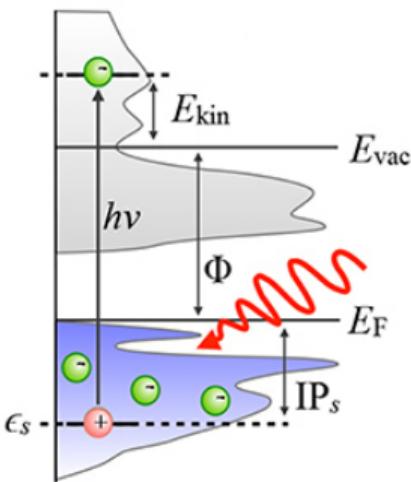


Koopmans functionals in practice

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



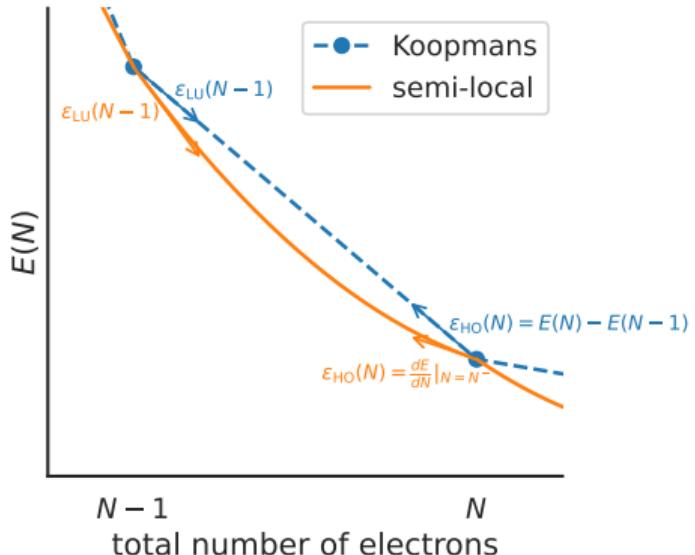
Goal: spectral properties (charged excitations) with a functional theory

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



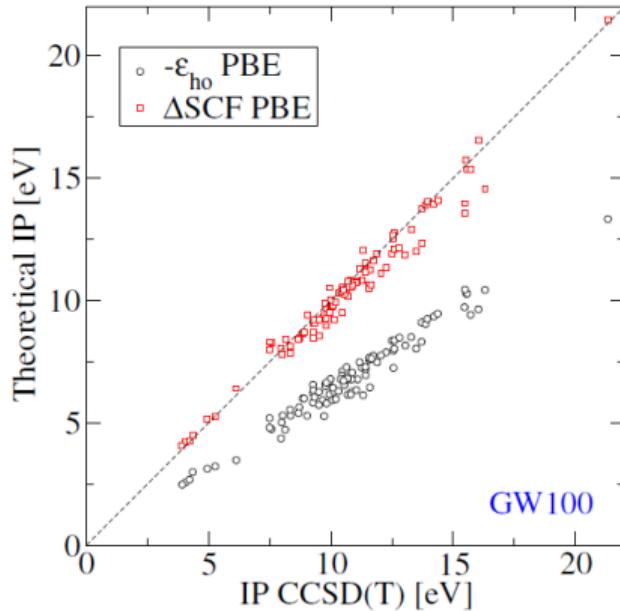
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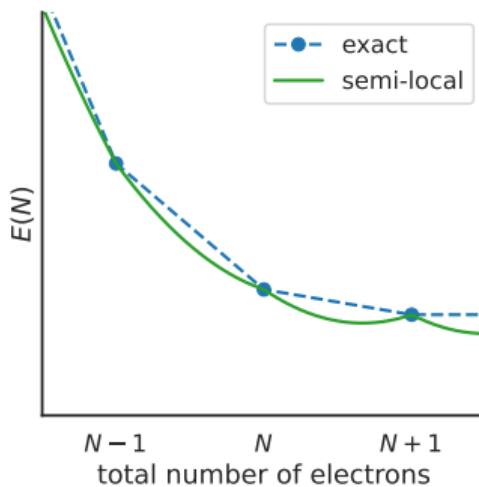
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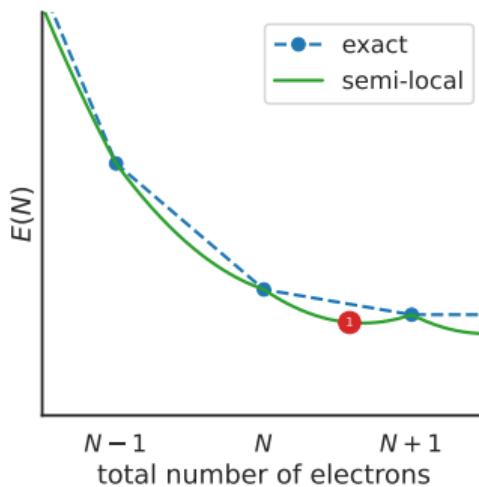
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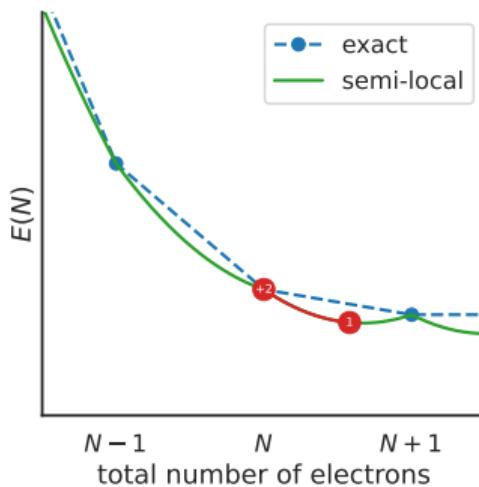
$$-\underbrace{\int_0^{f_i} \varepsilon_i(f) df}_{\text{removes curvature}} + \underbrace{f_i \eta_i}_{\text{restores linearity}}$$



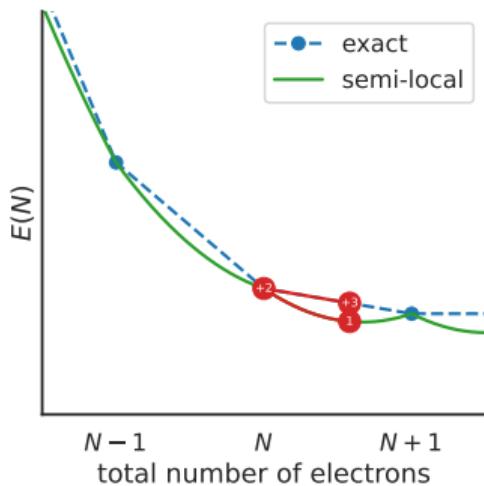
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- orbital-density dependence
- screening

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One degree of freedom: what should be the gradient of this linear term?

