



Accurate charged and neutral excitations with Koopmans functionals

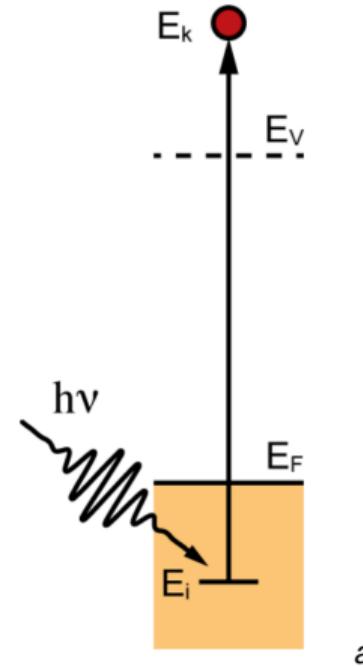
Koopmans functionals are a class of functionals that aim to reproduce spectral properties and total energies on the same footing

As a result they give band structures and orbital energies comparable to state-of-the-art GW

Koopmans can be used to replace GW when calculating neutral excitations with BSE

We have recently 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



Koopmans functionals: theory

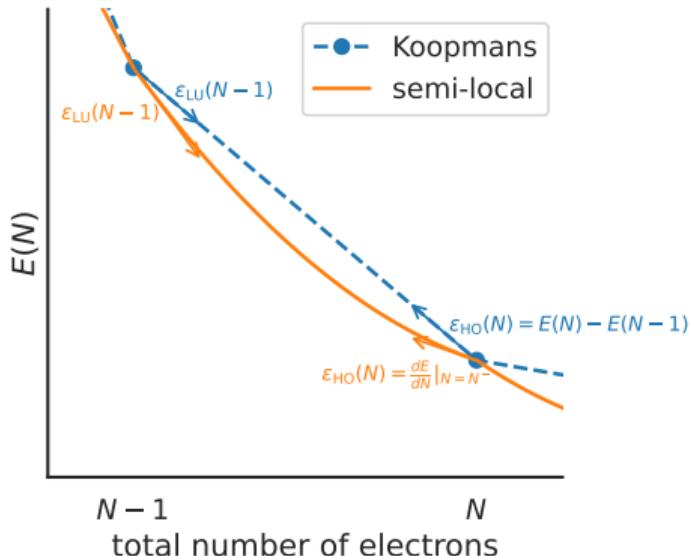
Goal: spectral properties (charged excitations) with a functional theory

Core idea: for every orbital i their energy

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

should be...

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



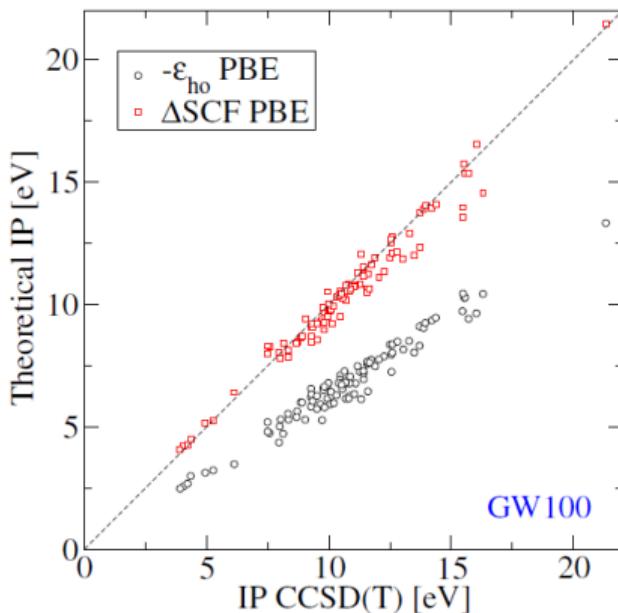
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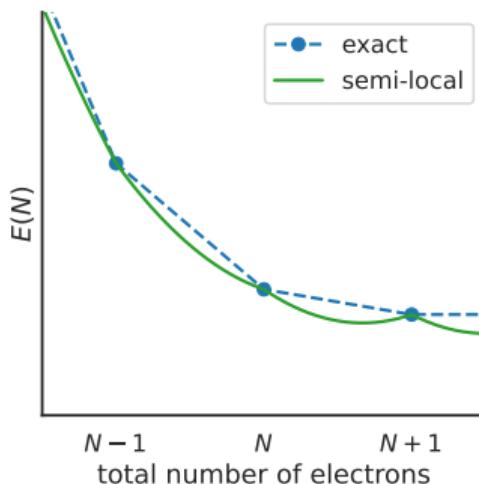
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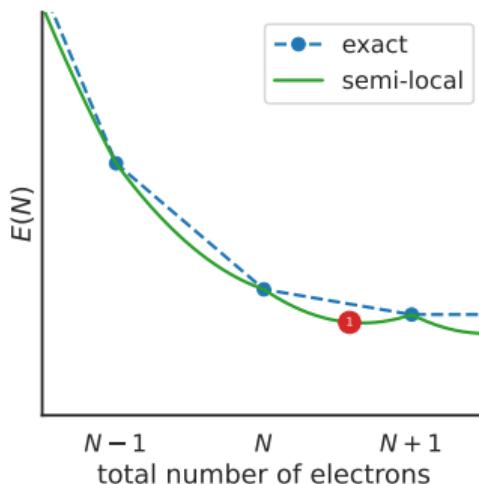
Koopmans functionals: theory

