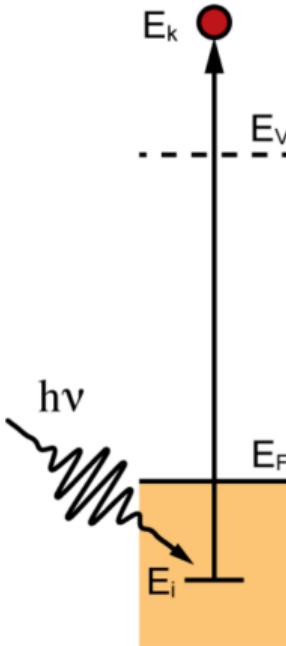




Koopmans functionals

accurately and efficiently predicting spectral properties
with a functional formulation

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

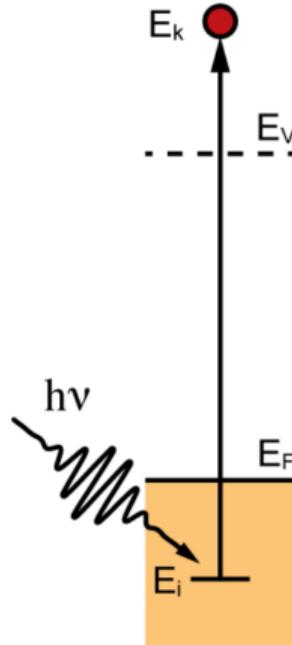


Koopmans functionals: theory

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

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

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

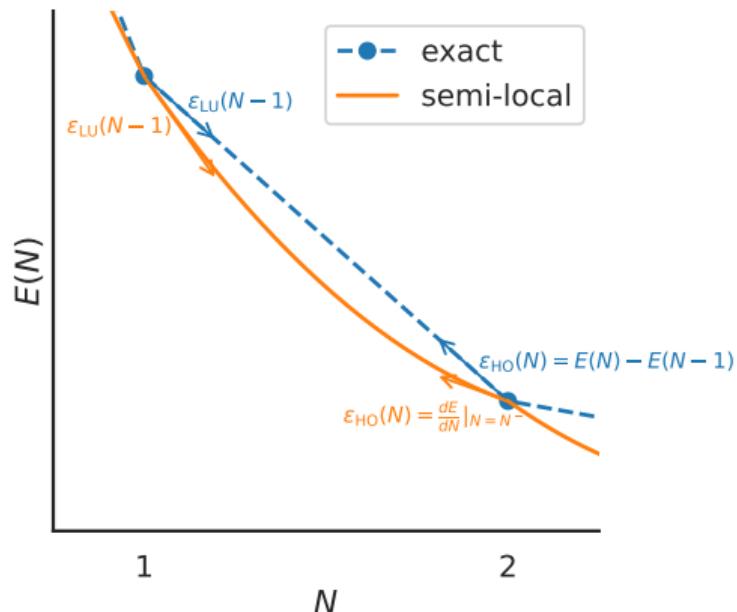


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For DFT, this condition is *not* satisfied in general

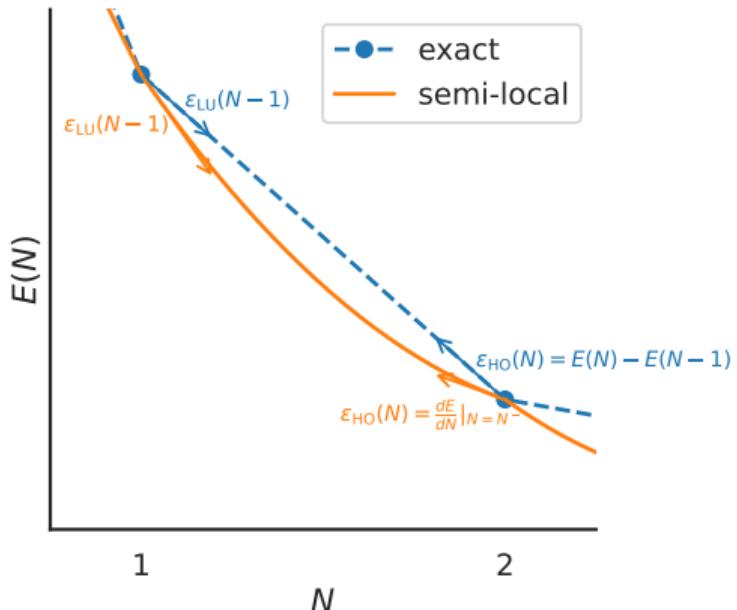


Core idea: for every orbital i their energy

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

ought to be...

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

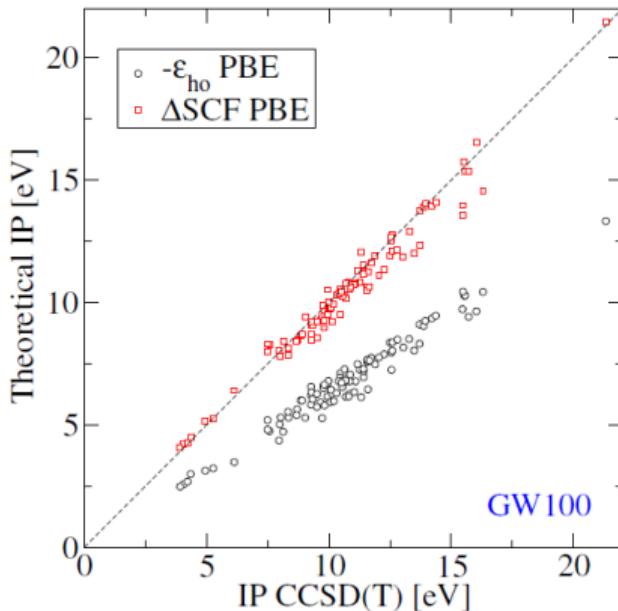


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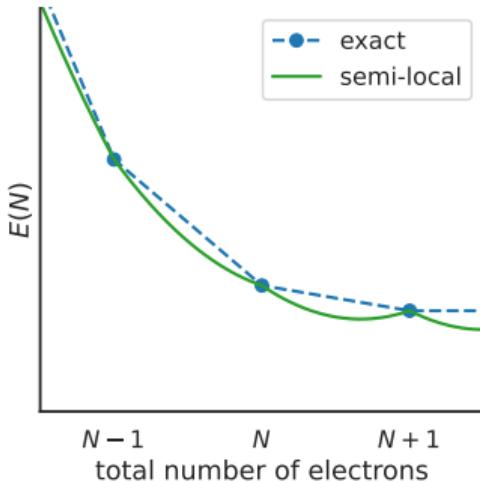
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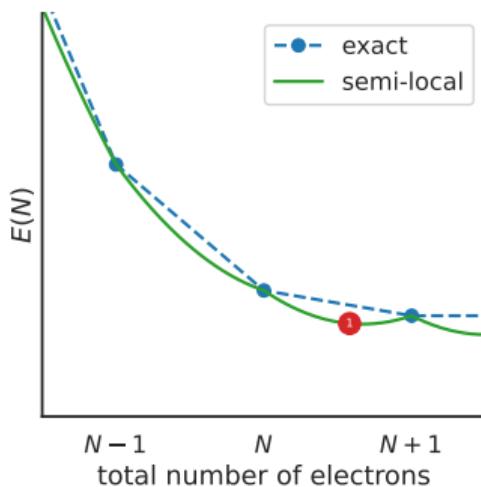
Koopmans functionals: theory

