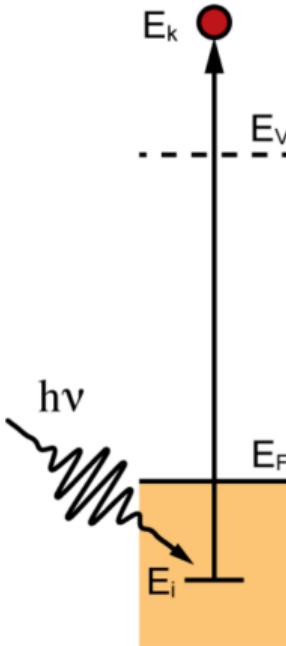




Koopmans functionals

accurately and efficiently predicting spectral properties
with a functional formulation

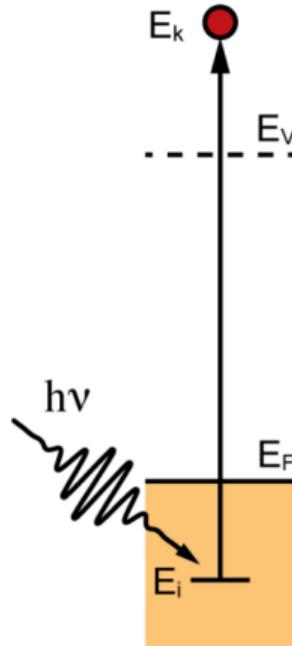
Goal: spectral properties (charged excitations) with a functional theory



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

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

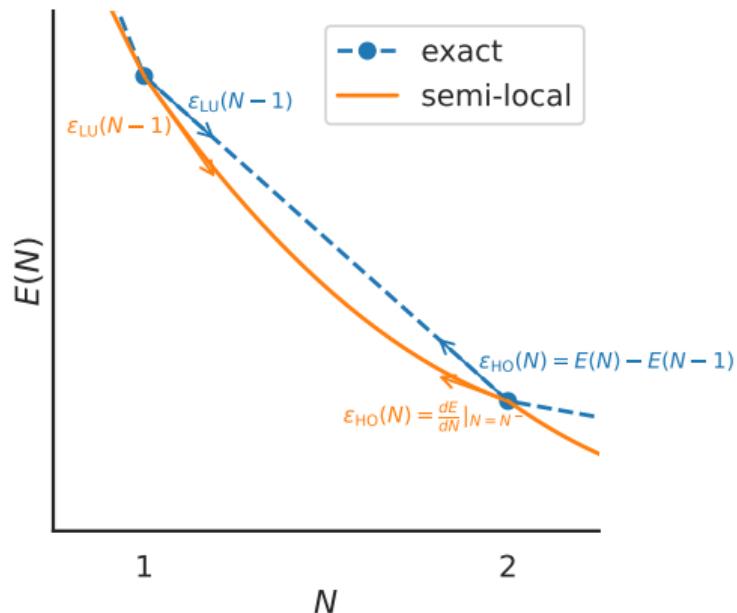


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For DFT, this condition is *not* satisfied in general

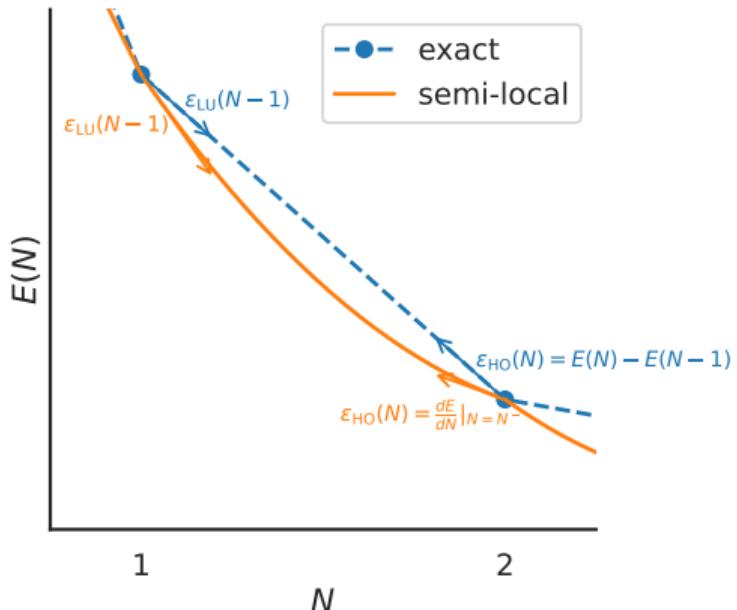


Core idea: for every orbital i their energy

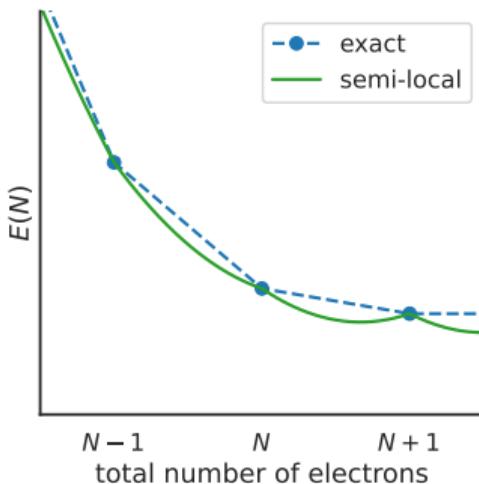
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

ought to be...

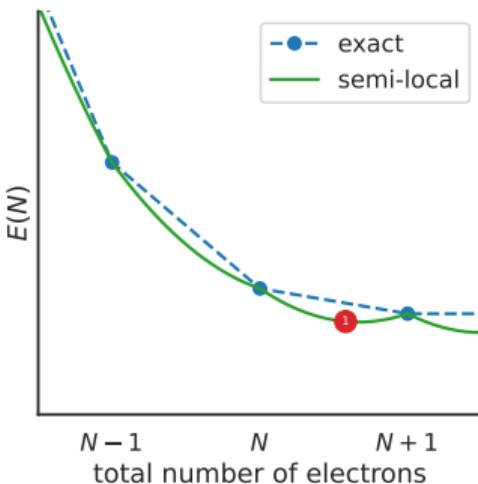
- independent of its own occupation f_i
- equal to the corresponding total energy difference $E_i(N - 1) - E(N)$