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- the base functional → “KI” (Koopmans integral). Enforces IP theorem. Does not affect energy/density!

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You might also see...

- “pKIPZ” = KIPZ Hamiltonian evaluated on the KI solution
- “K” = an earlier iteration based off half-filling rather than integer endpoints (no longer used)

$$-\int_0^{f_i} \varepsilon_i(f) df + f_i \int_0^1 \varepsilon_i(f) df = E_{\text{Hxc}}[\rho] + E_{\text{Hxc}}[\rho - \rho_i] + f_i (-E_{\text{Hxc}}[\rho - \rho_i] + E_{\text{Hxc}}[\rho - \rho_i + n_i])$$

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For more details see G. Borghi et al. *Phys. Rev. B* 91.15 (2015), 155112

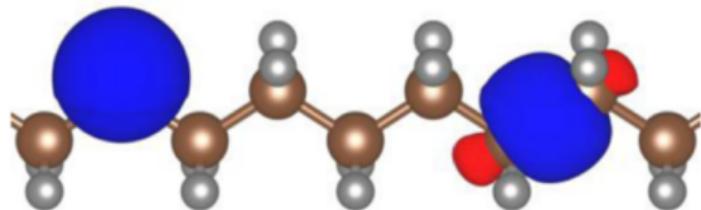
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(a) variational

Orbital-density-dependence

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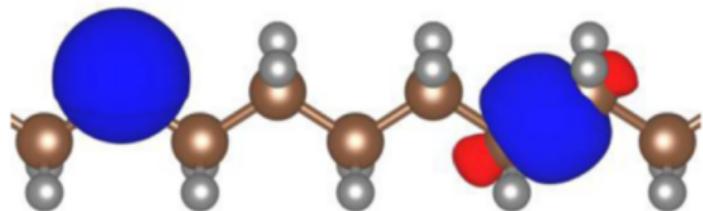
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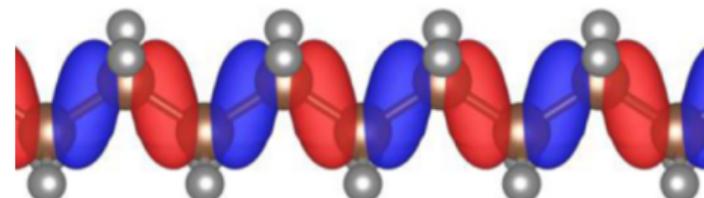
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Diagonalising at the minimum gives rise to diagonalising orbitals (delocalised/canonical)

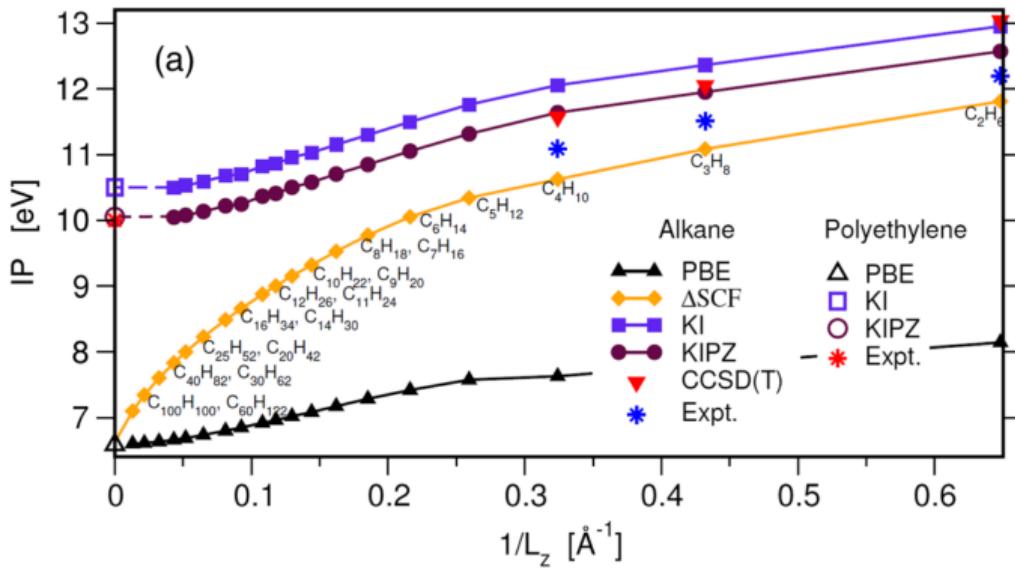


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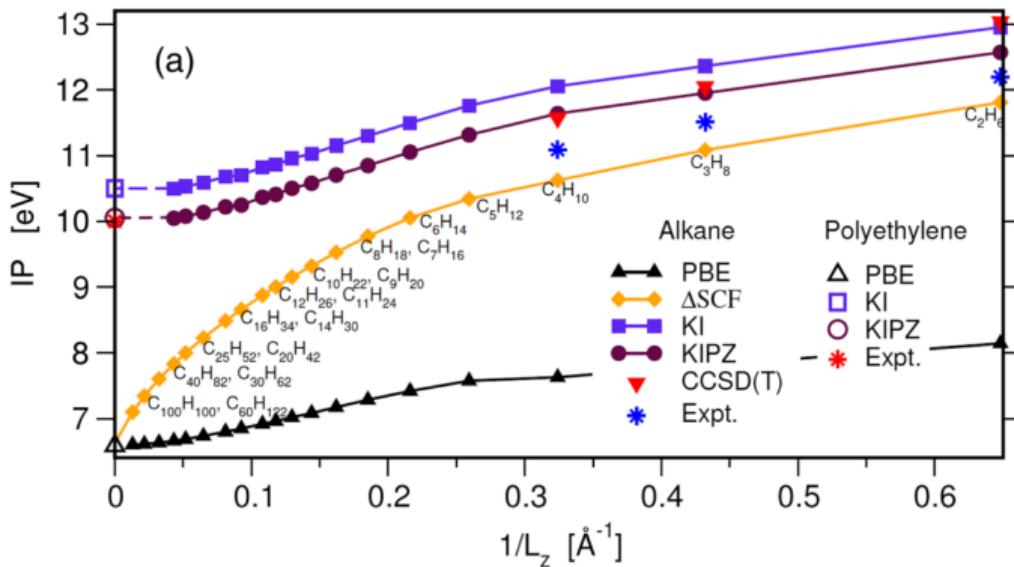


