



Koopmans functionals

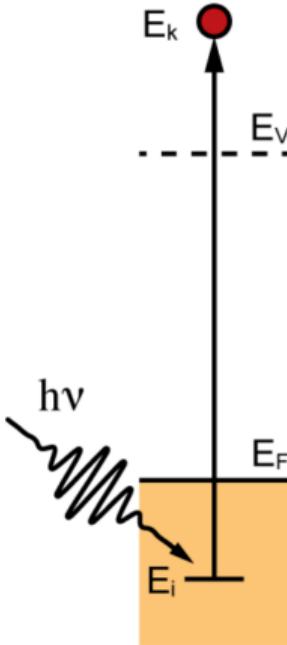
accurately and efficiently predicting spectral properties
with a functional formulation

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

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

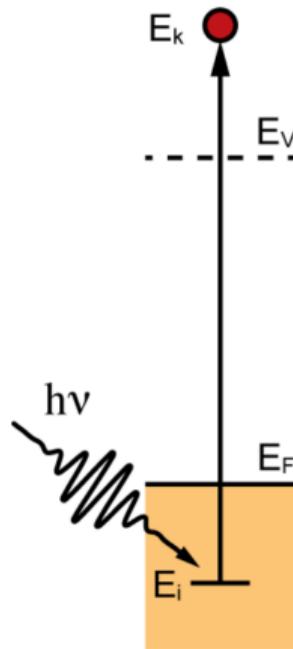
Goal: spectral properties (charged excitations) with a functional theory



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

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

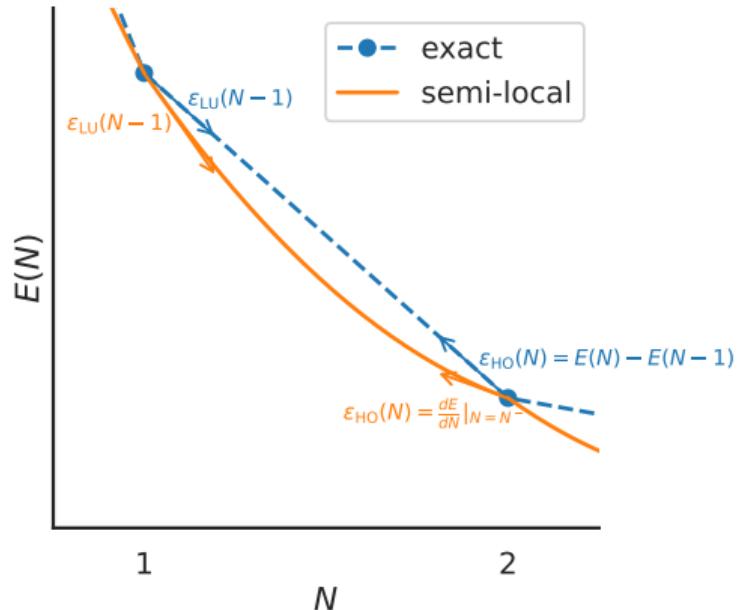


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For DFT, this condition is *not* satisfied



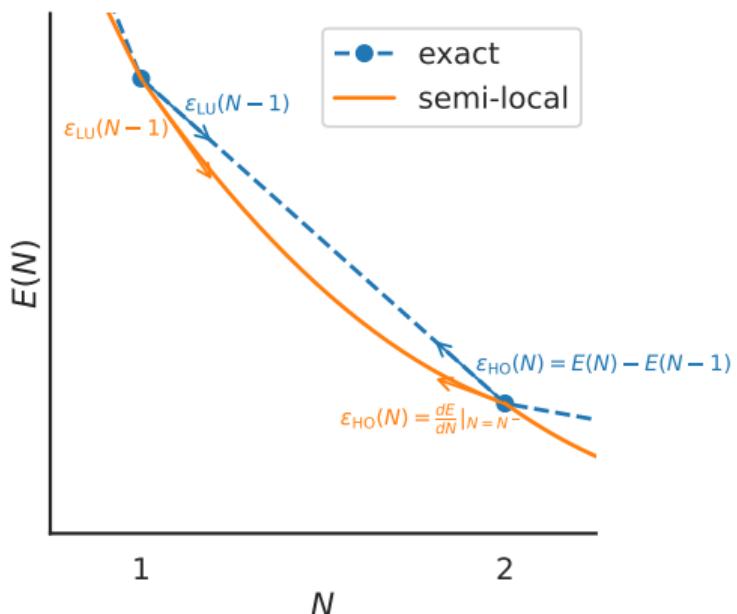
Koopmans functionals: theory

Core idea: for every orbital i their energy

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

ought to be...