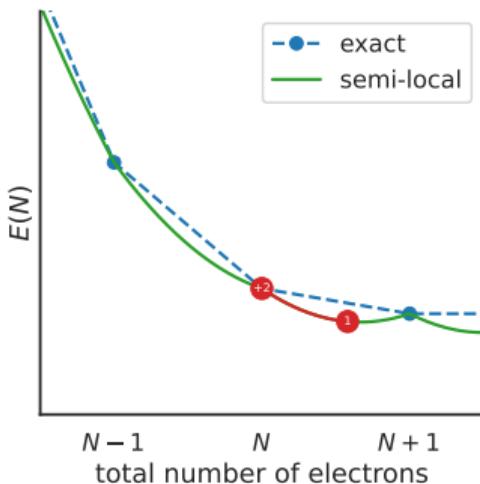
$$E_{\text{Koopmans}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{\text{DFT}}[\rho] + \sum_i \alpha_i \left(- \underbrace{\int_0^{f_i} \varepsilon_i(f) df}_{\text{removes curvature}} + \underbrace{f_i \eta_i}_{\text{restores linearity}} \right)$$



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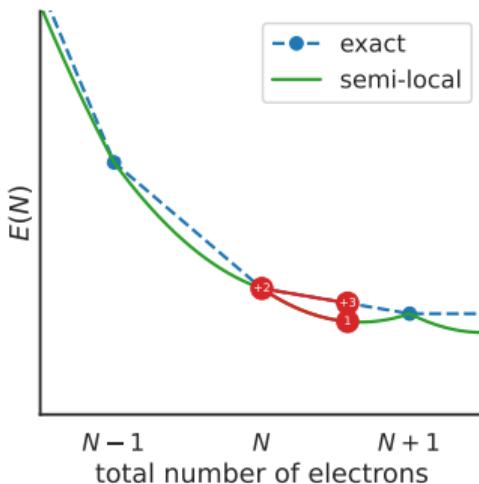


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Koopmans functionals: theory

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



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Features:

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Features:

- screening (calculated ab initio)

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Features:

- screening (calculated ab initio)
- different variants: KI (leaves total energy unchanged), KIPZ (exact for 1-electron systems), pKIPZ

$$\begin{aligned} E_{\text{KI}}[\rho, \{\rho_i\}, \{\alpha_i\}] = & E_{DFT}[\rho] + \sum_i \alpha_i \left(E_{\text{Hxc}}[\rho - \rho_i] - E_{\text{Hxc}}[\rho] \right. \\ & \left. + f_i (E_{\text{Hxc}}[\rho - \rho_i + n_i] - E_{\text{Hxc}}[\rho - \rho_i]) \right) \end{aligned}$$

Features:

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Features:

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

Consequences of ODD:

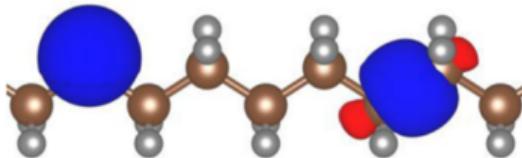
- a natural generalisation in the direction of spectral functional theory¹

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

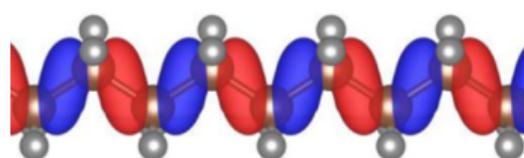
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

Consequences of ODD:

- a natural generalisation in the direction of spectral functional theory¹
- variational (localised, minimising) vs canonical (delocalised, diagonalising) orbitals



(a) variational



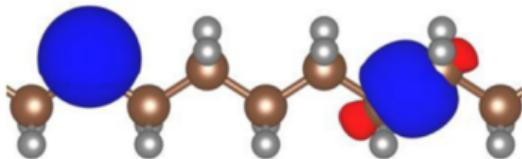
(b) canonical

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

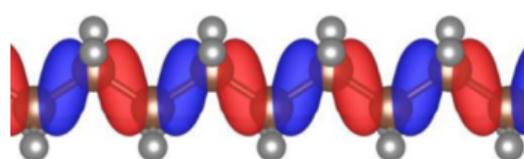
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Consequences of ODD:

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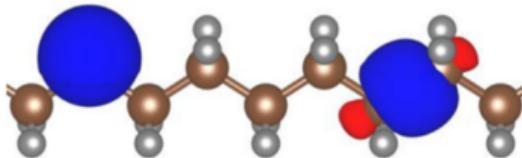
- Practically we can often use MLWFs

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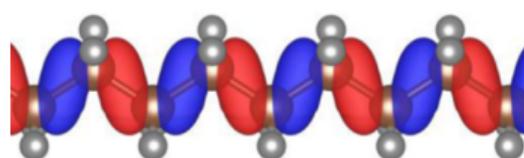
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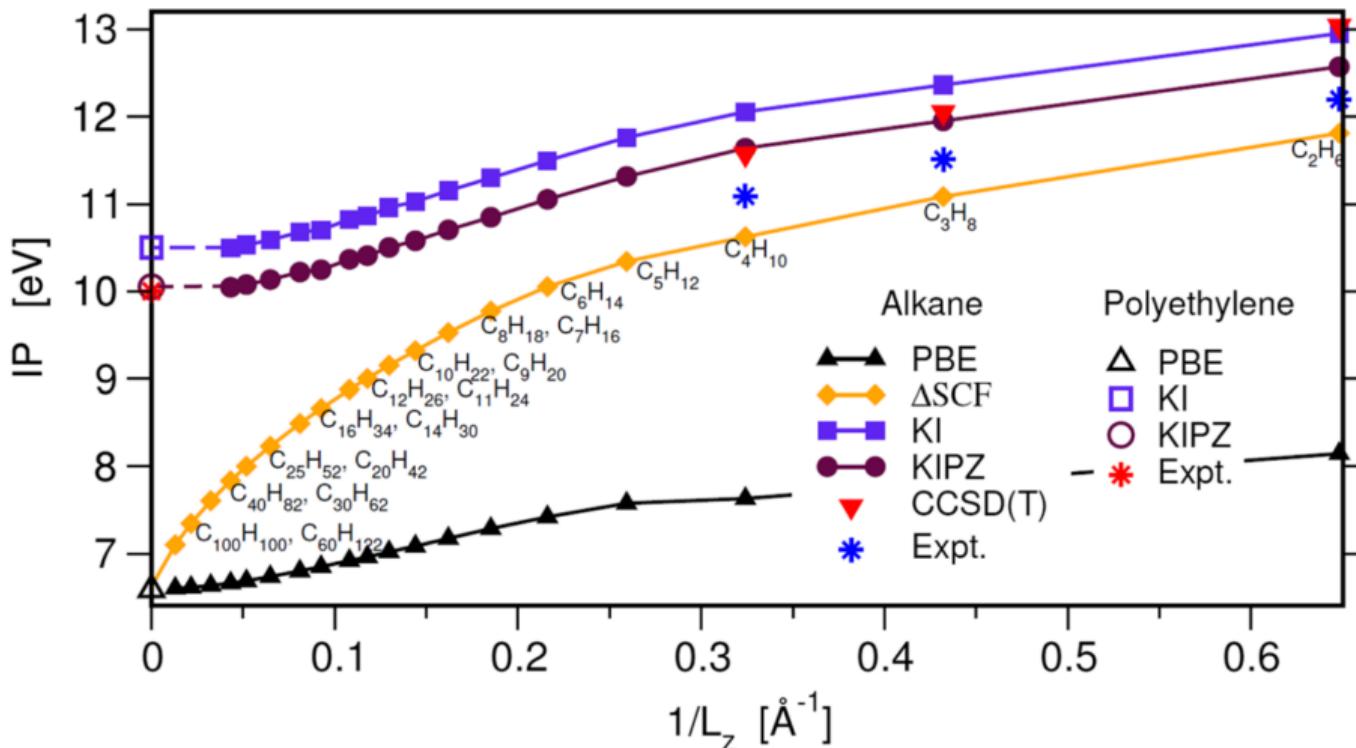
(b) canonical