(b) canonical

Importance of localisation

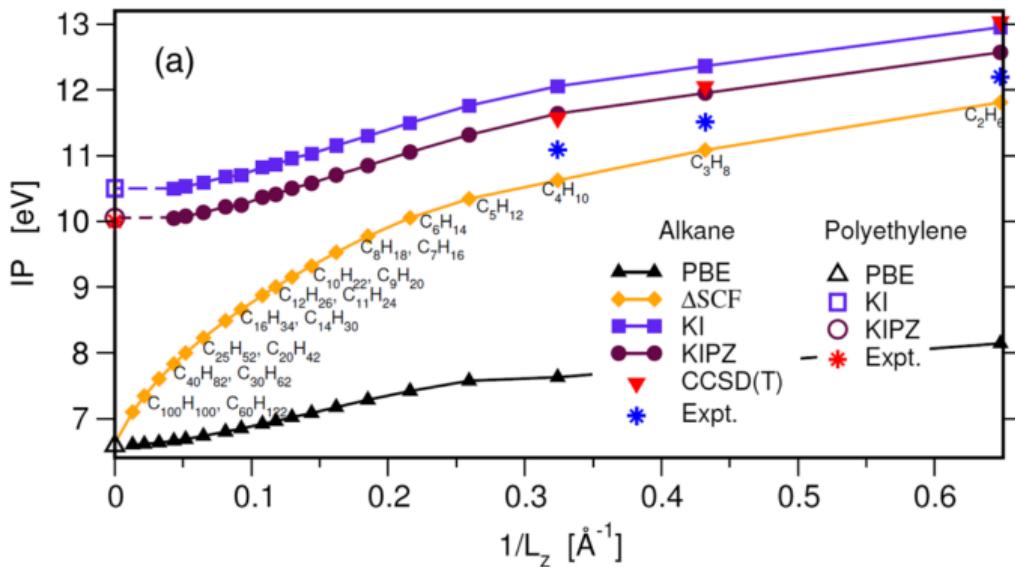


Importance of localisation



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

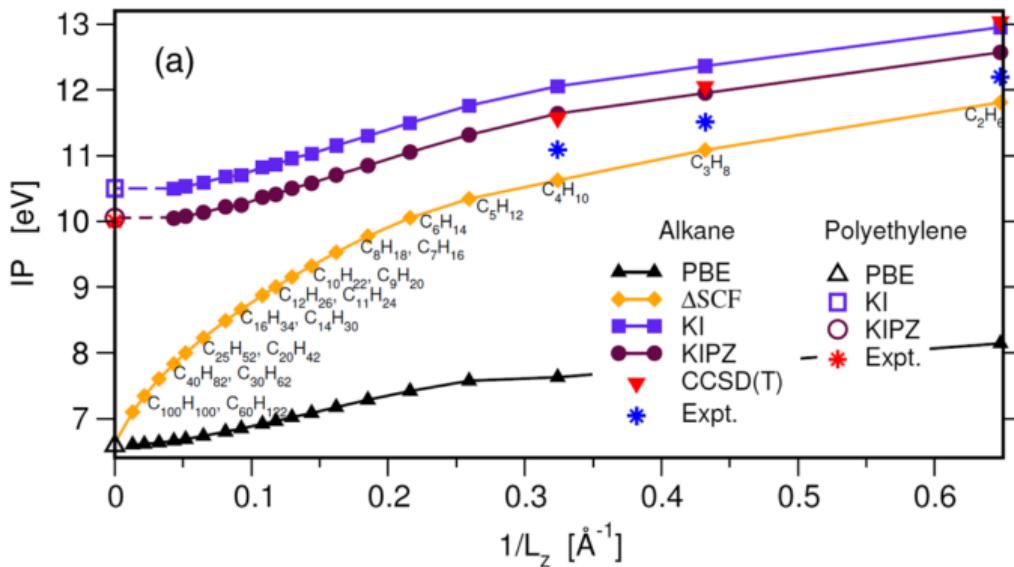
Importance of localisation



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

Importance of localisation



$$\lim_{n_i(r) \rightarrow 0} v_i^{\text{KI}}/\alpha_i = \lim_{n_i(r) \rightarrow 0} -E_H[n_i] + E_{xc}[\rho] - E_{xc}[\rho - n_i] - \int d\mathbf{r}' v_{xc}(\mathbf{r}', [\rho]) n_i(\mathbf{r}') = 0$$

Other features of orbital-density-dependence

- 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 (2014), 195134.

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- a natural generalisation in the direction of spectral functional theory (as discussed already by Andrea)¹

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- What is screening (in the context of Koopmans functionals)?