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



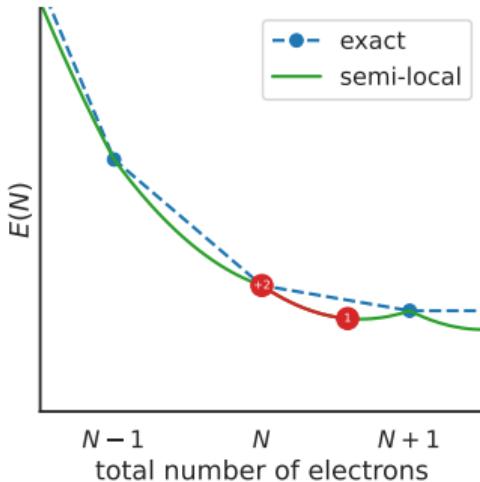
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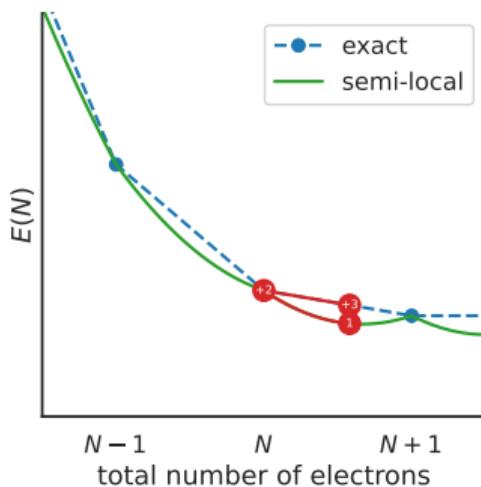
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Features:

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Features:

- screening

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

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

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

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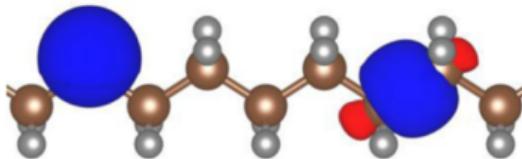
Features:

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- different variants: KI (leaves total energy unchanged), KIPZ (exact for 1-electron systems), pKIPZ
- orbital-density dependence

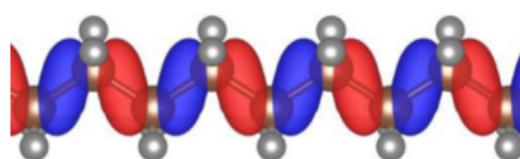
$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[\mathbf{n}_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - \mathbf{n}_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) \mathbf{n}_i(\mathbf{r}')$$

Consequences of ODD:

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



(a) variational



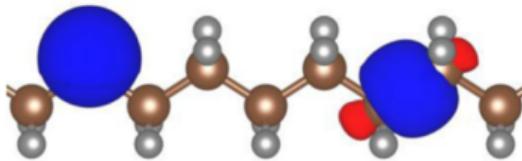
(b) canonical

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

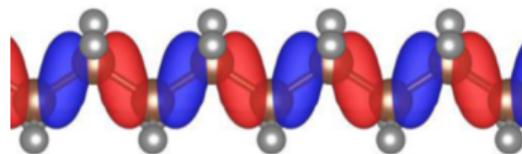
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

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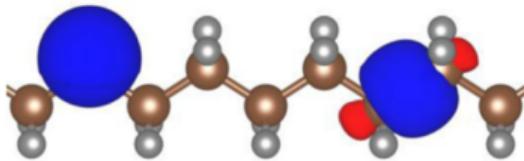
- localised variational orbitals naturally allow us to treat bulk systems

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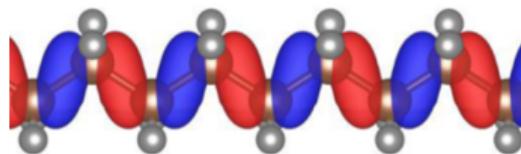
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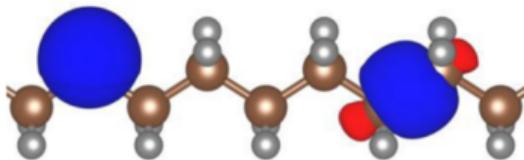
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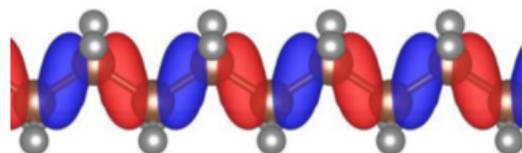
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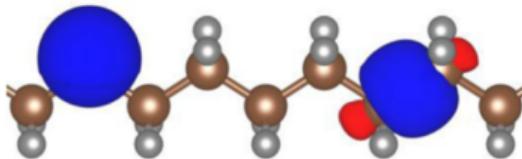
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- Practically we can often use MLWFs

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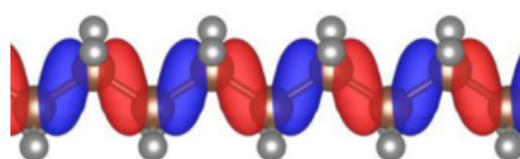
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Consequences of ODD:

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- localised variational orbitals naturally allow us to treat bulk systems
- 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
- a natural generalisation in the direction of spectral functional theory¹

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

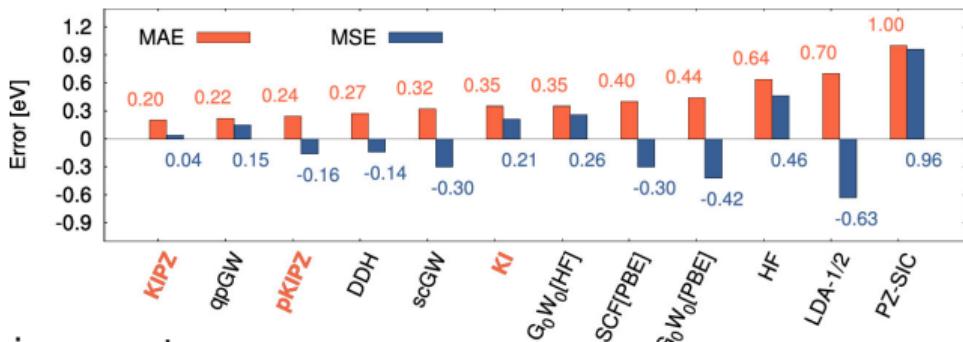
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

Resonance with other efforts:

