

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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Differences to semi-local functionals:

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- different flavours

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- different flavours
- orbital-density dependence

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Differences to semi-local functionals:

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- 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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- with a PZ correction → “KIPZ”

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

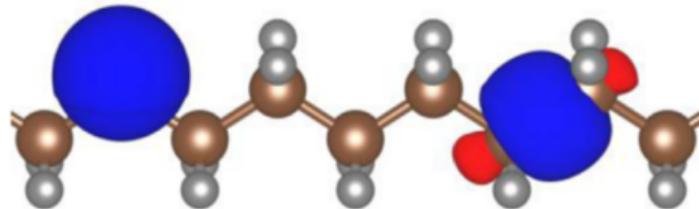
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(a) variational

Orbital-density-dependence

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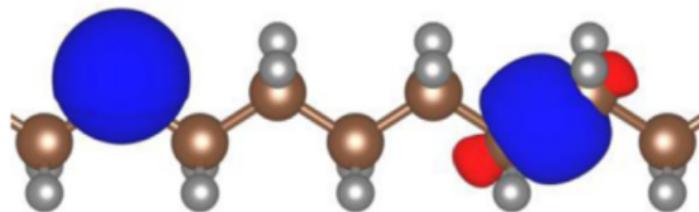
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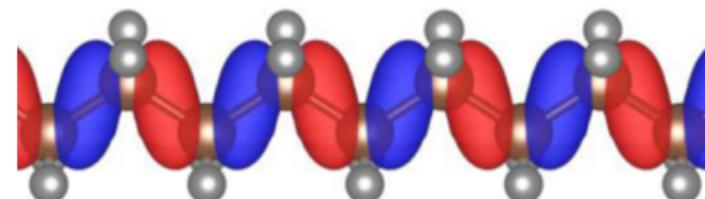
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Diagonalising at the minimum gives rise to diagonalising orbitals (delocalised/canonical)