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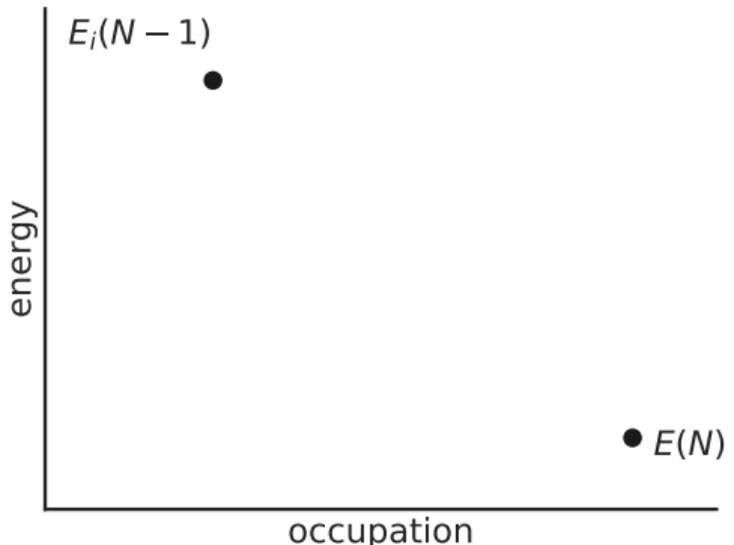
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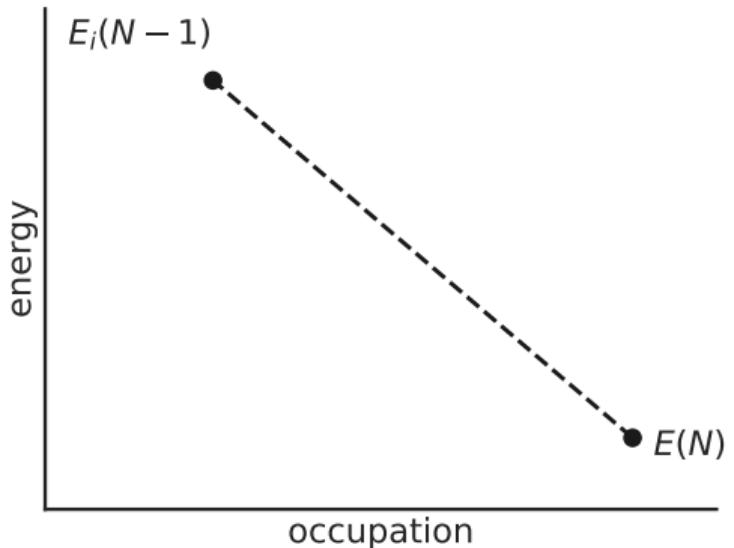
- How to choose an appropriate value for α_i ? Return to the original idea of Koopmans functionals:

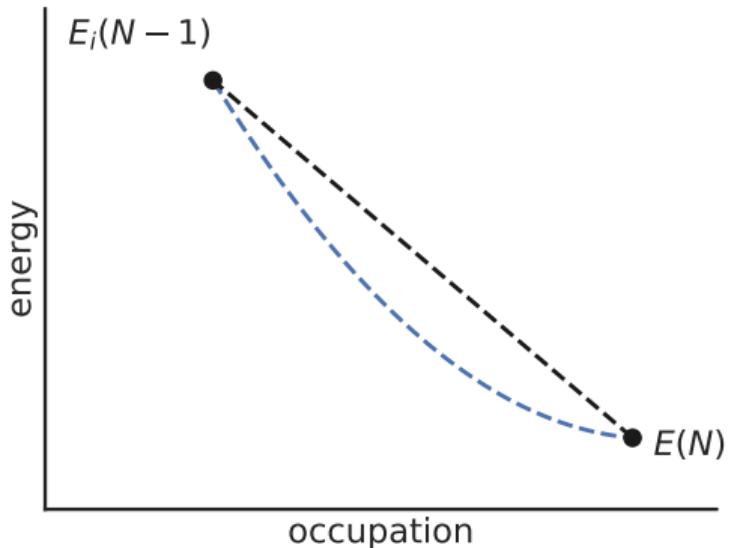
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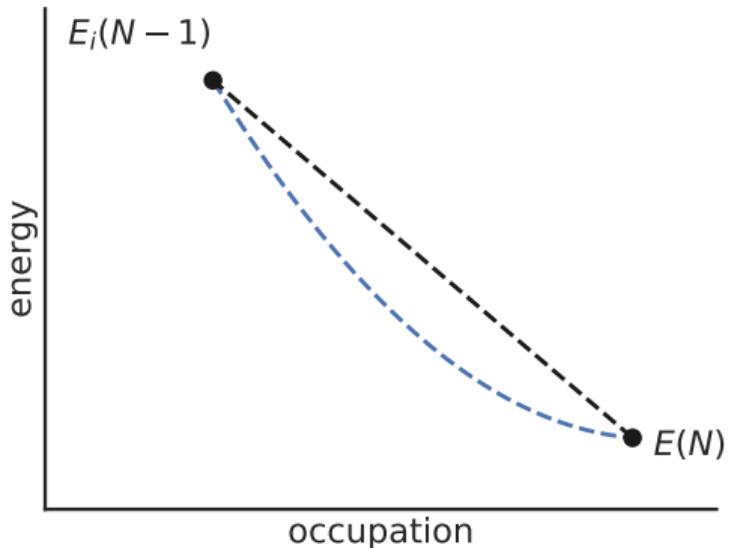
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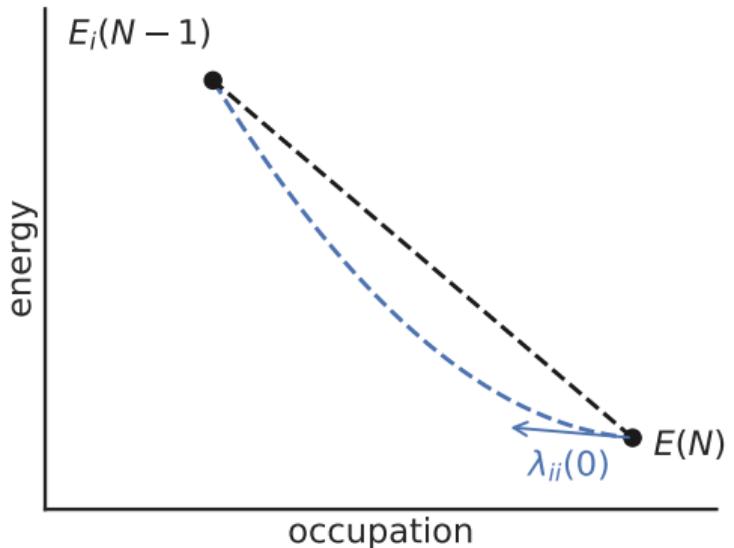
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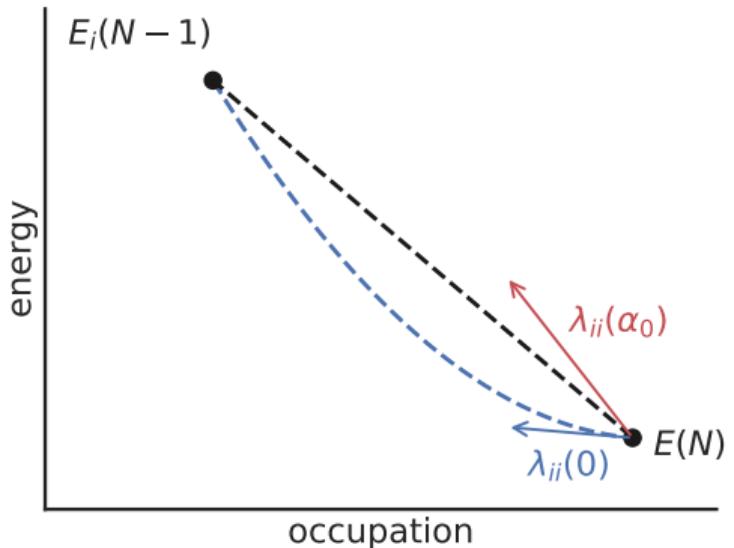