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



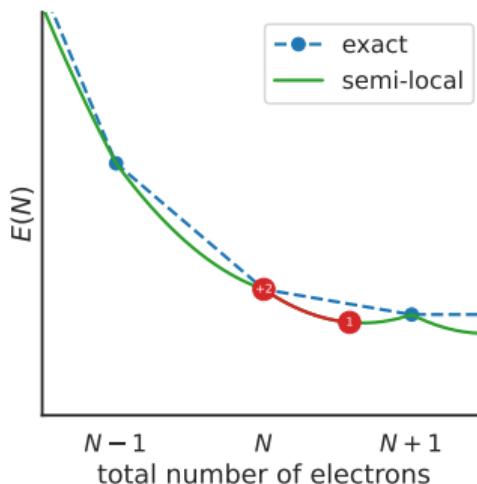
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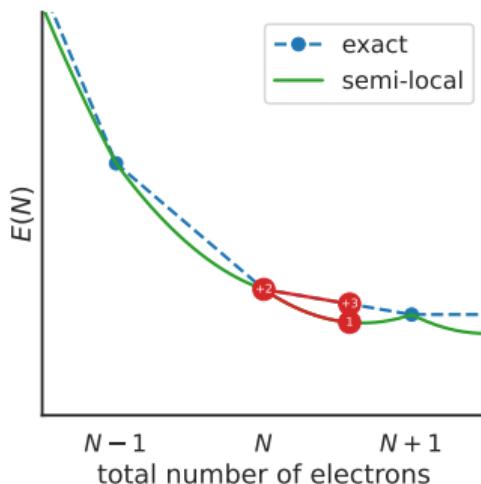
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Differences to semi-local functionals:

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Differences to semi-local functionals:

- screening

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

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

Differences to semi-local functionals:

- screening
- orbital-density dependence

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

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

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

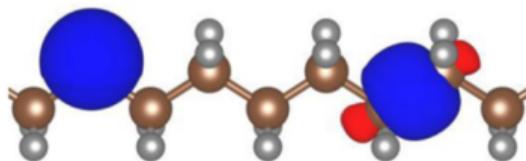
Differences to semi-local functionals:

- screening
- orbital-density dependence

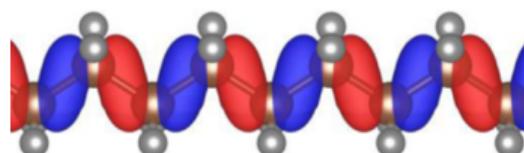
$$\frac{dE}{df_i} \approx \alpha_i \frac{\partial E}{\partial f_i} \Rightarrow \varepsilon_i^{\text{Koopmans}} = \frac{\partial E_{\text{Koopmans}}}{\partial f_i} \approx E_i(N-1) - E(N)$$

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

- 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

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

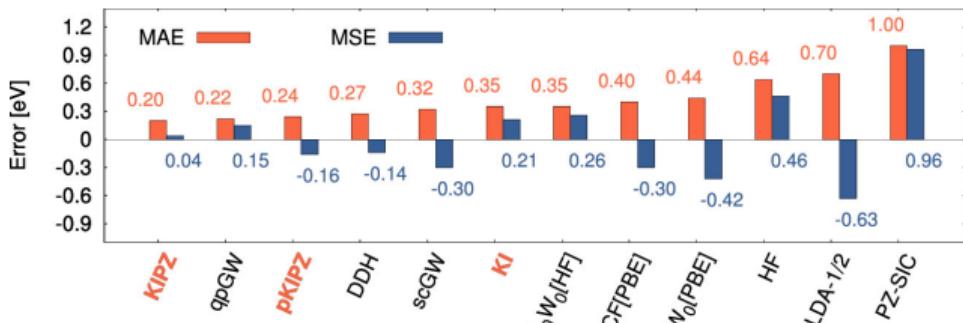
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (23, 2018), 021051

Resonance with other efforts:

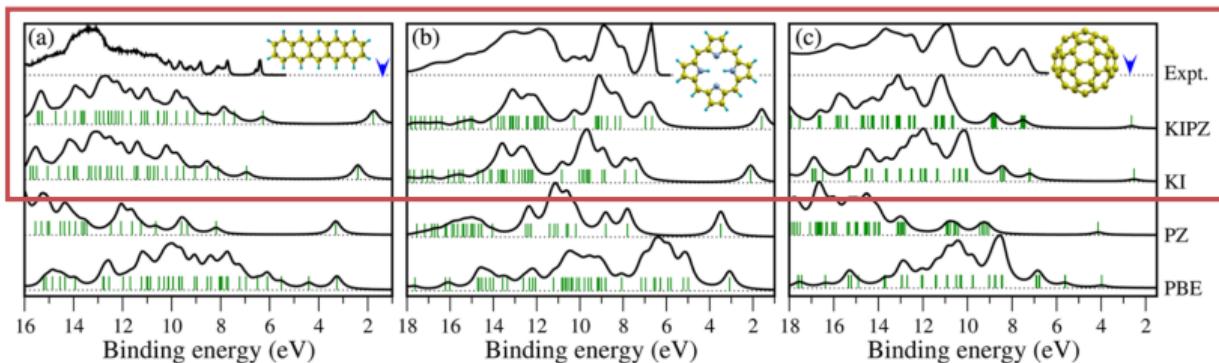
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (18, 2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (8, 2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (24, 2021), e2104556118
- Ensemble DFT of Kronik and co-workers E. Kraisler et al. *Phys. Rev. Lett.* 110.12 (19, 2013), 126403
- Koopmans-Wannier of Wang and co-workers J. Ma et al. *Sci. Rep.* 6.1 (1 26, 2016), 24924
- Dielectric-dependent hybrid functionals of Galli and co-workers J. H. Skone et al. *Phys. Rev. B* 93.23 (3, 2016), 235106
- LOSC functionals of Yang and co-workers C. Li et al. *Natl. Sci. Rev.* 5 (2018), 203

