



PSI

Center for Scientific Computing,
Theory and Data

Koopmans functionals

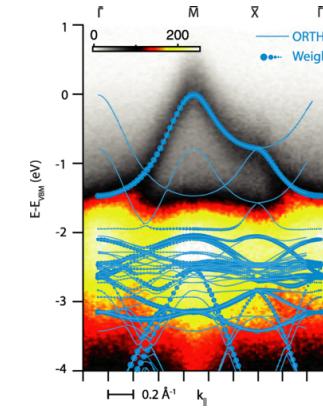
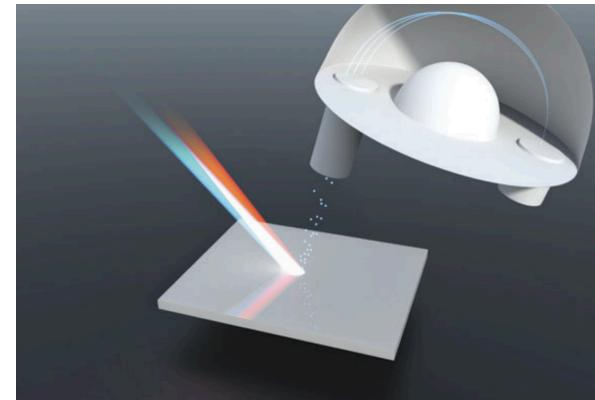
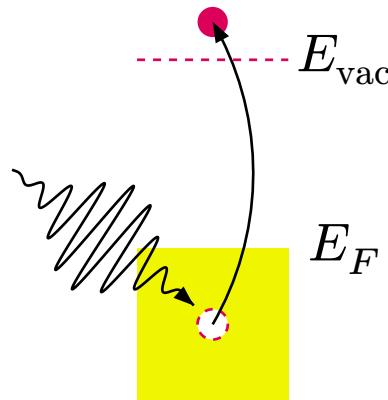
How satisfying piecewise linearity can yield reliable band structures

Edward Linscott

Psi-k, 27 August 2025

Predicting spectral properties

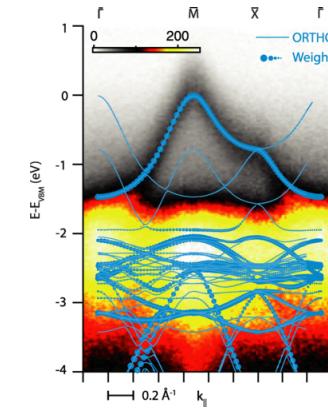
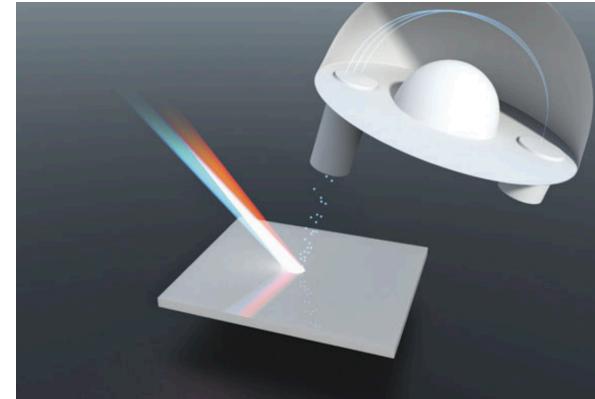
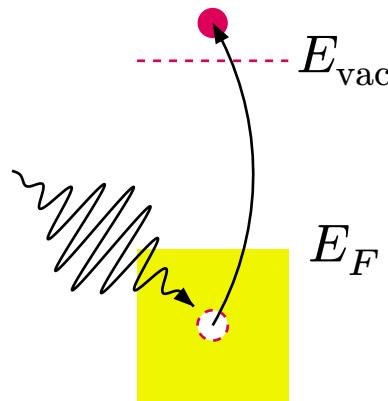
Spectral properties are fundamental to understanding materials...



¹A. de la Torre *et al.* *Rev. Mod. Phys.* **93**, 41002 (2021), M. Puppin *et al.* *Phys. Rev. Lett.* **124**, 206402 (2020)