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

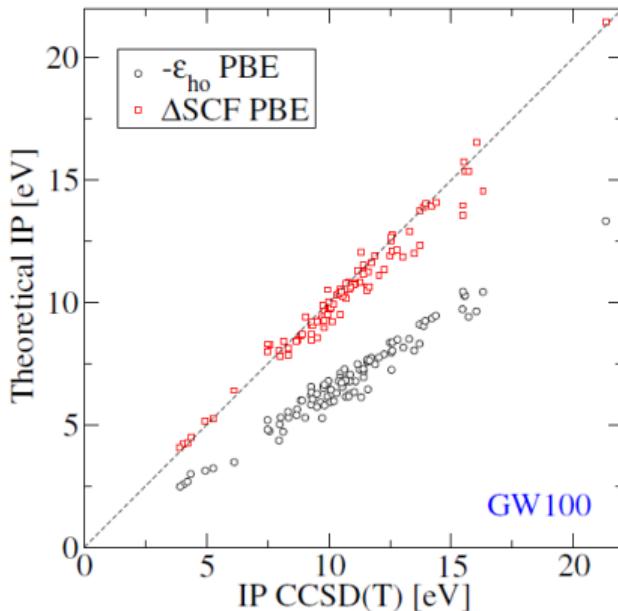


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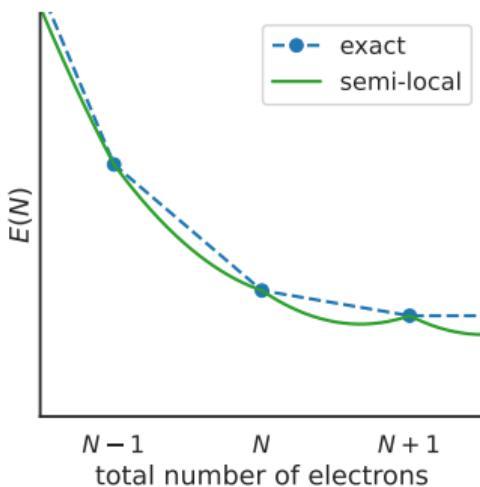
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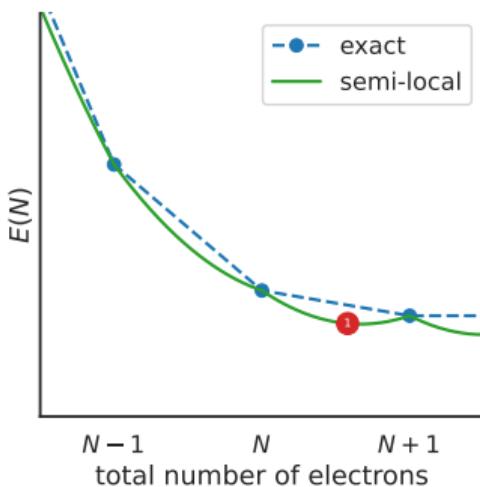
Koopmans functionals: theory

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



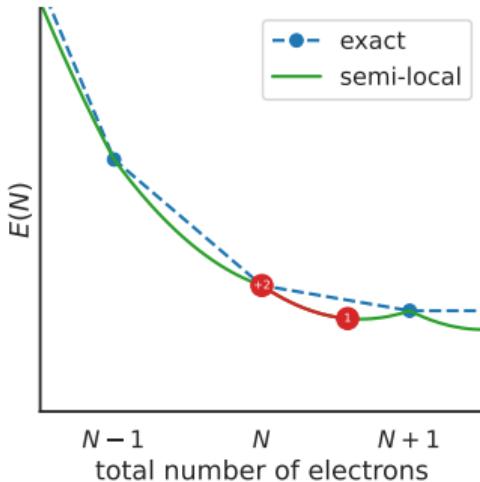
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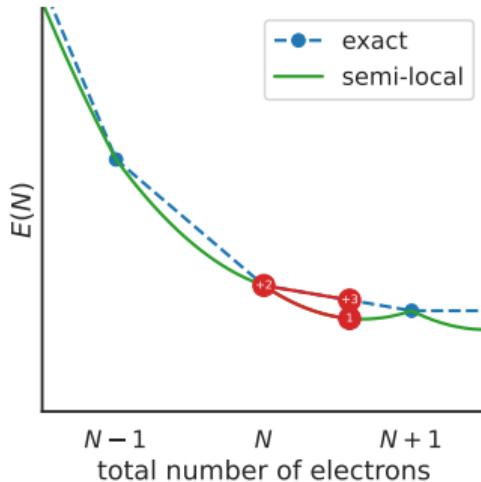
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Differences to semi-local functionals:

- flavours... TODO

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Differences to semi-local functionals:

- screening
- flavours... TODO

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

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Differences to semi-local functionals:

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

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

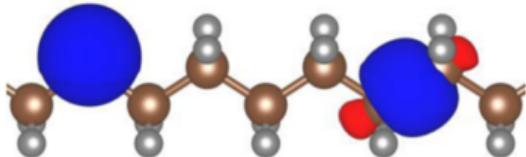
Differences to semi-local functionals:

- screening
- flavours... TODO
- orbital-density dependence

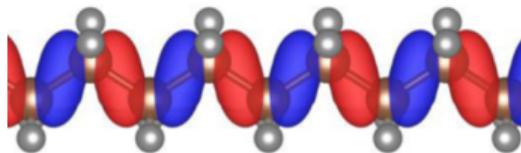
$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[\mathbf{n}_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - \mathbf{n}_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) \mathbf{n}_i(\mathbf{r}')$$

Consequences of ODD:

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



(a) variational



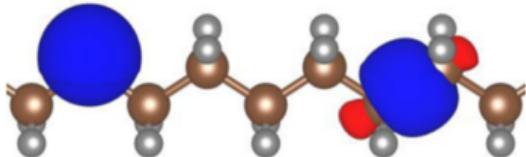
(b) canonical

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

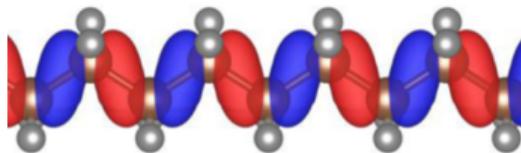
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

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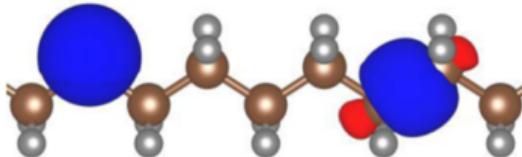
- ODD functional means that we know $\hat{H}|\varphi_i\rangle$ for variational orbitals $\{|\varphi_i\rangle\}$ but we don't know \hat{H} in general

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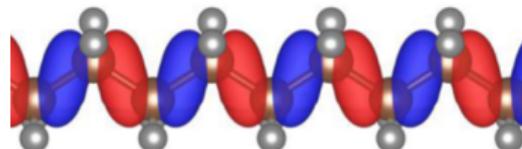
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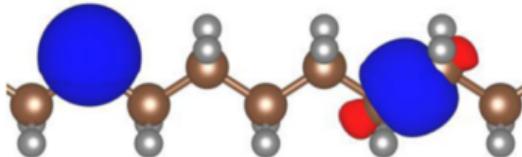
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- Practically we can often use MLWFs

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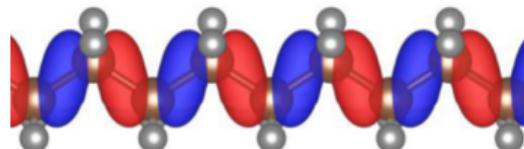
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- ODD functional means that we know $\hat{H}|\varphi_i\rangle$ for variational orbitals $\{|\varphi_i\rangle\}$ but we don't know \hat{H} in general
- Practically we can often use MLWFs
- a natural generalisation in the direction of spectral functional theory¹