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

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

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

Koopmans functionals: theory

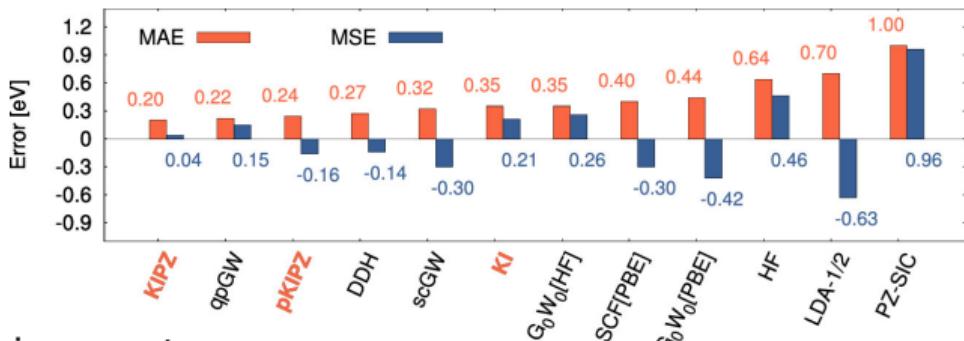


Resonance with other efforts:

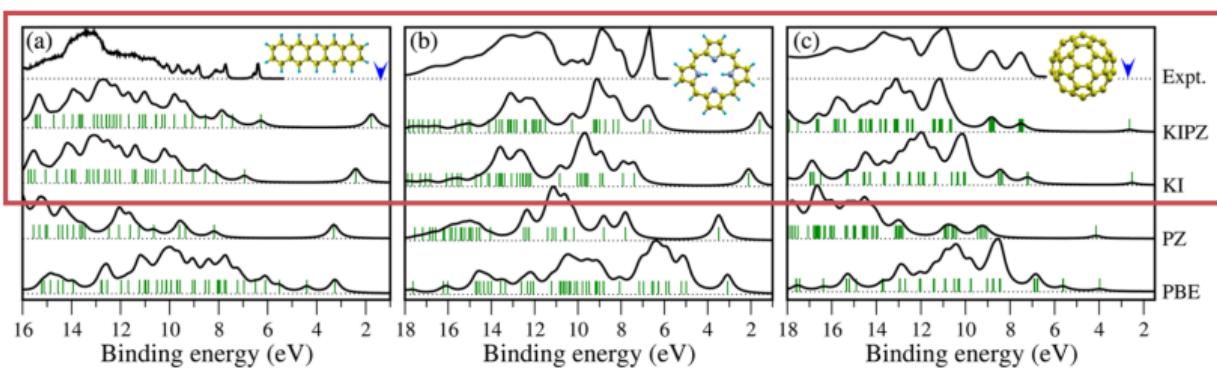
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021),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

Koopmans functionals: results for molecules

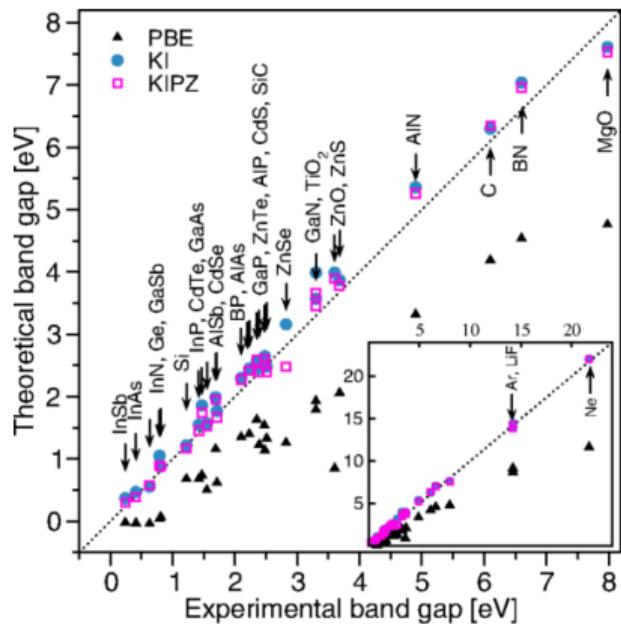
Ionisation potentials = $E(N - 1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