Predicting spectral properties

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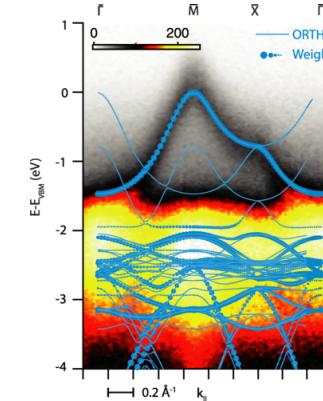
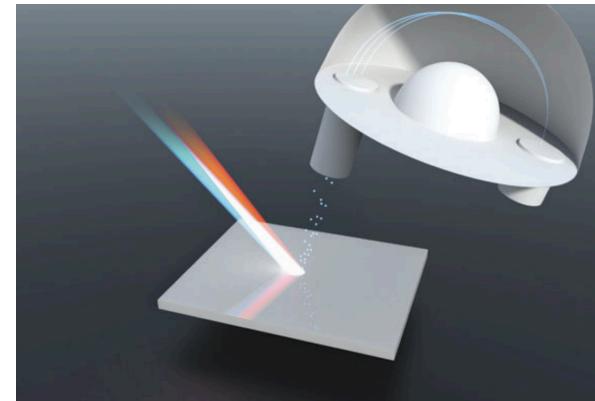
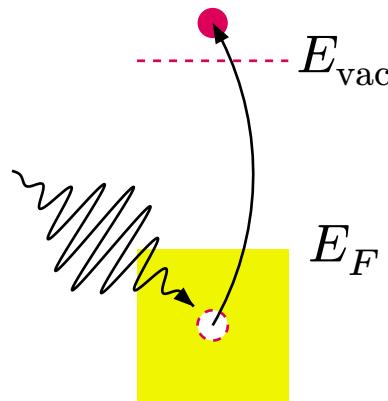


... but how can we routinely compute them?

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Predicting spectral properties

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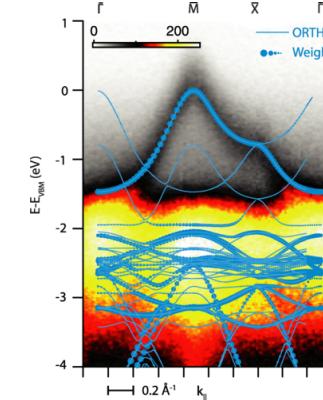
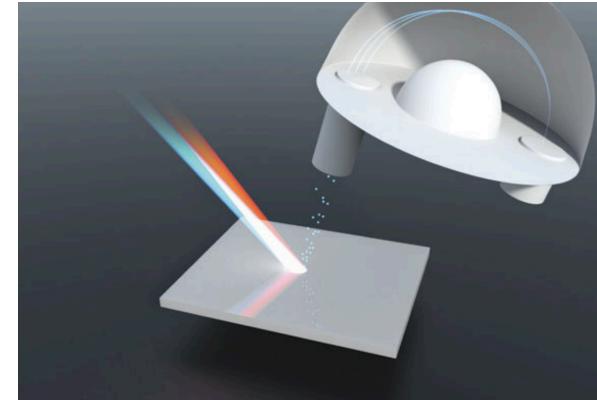
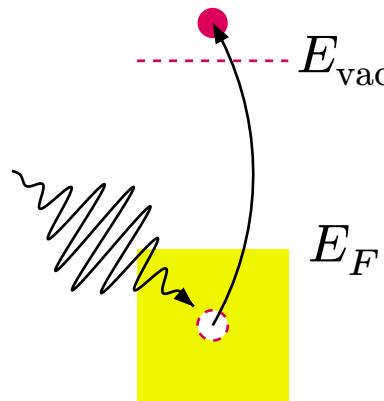
... but how can we routinely compute them?

- GW: accurate, expensive, often ill-behaved, diagrammatic
- DFT: plagued by intrinsic errors

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Predicting spectral properties

Spectral properties are fundamental to understanding materials...



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 Koopmans functionals: overcome limitations of DFT → a functional that can accurately predict single-particle excitations

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The failures of DFT

Total energy differences vs. eigenvalues

We all know that DFT underestimates the band gap. But why?

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The exact Green's function has poles that correspond to total energy differences