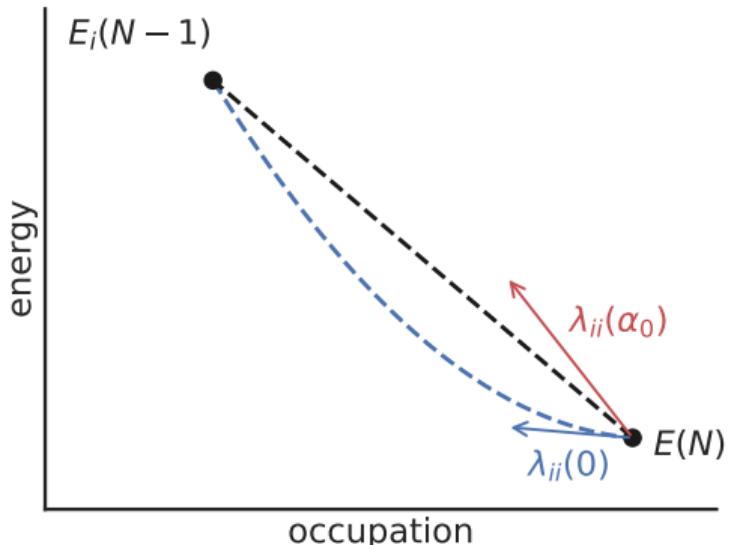
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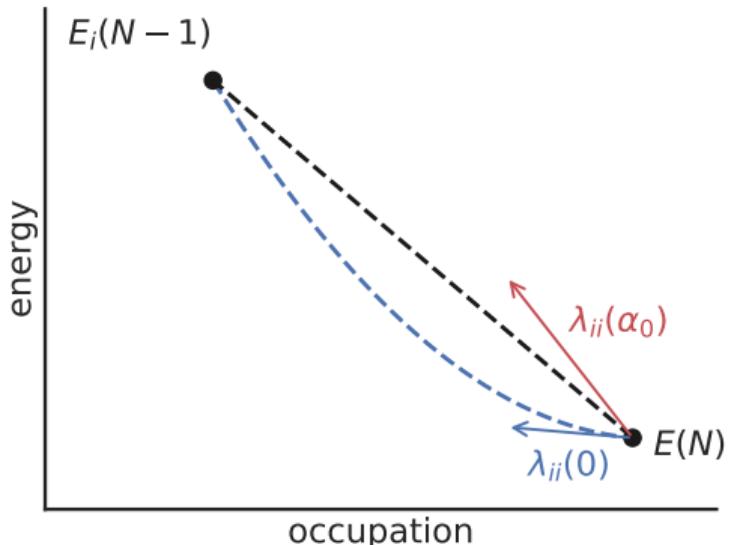
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total energy
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↑
↑
↑

expectation value
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$$\alpha^{n+1} = \alpha^n \frac{E_i(N-1) - E(N) - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^n) - \lambda_{ii}(0)}$$

total energy with electron removed from orbital i

total energy of neutral system

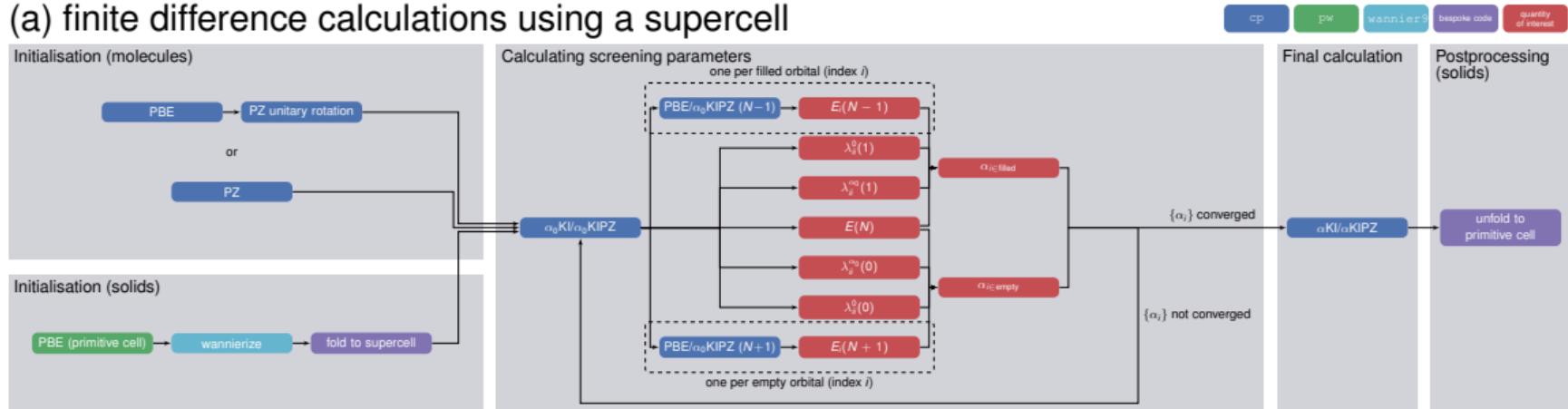
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Workflows for calculating screening parameters