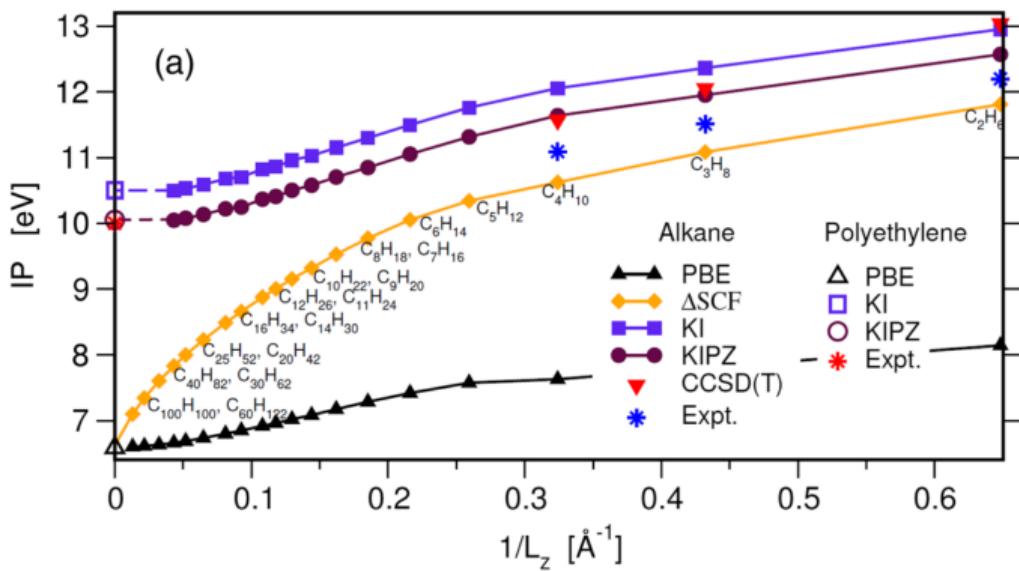


(a) variational

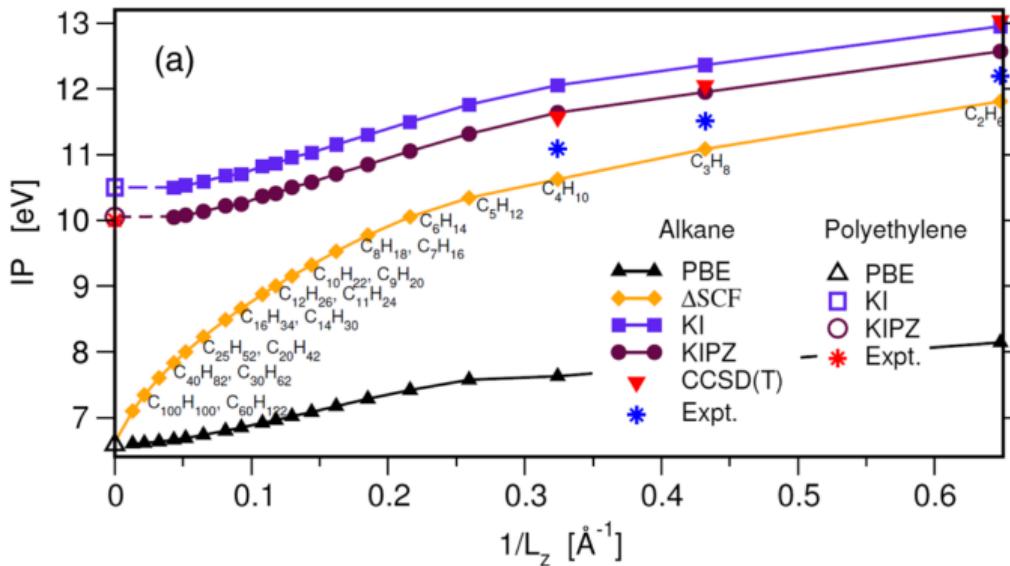


(b) canonical

Importance of localisation

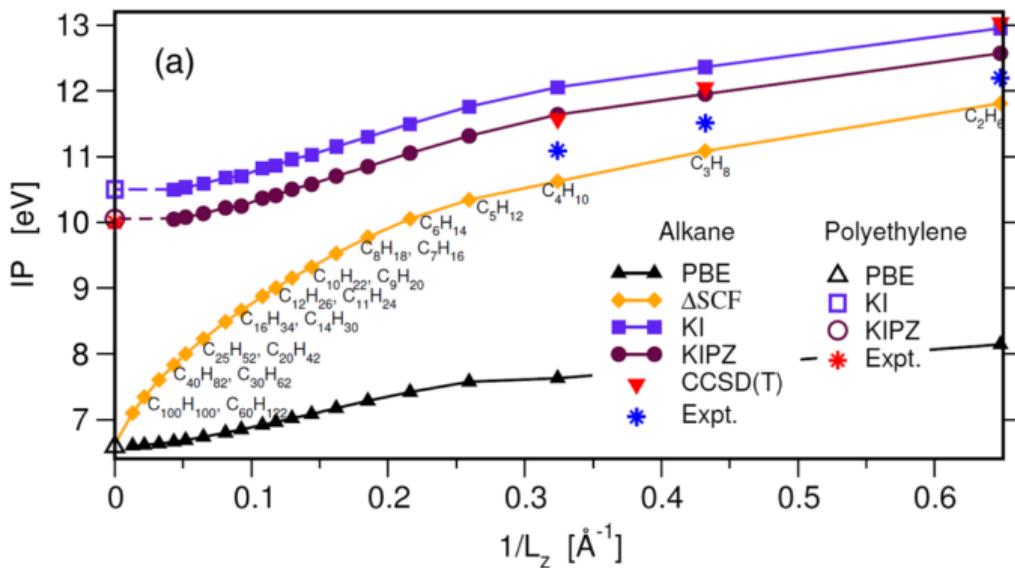


Importance of localisation



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

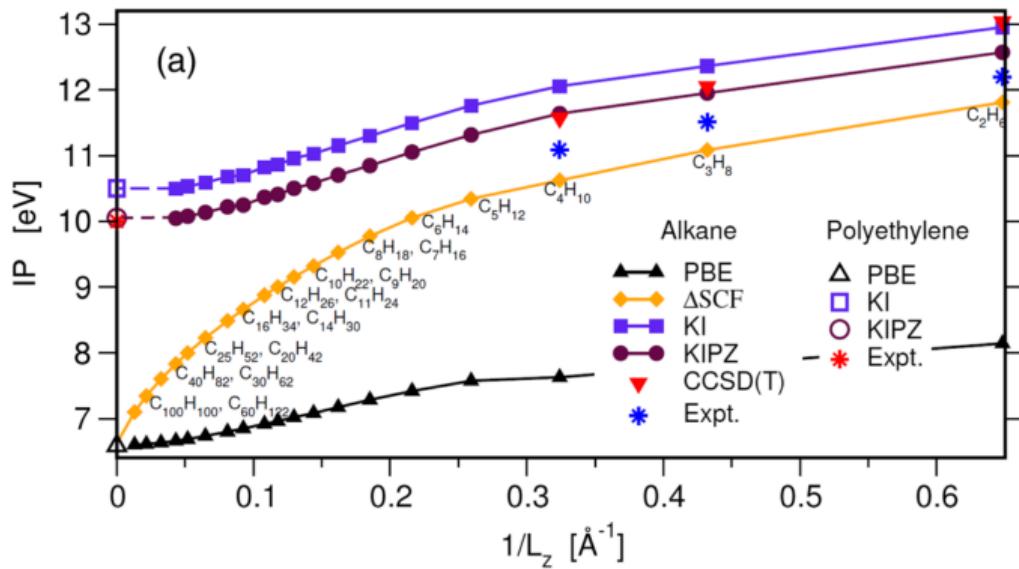
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Across all the cells $\Delta E = \frac{1}{\delta N} (E(N - \delta N) - E(N)) = -\frac{dE}{dN} = -\varepsilon_{HO}$

Importance of localisation



$$\lim_{n_i(r) \rightarrow 0} v_i^{\text{KI}} / \alpha_i = \lim_{n_i(r) \rightarrow 0} -E_H[n_i] + E_{xc}[\rho] - E_{xc}[\rho - n_i] - \int d\mathbf{r}' v_{xc}(\mathbf{r}', [\rho]) n_i(\mathbf{r}') = 0$$

Other features of orbital-density-dependence

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

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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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- 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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- Account for screening post-hoc:

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

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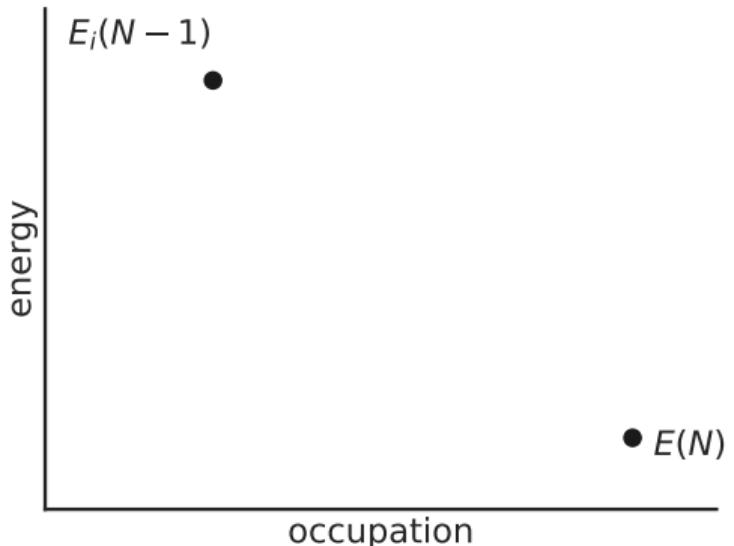
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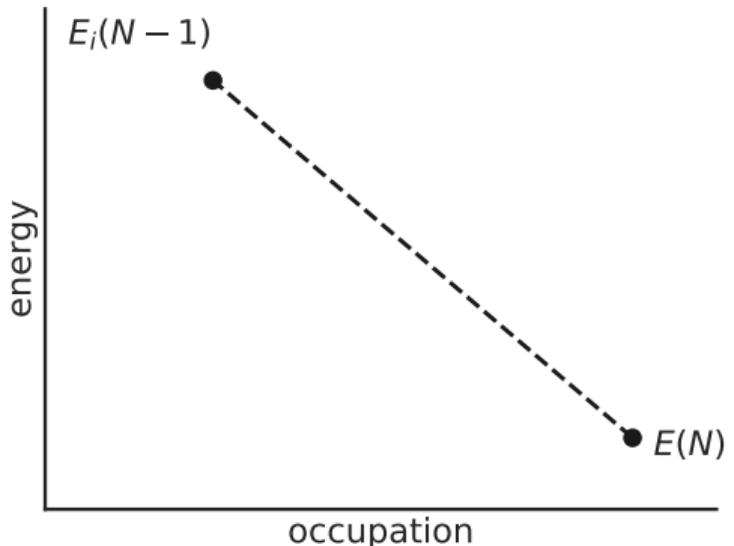
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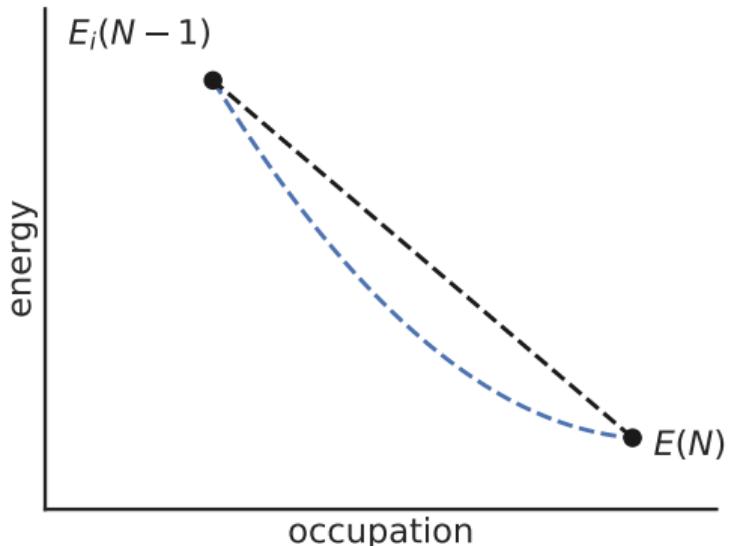
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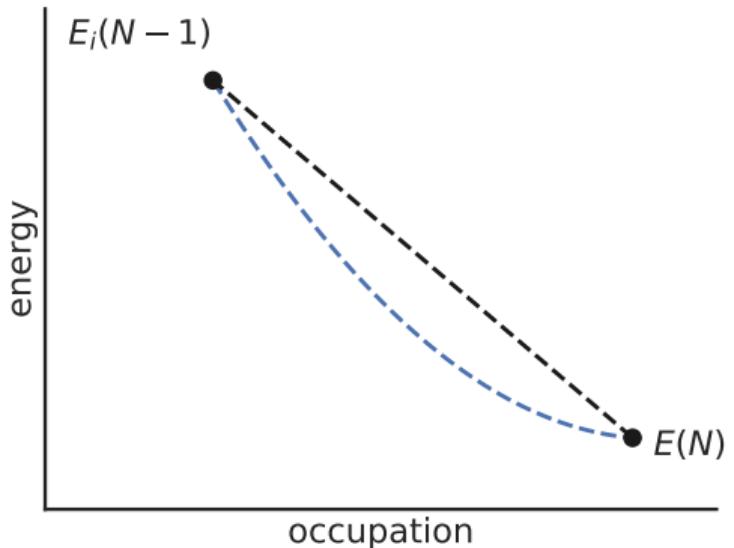
- How to choose an appropriate value for α_i ? Return to the original idea of Koopmans functionals:

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

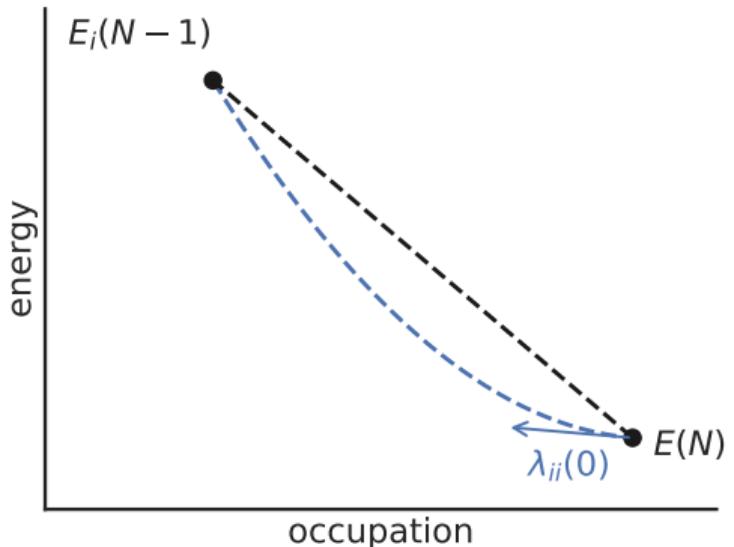




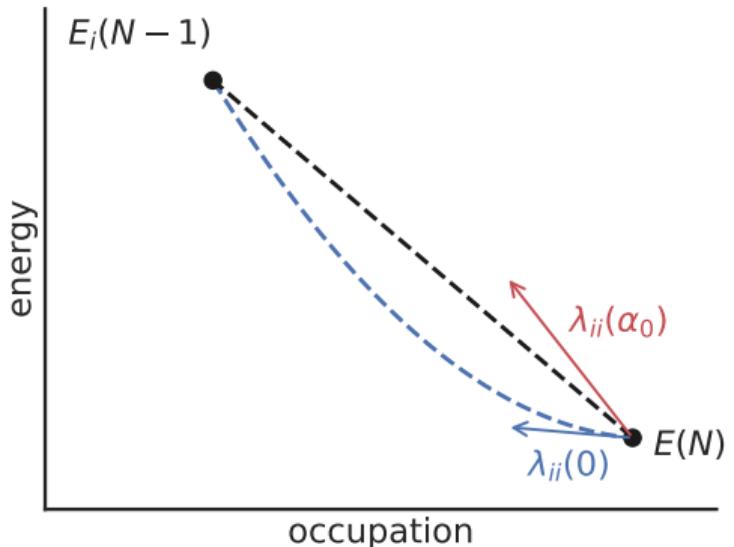




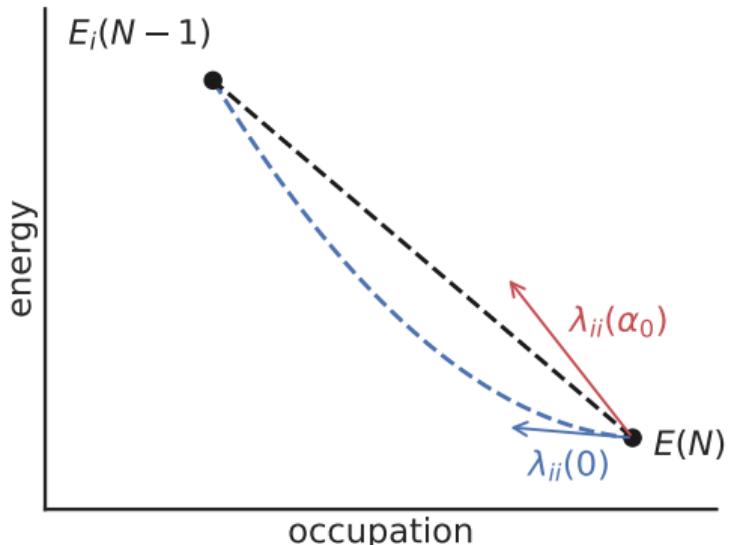
$$\lambda_{ii}(\alpha) \equiv \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}^{\text{Koopmans}} | \varphi_i \rangle = \frac{dE^{\text{Koopmans}}}{df_i} \Big|_{f_i=s}$$



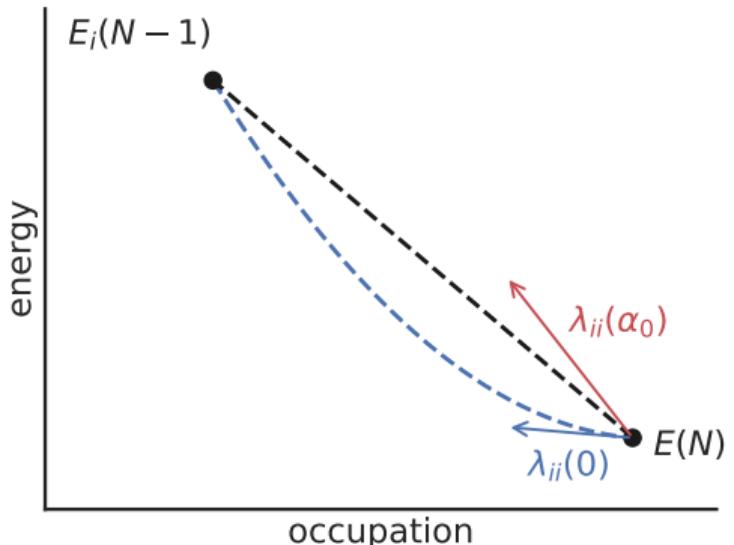
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$$\alpha_{n+1} = \alpha_n \frac{E_i(N-1) - E(N) - \lambda_{ii}(0)}{\lambda_{ii}(\alpha_n) - \lambda_{ii}(0)}$$

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total energy
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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}

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

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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Reformulate in terms of DFPT¹...

