

Koopmans functionals in practice

minimisation, screening coefficients, automation, and more...

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

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- different flavours

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- different flavours
- orbital-density dependence

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Differences to semi-local functionals:

- different flavours
- orbital-density dependence
- screening

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

$$E_{\text{KI}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{DFT}[\rho] + \sum_i \alpha_i \left(- \int_0^{f_i} \varepsilon_i(f) df + f_i \int_0^1 \varepsilon_i(f) df \right)$$

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

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

$$E_{\text{KIPZ}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{DFT}[\rho] + \sum_i \alpha_i \left(- \int_0^{f_i} \varepsilon_i(f) df + f_i \left\{ \int_0^1 \varepsilon_i(f) df - E_{Hxc}[n_i] \right\} \right)$$

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You might also see...

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

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

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For filled orbitals with KI:

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

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

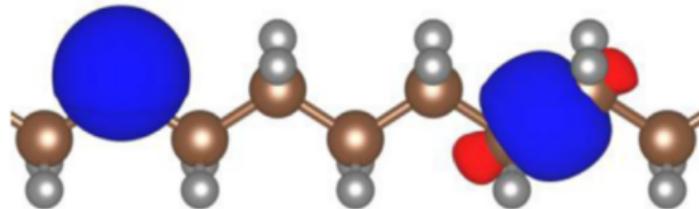
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(a) variational

Orbital-density-dependence

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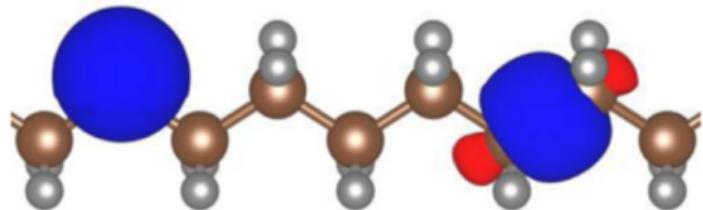
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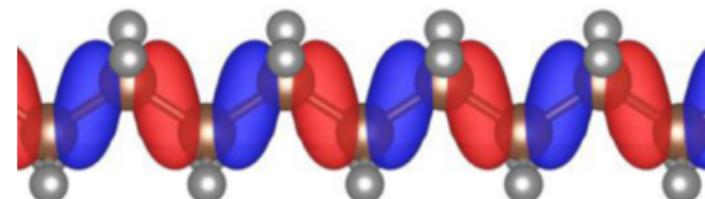
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Diagonalising at the minimum gives rise to diagonalising orbitals (delocalised/canonical)

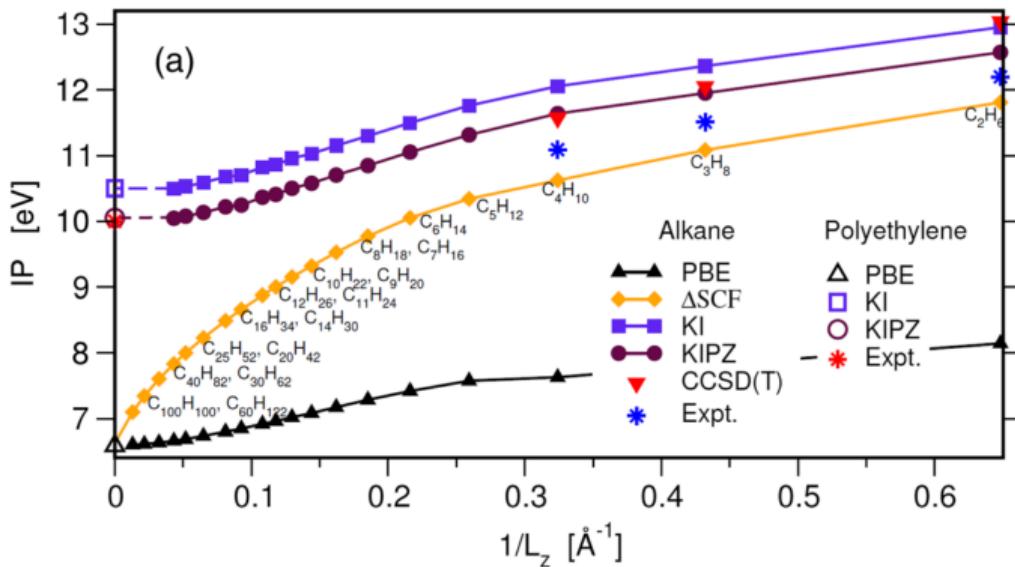


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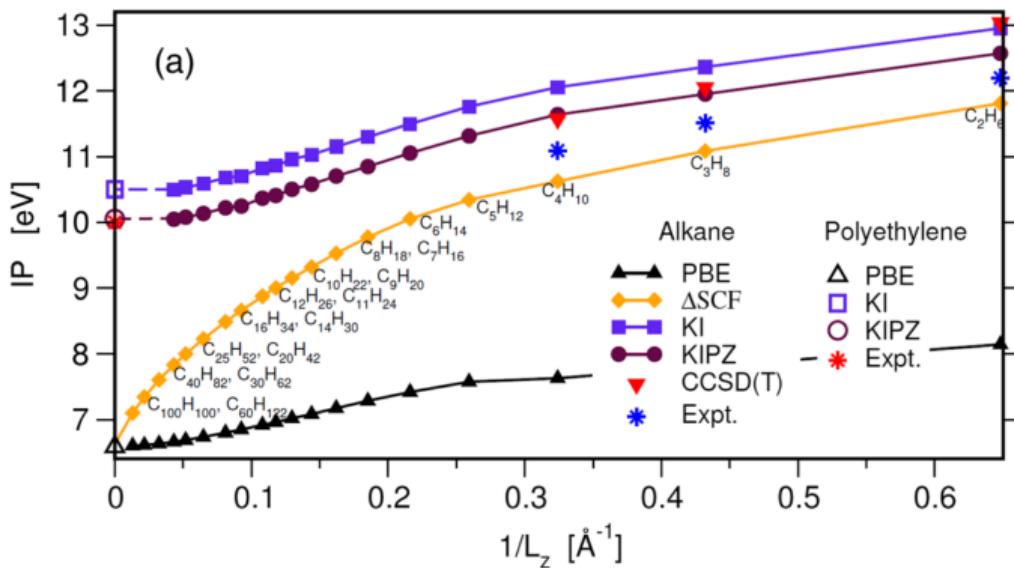