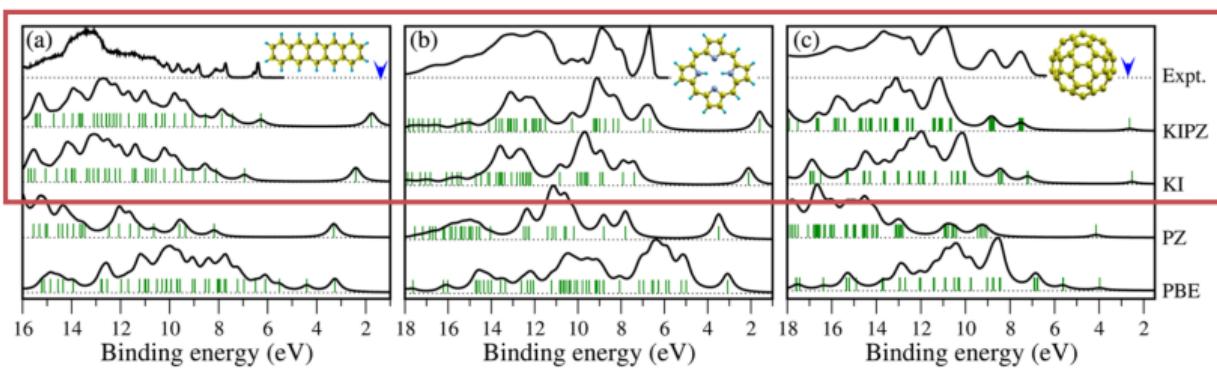
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021), 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

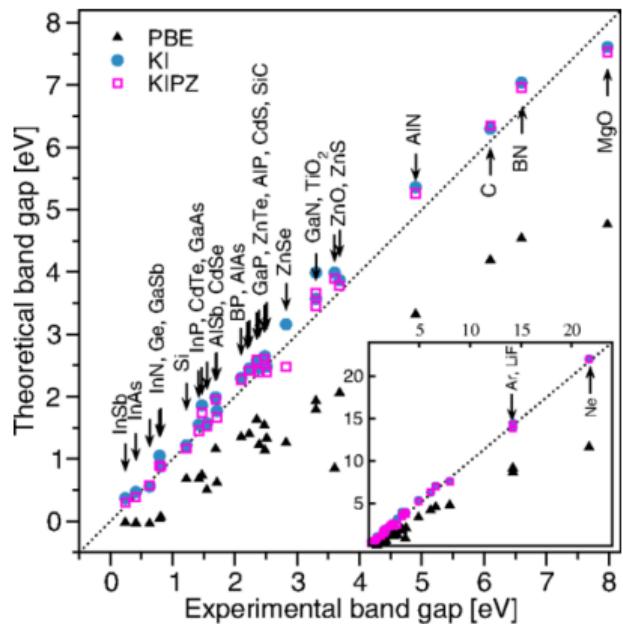
Ionisation potentials = $E(N - 1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



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

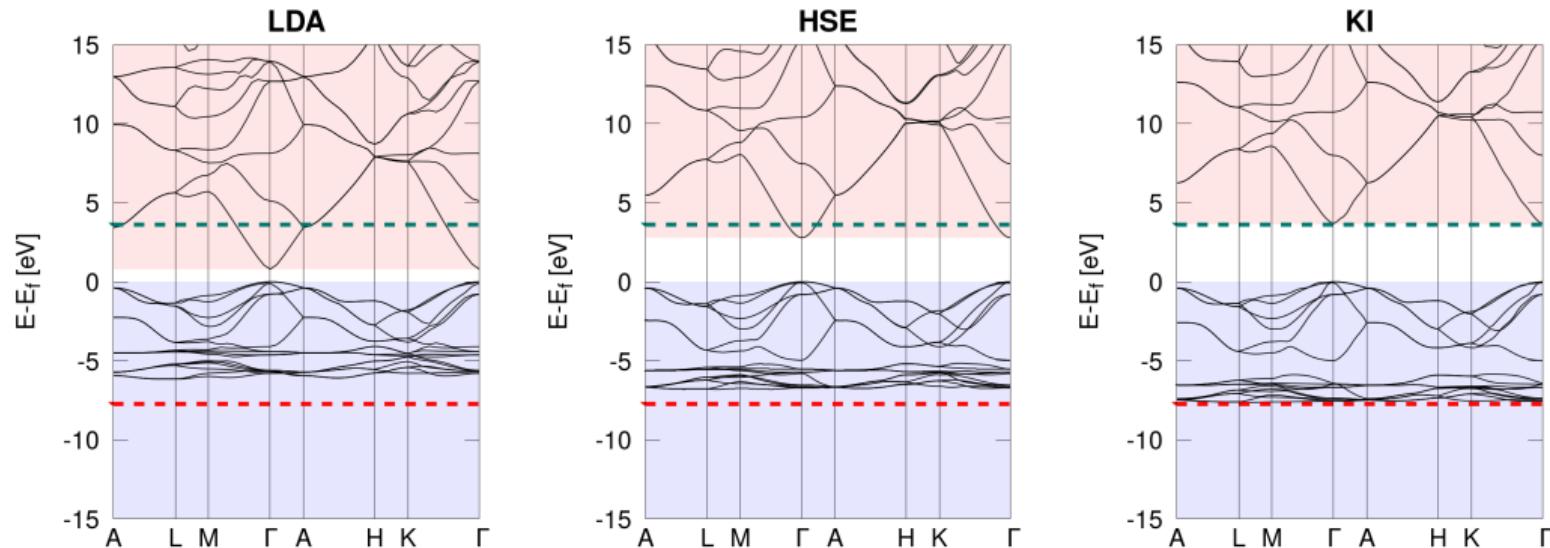
	PBE	$G_0W_0^1$	scGW 2	KI@[PBE,MLWFs]	KIPZ@PBE	exp 3
E_g	0.49	1.06	1.14	1.16	1.15	1.17
$\Gamma_{1v} \rightarrow \Gamma_{25'v}$	11.97	12.04		11.97	12.09	12.5 ± 0.6
$X_{1v} \rightarrow \Gamma_{25'v}$	7.82			7.82		7.75
$X_{4v} \rightarrow \Gamma_{25'v}$	2.85	2.99		2.85	2.86	2.90
$L_{2'v} \rightarrow \Gamma_{25'v}$	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. B* 75.23 (2007), 235102 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. Lett.* 99.24 (2007), 246403.

³ O. Madelung. *Semiconductors*. 3rd ed. Berlin: Springer-Verlag, 2004.