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

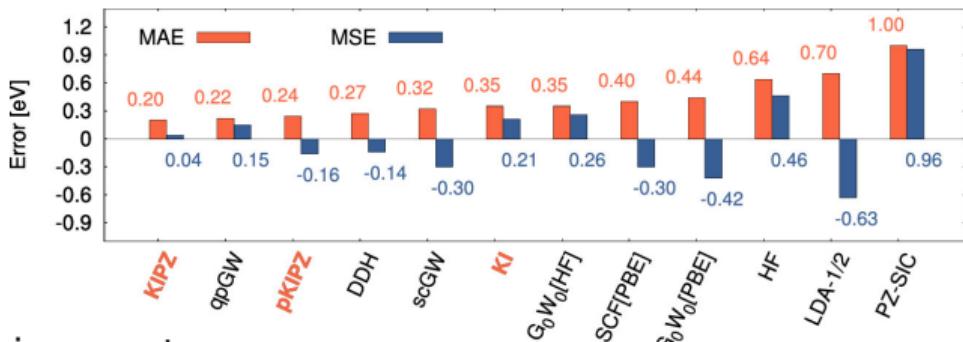
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Resonance with other efforts:

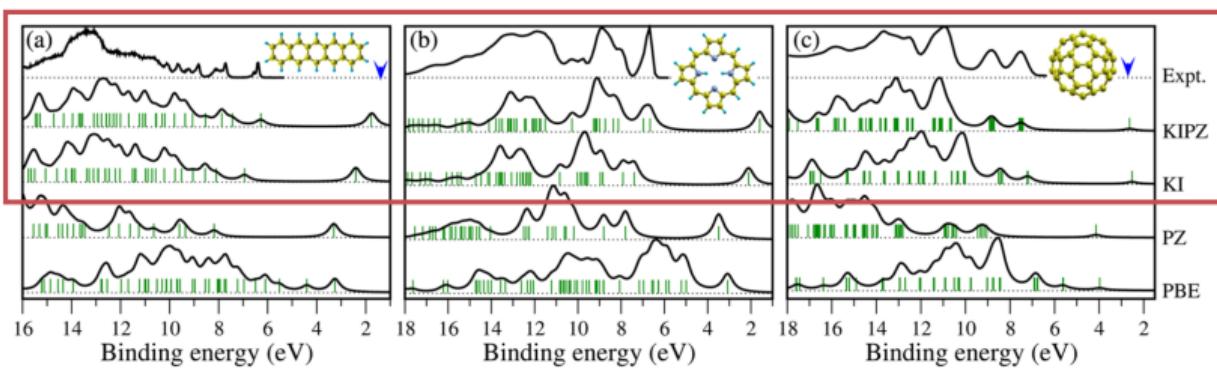
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021),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

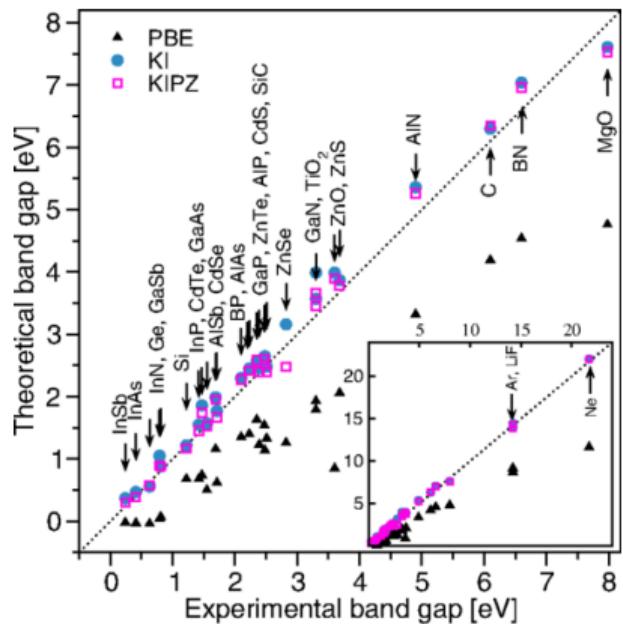
Ionisation potentials = $E(N - 1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



Ultraviolet photoemission spectra



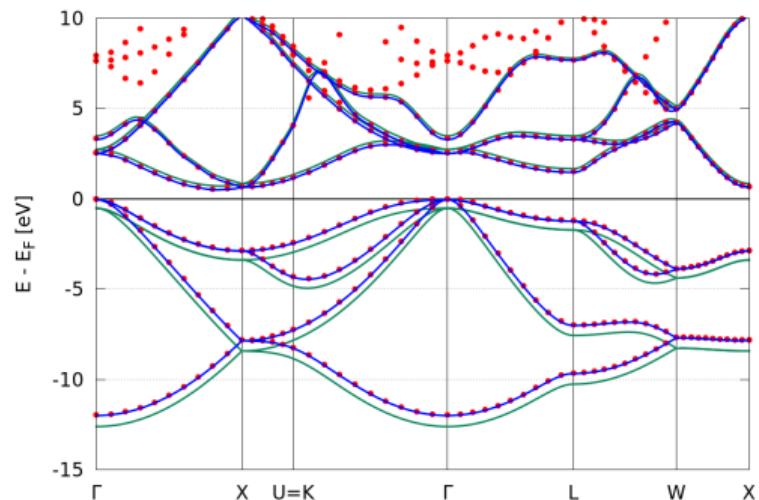
Koopmans functionals: results for solids



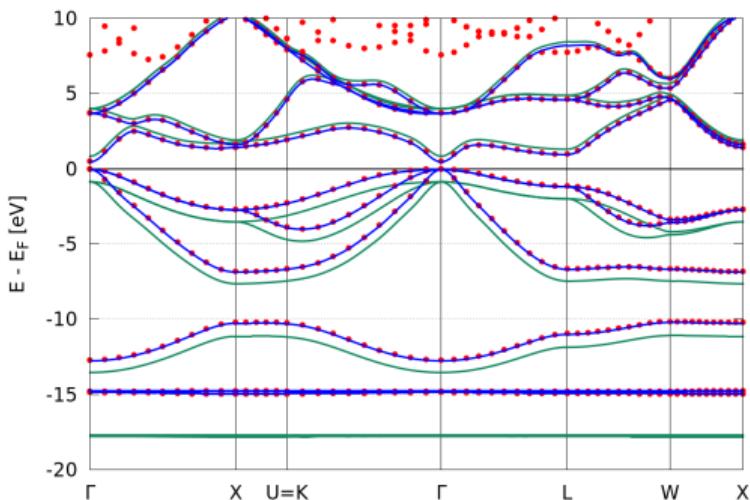
Mean absolute error (eV) across prototypical semiconductors and insulators