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

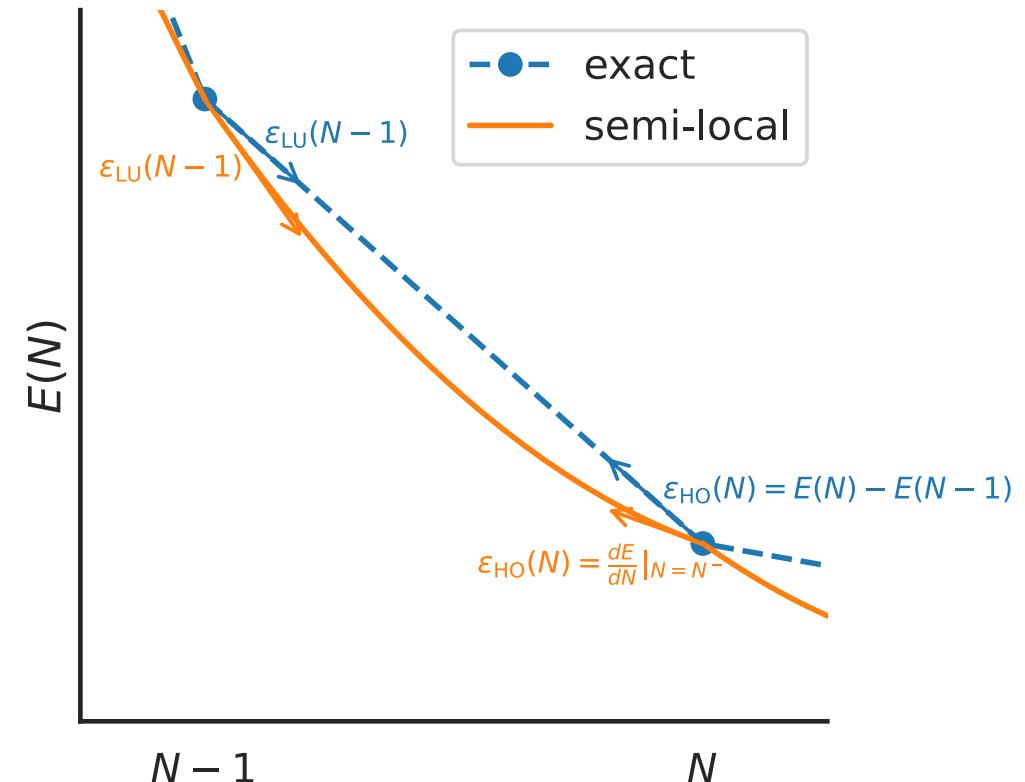
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but DFT does *not*



**Core idea: impose this condition on
DFT**

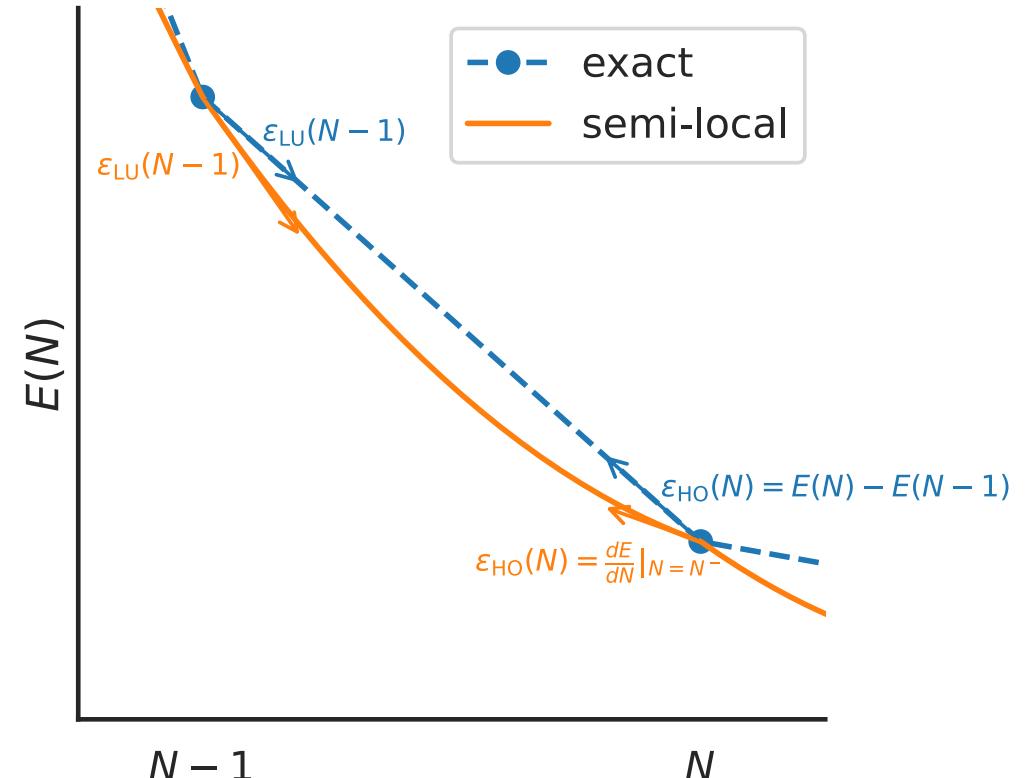
Imposing generalised piecewise linearity

Formally, every orbital i should have an eigenenergy

$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | \hat{H} | \varphi_i \rangle = \frac{dE}{df_i}$$