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

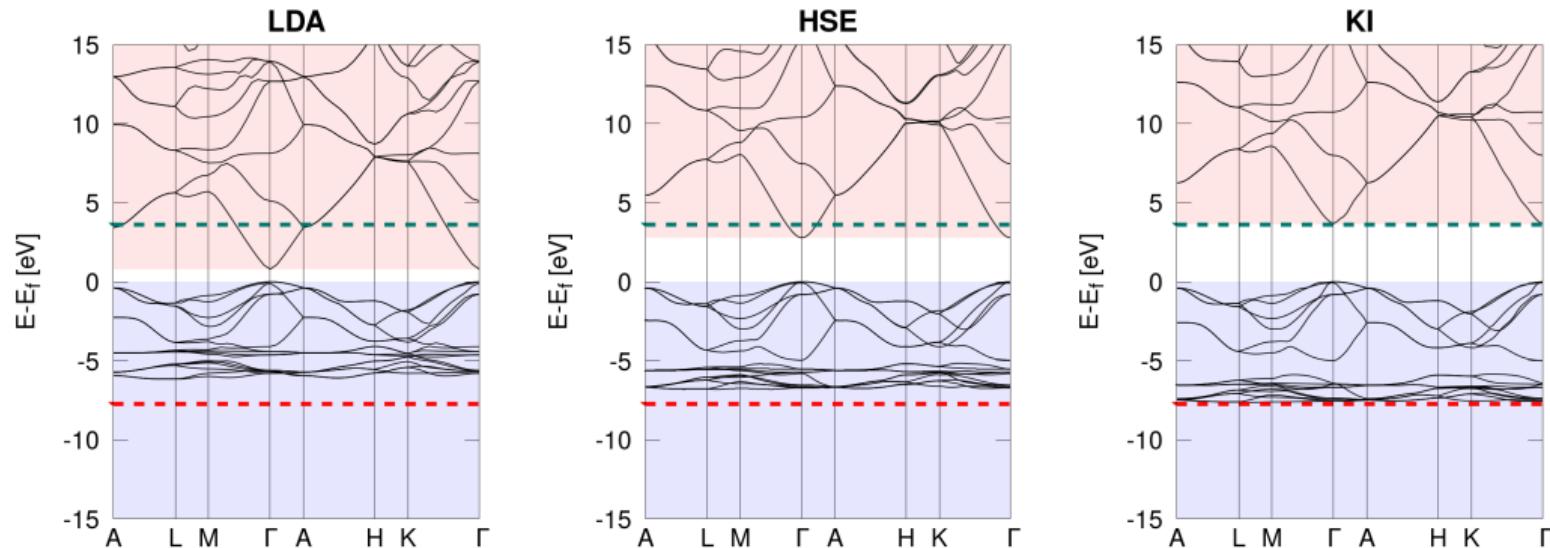
	PBE	$G_0W_0^1$	scGW 2	KI@[PBE,MLWFs]	KIPZ@PBE	exp 3
E_g	0.49	1.06	1.14	1.16	1.15	1.17
$\Gamma_{1v} \rightarrow \Gamma_{25'v}$	11.97	12.04		11.97	12.09	12.5 ± 0.6
$X_{1v} \rightarrow \Gamma_{25'v}$	7.82			7.82		7.75
$X_{4v} \rightarrow \Gamma_{25'v}$	2.85	2.99		2.85	2.86	2.90
$L_{2'v} \rightarrow \Gamma_{25'v}$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

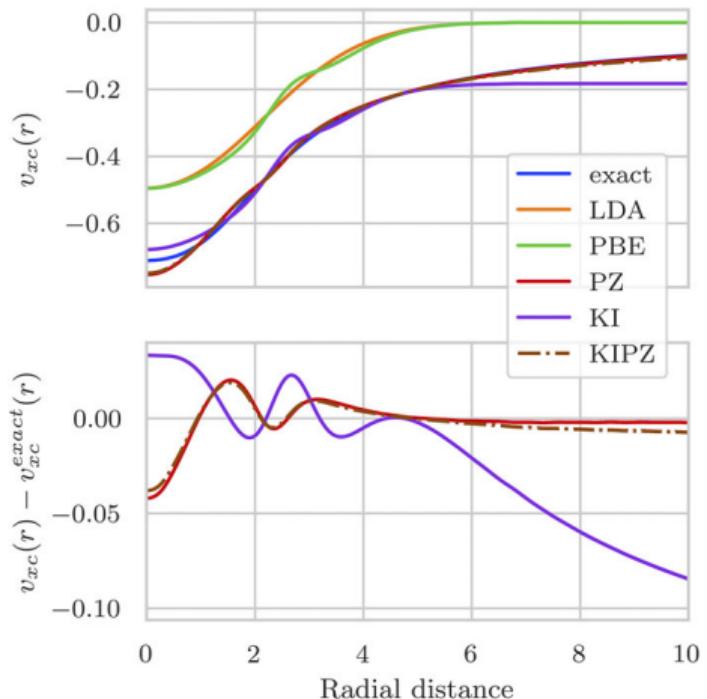
Koopmans functionals: results for solids



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

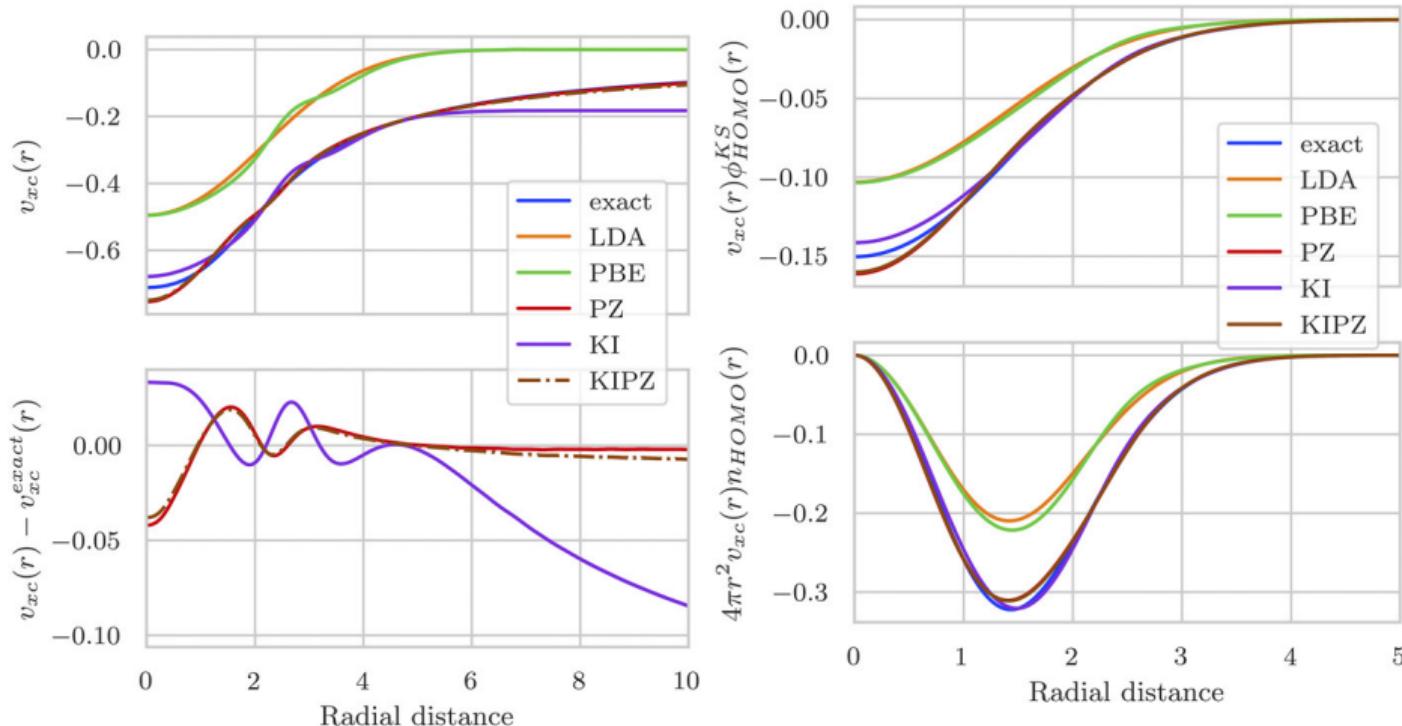
Koopmans functionals: results for toy systems

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)



- will *not* solve H_2^+ !