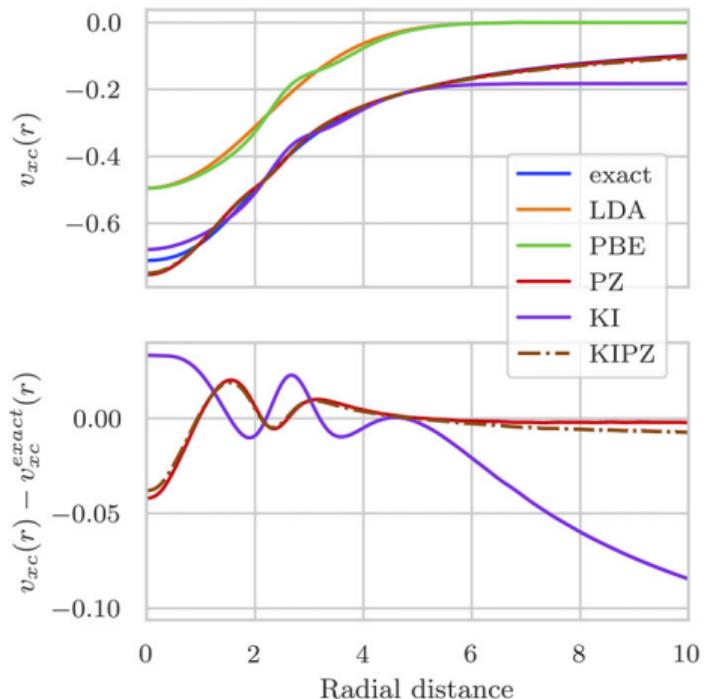
Koopmans functionals: results for solids



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

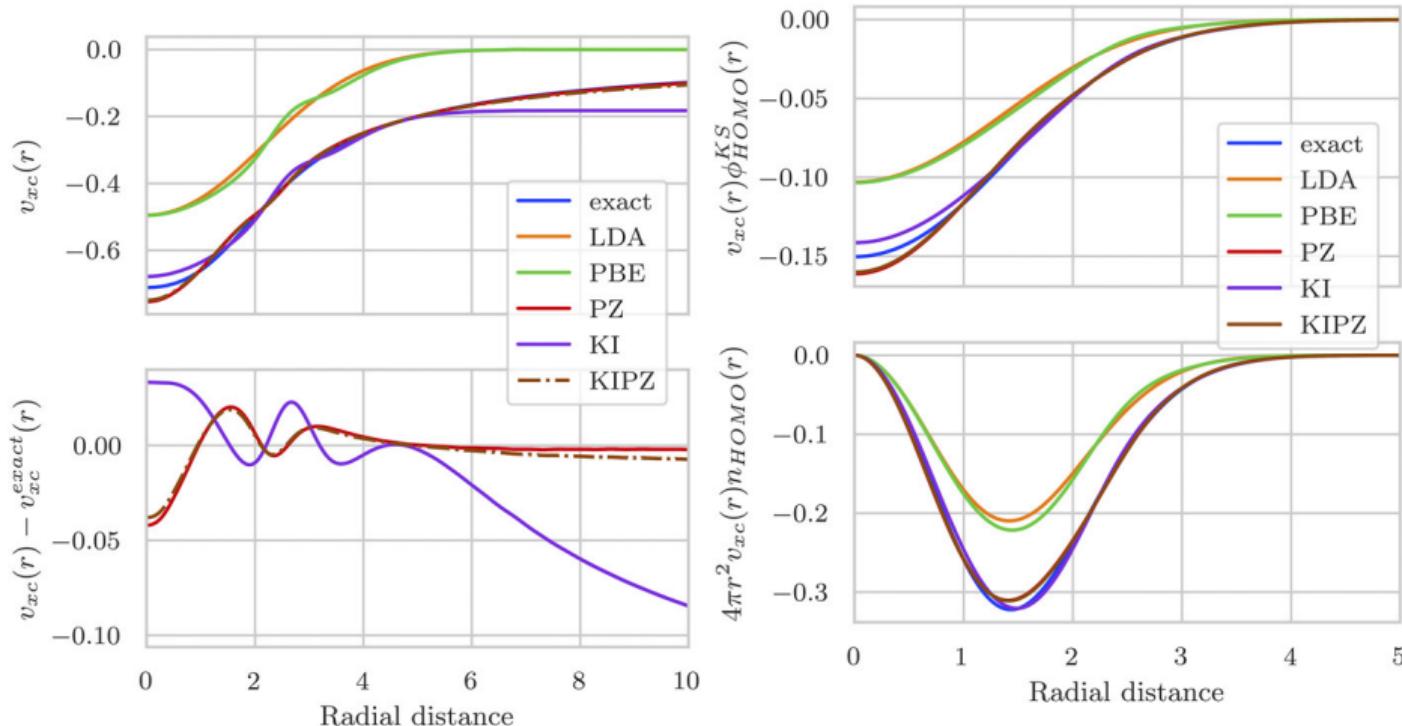
Koopmans functionals: results for toy systems

For Hooke's atom (two electrons in a harmonic confining potential with Coulombic repulsion)



Koopmans functionals: results for toy systems

For Hooke's atom (two electrons in a harmonic confining potential with Coulombic repulsion)



- restricted to systems with a non-zero band gap

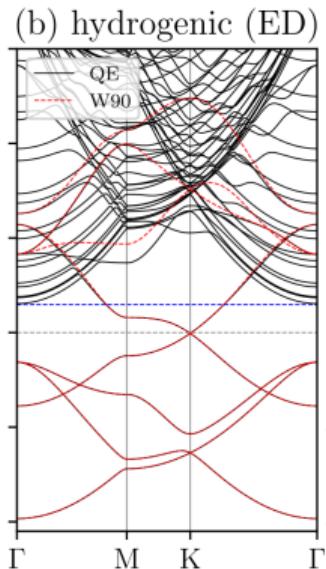
- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit

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

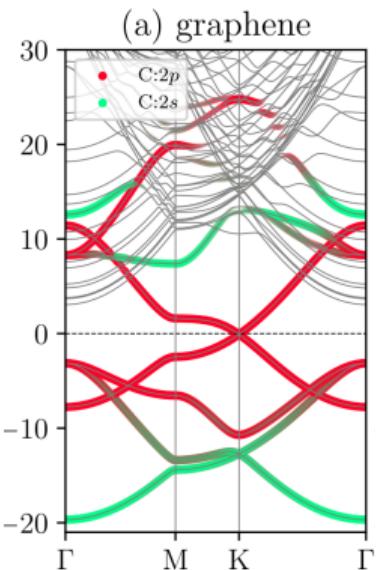
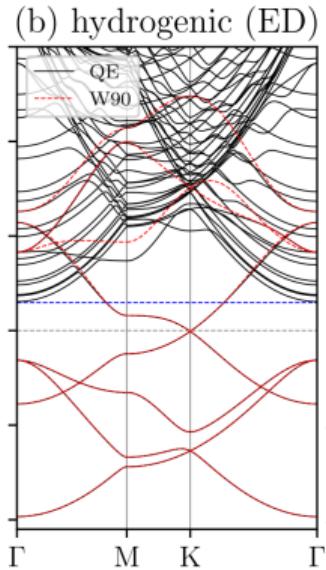
The general workflow:

