

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

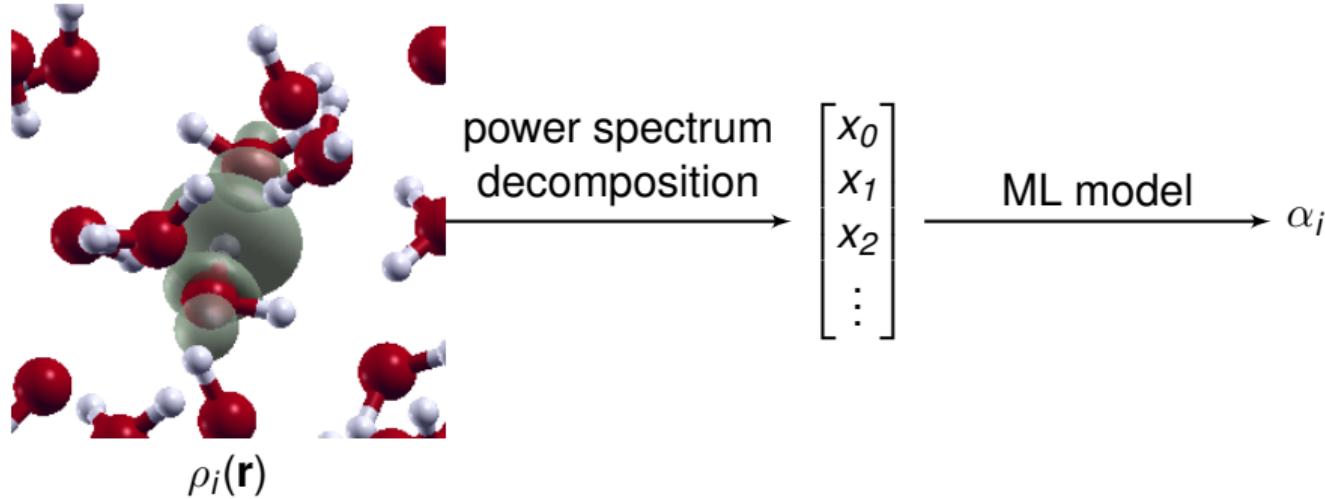
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are...

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

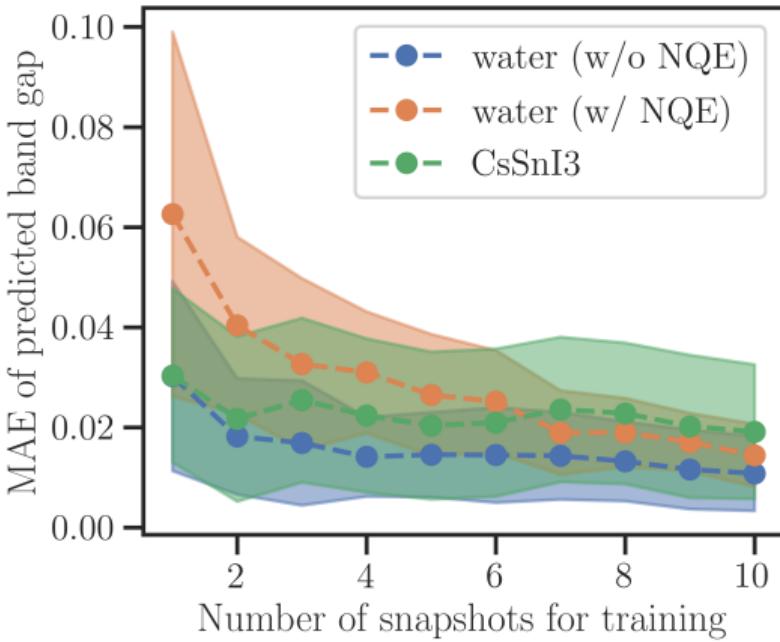
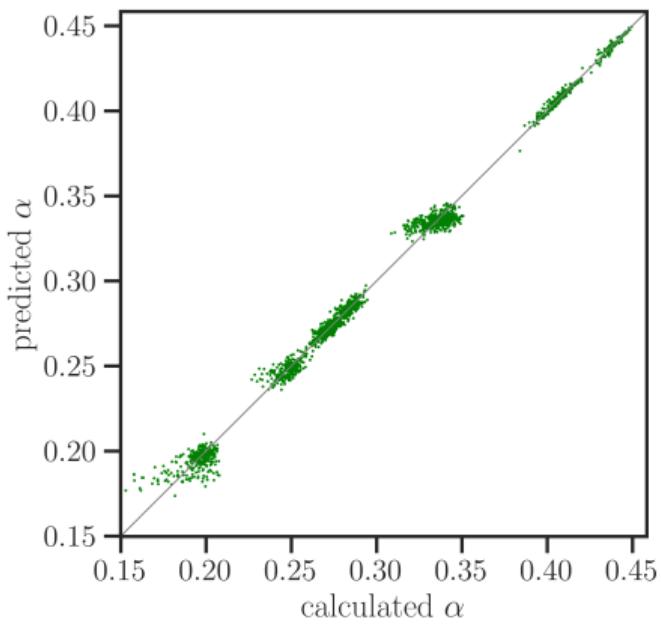
Learning the screening parameters



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

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

Learning the screening parameters



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