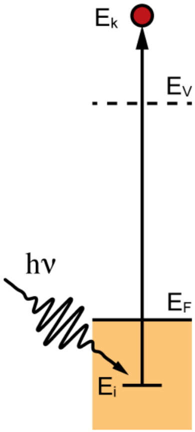
Koopmans functionals

accurately and efficiently predicting spectral properties with a functional formulation

Edward Linscott | EPFL | MARVEL junior seminar, Lausanne | 19 Oct 2023

The goal: charged excitations with a functional theory

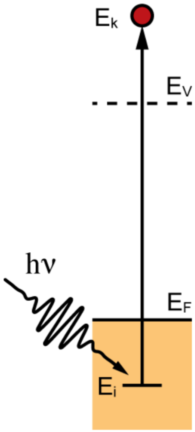


R. Costantini et al. "Exciton Dynamics in Molecular Heterojunctions". https://bib-pubdb1.desy.de/record/453801/. PhD thesis. Universita degli Studi di Trieste, 2020

The goal: charged excitations with a functional theory

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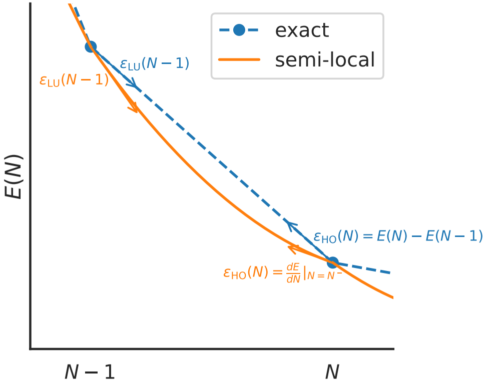
For DFT, this condition is *not* satisfied in general



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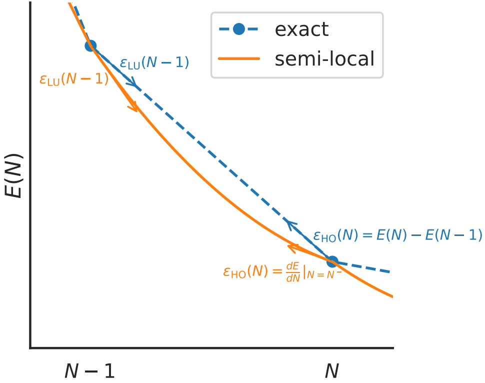
Core idea: for every orbital i their energy

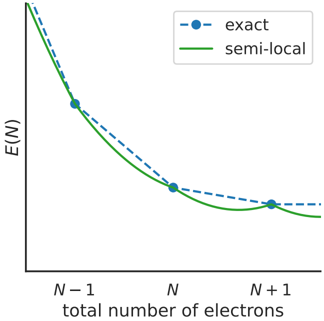
$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

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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Koopmans functionals: theory

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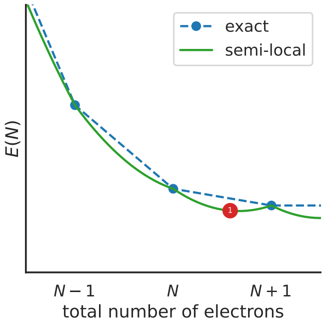

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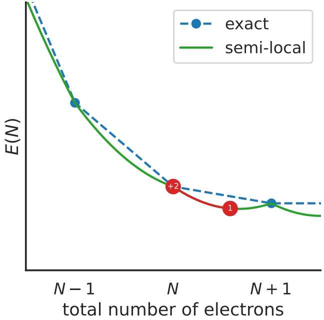

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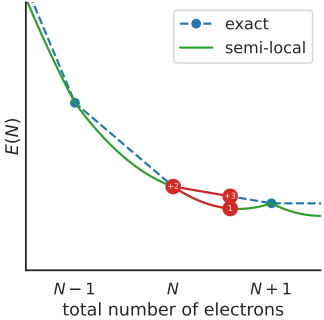

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- screening (calculated ab initio)

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Features:

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

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Koopmans functionals: theory

$$E_{\mathrm{KI}}[\rho, \{\rho_i\}, \{\alpha_i\}] = E_{\mathrm{DFT}}[\rho] + \sum_i \alpha_i \Big(E_{\mathrm{Hxc}}[\rho - \rho_i] - E_{\mathrm{Hxc}}[\rho] + f_i \left(E_{\mathrm{Hxc}}[\rho - \rho_i + n_i] - E_{\mathrm{Hxc}}[\rho - \rho_i] \right) \Big)$$

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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

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Consequences of ODD:

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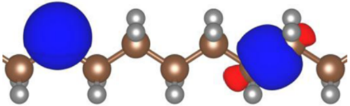
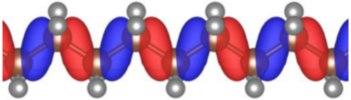
- variational (localized, minimizing) vs canonical (delocalized, diagonalizing) orbitals



(a) variational



(b) canonical

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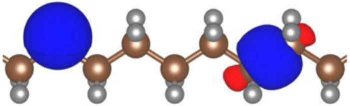

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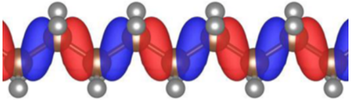

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- Practically we can often use MLWFs

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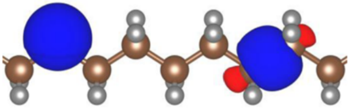

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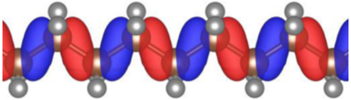


(b) canonical

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

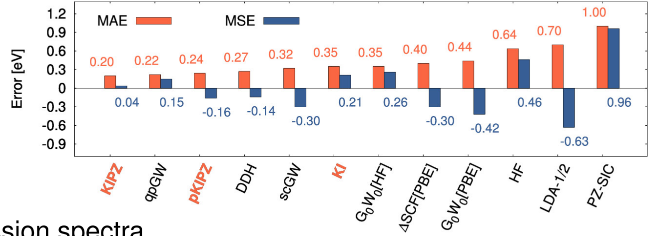
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051

Resonance with other efforts:

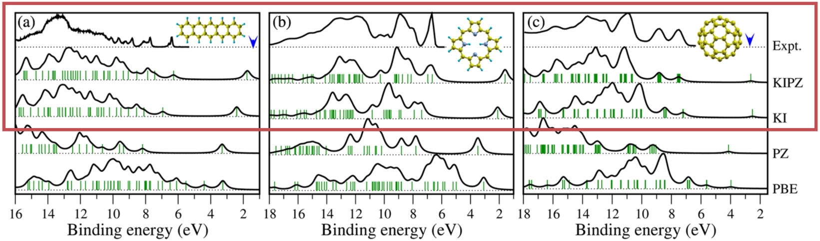
- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021),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

Ionization potentials for the GW100 set cf. CCSD(T)

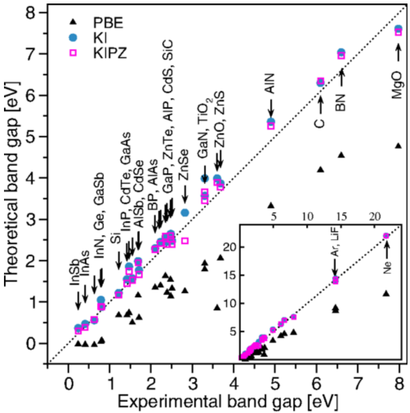


Ultraviolet photoemission spectra



N. Colonna et al. *J. Chem. Theory Comput.* 14.5 (2018), 2549; N. L. Nguyen et al. *Phys. Rev. Lett.* 114.16 (2015), 166405

Koopmans functionals: results for solids



Mean absolute error (eV) across prototypical semiconductors and insulators

	PBE	G_0W_0	**KI**	**KIPZ**	QSG$\tilde{W}$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