| | 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



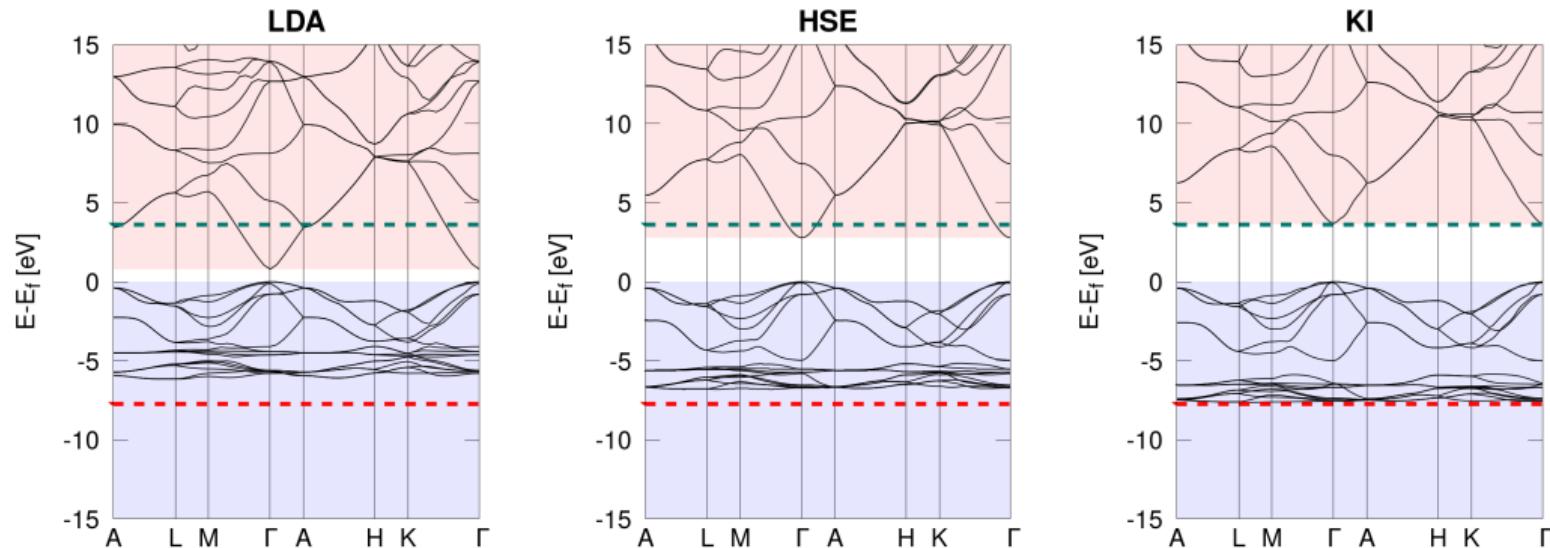
(a) Si, KIPZ



(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 |

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 | |

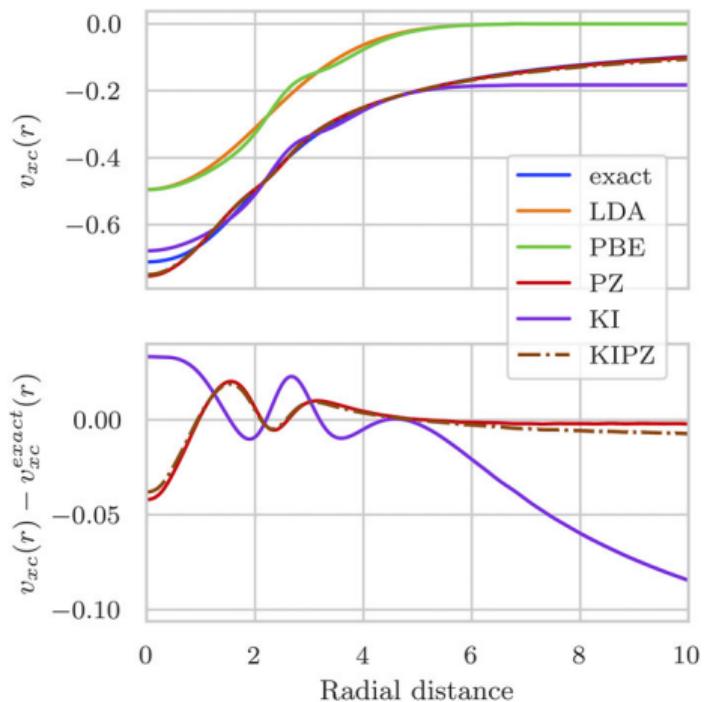
¹ M. Shishkin et al. *Phys. Rev. B* 75.23 (2007), 235102 for E_g and M. S. Hybertsen et al. *Phys. Rev. B* 34.8 (1986), 5390 for the transitions;

² M. Shishkin et al. *Phys. Rev. Lett.* 99.24 (2007), 246403.