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- restricted to systems with a non-zero band gap

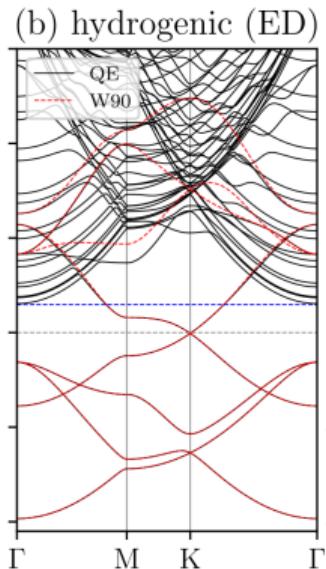
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- will *not* solve H_2^+ !
- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit
- can potentially break the crystal point group symmetry

The general workflow:

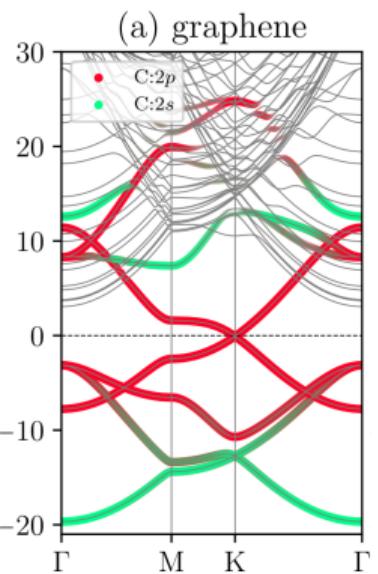
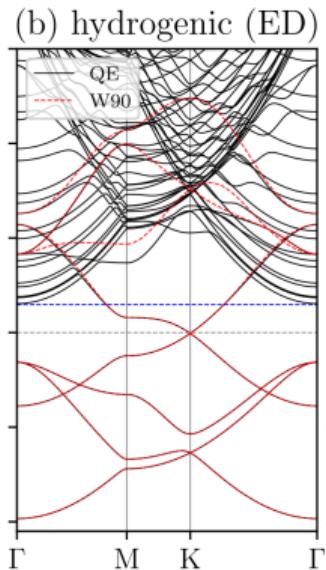
- define/initialize a set of variational orbitals
- calculate the screening parameters $\{\alpha_i\}$
- construct and diagonalize the Hamiltonian

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



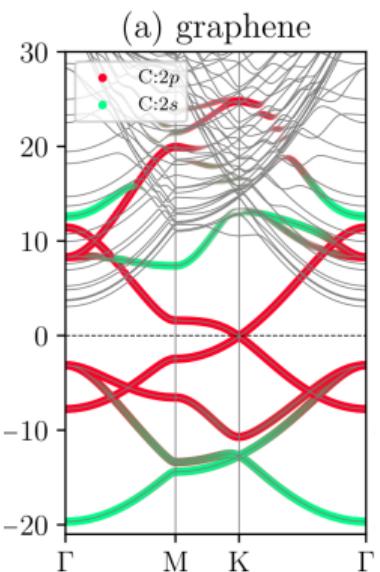
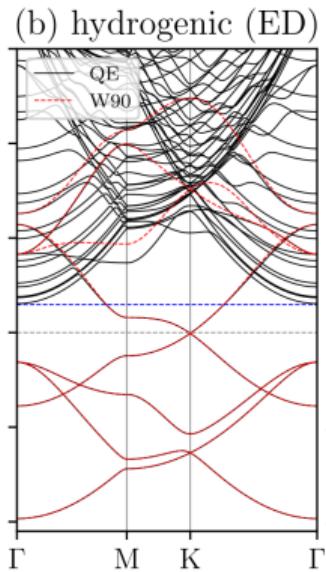
Accelerating improvements: easier Wannierization

Edward Linscott
EPFL | 15/23



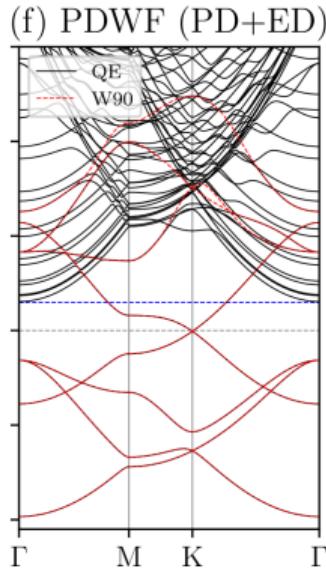
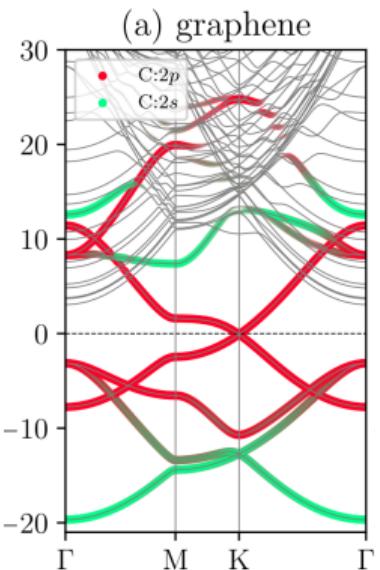
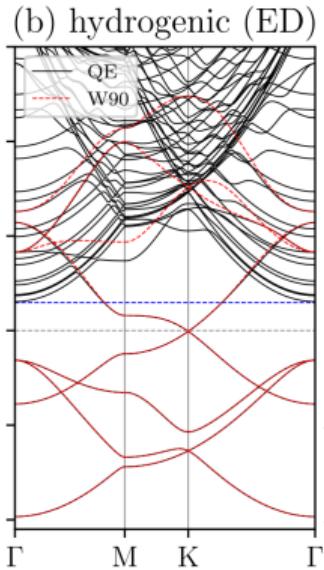
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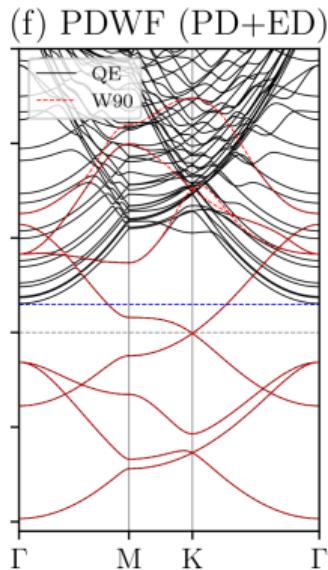
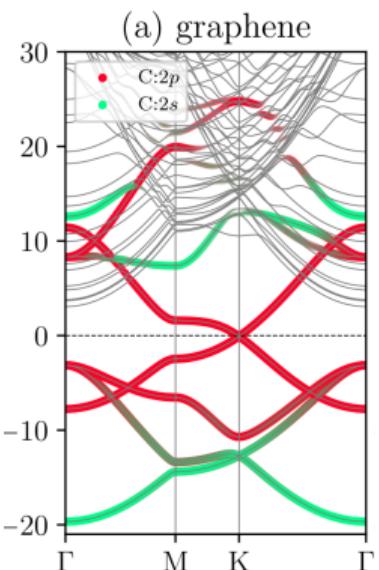
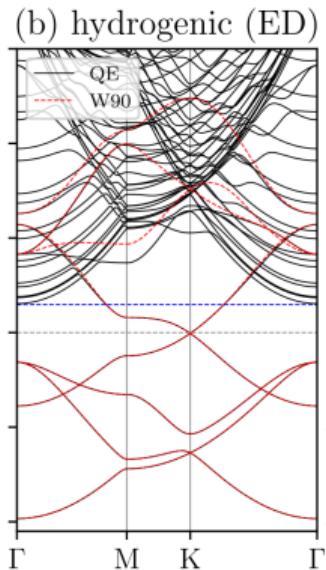