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

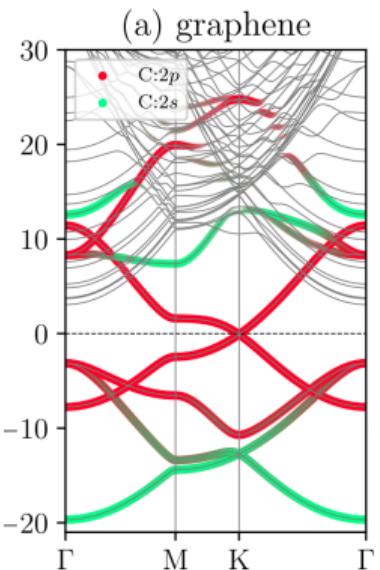
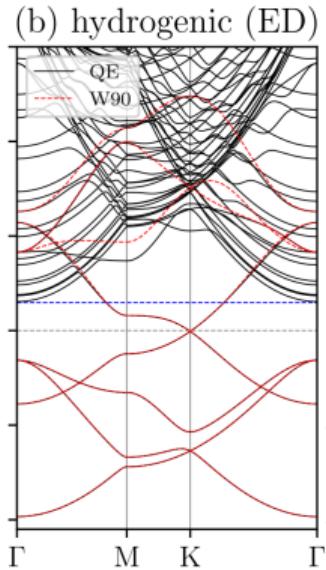
Recent advances make some of these steps a lot easier...



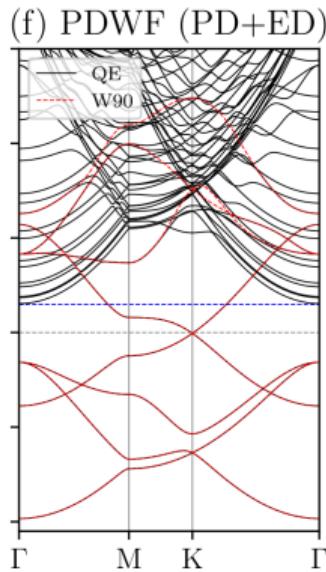
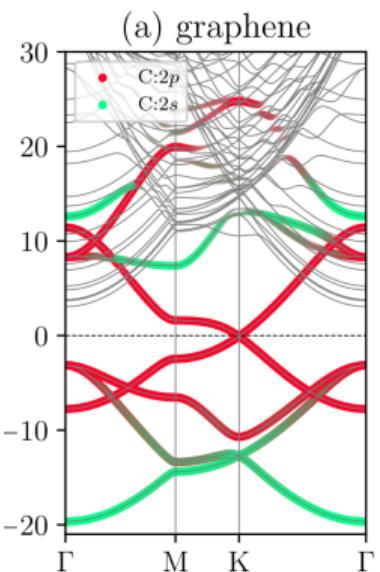
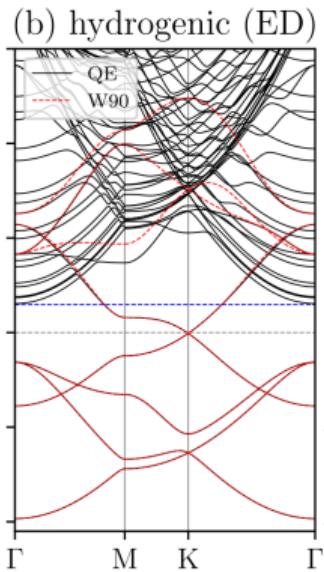
Accelerating improvements: easier Wannierization



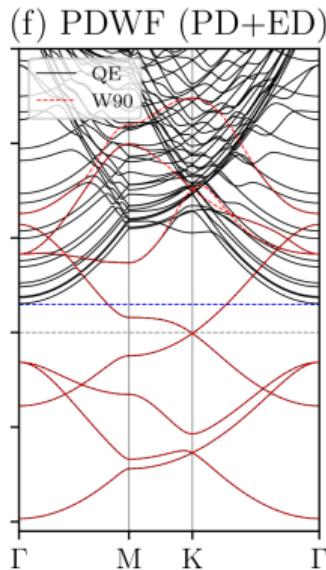
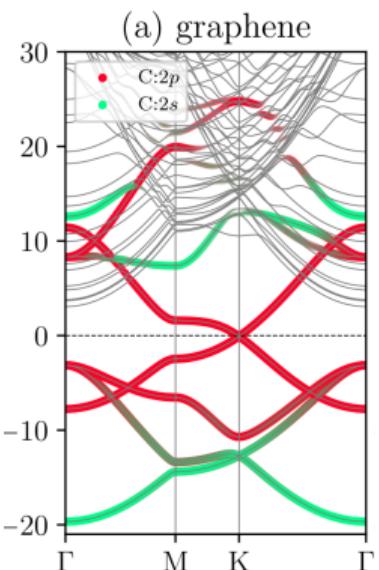
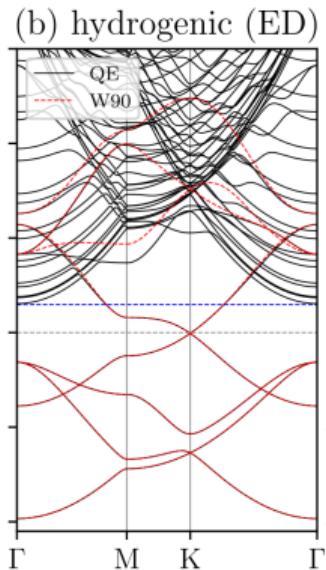
Accelerating improvements: easier Wannierization



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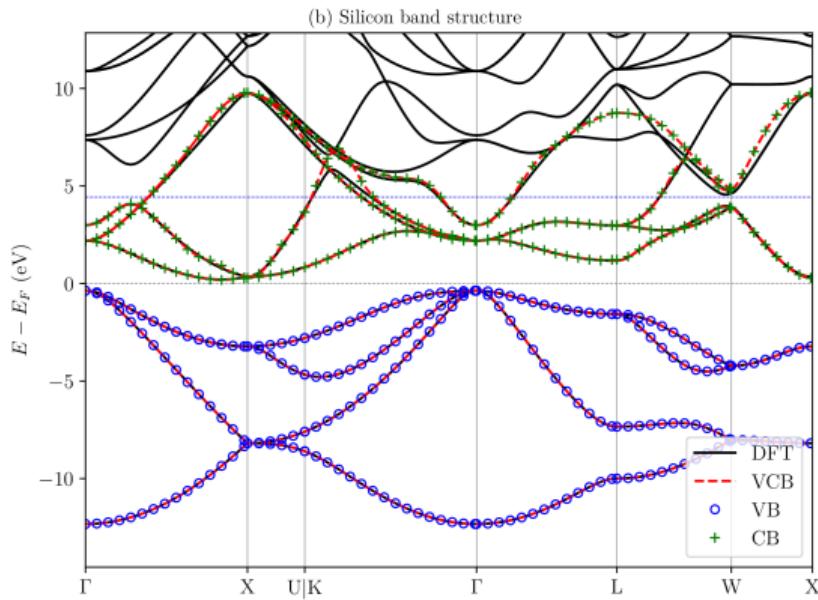
Accelerating improvements: easier Wannierization



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

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

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



Original formulation requires explicit charged defect calculations in a supercell

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

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 DFPT¹...