Koopmans functionals: results for molecules

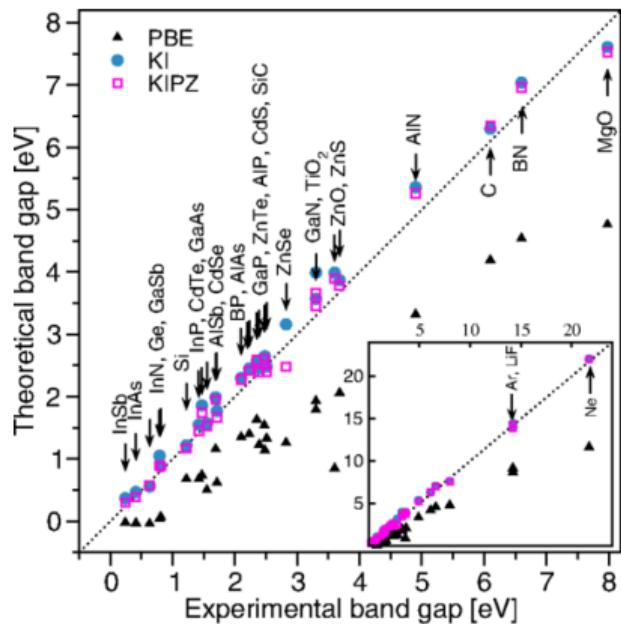
Ionisation potentials = $E(N - 1) - E(N)$? $= -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



Ultraviolet photoemission spectra



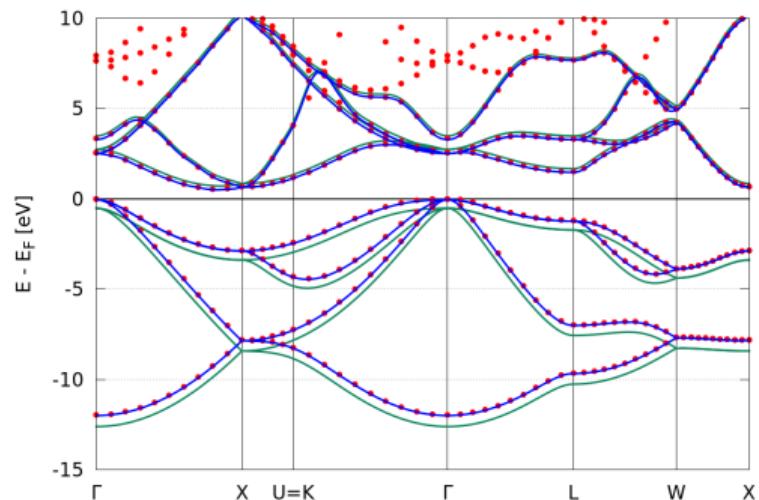
Koopmans functionals: results for solids



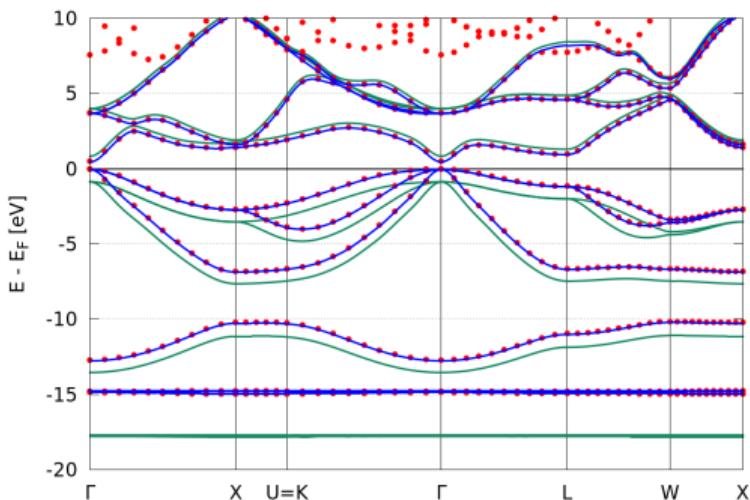
Mean absolute error (eV) across prototypical semiconductors and insulators