(b) canonical

Importance of localisation

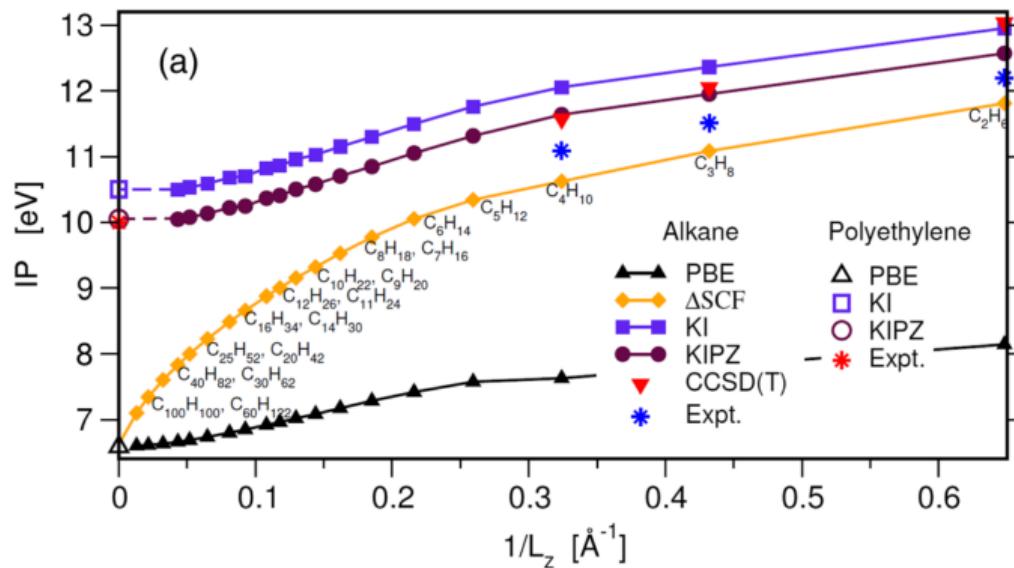


Importance of localisation



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

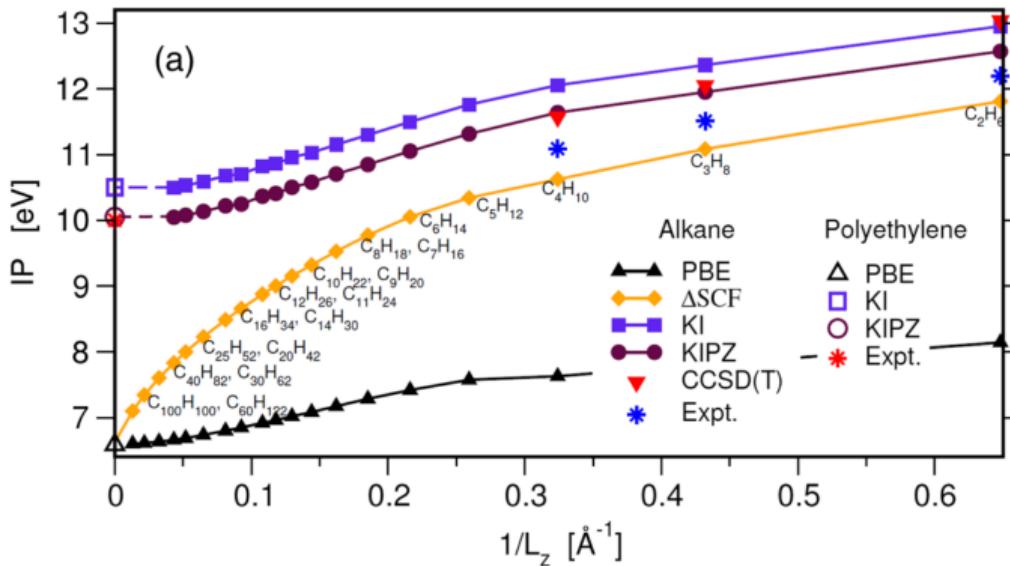
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In the bulk limit for one cell $\Delta E = E(N - \delta N) - E(N)$

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

Importance of localisation



Other features of orbital-density-dependence

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

Other features of orbital-density-dependence

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

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- Practically we can often use MLWFs
- a natural generalisation in the direction of spectral functional theory (as discussed already by Andrea)¹

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- In Hartree-Fock (the original “Koopmans’ theorem”):

$$E_{ee}^{HF} = \frac{1}{2} \sum_{ij} f_i f_j \int d\mathbf{r} d\mathbf{r}' \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{\mathbf{r} - \mathbf{r}'} - \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') \psi_j(\mathbf{r})}{\mathbf{r} - \mathbf{r}'}$$