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

Koopmans functionals: results for solids

	PBE	G_0W_0[1]	sc$G\tilde{W}$[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 $\pm$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 $\pm$0.4
$L_{1v} \rightarrow \Gamma_{25'v}$	6.98	7.18		6.98	7.04	6.8 $\pm$0.2
$L_{3'v} \rightarrow \Gamma_{25'v}$	1.19	1.27		1.19		1.2 $\pm$0.2
$\Gamma_{25'v} \rightarrow \Gamma_{15c}$	2.48	3.29		3.17	3.20	3.35$\pm$0.01
$\Gamma_{25'v} \rightarrow \Gamma_{2'c}$	3.28	4.02		3.95	3.95	4.15$\pm$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$\pm$0.06
$\Gamma_{25'v} \rightarrow L_{3c}$	3.24	4.18		3.91	3.94	3.9 $\pm$0.1
MSE	0.35	0.02		0.01	0.03	
MAE	0.44	0.21		0.14	0.17	

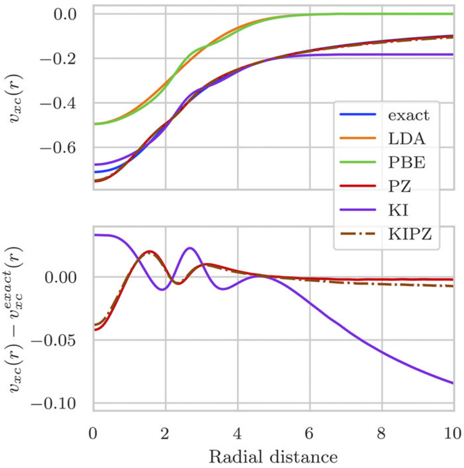
[1] M. Shishkin et al. *Phys. Rev. B* 75.23 (2007), 235102 for E_g and M. S. Hybertsen et al. *Phys. Rev. B* 34.8 (1986), 5390 for the transitions;

[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

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



Y. Schubert et al. *J. Chem. Phys.* 158.14 (2023), 144113

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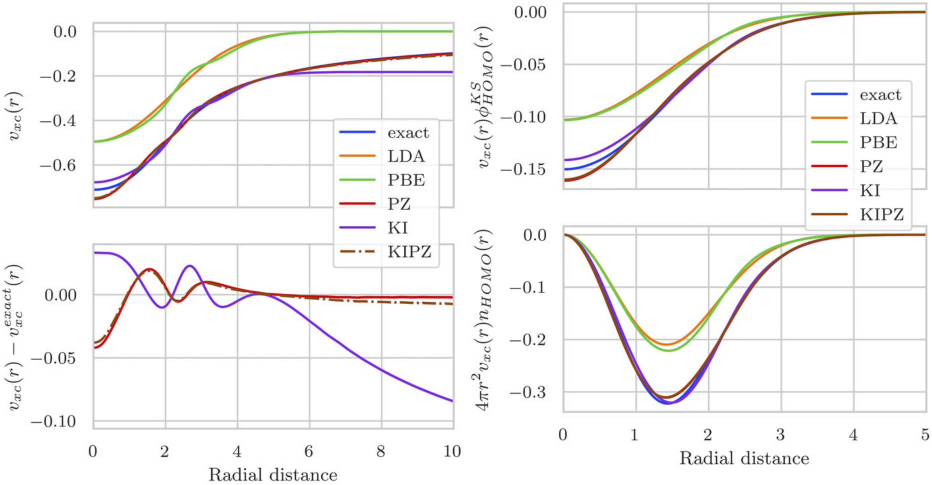

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N. Q. Su et al. *J. Phys. Chem. Lett.* 11.4 (2020), 1528

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Koopmans functionals: caveats

- restricted to systems with a non-zero band gap
- empty state localization in the bulk limit

N. Q. Su et al. *J. Phys. Chem. Lett.* 11.4 (2020), 1528

Koopmans functionals: caveats

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

N. Q. Su et al. *J. Phys. Chem. Lett.* 11.4 (2020), 1528

The general workflow:

- 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 improvements: screening via DFPT

Original formulation requires explicit charged defect calculations in a supercell

$$\alpha_i^{n+1} = \alpha_i^n \frac{\Delta E_i^{\text{Koopmans}} - \lambda_{ii}(0,1)}{\lambda_{ii}(\alpha_i^n,1) - \lambda_{ii}(0,1)}; \qquad \Delta E_i^{\text{Koopmans}} = E^{\text{Koopmans}}(N) - E_i^{\text{Koopmans}}(N-1)$$

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[2] N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435.