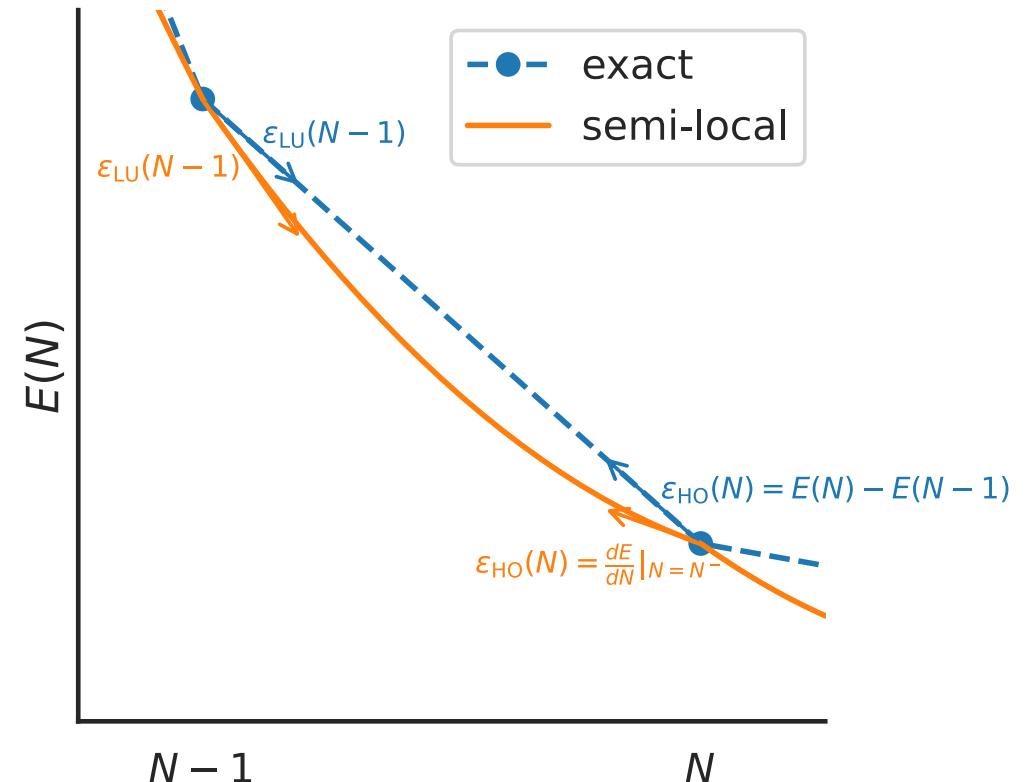
that is

- independent of f_i
- equal to ΔE of explicit electron addition/
removal



Imposing generalised piecewise linearity

$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

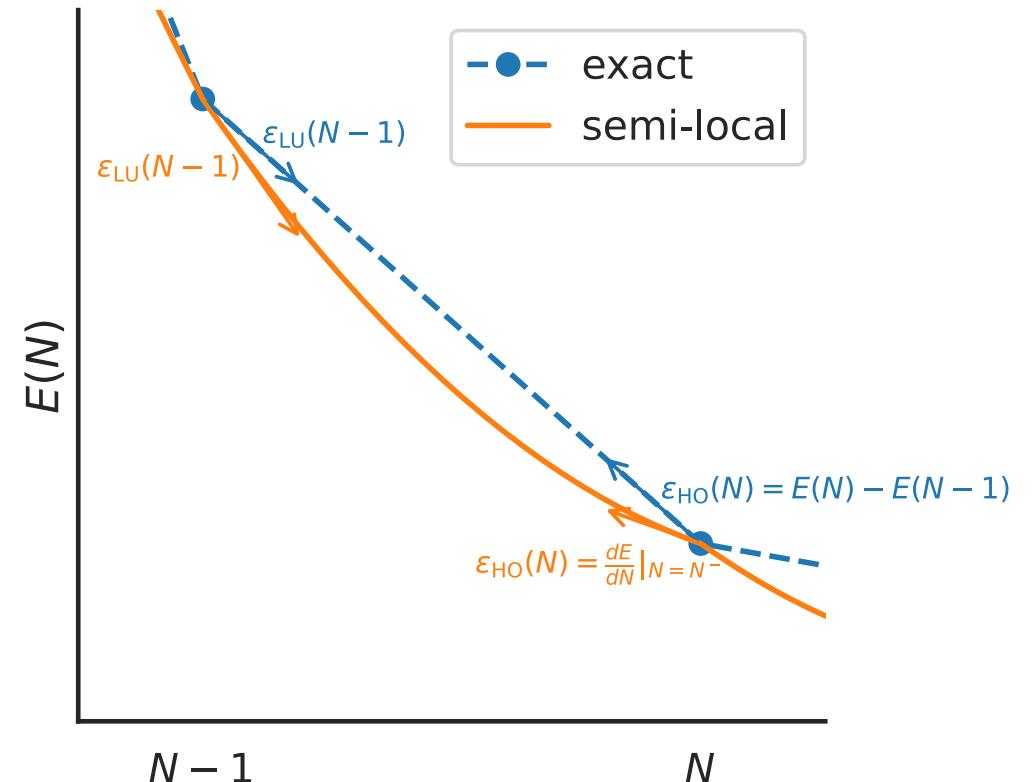


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removes dependence on f_i



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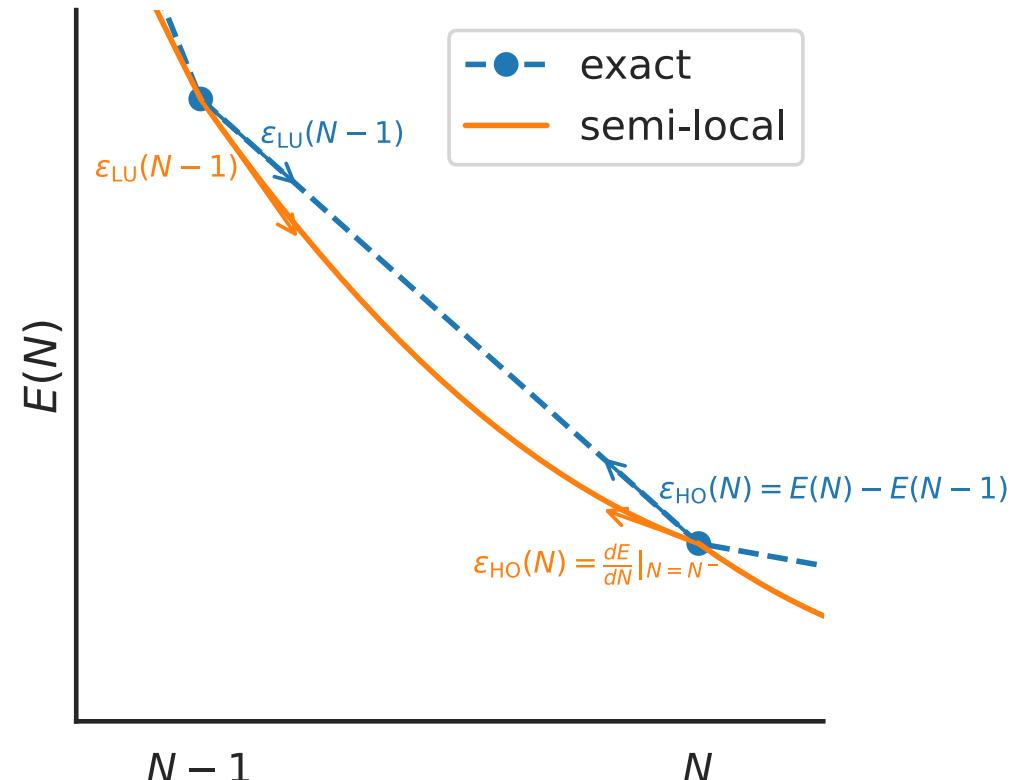
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removes dependence on f_i

restores linear dependence on f_i



Comparison with DFT+*U* (and BLOR)

DFT+*U*

*seeks to
correct...*

in practice...

*correction
applied to...*

*orbitals defined
by...*

*parametrised
by...*

Koopmans

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Electronic screening via parameters