	PBE	G ₀ W ₀	KI	KIPZ	QSGW̃
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

Koopmans functionals: results for solids



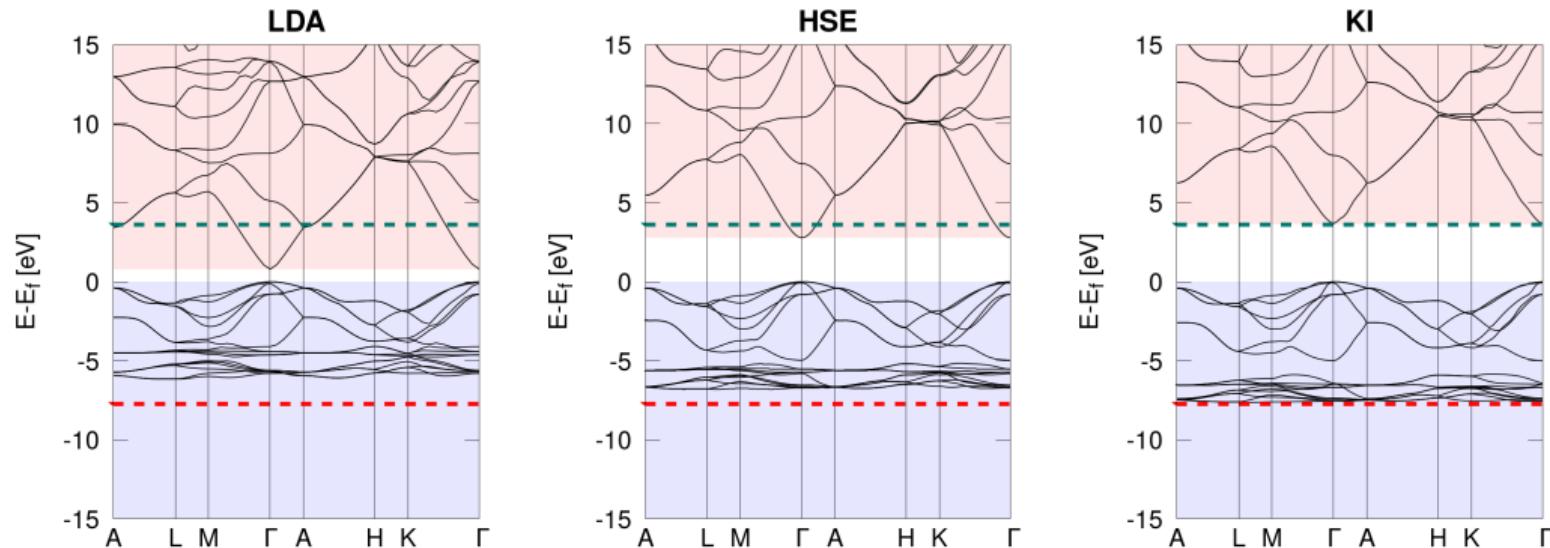
(a) Si, KIPZ



(b) GaAs, KI

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

Koopmans functionals: results for solids



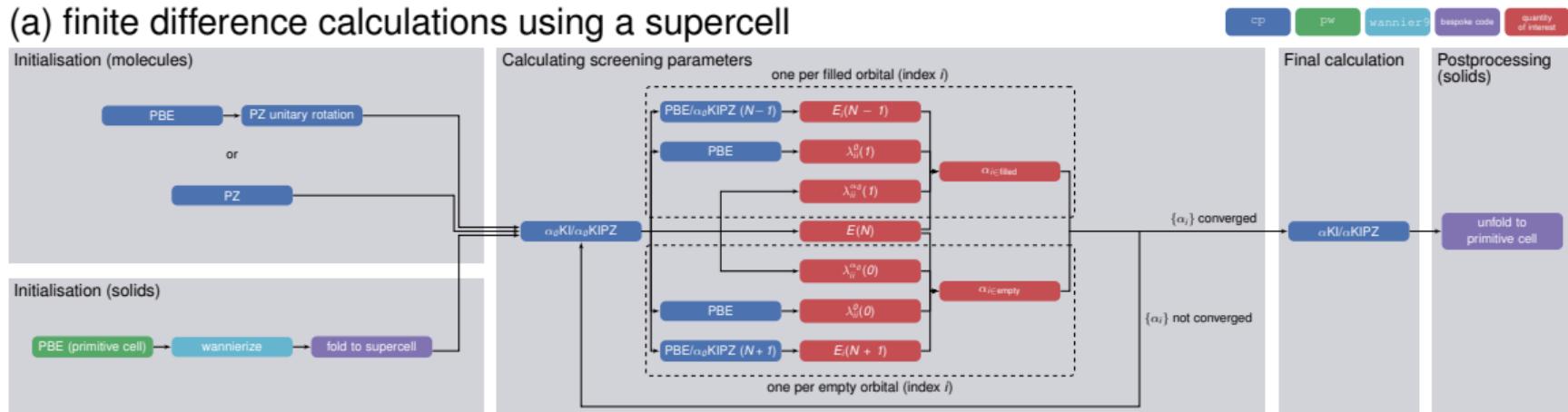
ZnO	LDA	HSE	GW_0	$scG\tilde{W}$	KI	exp
E_{gap} (eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle \varepsilon_d \rangle$ (eV)	-5.1	-6.1	-6.4	-6.7	-6.9	-7.5/-8.0

Screening coefficients $\{\alpha_i\}$ must be determined first, via...

Koopmans functionals: the workflows

Screening coefficients $\{\alpha_i\}$ must be determined first, via...