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

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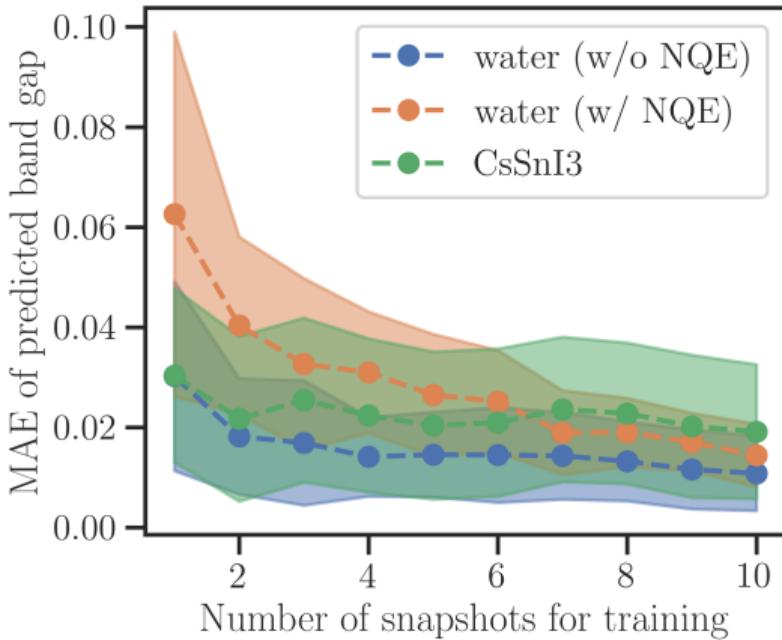
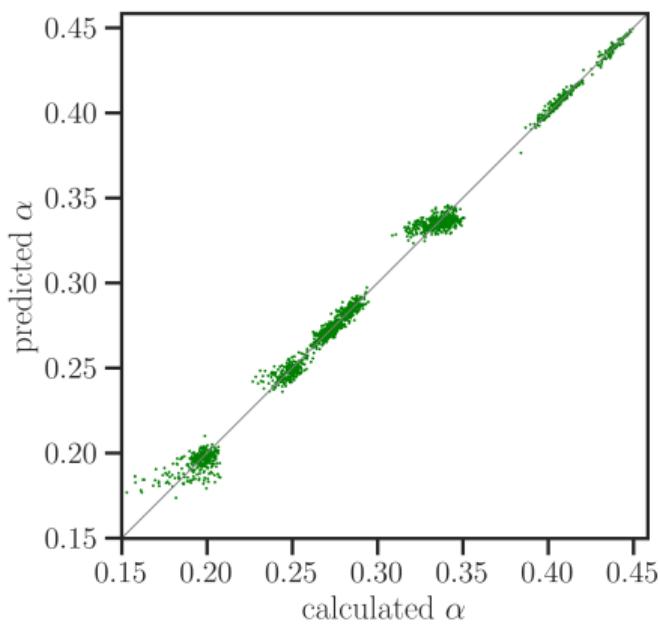
... in reciprocal space²

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

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

Accelerating improvements: screening via ML

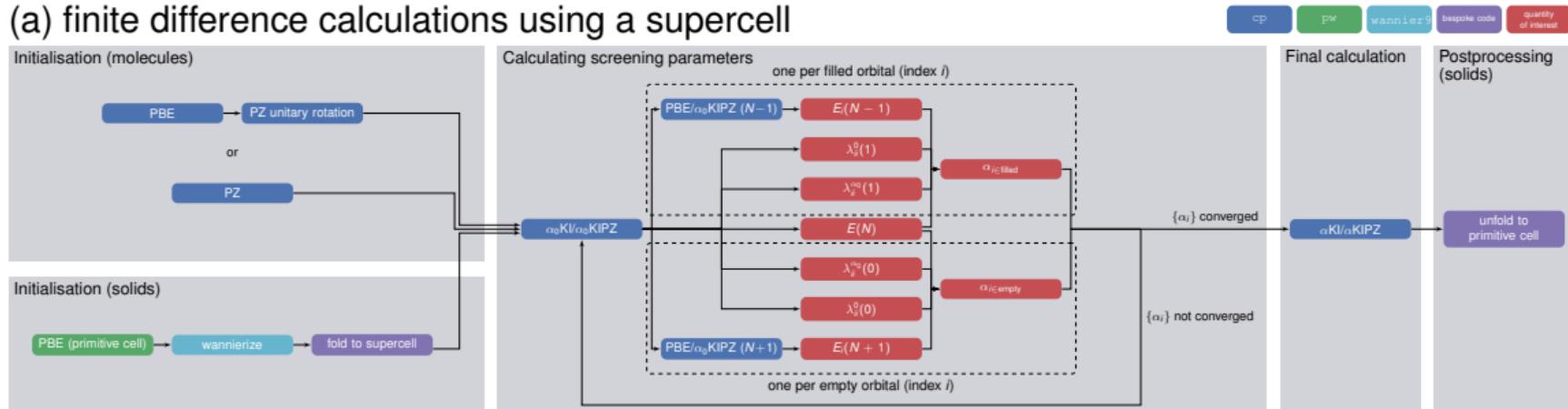


loss of accuracy of the band gap of ~ 0.02 eV
(cf. when calculating screening parameters *ab initio*)
speedup of 70 \times

We have complicated workflows, with either...

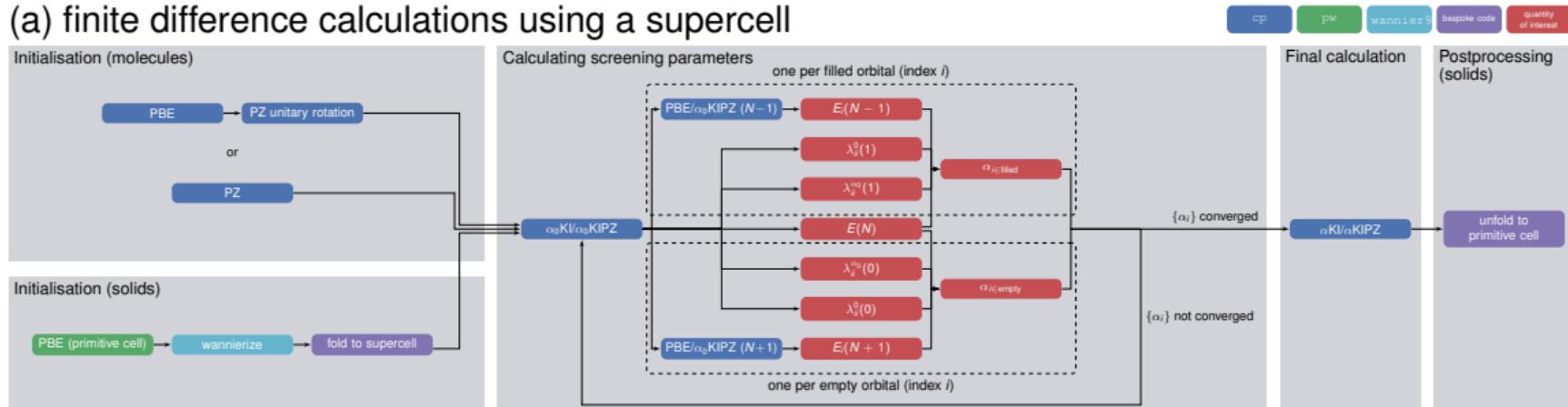
We have complicated workflows, with either...