$$E^{\text{KI}}[\{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

Electronic screening via parameters

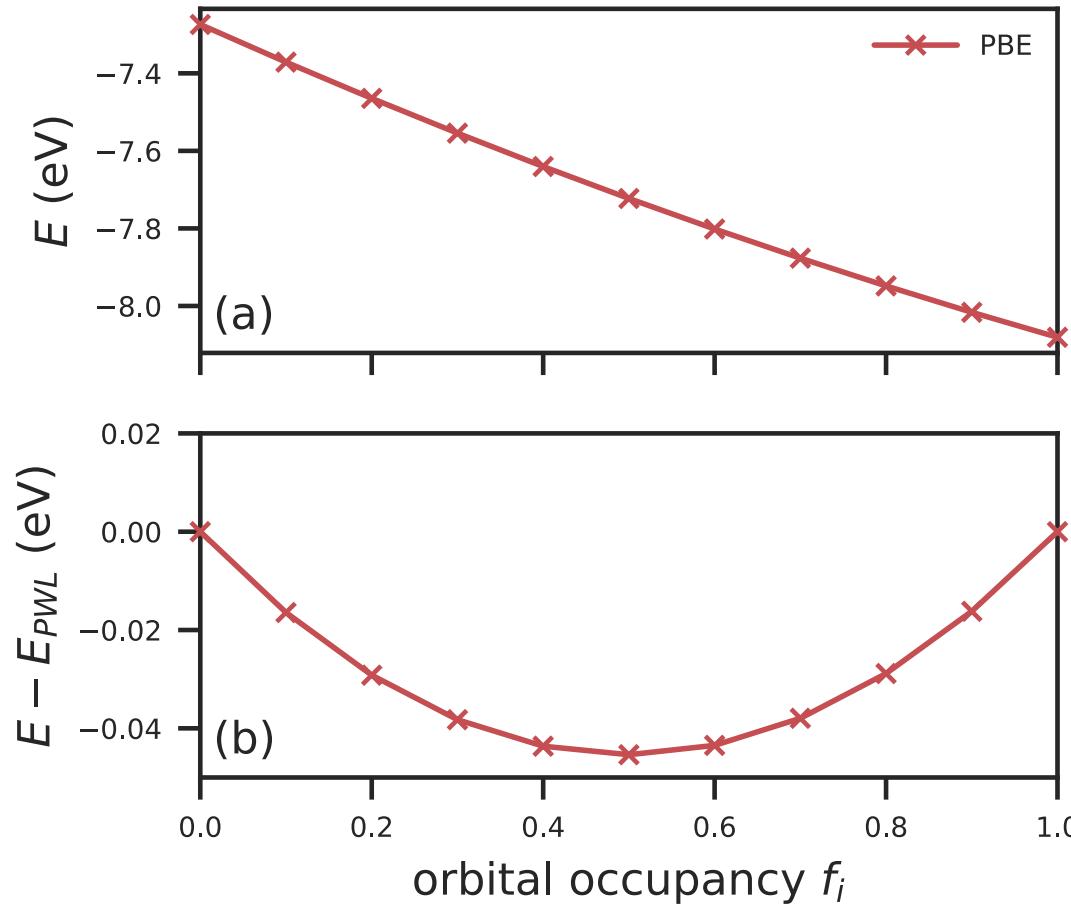
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 &= E^{\text{DFT}}[\rho] + \sum_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}
 \end{aligned}$$

Electronic screening via parameters

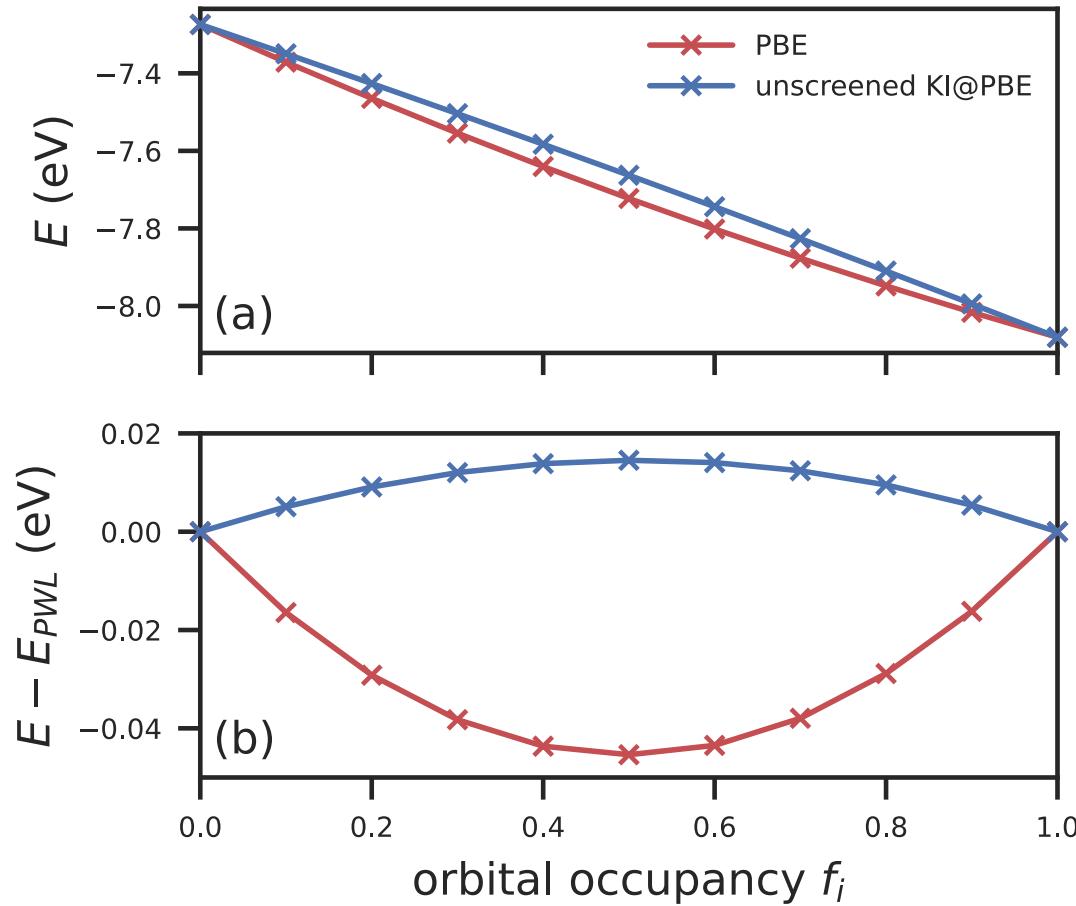
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cannot evaluate directly cannot evaluate directly cannot evaluate directly