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Now reformulated in terms of DFPT[1]...

$$\alpha_i = 1 + \frac{\langle v_{\text{pert}}^i | \Delta^i n \rangle}{\langle n_i | v_{\text{pert}}^i \rangle}.$$

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Now reformulated in terms of DFPT[1]...

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... in reciprocal space[2]

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

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[1] N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.
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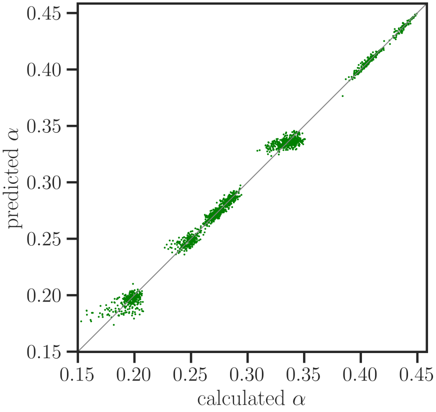
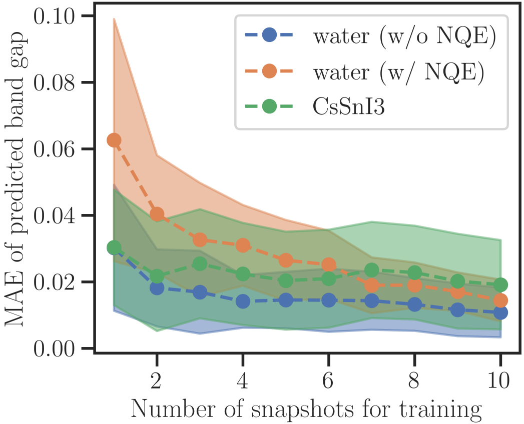
Recent improvements: screening via ML





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

Recent improvements: automated workflows

We have complicated workflows, with either...

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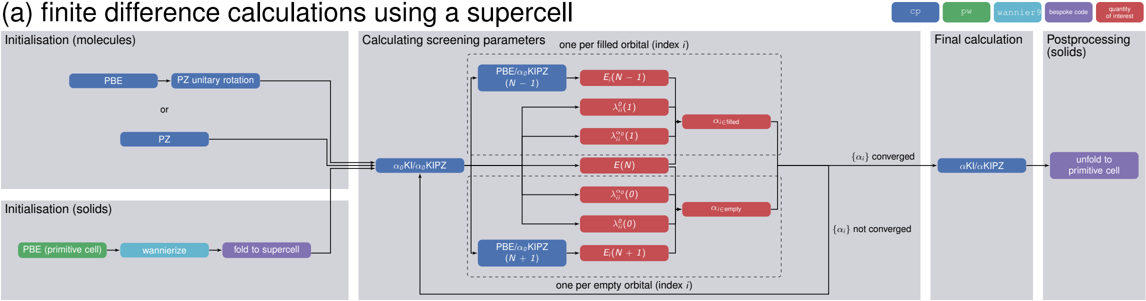
(a) finite difference calculations using a supercell