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... in reciprocal space²

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

(See Nicola Colonna's talk)

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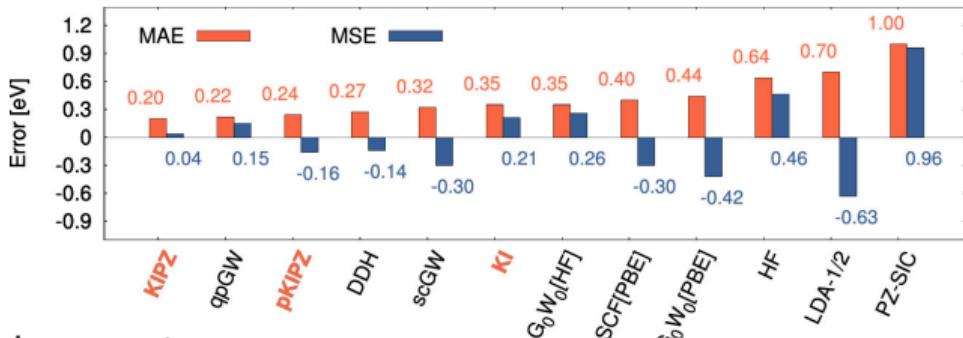
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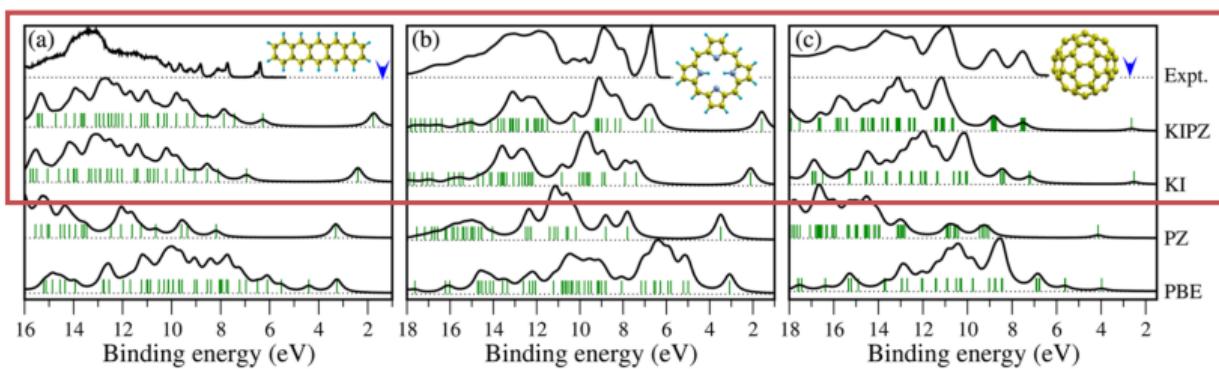
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- how are we calculating the screening parameters? (finite differences, DFPT, ML...)

Koopmans functionals: results for molecules

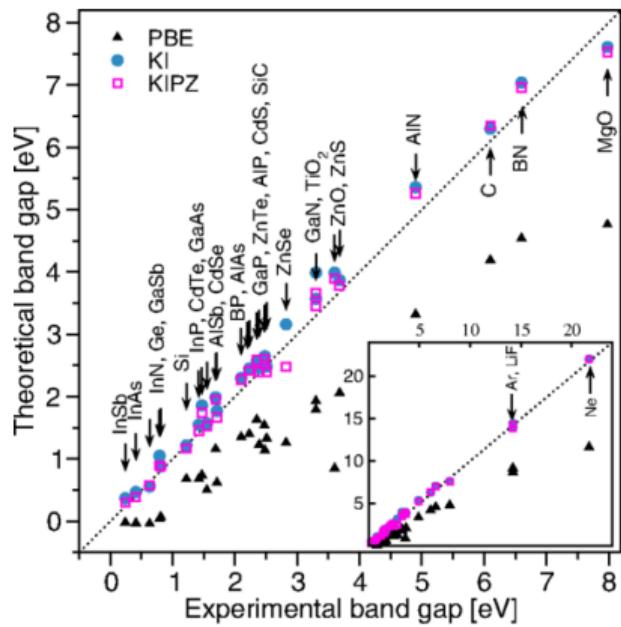
Ionisation potentials of 100 molecules cf. CCSD(T)



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	

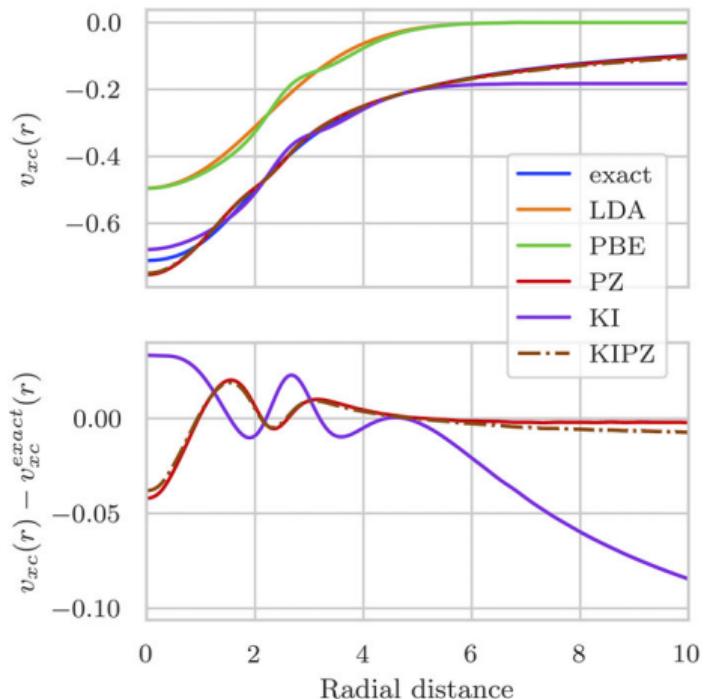
¹ M. Shishkin et al. *Phys. Rev. B* 75.23 (2007), 235102 for E_g and M. S. Hybertsen et al. *Phys. Rev. B* 34.8 (1986), 5390 for the transitions;