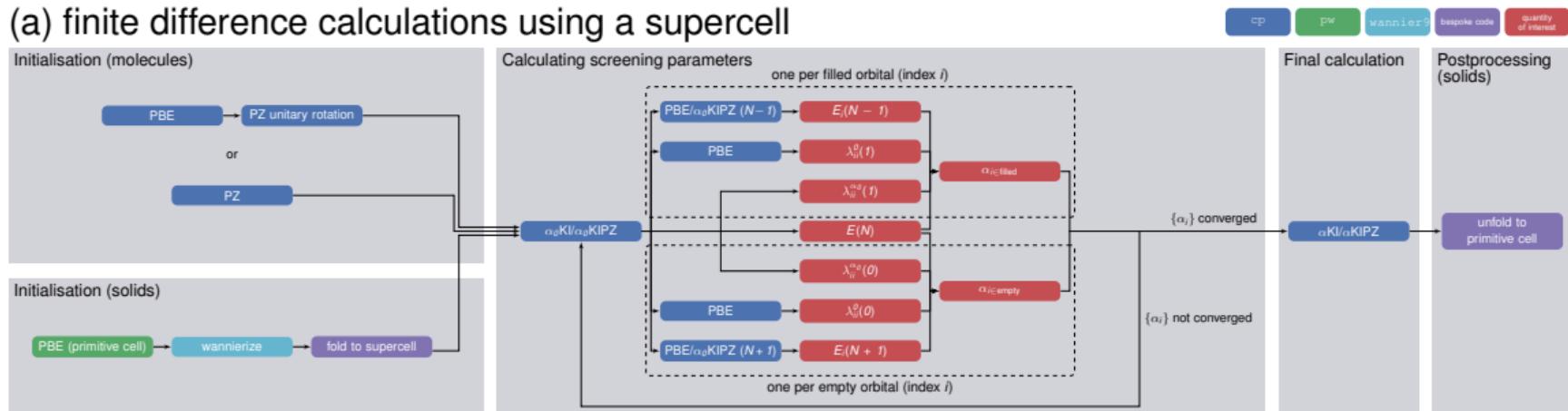
(a) finite difference calculations using a supercell



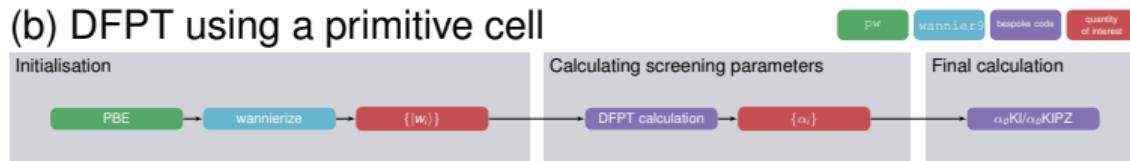
Koopmans functionals: the workflows

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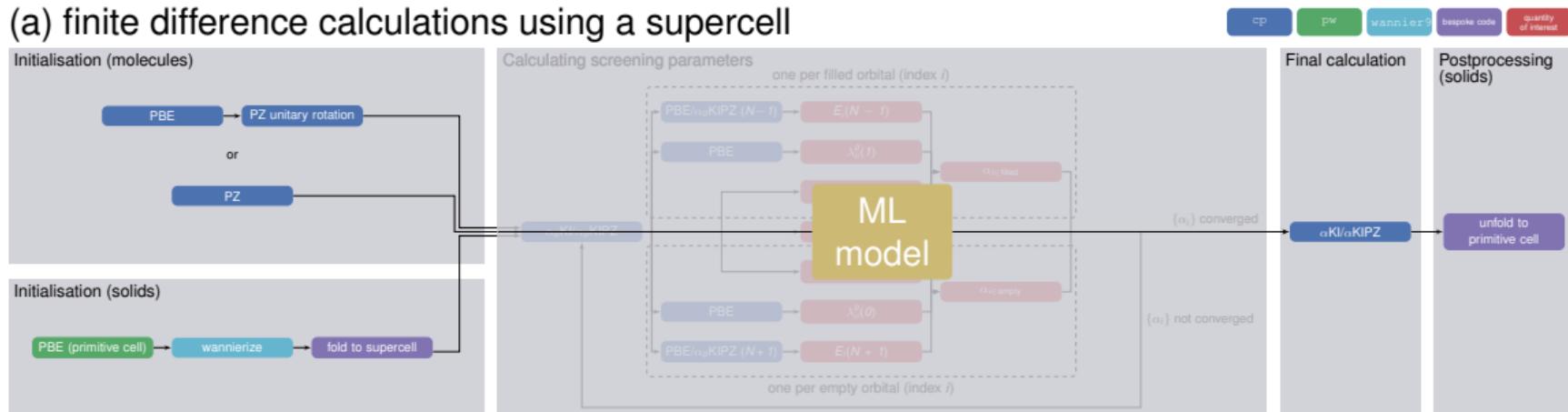
(b) DFPT using a primitive cell