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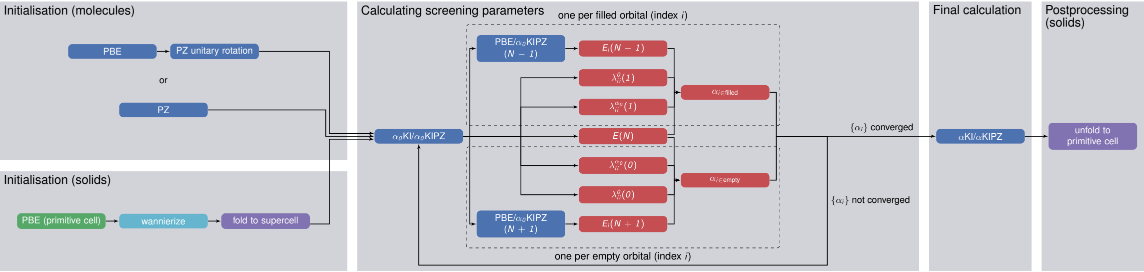
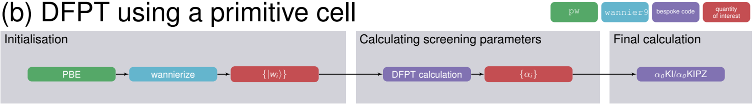


(b) DFPT using a primitive cell



E. B. Linscott et al. *J. Chem. Theory Comput.* (2023)

Recent improvements: automated workflows

Complicated workflows mean that...

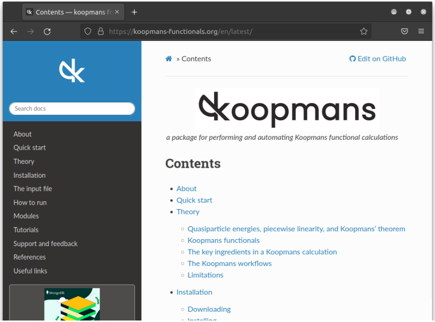
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- v1.0 released earlier this year[1]
- implementations of Koopmans functionals within Quantum ESPRESSO
- automated workflows
  - start-to-finish Koopmans calculations
  - Wannierization
  - dielectric tensor
  - convergence tests
  - ...
- built on top of ASE[2]
- does not require expert knowledge

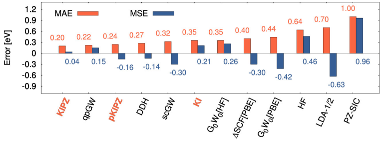
koopmans-functionals.org

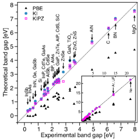


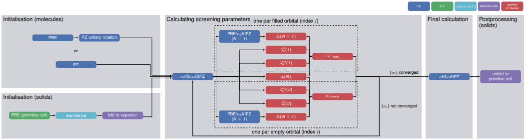
[1] E. B. Linscott et al. *J. Chem. Theory Comput.* (2023)

[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

JCTC Journal of Chemical Theory and Computation

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koopmans: An Open-Source Package for Accurately and Efficiently Predicting Spectral Properties with Koopmans Functionals

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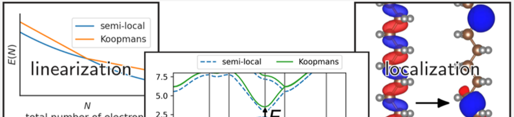
ABSTRACT: Over the past decade we have developed Koopmans functionals, a computationally efficient approach for predicting spectral properties with an orbital-density-dependent functional framework. These functionals impose a generalized piecewise linearity condition to the entire electronic manifold, ensuring that



Acknowledgements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Nicola Colonna


Riccardo De Gennaro


Yannick Schubert

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MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

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

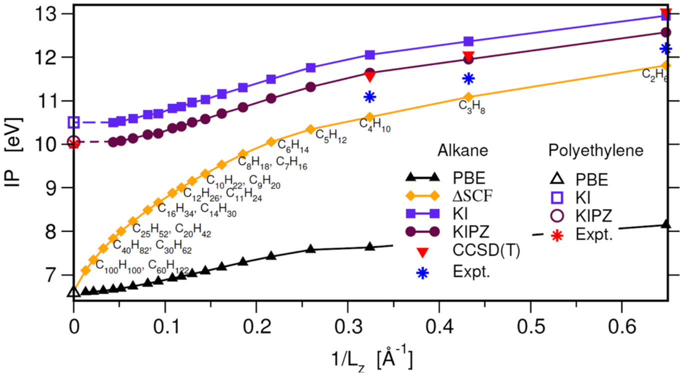
Recordings of lectures and tutorials can be found on the Materials Cloud YouTube channel