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

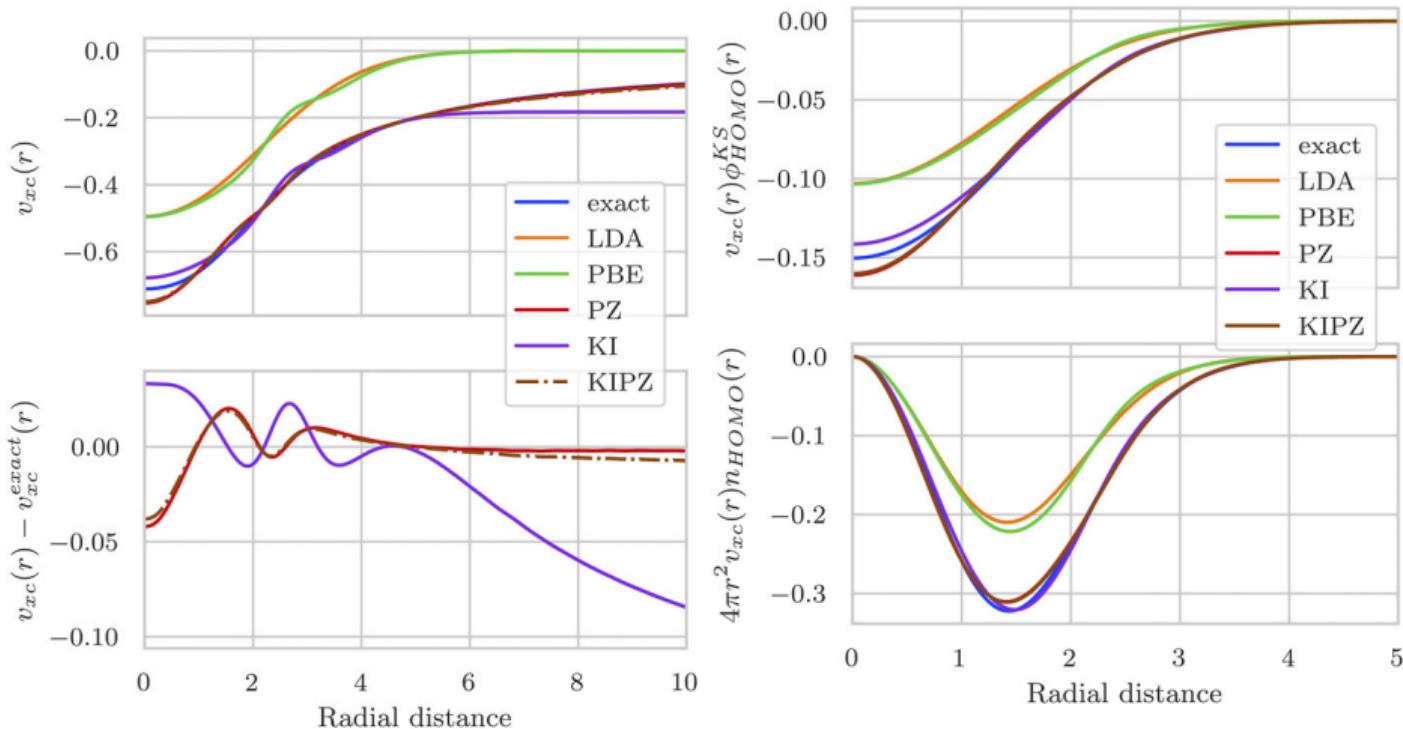
Koopmans functionals: results for toy systems

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



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



- restricted to systems with a non-zero band gap

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- empty state localization in the bulk limit

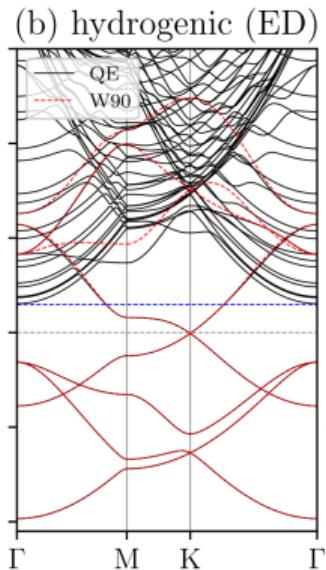
- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit
- can potentially break the crystal point group symmetry

The general workflow:

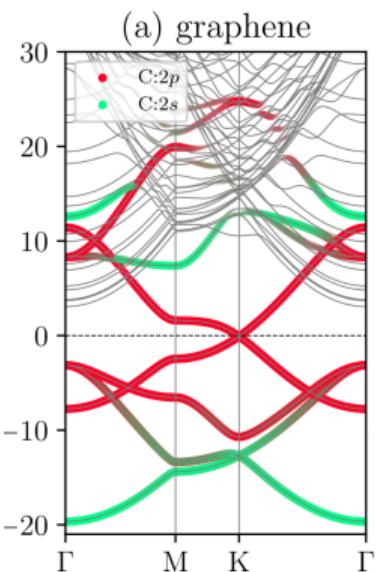
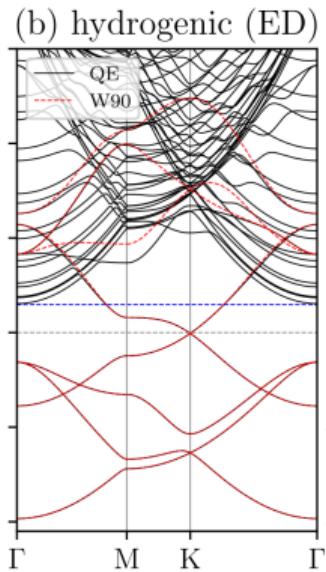
- define/initialize a set of variational orbitals
- calculate the screening parameters $\{\alpha_i\}$
- construct and diagonalize the Hamiltonian

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

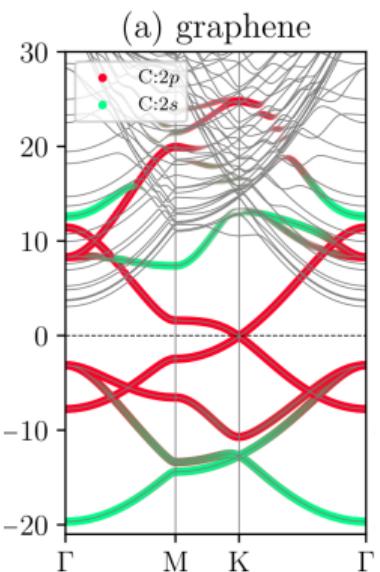
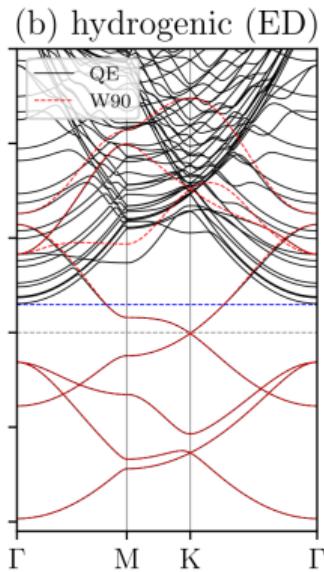
Recent advances: easier Wannierization