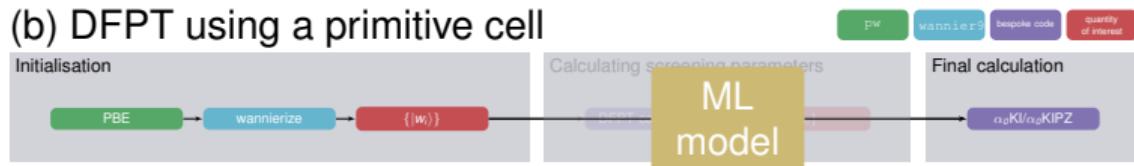
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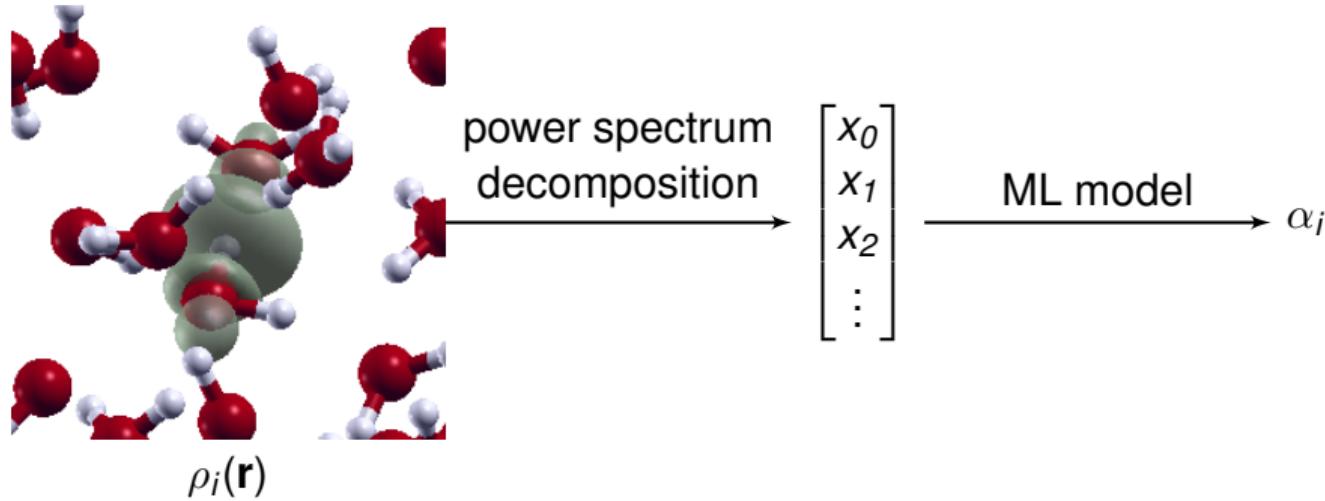


(b) DFPT using a primitive cell



(c) via machine learning (resulting band gaps within ~ 0.02 eV of explicit approach)

Learning the screening parameters



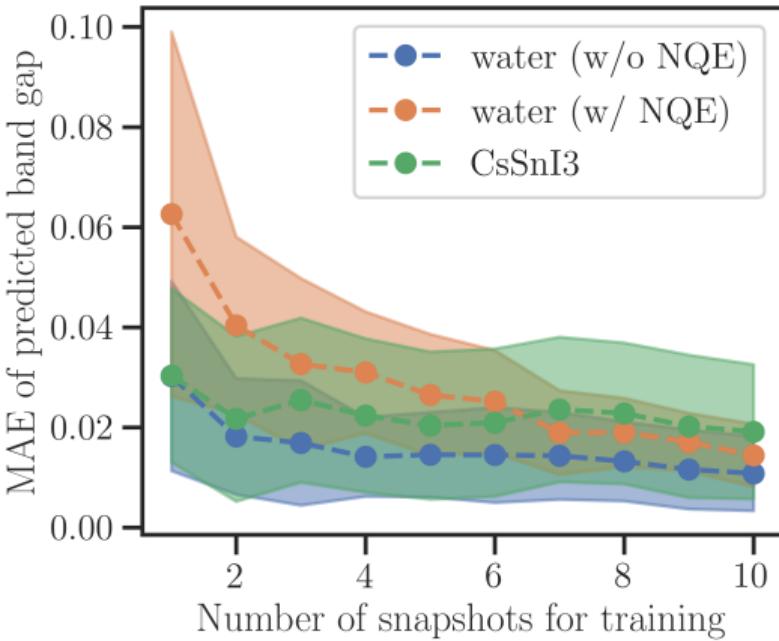
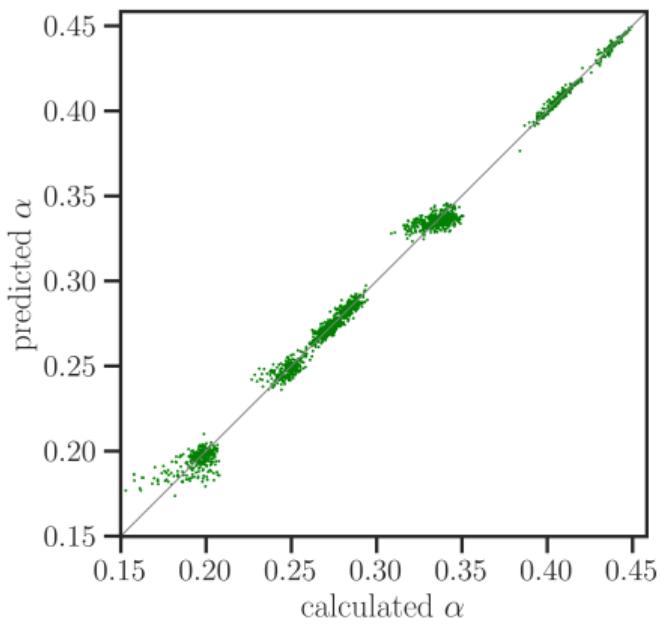
$$c_{nlm, k=\text{orbital}}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) \rho^i(\mathbf{r} - \mathbf{R}^i)$$

g_{nl} = orthonormalised radial Gaussian basis functions

Y_{lm} = spherical harmonics

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

Learning the screening parameters



loss of accuracy of the band gap of $\sim 0.02
(cf. when calculating screening parameters *ab initio*)$

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

But complex workflows mean that...