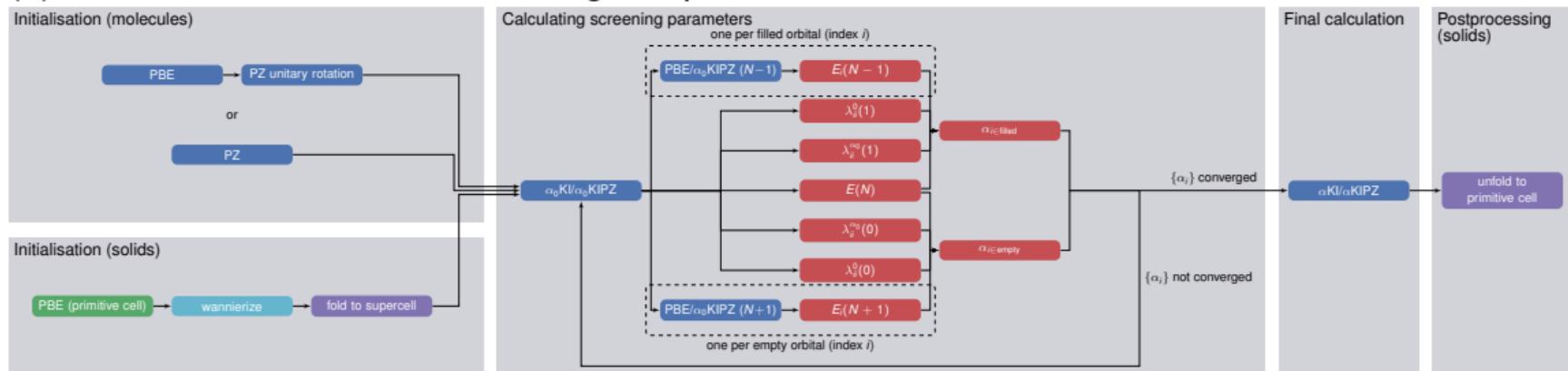
Workflows for calculating screening parameters

(a) finite difference calculations using a supercell

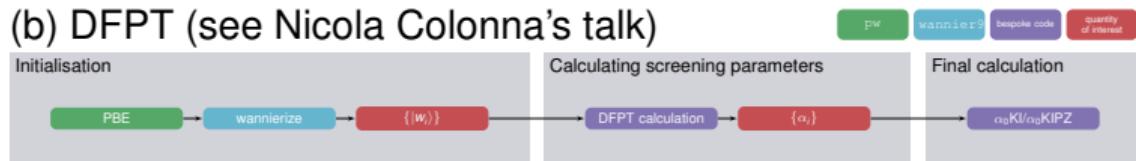


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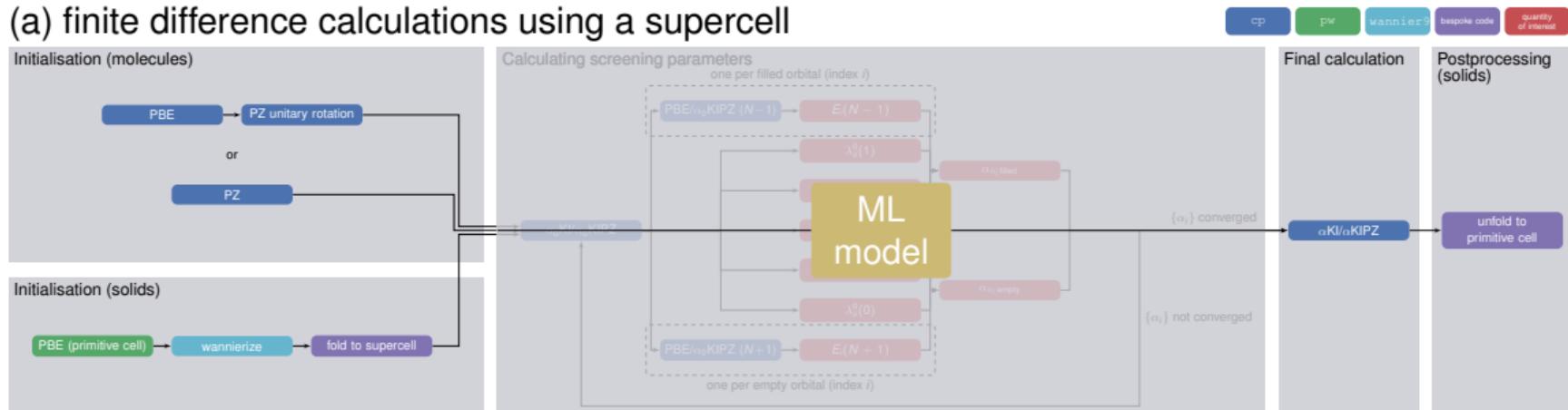


(b) DFPT (see Nicola Colonna's talk)

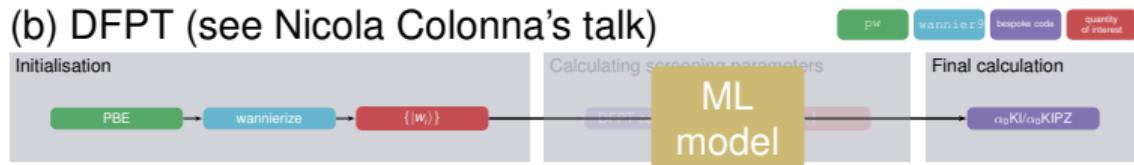


Workflows for calculating screening parameters

(a) finite difference calculations using a supercell



(b) DFPT (see Nicola Colonna's talk)



(c) via machine learning (see Yannick Schubert's talk)

- 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 (refer back to Leeor's talk on Wednesday) 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