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

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

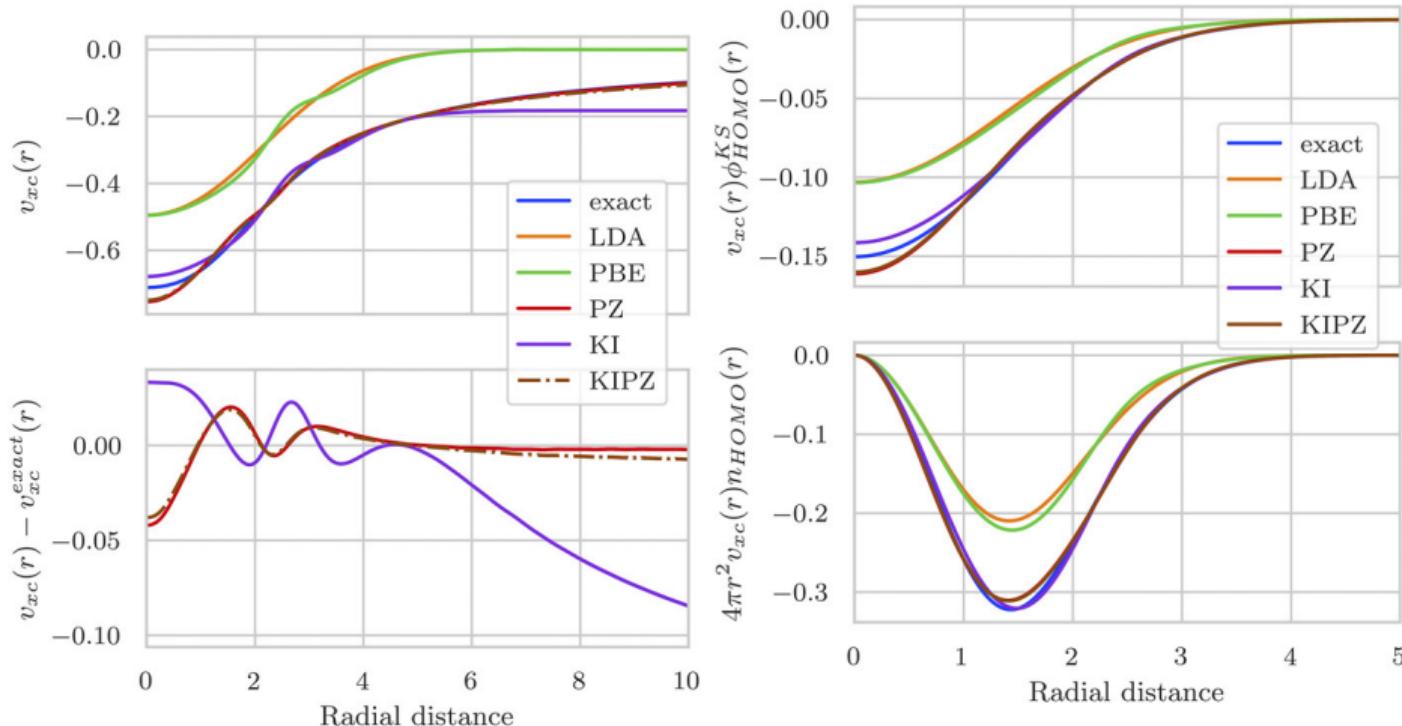
Koopmans functionals: results for toy systems

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



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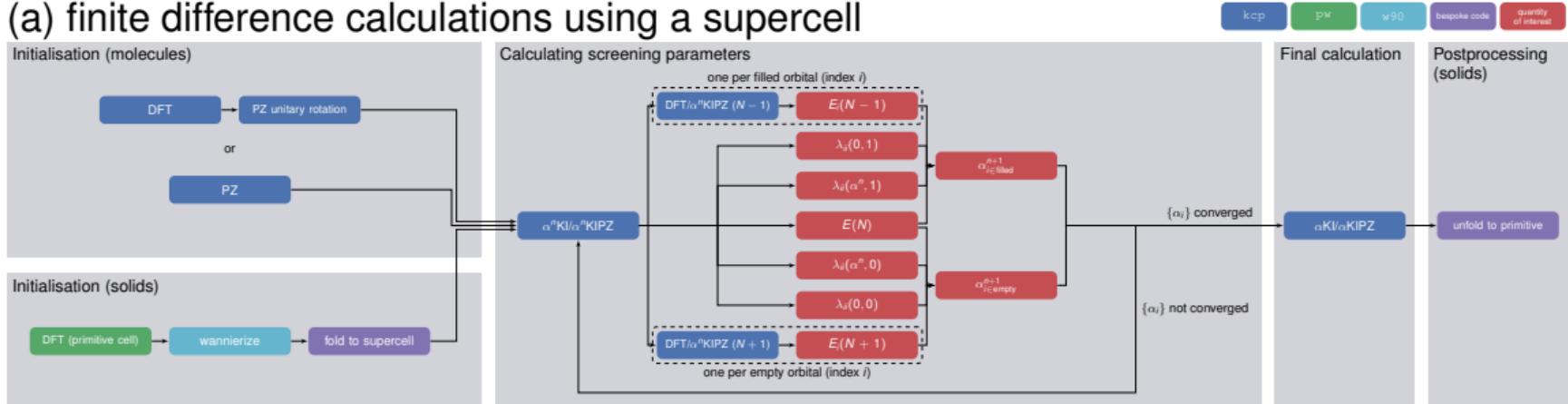
- will *not* solve H_2^+ !
- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit
- can potentially break the crystal point group symmetry