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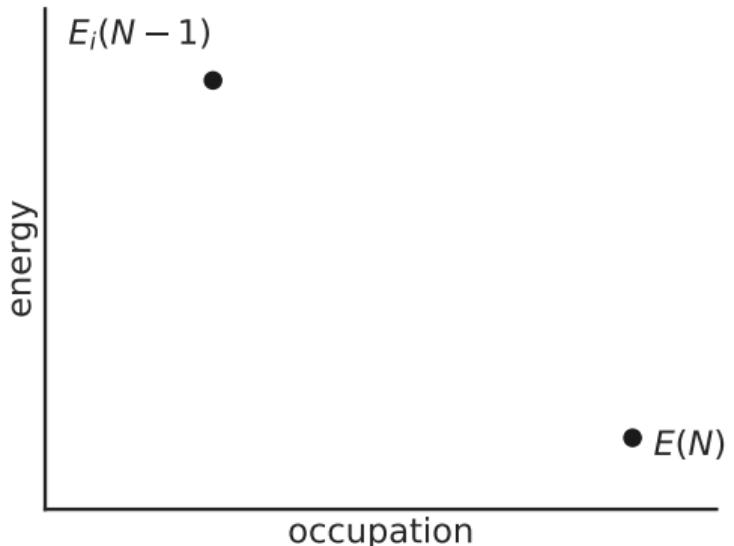
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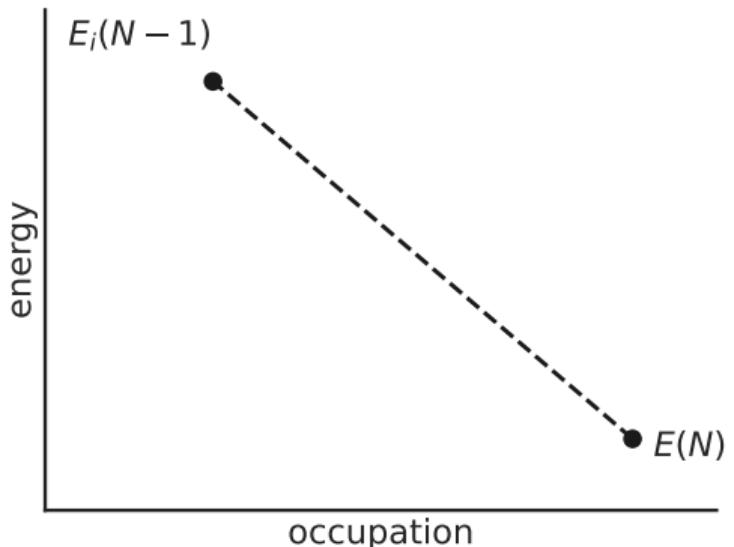
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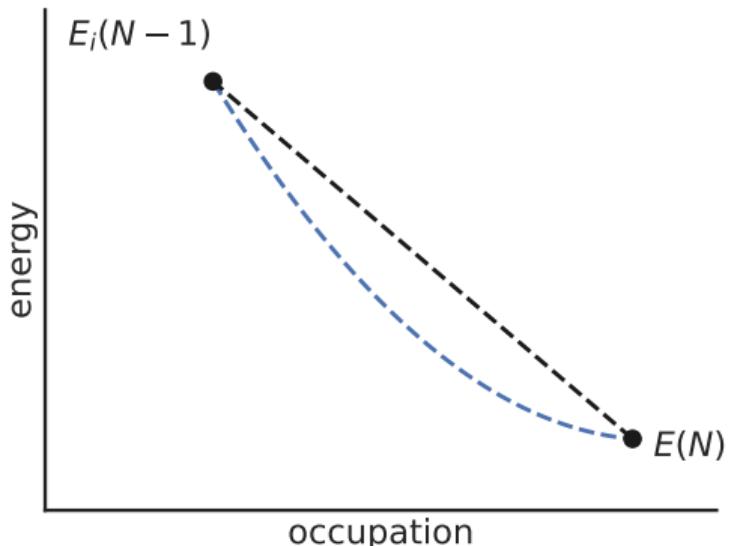
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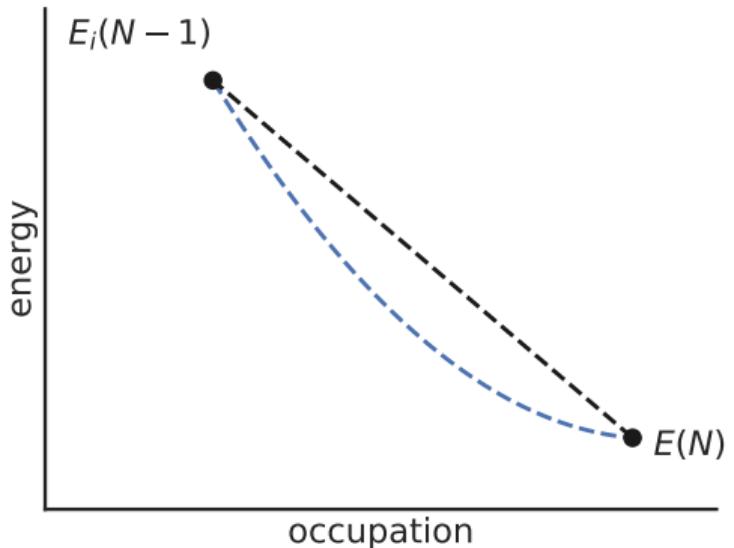
- How to choose an appropriate value for α_i ? Return to the original idea of Koopmans functionals:

$$\varepsilon_i^{\text{Koopmans}} = E_i(N-1) - E(N)$$

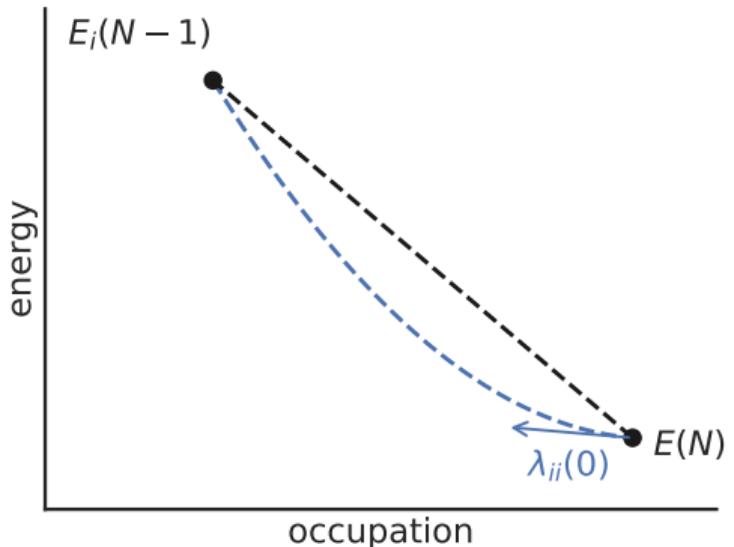




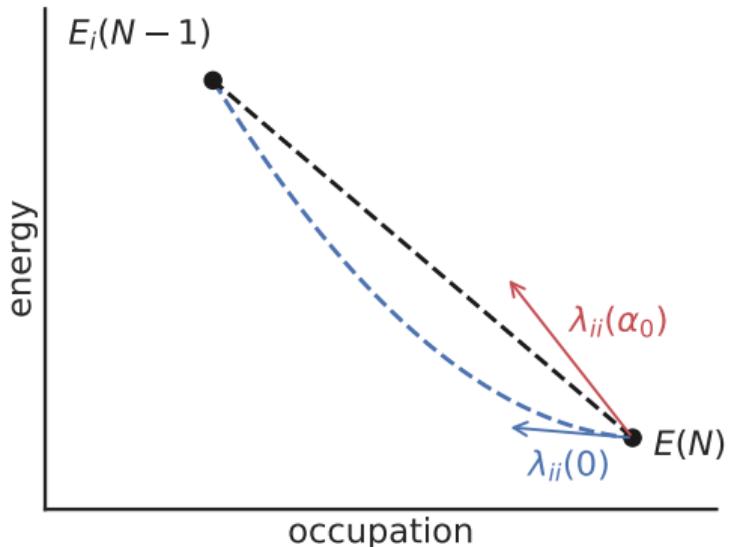




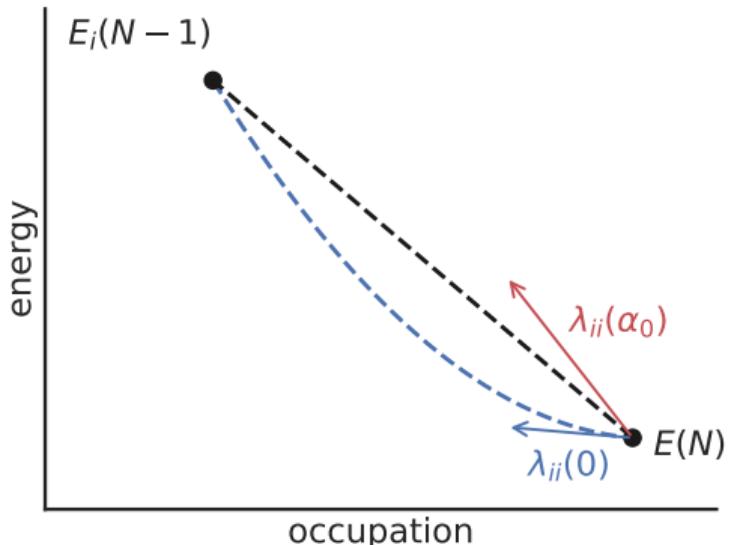
$$\lambda_{ii}(\alpha) \equiv \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}^{\text{Koopmans}} | \varphi_i \rangle = \frac{dE^{\text{Koopmans}}}{df_i} \Big|_{f_i=s}$$



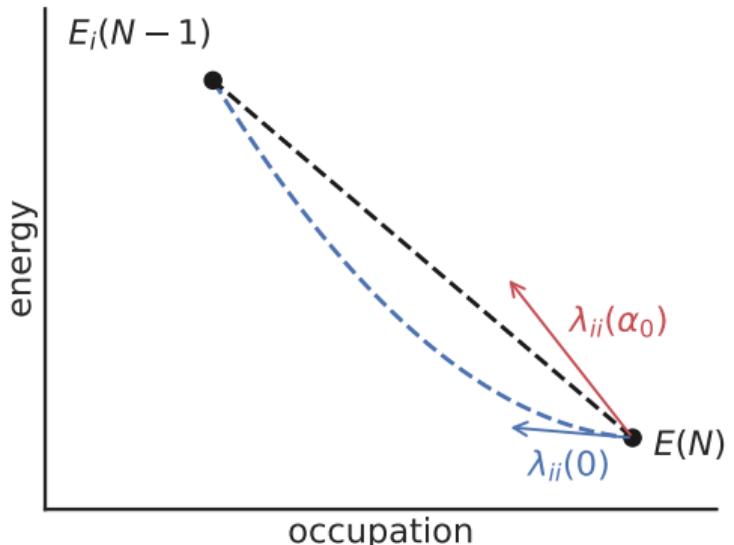
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$$\alpha_{n+1} = \alpha_n \frac{E_i(N-1) - E(N) - \lambda_{ii}(0)}{\lambda_{ii}(\alpha_n) - \lambda_{ii}(0)}$$

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↑
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total energy with electron removed from orbital i

total energy of neutral system

expectation value of \hat{H}^{DFT}

expectation value of $\hat{H}^{\text{Koopmans}}$

How can we avoid explicit charged defect calculations in a supercell?

¹ N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.