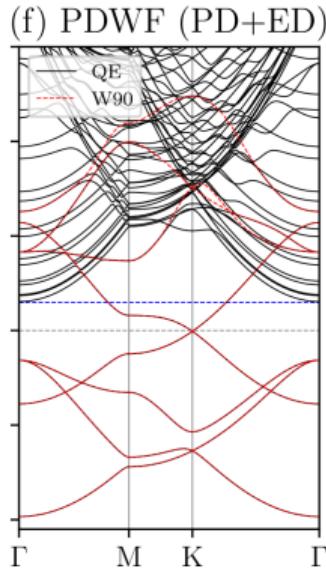
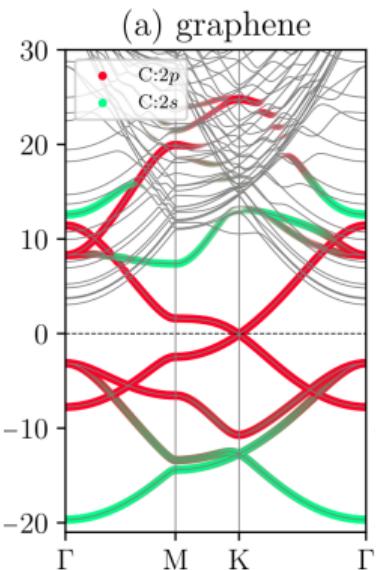
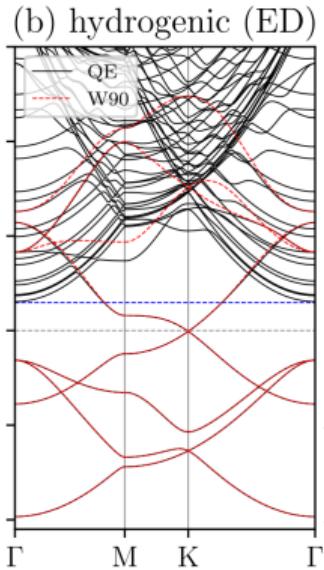
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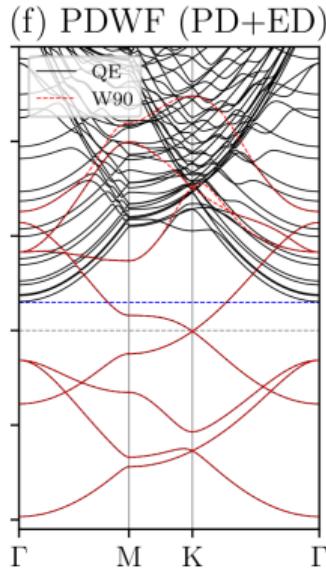
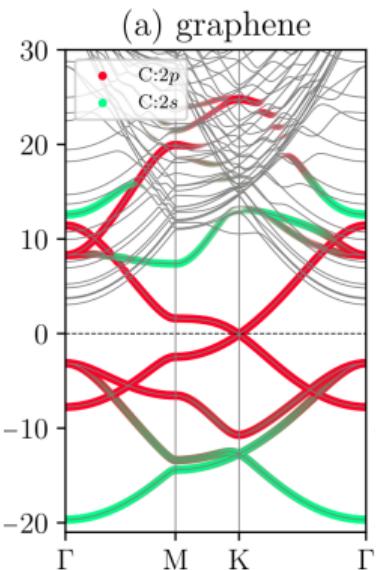
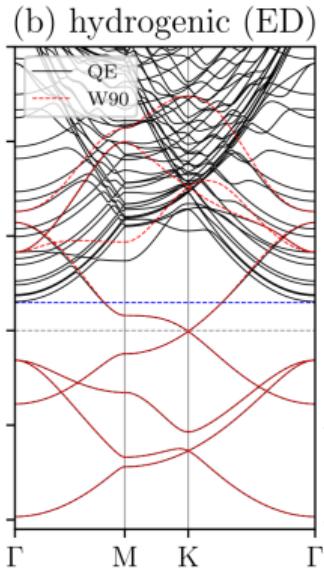
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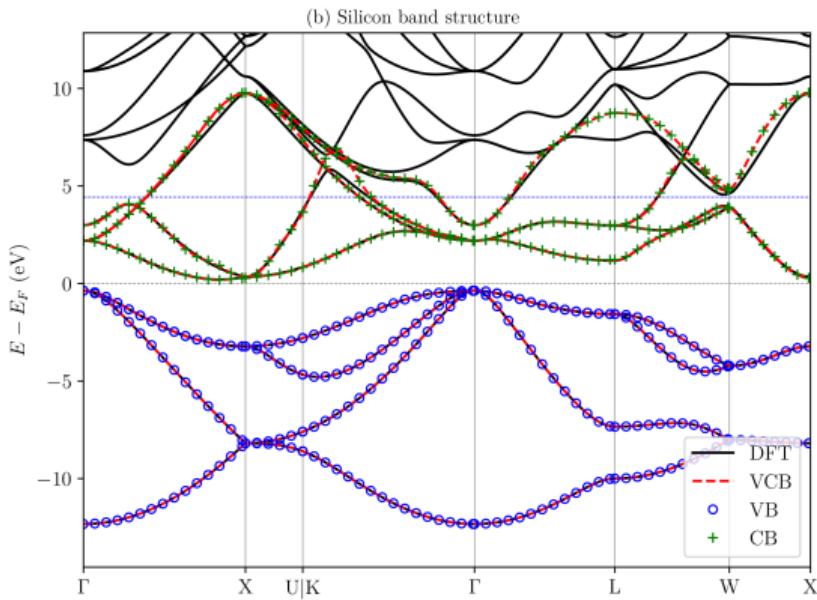


Demonstrated on >20,000 materials → black-box Wannierization!

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

Recent advances: easier Wannierization

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.* (2022).