The general workflow:

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

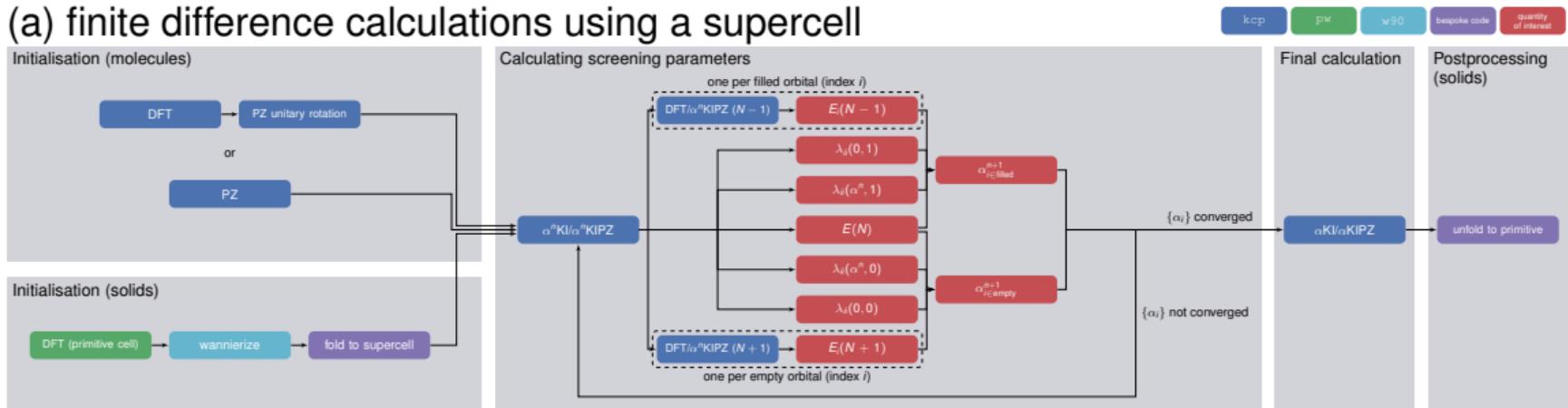
The workflows

(a) finite difference calculations using a supercell

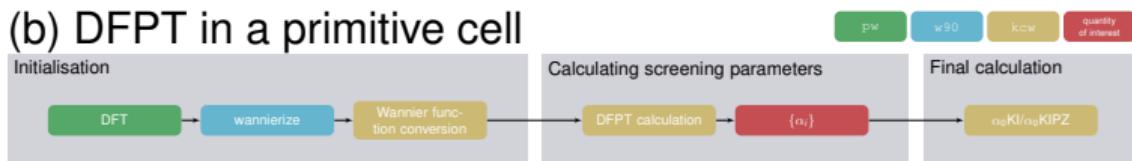


The workflows

(a) finite difference calculations using a supercell



(b) DFPT in a primitive cell



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- expert knowledge required

How do I run these calculations?

Complicated workflows mean that...

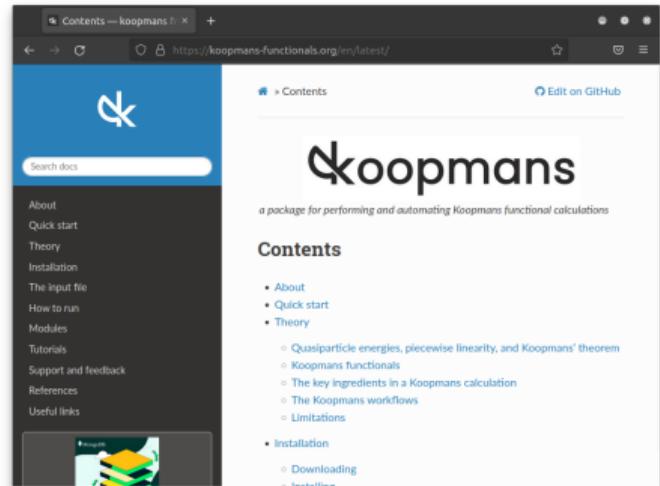
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

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

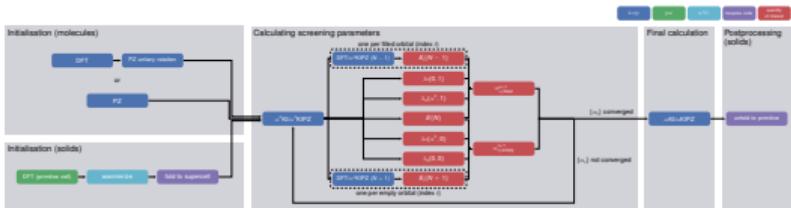
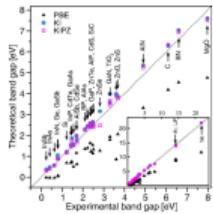
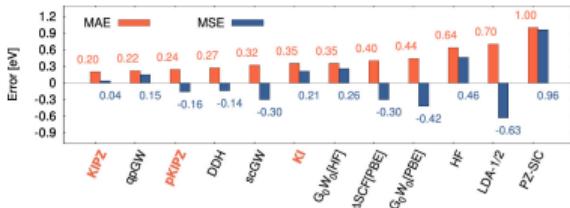
`atoms` an ASE Atoms object
`calculations` a list of ASE calculators
`kpoints` a custom class containing *k*-point information
`pseudopotentials` a dictionary of pseudopotentials