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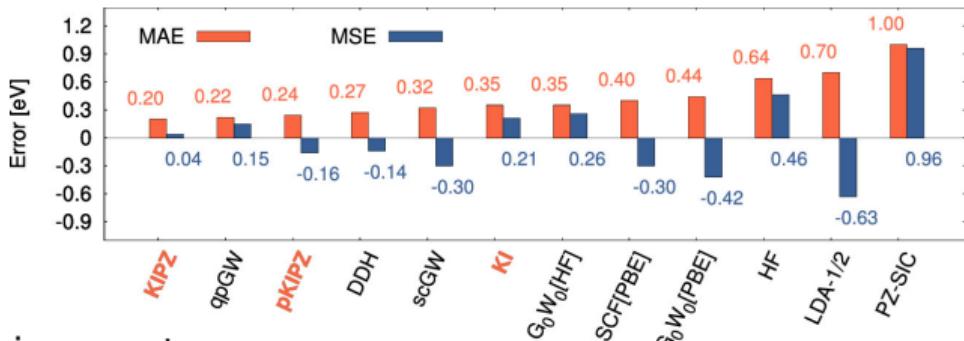
	DFT+ <i>U</i>	Koopmans
the functional...	corrects local curvature in total energies	removes dependence of ε_i on f_i and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$
correction applied to...	selected subspaces only (e.g. 3d orbitals)	every variational orbital in the entire system
orbitals defined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

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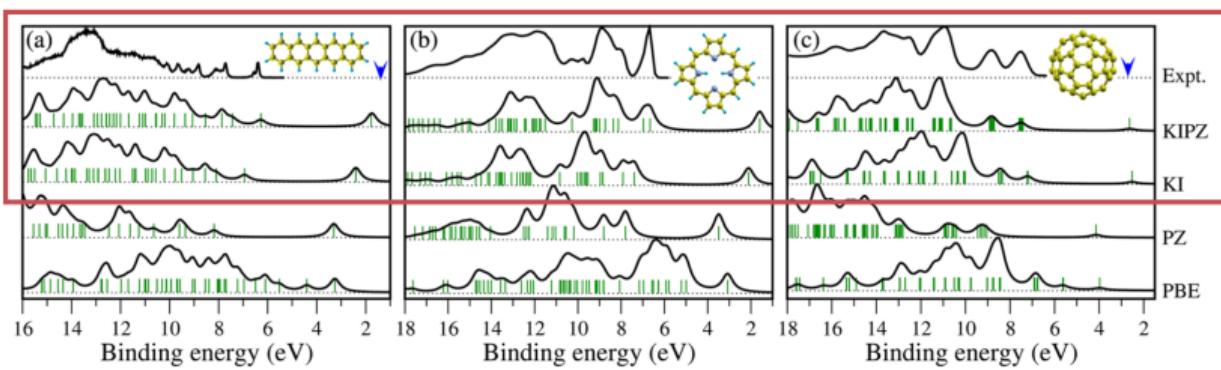
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corrective parameters are...	$\{U^I\}$, defined with respect to charge-neutral excitations (if using LR)	$\{\alpha_i\}$, defined with respect to charged excitations

Koopmans functionals: results for molecules

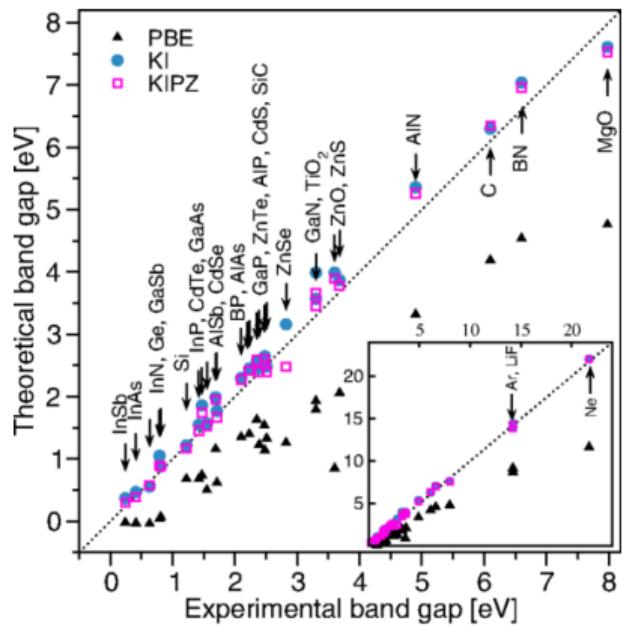
Ionisation potentials = $E(N - 1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



Ultraviolet photoemission spectra



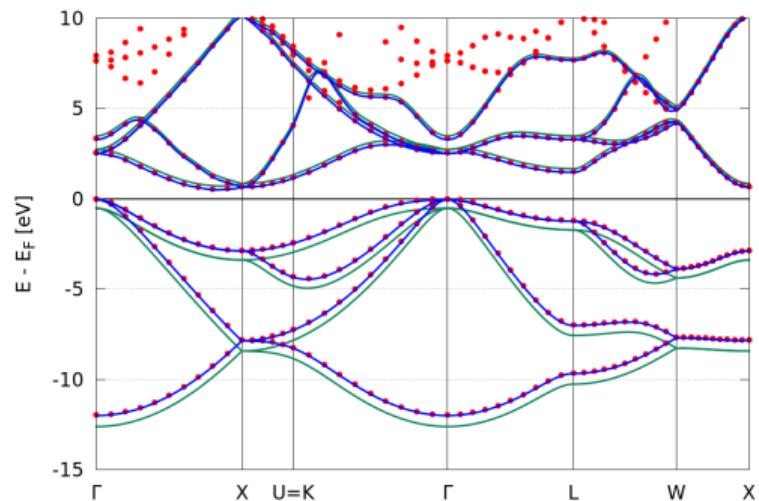
Koopmans functionals: results for solids



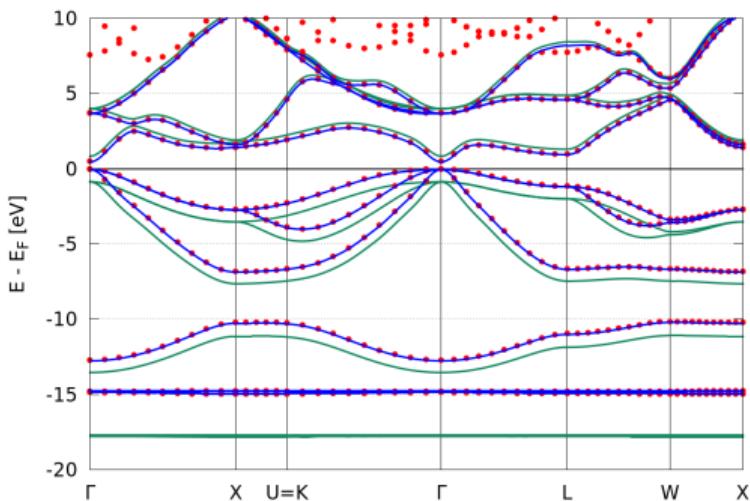
Mean absolute error (eV) across prototypical semiconductors and insulators