Accelerating improvements: easier Wannierization

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Accelerating improvements: easier Wannierization



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

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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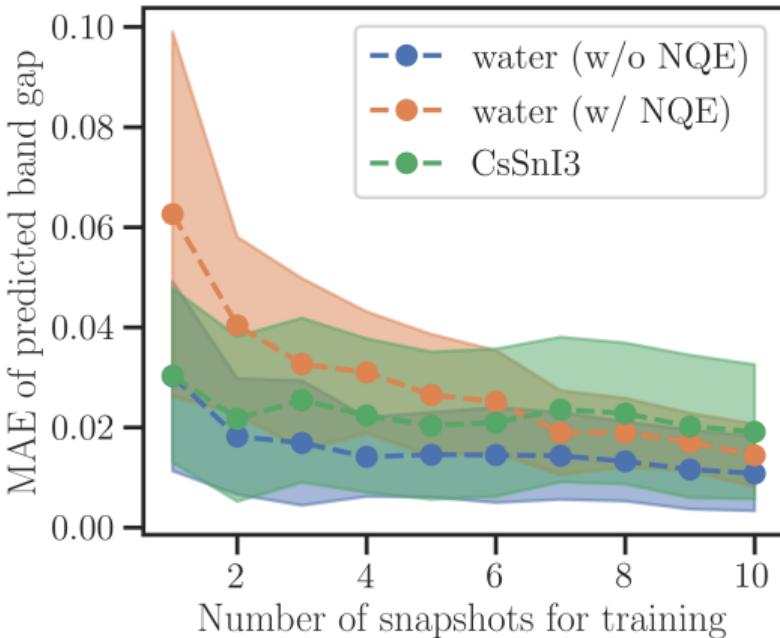
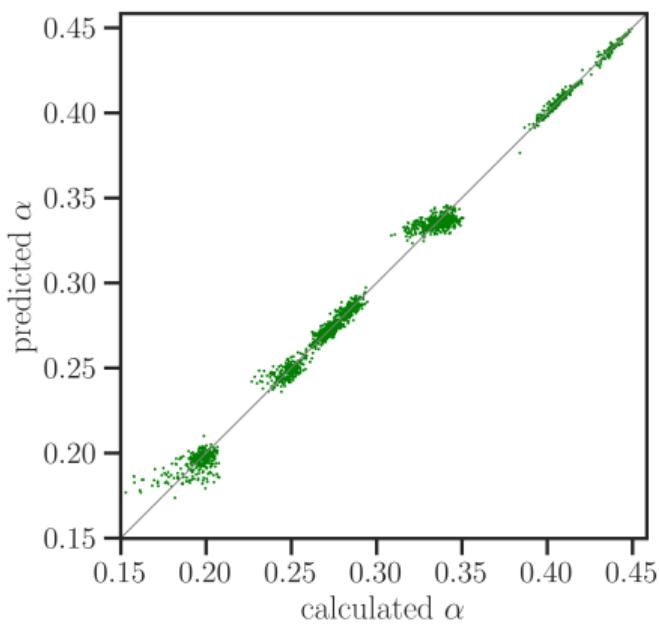
... in reciprocal space²

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

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Accelerating improvements: screening via ML

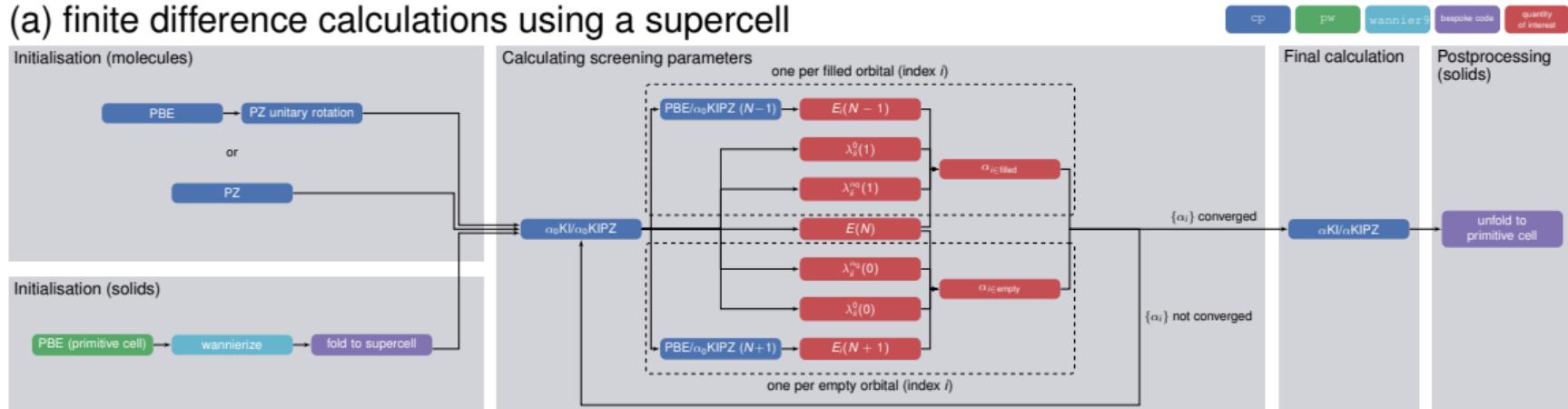


loss of accuracy of the band gap of ~ 0.02 eV
(cf. when calculating screening parameters *ab initio*)
speedup of 70×

We have complicated workflows, with either...