Masters projects available (search on `sirop.org`)

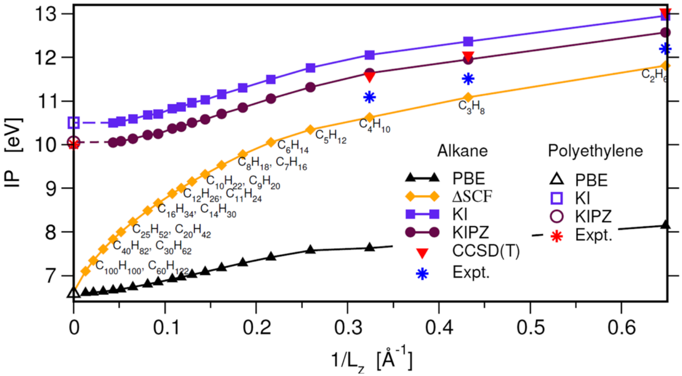
Follow @ed_linscott for updates | Slides available at github/elinscott

SPARE SLIDES

Koopmans functionals: the bulk limit



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



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

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

Koopmans functionals: the bulk limit

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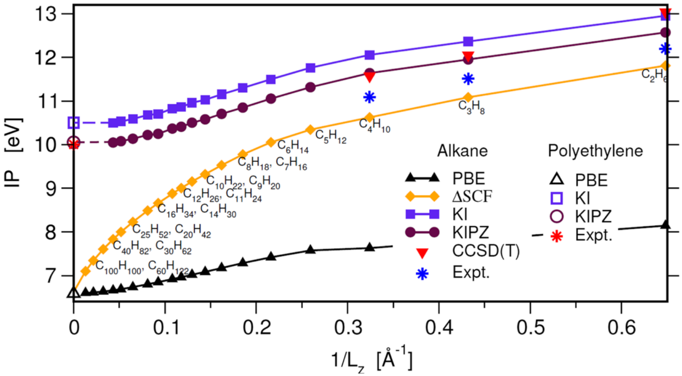
EPFL



In the bulk limit for one cell $\Delta E_{\text{one cell}} = E(N - \delta N) - E(N)$
Across all the cells $\Delta E_{\text{all cells}} = \frac{1}{\delta N}\left(E(N - \delta N) - E(N)\right) = -\frac{dE}{dN} = -\varepsilon_{\text{HO}}$

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

Koopmans functionals: off-diagonal occupancies

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Recap from earlier

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

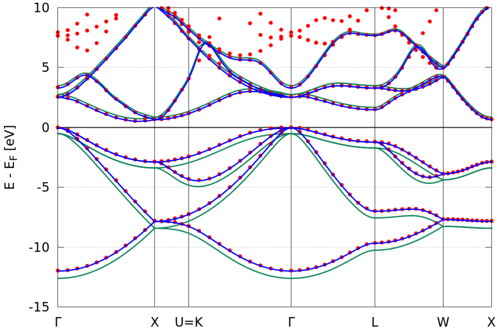
$$\varepsilon_i^{\text{Koopmans}} = \langle\varphi_i|H|\varphi_i\rangle = \partial E_{\text{Koopmans}}/\partial f_i$$

are...

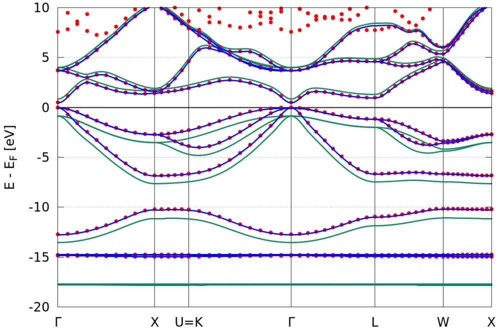
- independent of the corresponding occupancies f_i
- equal to the corresponding total energy difference $E_i(N-1) - E(N)$