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(See Nicola Colonna's talk)

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N.B. even for the supercell, we can still reconstruct a band structure³

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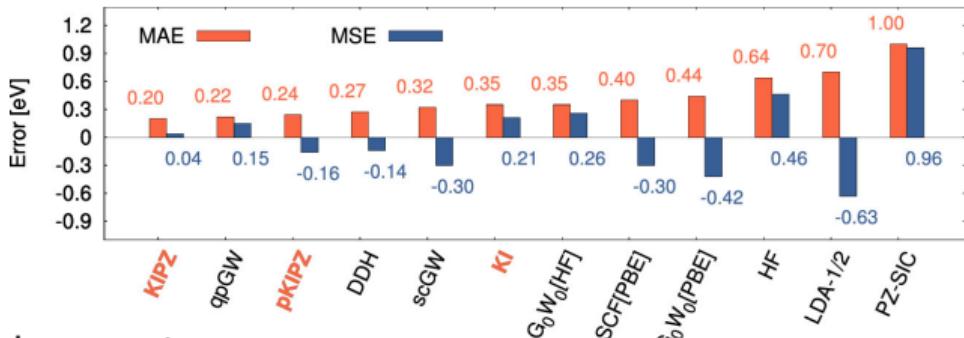
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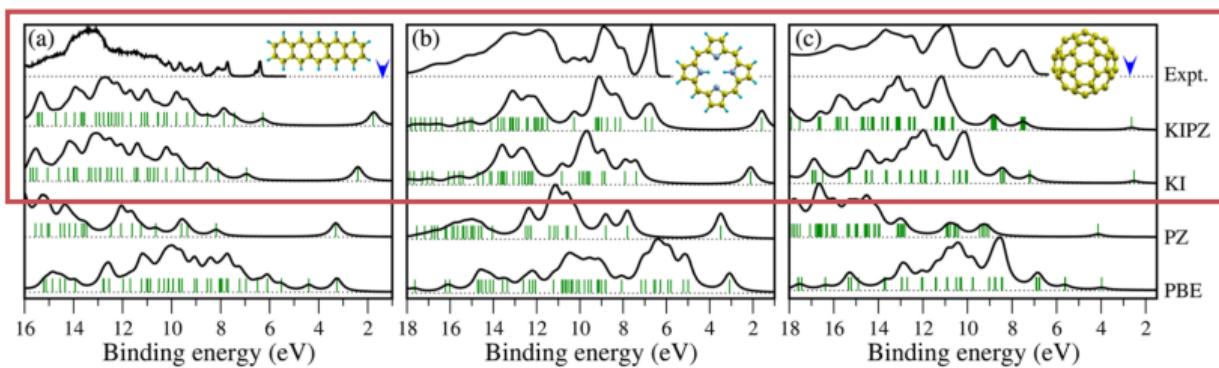
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- how are we calculating the screening parameters? (finite differences, DFPT, ML...)

Koopmans functionals: results for molecules

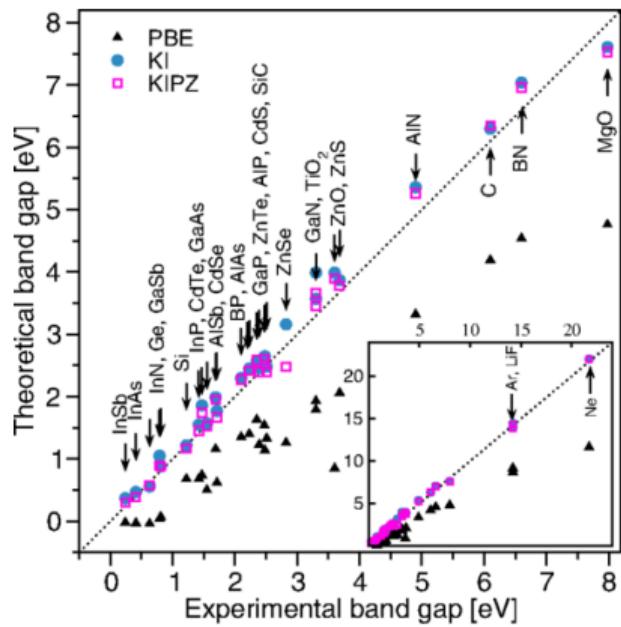
Ionisation potentials of 100 molecules cf. CCSD(T)



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	

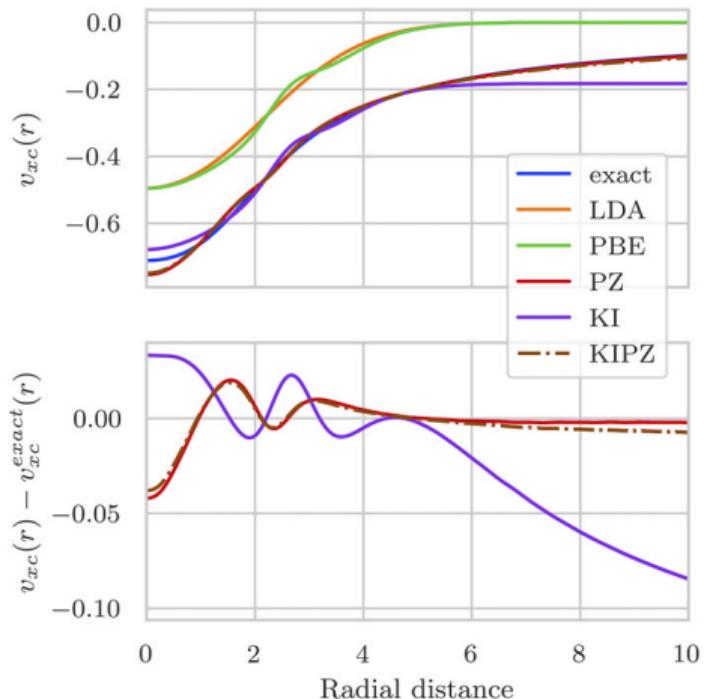
¹ M. Shishkin et al. *Phys. Rev. B* 75.23 (2007), 235102 for E_g and M. S. Hybertsen et al. *Phys. Rev. B* 34.8 (1986), 5390 for the transitions;