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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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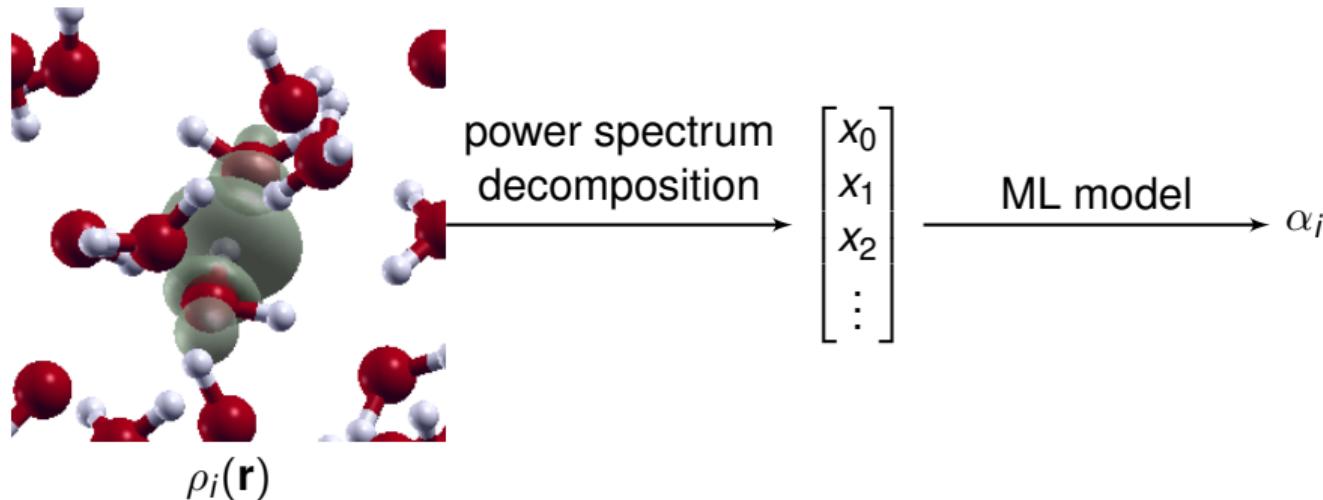
... in reciprocal space²

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

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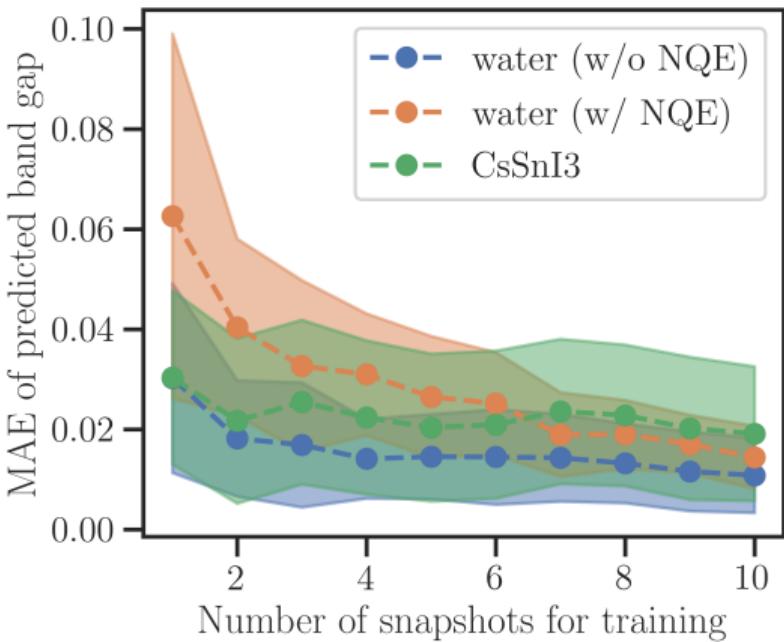
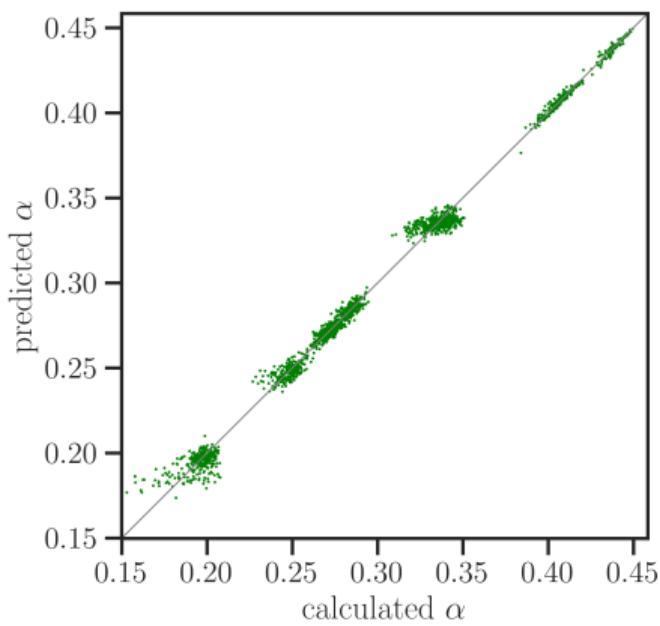
Recent advances: screening parameters via ML



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

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

Recent advances: screening parameters via ML



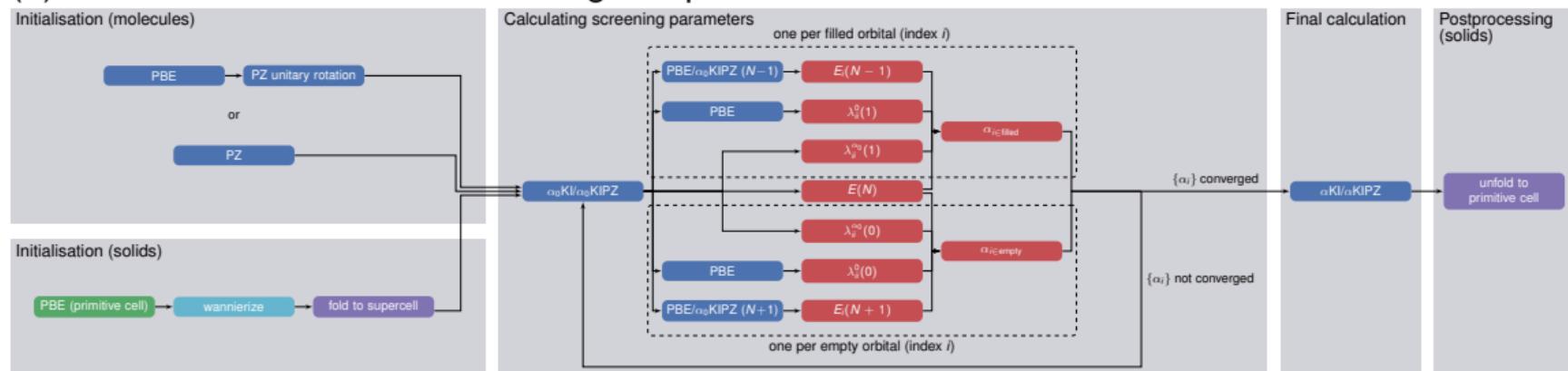
loss of accuracy of the band gap of ~ 0.02 eV
(cf. when calculating screening parameters *ab initio*)
speedup of 70 \times

We have complicated workflows, with either...