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

Koopmans functionals: results for solids



(a) Si, KIPZ



(b) GaAs, KI

		PBE	QSG$\tilde{W}$	**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

R. De Gennaro et al. *Phys. Rev. B* 106.3 (2022), 035106

Koopmans functionals: results for solids

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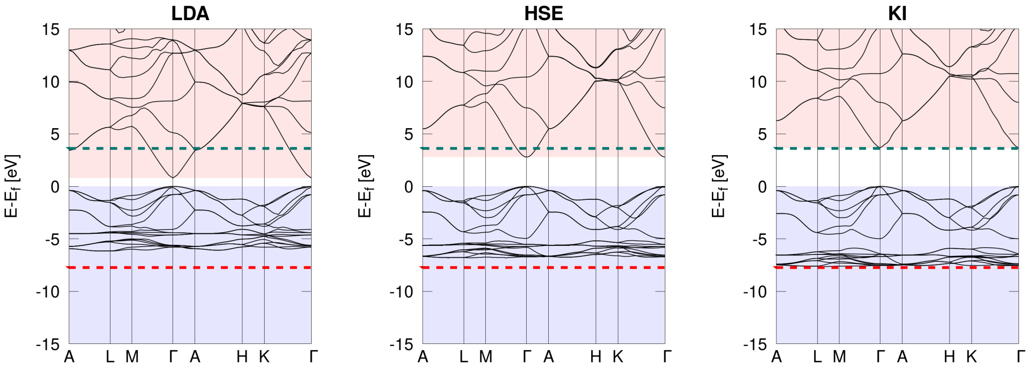

ZnO	LDA	HSE	GW_0	$scG\tilde{W}$	**KI**	exp
E_{gap} (eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle \varepsilon_d \rangle$ (eV)	−5.1	−6.1	−6.4	−6.7	−6.9	-7.5/-8.0

N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435

Recent improvements: easier Wannierization

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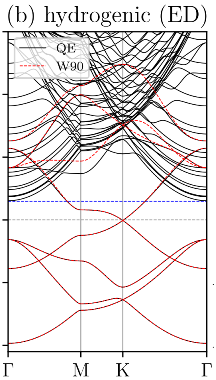

J. Qiao et al. *Projectability Disentanglement for Accurate and Automated Electronic-Structure Hamiltonians.* `http://arxiv.org/abs/2303.07877`. 2023

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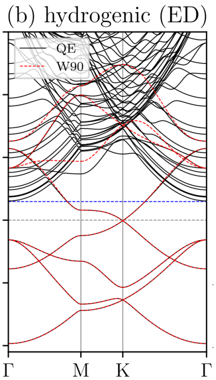

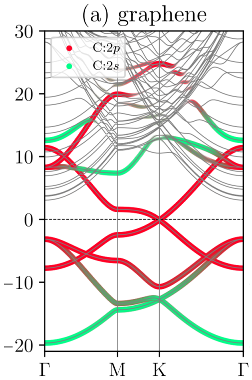

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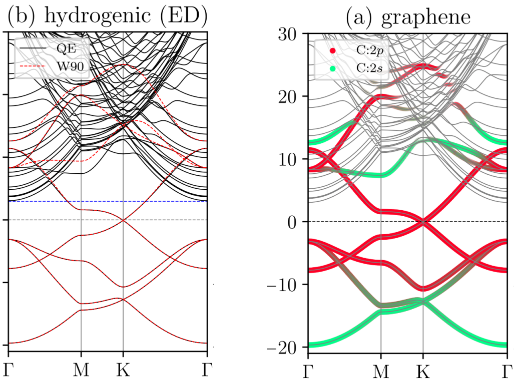