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

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

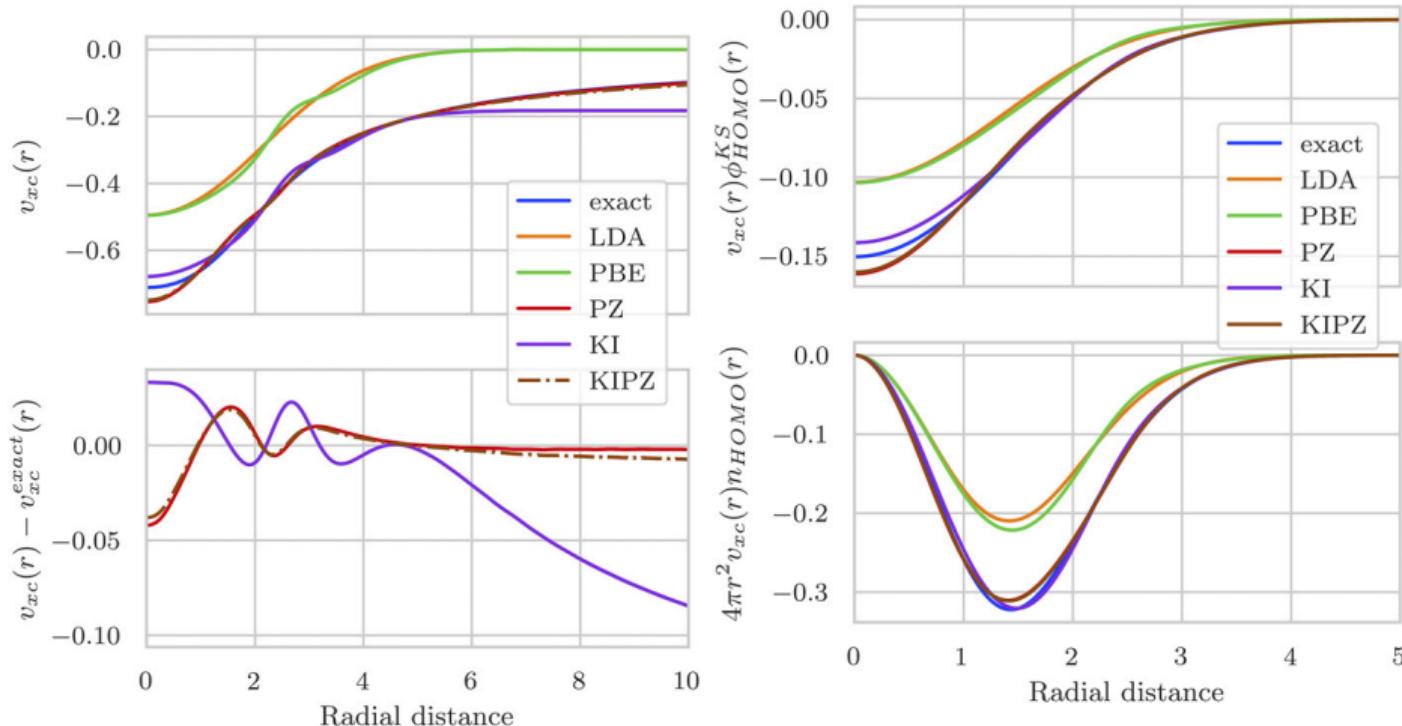
Koopmans functionals: results for toy systems

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



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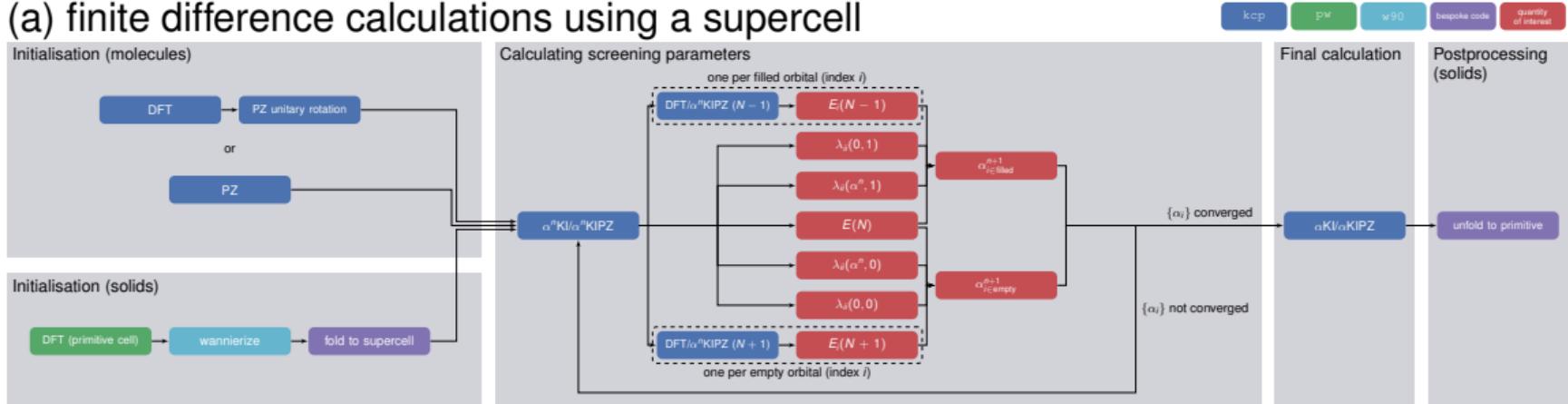
- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit
- can potentially break the crystal point group symmetry

The general workflow:

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

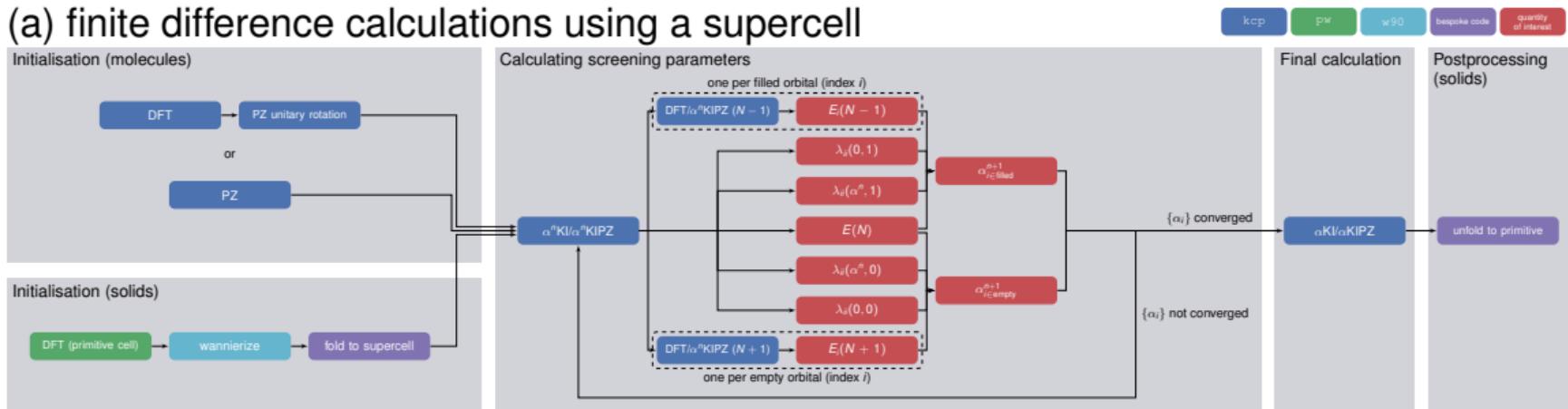
The workflows

(a) finite difference calculations using a supercell

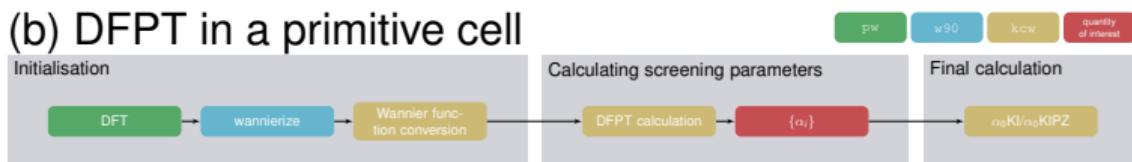


The workflows

(a) finite difference calculations using a supercell



(b) DFPT in a primitive cell



How do I run these calculations?

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- lots of different codes that need to handshake