(a) finite difference calculations using a supercell

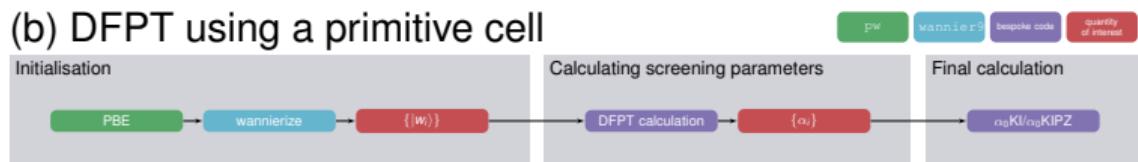


We have complicated workflows, with either...

(a) finite difference calculations using a supercell



(b) DFPT using a primitive cell



But complex workflows mean that...

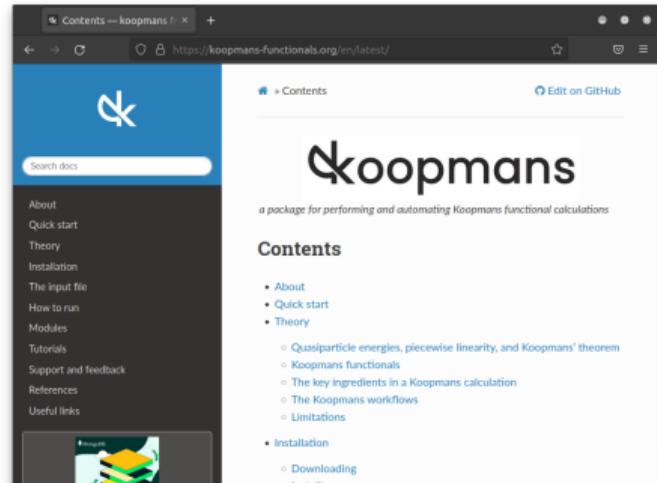
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- v1.0 released earlier this year¹
- implementations of Koopmans functionals within Quantum ESPRESSO
- 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



¹ E. B. Linscott et al. *J. Chem. Theory Comput.* (2023)

² 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",  
        "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

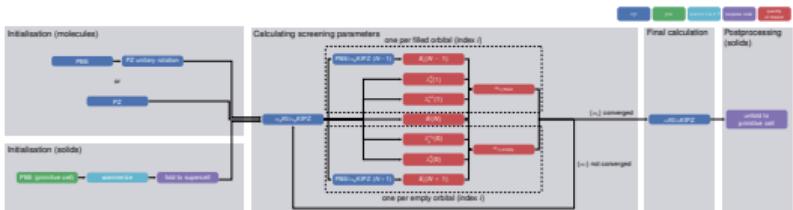
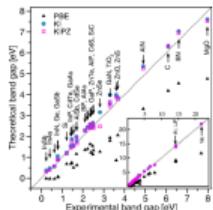
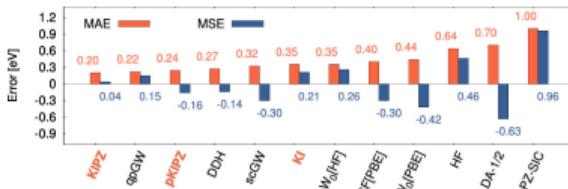
# Use ASE to create bulk silicon
atoms = bulk('Si')

# 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

koopmans: An Open-Source Package for Accurately and Efficiently Predicting Spectral Properties with Koopmans Functionals

Edward B. Linscott,*[△] Nicola Colonna,[△] Riccardo De Gennaro, Ngoc Linh Nguyen, Giovanni Borghi, Andrea Ferretti, Ismaila Dabo, and Nicola Marzari*



Cite This: <https://doi.org/10.1021/acs.jctc.3c00652>



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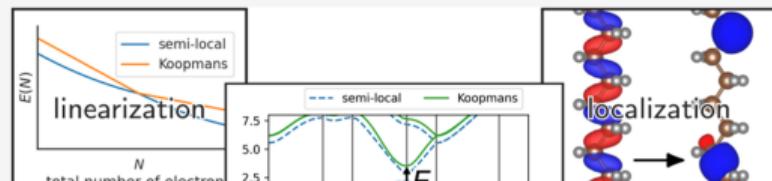
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Article Recommendations

Supporting Information

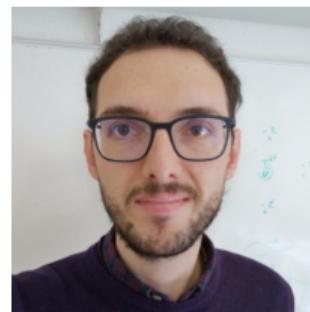
ABSTRACT: Over the past decade we have developed Koopmans functionals, a computationally efficient approach for predicting spectral properties with an orbital-density-dependent functional framework. These functionals impose a generalized piecewise linearity condition to the entire electronic manifold, ensuring that



Acknowledgements



Nicola Marzari



Nicola Colonna



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**Swiss National
Science Foundation**

MARVEL
The logo for MARVEL consists of four red hexagons arranged in a horizontal row, with each hexagon having a thin black outline.

NATIONAL CENTRE OF COMPETENCE IN RESEARCH

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

Next week in Pavia, Italy *Advanced Quantum ESPRESSO school: Hubbard and Koopmans functionals from linear response*. Recordings can be found on the Materials Cloud youtube page

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

SPARE SLIDES

Recap from earlier

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

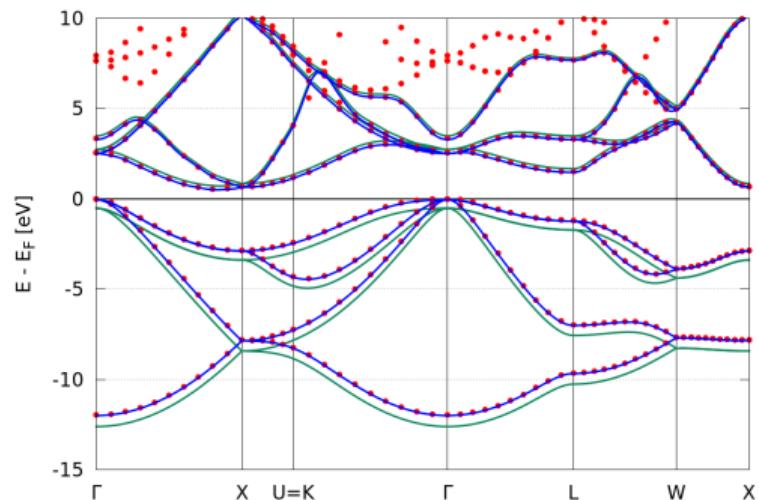
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

are...