	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



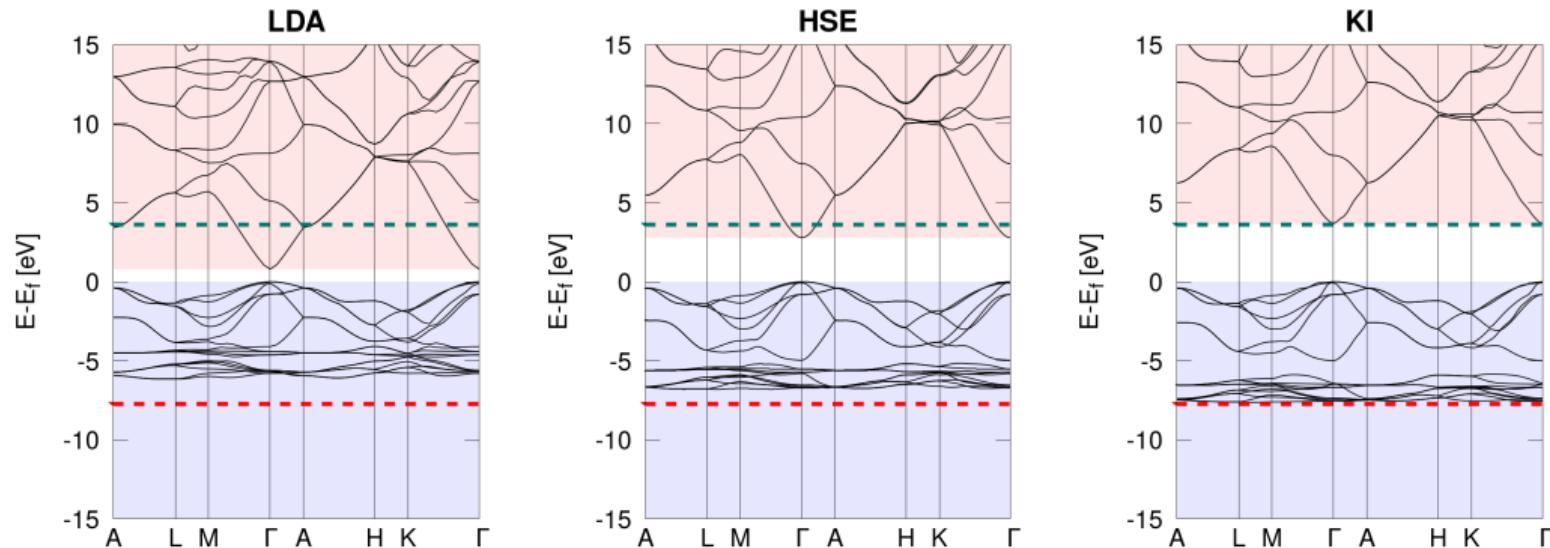
(a) Si, KIPZ



(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

`kcp.x` (supercell implementation) is available publically

But complex workflows mean that...

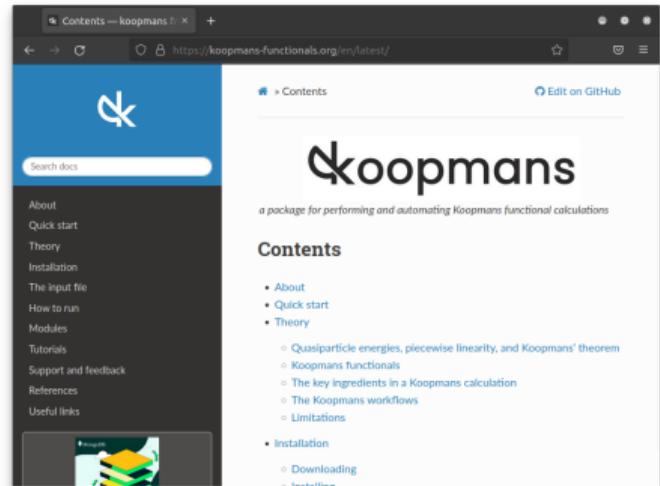
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- beta version released earlier this year¹
- implementations of Koopmans functionals
- automated workflows
 - start-to-finish Koopmans calculations
 - Wannierisation
 - dielectric tensor
 - ...
- built on top of ASE²
- under the hood, calls Quantum ESPRESSO
- does not require expert knowledge

koopmans-functionals.org



¹Linscott et al., in prep

²A. 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",  
        "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

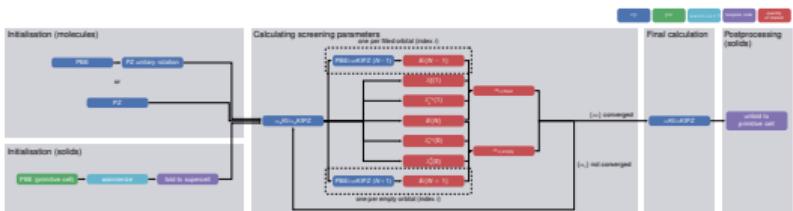
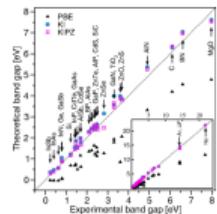
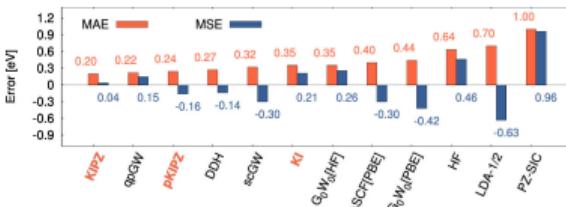
# Use ASE to create bulk silicon
atoms = bulk('Si')

# 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
- Koopmans functionals are implemented in Quantum ESPRESSO, and we can use koopmans to run these calculations easily

Acknowledgements



Nicola Marzari



Nicola Colonna



Riccardo
De Gennaro



Yannick
Schubert



**Swiss National
Science Foundation**



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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