Koopmans functionals: the workflows

We have complicated workflows, with either...

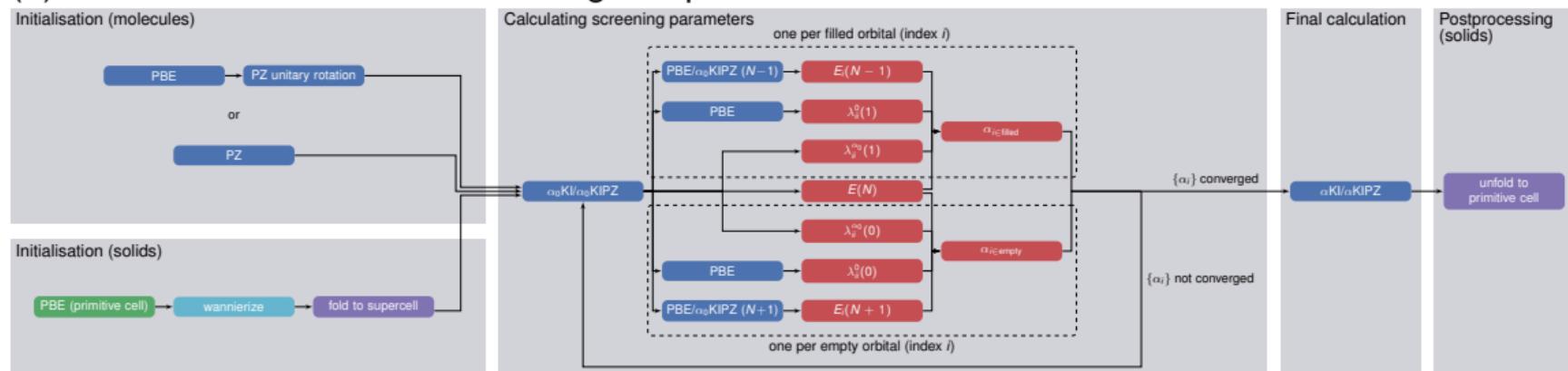
(a) finite difference calculations using a supercell



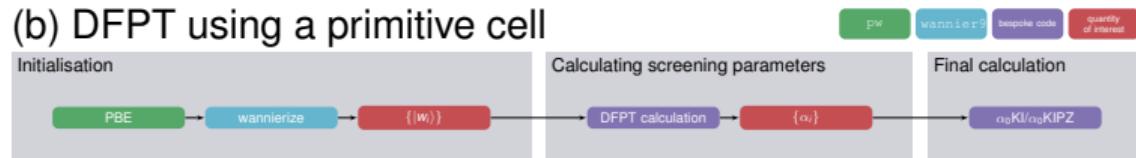
Koopmans functionals: the workflows

We have complicated workflows, with either...

(a) finite difference calculations using a supercell



(b) DFPT using a primitive cell



But complex workflows mean that...

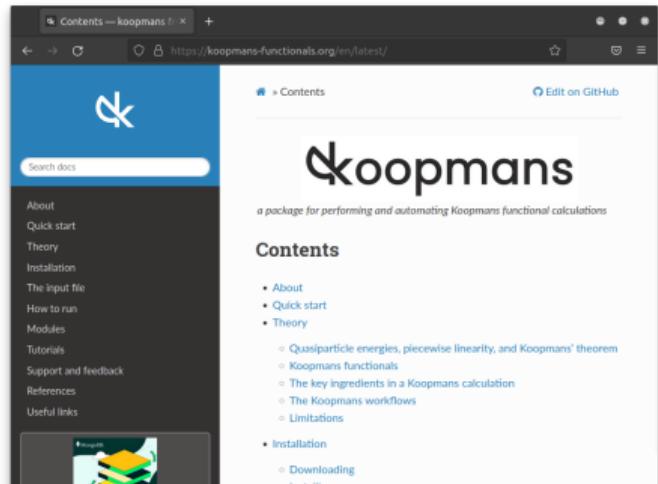
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- v1.0 released earlier this year¹
- implementations of Koopmans functionals
- 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 (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

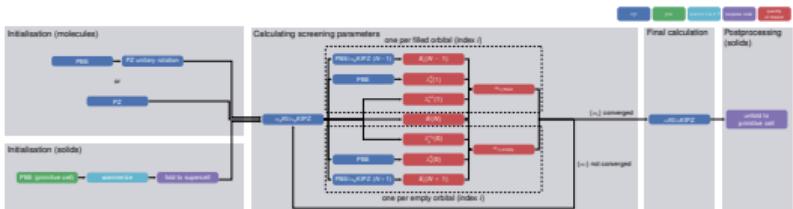
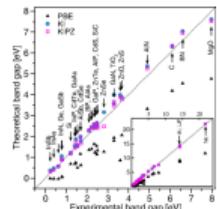
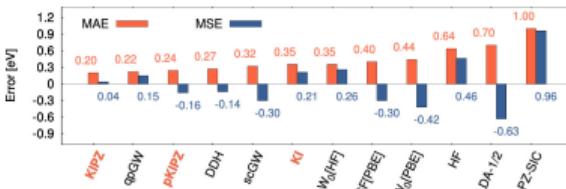
# Use ASE to create bulk silicon
atoms = bulk('Si')

# 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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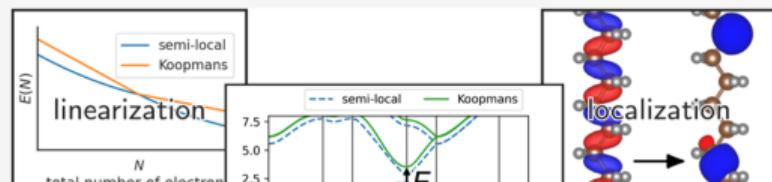
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Supporting Information

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



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Nicola Colonna



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**Swiss National
Science Foundation**

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

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