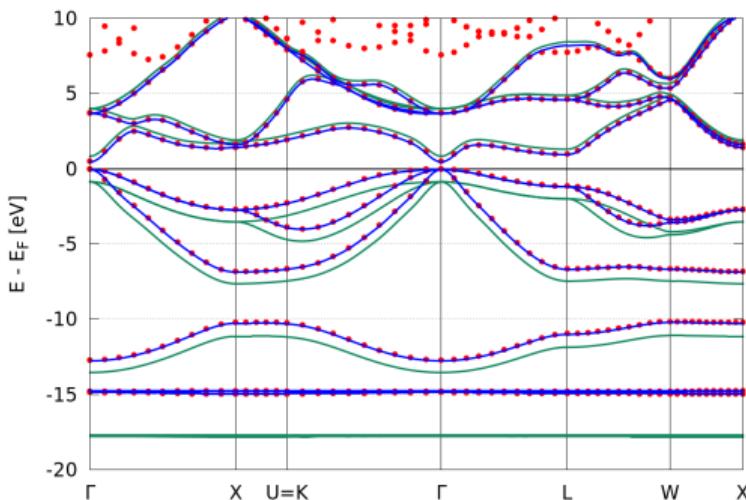
- independent of the corresponding occupancies f_i
- equal to the corresponding total energy difference $E_i(N - 1) - E(N)$

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

Koopmans functionals: results for solids



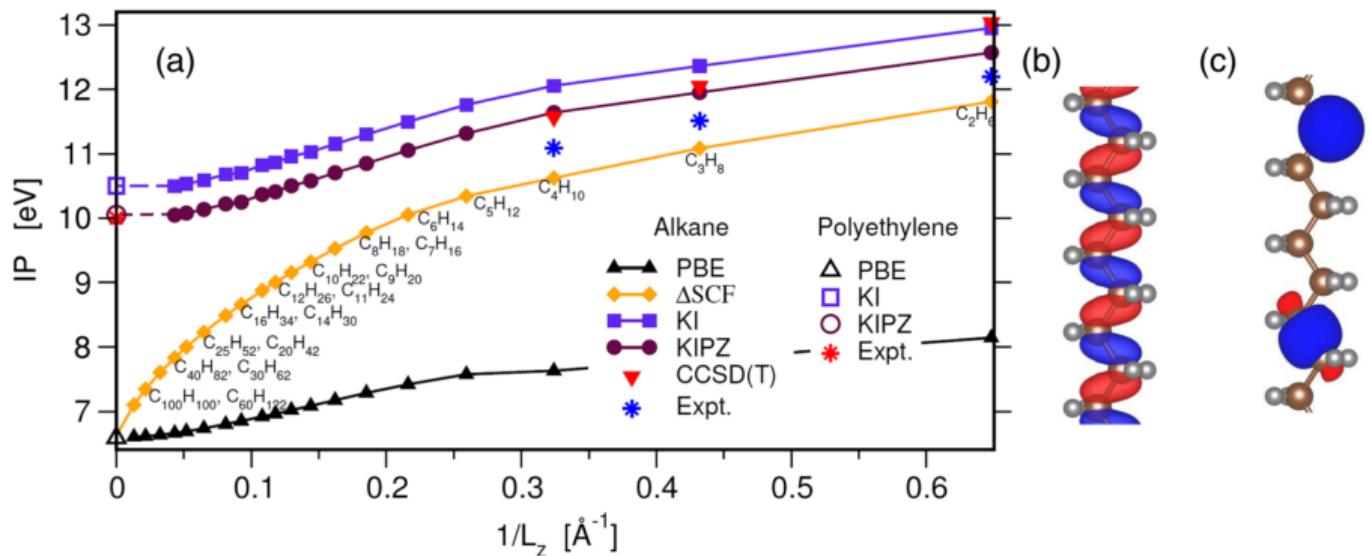
(a) Si, KIPZ



(b) GaAs, KI

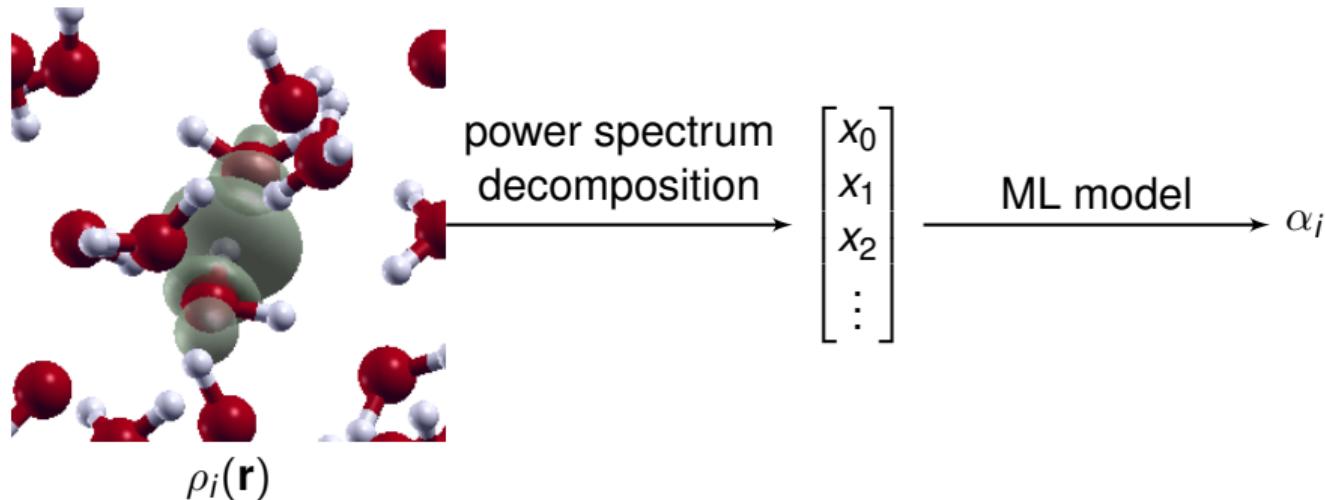
		PBE	QSGW	KI	pKIPZ	KIPZ	exp
Si	E_{gap}	0.55	1.24	1.18	1.17	1.19	1.17
GaAs	E_{gap}	0.50	1.61	1.53	1.49	1.50	1.52
	$\langle \varepsilon_d \rangle$	14.9	17.6	16.9	17.7	18.9	

Extrapolating properly to the bulk limit



Accelerating improvements: screening via ML

Edward Linscott
EPFL



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

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