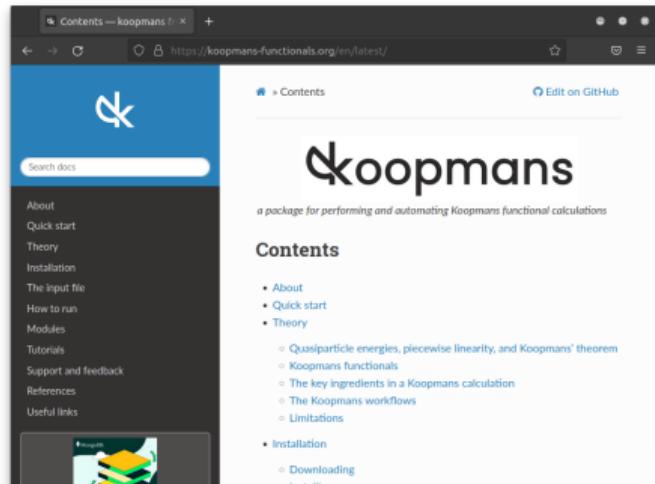
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- beta version released earlier this year¹
- implementations of Koopmans functionals
- automated workflows
 - start-to-finish Koopmans calculations
 - Wannierisation
 - dielectric tensor
 - convergence tests
 - ...
- built on top of ASE²
- does not require expert knowledge

koopmans-functionals.org



¹Linscott et al., in prep

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

koopmans: the input file

```
{  
    "workflow": {  
        "task": "singlepoint",  
        "functional": "ki",  
        "method": "dscf",  
        "init_orbitals": "mlwfs",  
        "alpha_guess": 0.1  
    },  
    "atoms": {  
        "atomic_positions": {  
            "units": "crystal",  
            "positions": [[{"Si": 0.00, 0.00, 0.00},  
                          {"Si": 0.25, 0.25, 0.25}]]  
        },  
        "cell_parameters": {  
            "periodic": true,  
            "ibrav": 2,  
            "celldm(1)": 10.262  
        }  
    },  
}
```

```
"k_points": {  
    "grid": [8, 8, 8],  
    "path": "LGXKG"  
},  
"calculator_parameters": {  
    "ecutwfc": 60.0,  
    "w90": {  
        "projections": [  
            [{"fsite": [0.125, 0.125, 0.125],  
             "ang_mtm": "sp3"}],  
            [{"fsite": [0.125, 0.125, 0.125],  
             "ang_mtm": "sp3"}]  
        ],  
        "dis_froz_max": 11.5,  
        "dis_win_max": 17.0  
    }  
}
```

koopmans is scriptable

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

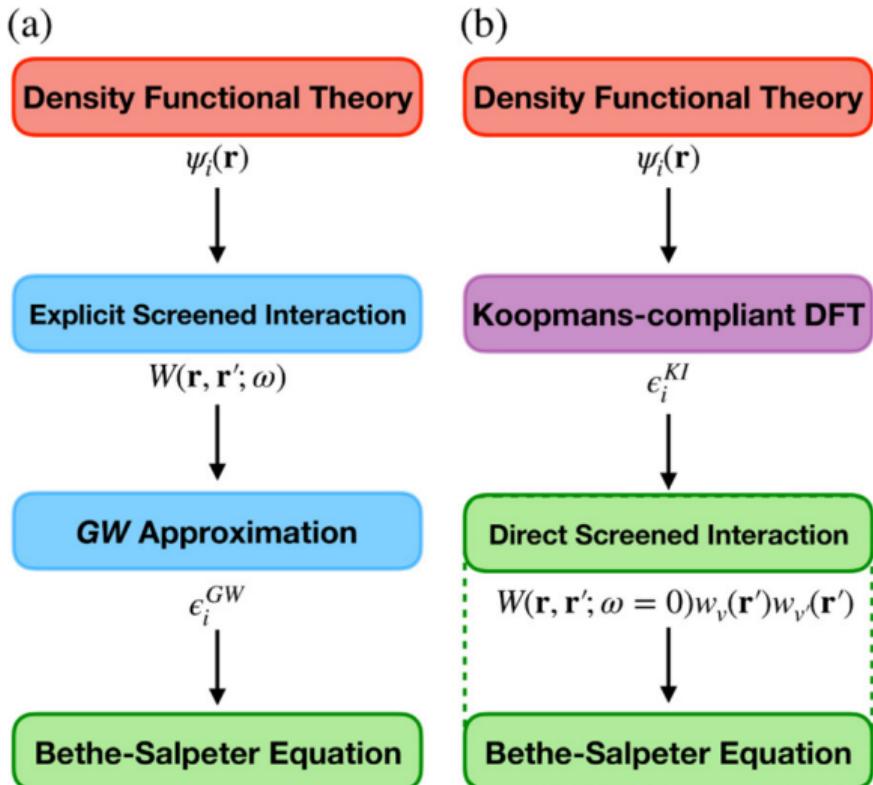
# Use ASE to create bulk silicon
atoms = bulk('Si')

# Define the projections for the Wannierization (same for filled and empty manifold)
si_proj = [{'fsite': [0.25, 0.25, 0.25], 'ang_mtm': 'sp3'}]
si_projs = ProjectionBlocks.from_list([si_proj, si_proj], atoms=atoms)