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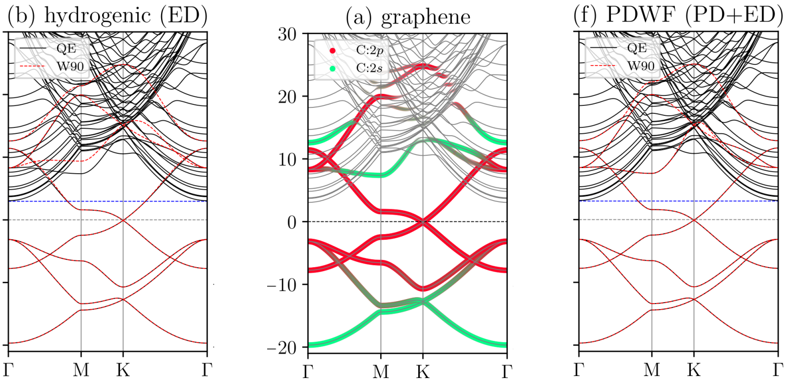

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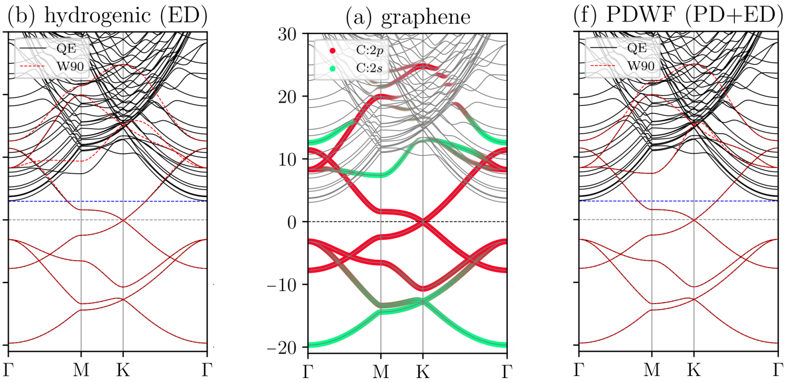

Demonstrated on >20,000 materials → black-box Wannierization!

J. Qiao et al. *Projectability Disentanglement for Accurate and Automated Electronic-Structure Hamiltonians.* `http://arxiv.org/abs/2303.07877`. 2023

Recent improvements: easier Wannierization

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

J. Qiao et al. *Automated Mixing of Maximally Localized Wannier Functions into Target Manifolds*. `http://arxiv.org/abs/2306.00678`. 2023

Recent improvements: easier Wannierization

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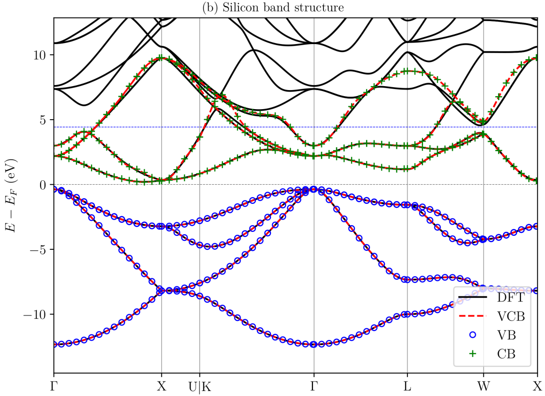
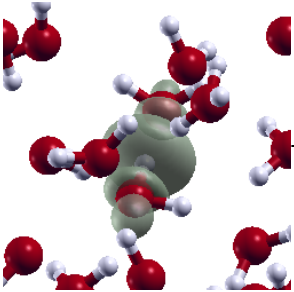
Separation of target manifolds via parallel transport to obtain separate occupied and empty manifolds



J. Qiao et al. *Automated Mixing of Maximally Localized Wannier Functions into Target Manifolds.* `http://arxiv.org/abs/2306.00678`. 2023

Accelerating improvements: screening via ML



$\rho_i(\mathbf{r})$

$$\rho_i(\mathbf{r}) \xrightarrow{\text{power spectrum decomposition}} \begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix} \xrightarrow{\text{ML model}} \alpha_i$$

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

$$p^i_{n_1 n_2 l, k_1 k_2} = \pi \sqrt{\frac{8}{2l+1}} \sum_m c^{i*}_{n_1 lm, k_1} c^i_{n_2 lm, k_2}$$

Y. Schubert. “Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations”. MA thesis. ETH Zürich, 2022

koopmans: the input file

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```
{
  "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

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```python
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()
```