Workflow

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

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>



Read Online

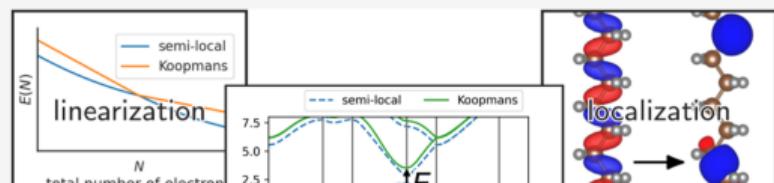
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Metrics & More

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



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

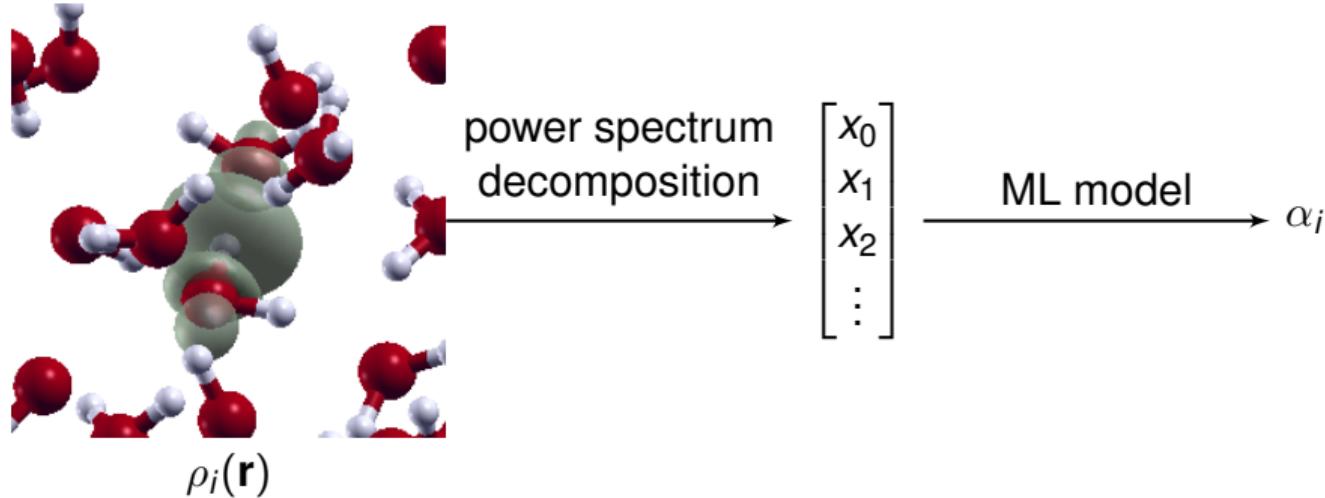
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

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

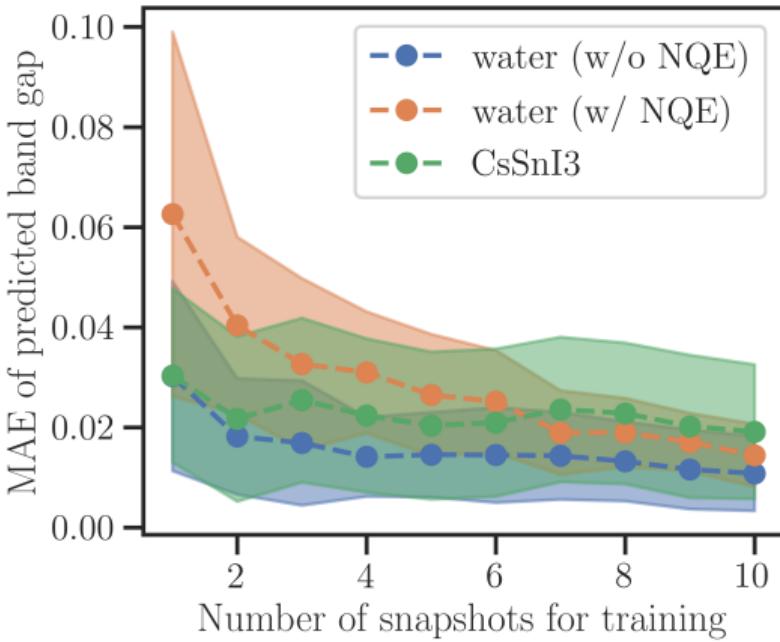
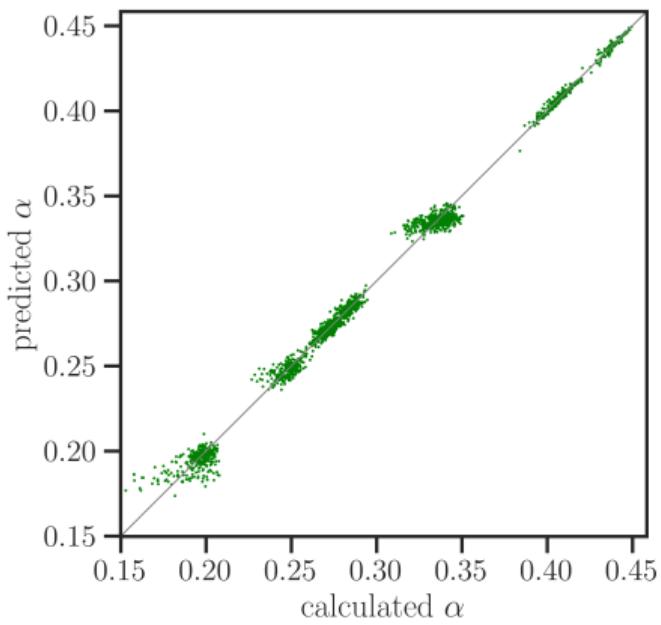
Learning the screening parameters



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

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

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