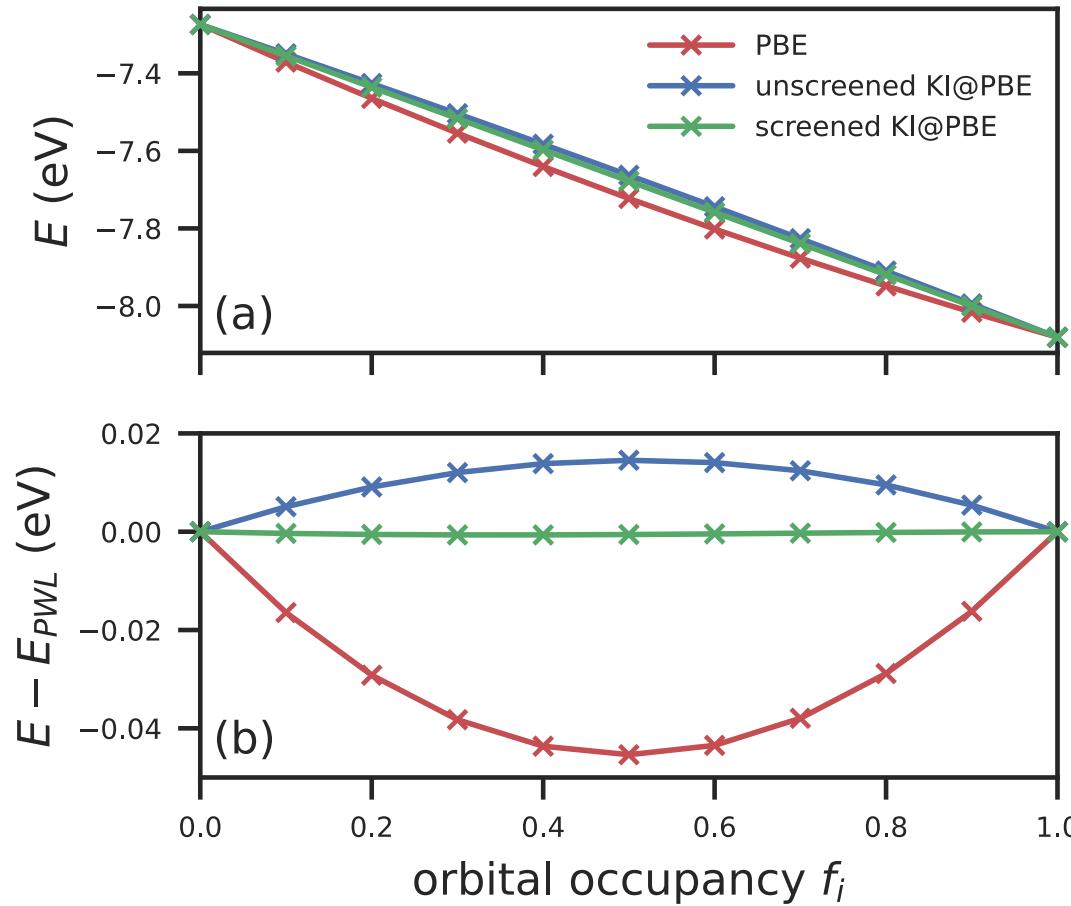
Electronic screening via parameters



Electronic screening via parameters



Electronic screening via parameters



Electronic screening via parameters

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

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uses frozen orbitals uses frozen orbitals uses frozen orbitals

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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

which is easy to evaluate e.g.

$$H_{ij}^{\text{KI}} = \langle \varphi_j | \hat{h}^{\text{DFT}} + \alpha_i \hat{v}_i^{\text{KI}} | \varphi_i \rangle \quad \hat{v}_i^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$

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Screening parameters *not* a fitting parameter!

Orbital-density dependence

The potential is orbital-density-dependent!