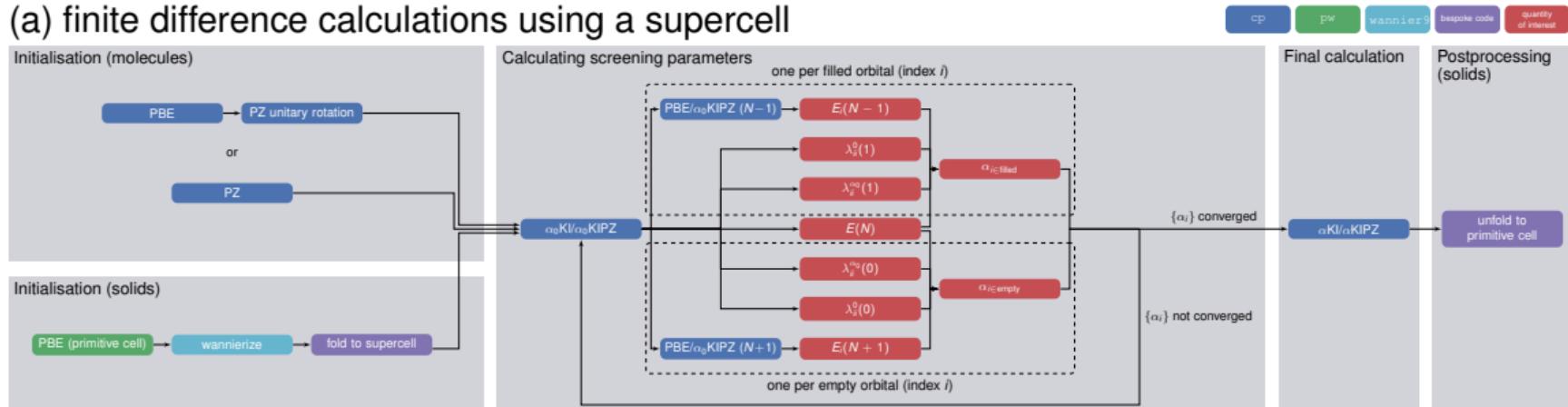
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(a) finite difference calculations using a supercell

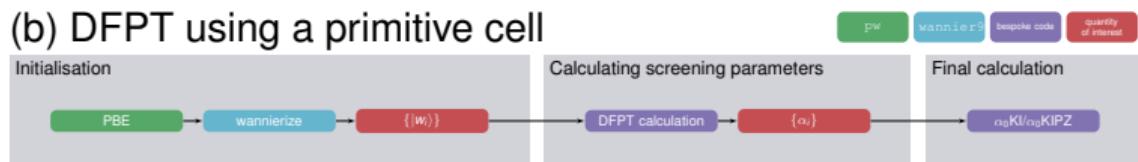


We have complicated workflows, with either...

(a) finite difference calculations using a supercell



(b) DFPT using a primitive cell



Complicated workflows mean that...

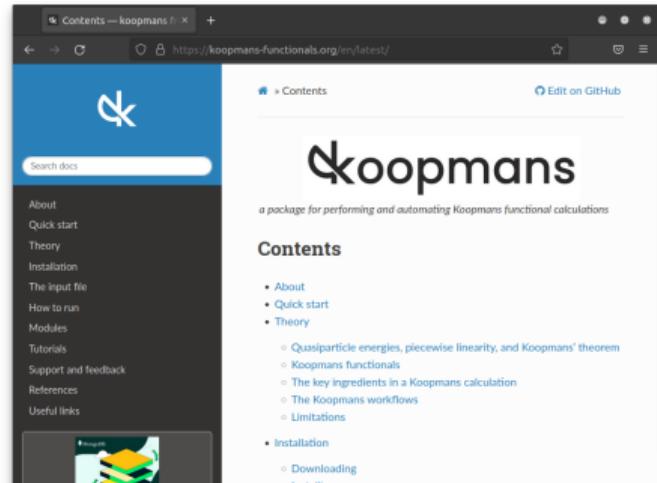
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

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

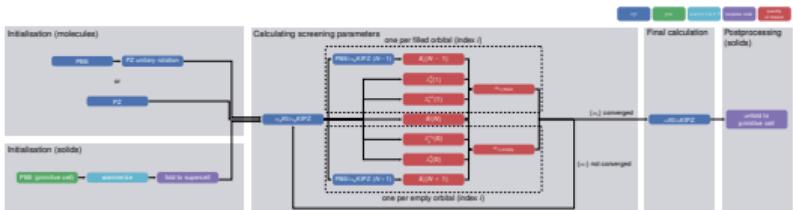
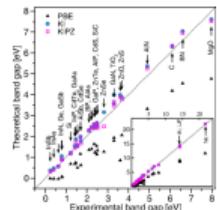
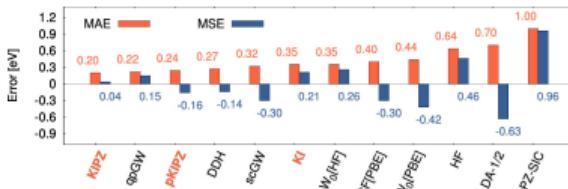
koopmans-functionals.org



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

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*



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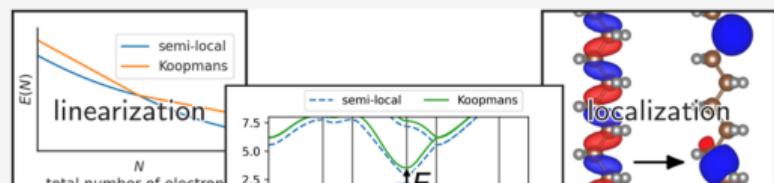
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Supporting Information

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



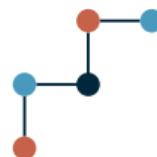
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**Swiss National
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MARVEL
The logo for MARVEL consists of four red hexagons of increasing size arranged horizontally.