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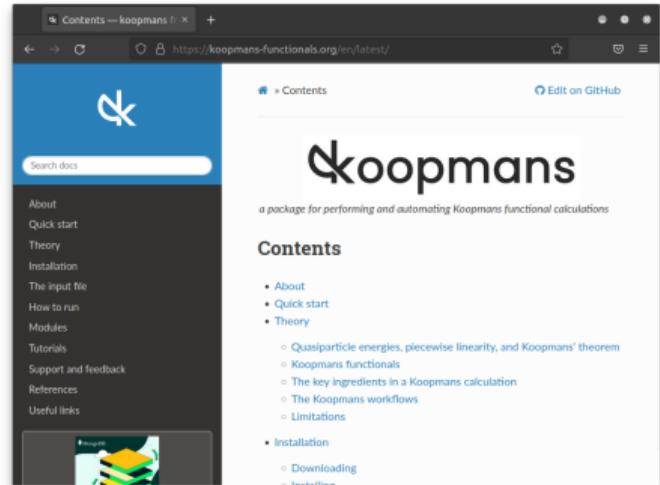
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- v1.0 released earlier this year¹
- implementations of Koopmans functionals
- automated workflows
 - start-to-finish Koopmans calculations
 - Wannierisation
 - dielectric tensor
 - ...
- built on top of ASE²
- under the hood, calls Quantum ESPRESSO
- 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()
```

Workflow

Workflow

atoms an ASE Atoms object

Workflow

atoms **an** ASE Atoms **object**
calculations **a list of** ASE **calculators**

Workflow

- `atoms` an ASE Atoms object
- `calculations` a list of ASE calculators
- `kpoints` a custom class containing *k*-point information

Workflow

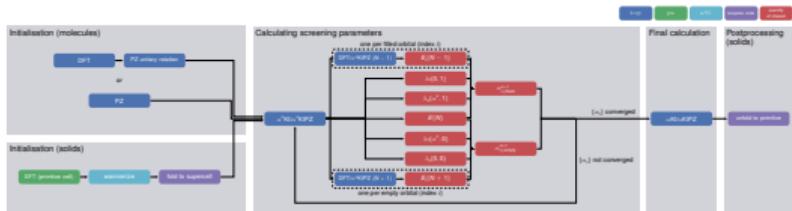
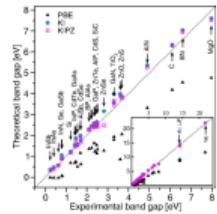
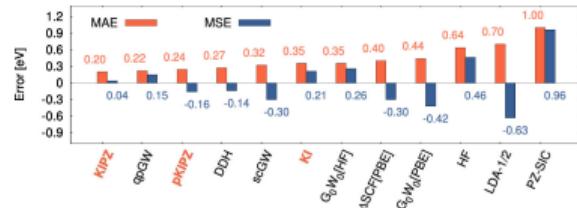
`atoms` an ASE Atoms object
`calculations` a list of ASE calculators
`kpoints` a custom class containing *k*-point information
`pseudopotentials` a dictionary of pseudopotentials

Workflow

`atoms` an ASE Atoms object
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We will see examples in the hands-on!

Take home messages



- Koopmans functionals are more complicated than a simple semi-local DFT calculation, because of...
 - orbital-density-dependence
 - screening parameters
 - Koopmans functionals are implemented in Quantum ESPRESSO
 - the complexity of the workflows are handled by the `koopmans` package

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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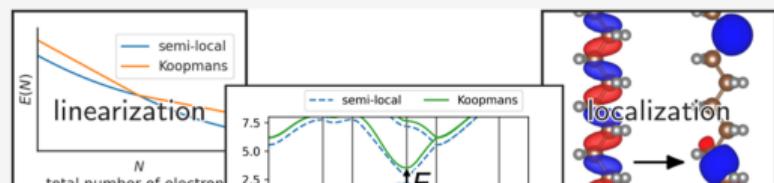
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Article Recommendations

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



Riccardo De Gennaro



Yannick Schubert



NATIONAL CENTRE OF COMPETENCE IN RESEARCH

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

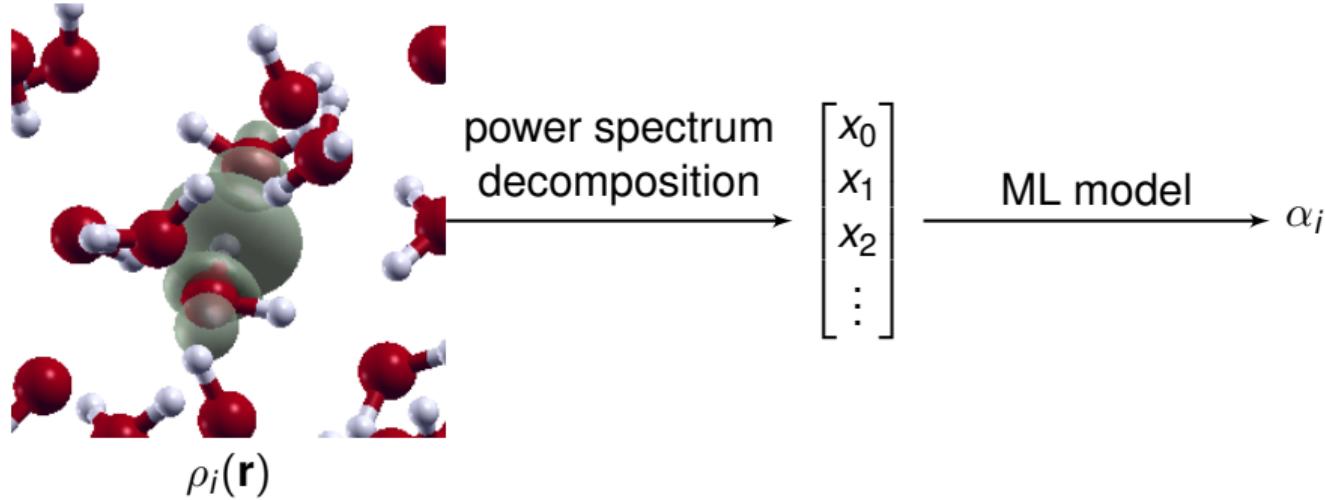
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

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

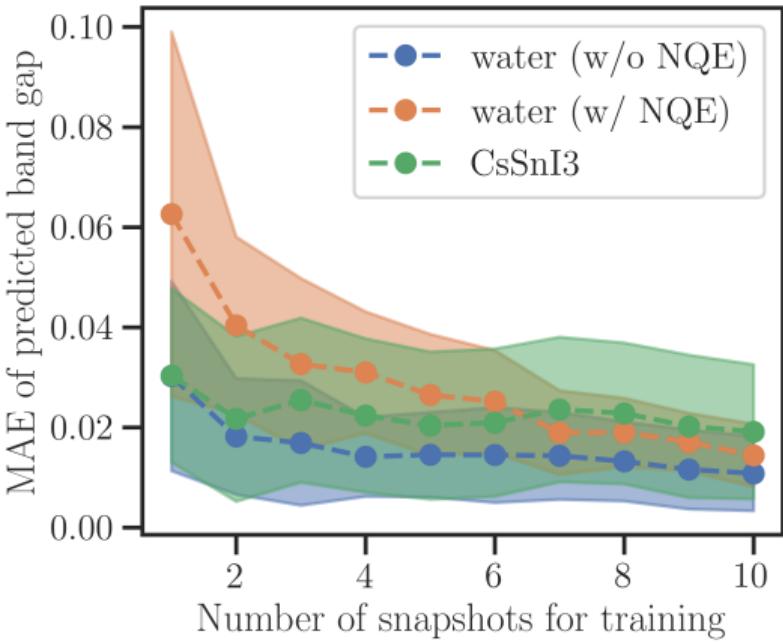
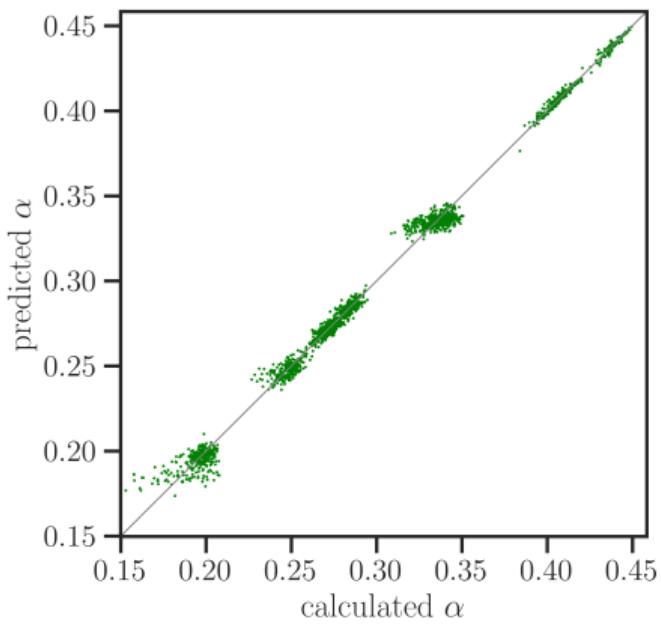
Learning the screening parameters



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

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

Learning the screening parameters



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

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 (refer back to Leeor's talk on Wednesday) L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021), e2104556118
- Ensemble DFT of Kronik and co-workers E. Kraisler et al. *Phys. Rev. Lett.* 110.12 (2013), 126403
- Koopmans-Wannier of Wang and co-workers J. Ma et al. *Sci. Rep.* 6.1 (2016), 24924
- Dielectric-dependent hybrid functionals of Galli and co-workers J. H. Skone et al. *Phys. Rev. B* 93.23 (2016), 235106
- LOSC functionals of Yang and co-workers C. Li et al. *Natl. Sci. Rev.* 5 (2018), 203