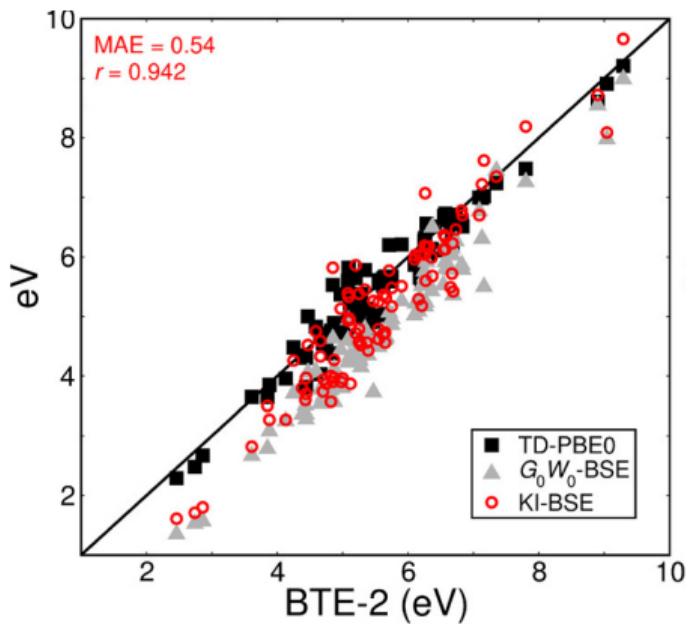
# Create the workflow
workflow = SinglepointWorkflow(atoms = atoms,
                                projections = si_projs,
                                ecutwfc = 40.0,
                                kpoints = Kpoints(grid=[8, 8, 8], path='LGXKG', cell=atoms.cell),
                                calculator_parameters = {'pw': {'nbnd': 10},
                                                        'w90': {'dis_froz_max': 10.6, 'dis_win_max': 16.9}})

# Run the workflow
workflow.run()
```

Neutral excitations with Koopmans

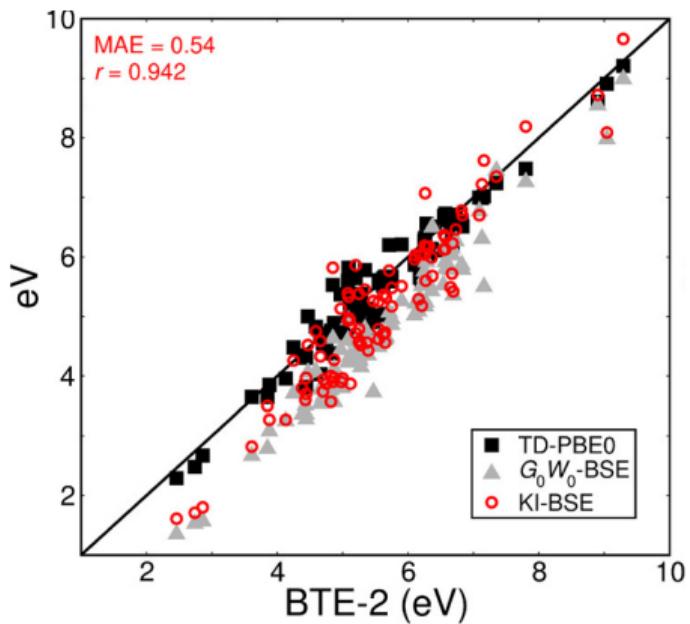


Neutral excitations with Koopmans



Thiel's set	KI-BSE PBE	G_0W_0 -BSE PBE	TDDFT PBE	G_0W_0 -BSE B3LYP	TDDFT B3LYP
MAE (eV)	0.54	0.83	0.55	0.46	0.27

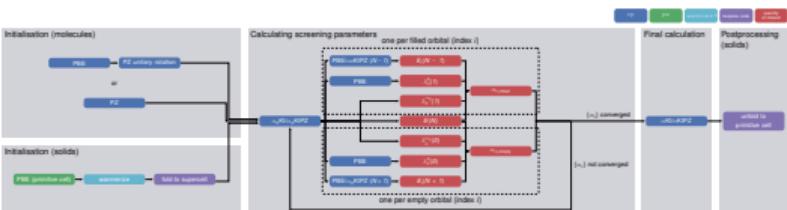
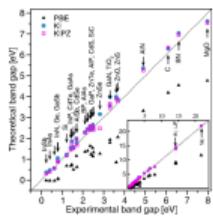
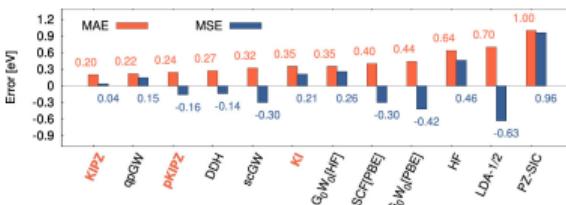
Neutral excitations with Koopmans



Thiel's set	KI-BSE PBE	G_0W_0 -BSE PBE	G_0W_0 -BSE B3LYP	TDDFT PBE	TDDFT B3LYP
MAE (eV)	0.54	0.83	0.46	0.55	0.27

Based on RPA → room for improvement with finite-field approaches

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 can replace GW when calculating neutral excitations with BSE

Acknowledgements

Edward Linscott
EPFL | 22/22



Nicola Marzari



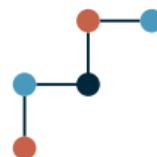
Nicola Colonna



Riccardo De Gennaro



Yannick Schubert



**Swiss National
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MARVEL



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

Free online school Nov 9-11 2022 *Advanced Quantum ESPRESSO tutorial: Hubbard and Koopmans functionals from linear response*. Too late to register but it will be recorded!

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