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

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Recap from earlier

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

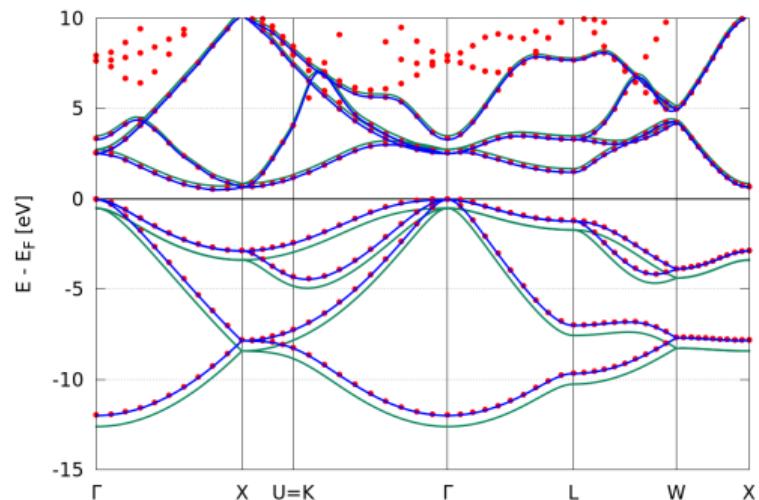
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

are...

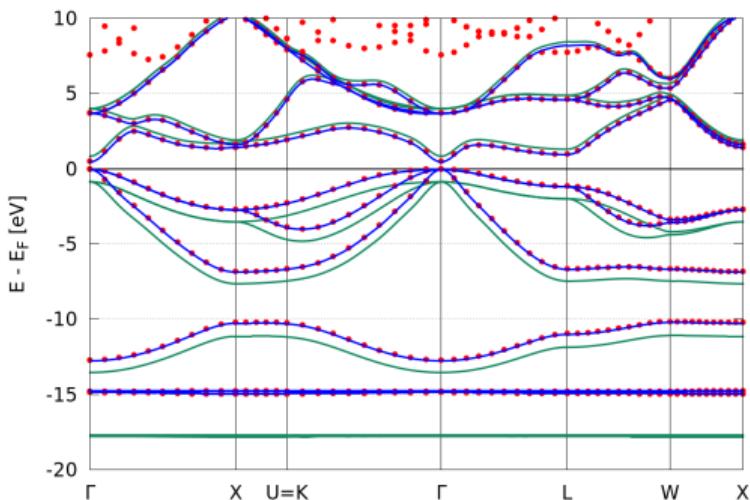
- independent of the corresponding occupancies f_i
- equal to the corresponding total energy difference $E_i(N - 1) - E(N)$

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

Koopmans functionals: results for solids



(a) Si, KIPZ



(b) GaAs, KI

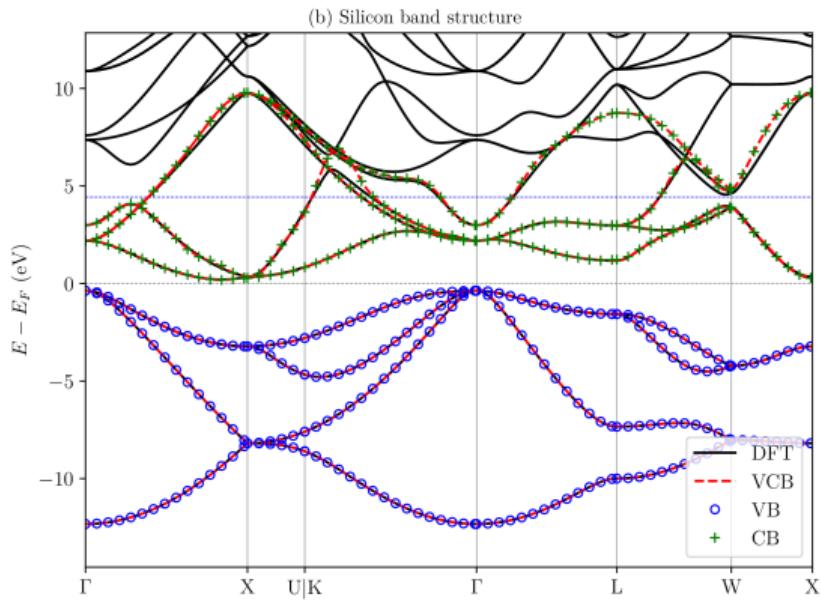
		PBE	QSGW	KI	pKIPZ	KIPZ	exp
Si	E_{gap}	0.55	1.24	1.18	1.17	1.19	1.17
GaAs	E_{gap}	0.50	1.61	1.53	1.49	1.50	1.52
	$\langle \varepsilon_d \rangle$	14.9	17.6	16.9	17.7	18.9	

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

Accelerating improvements: easier Wannierization

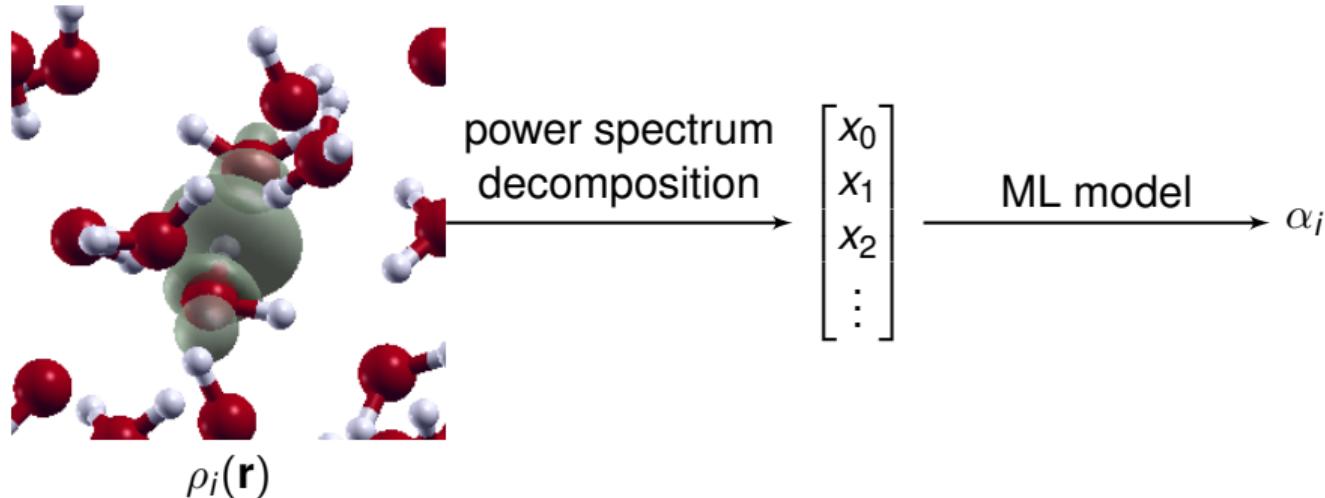
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EPFL

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



Accelerating improvements: screening via ML

Edward Linscott
EPFL



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

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

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()
```