$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018)

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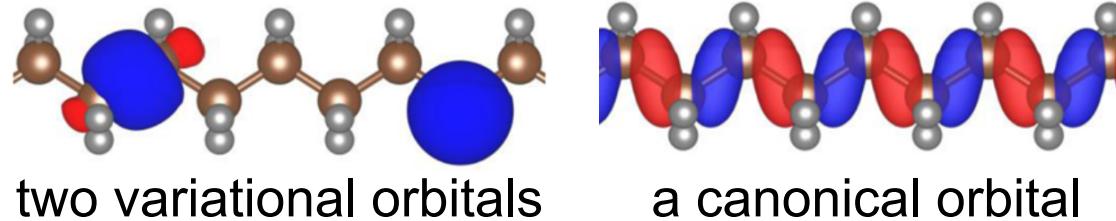
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- loss of unitary invariance¹



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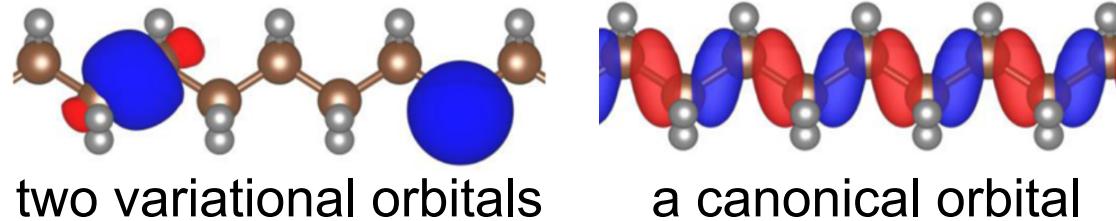
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- we can use MLWFs²

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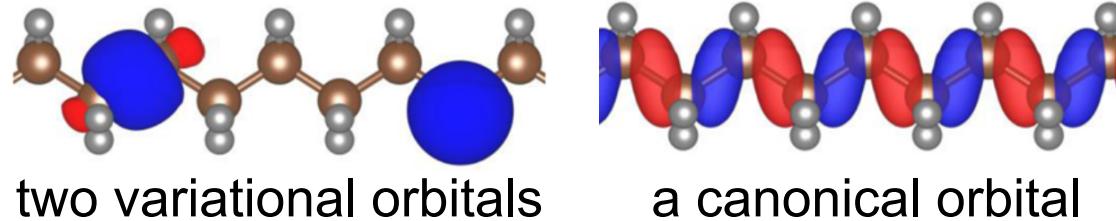
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- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}

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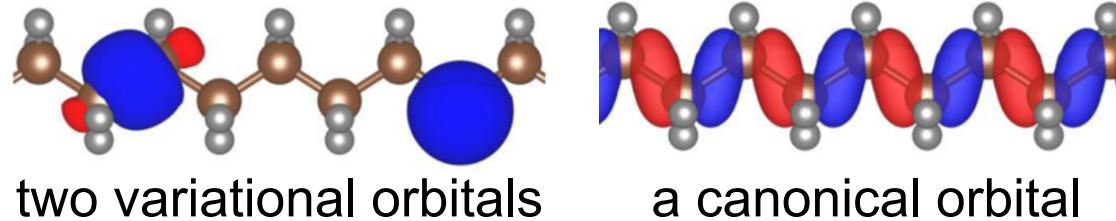
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- we can use MLWFs²
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}
- a natural generalisation of DFT towards spectral functional theory³

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To summarise...

$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) \right. \\ \left. + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

- an orbital-by-orbital correction to DFT
- screening parameters
- orbital-density-dependence
- total energy at integer occupations unchanged!

Comparison with DFT+ U (and BLOR)

| | DFT+ U | Koopmans |
|---------------------------------|---|---|
| <i>seeks to correct...</i> | erroneous global curvature in total energies w.r.t. N | erroneous global curvature in total energies w.r.t. orbital occupancies |
| <i>in practice...</i> | corrects curvature in total energies w.r.t. local manifold (BLOR does so more faithfully) | removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$ |
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Comparison with DFT+ U (and BLOR)

| | DFT+ U | Koopmans |
|---------------------------------|---|--|
| seeks to correct... | erroneous global curvature in total energies w.r.t. N | erroneous global curvature in total energies w.r.t. canonical orbital occupancies |
| <i>in practice...</i> | corrects curvature in total energies w.r.t. local manifold (BLOR does so more faithfully) | removes dependence of ε_i on variational orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$ |
| <i>correction applied to...</i> | selected subspaces (e.g. 3d orbitals) | the entire system |
| <i>orbitals defined by...</i> | Hubbard projectors (atom-centred, frozen, incomplete) | variational (localised) orbitals |
| <i>parametrised by...</i> | $\{U_I\}$ | |

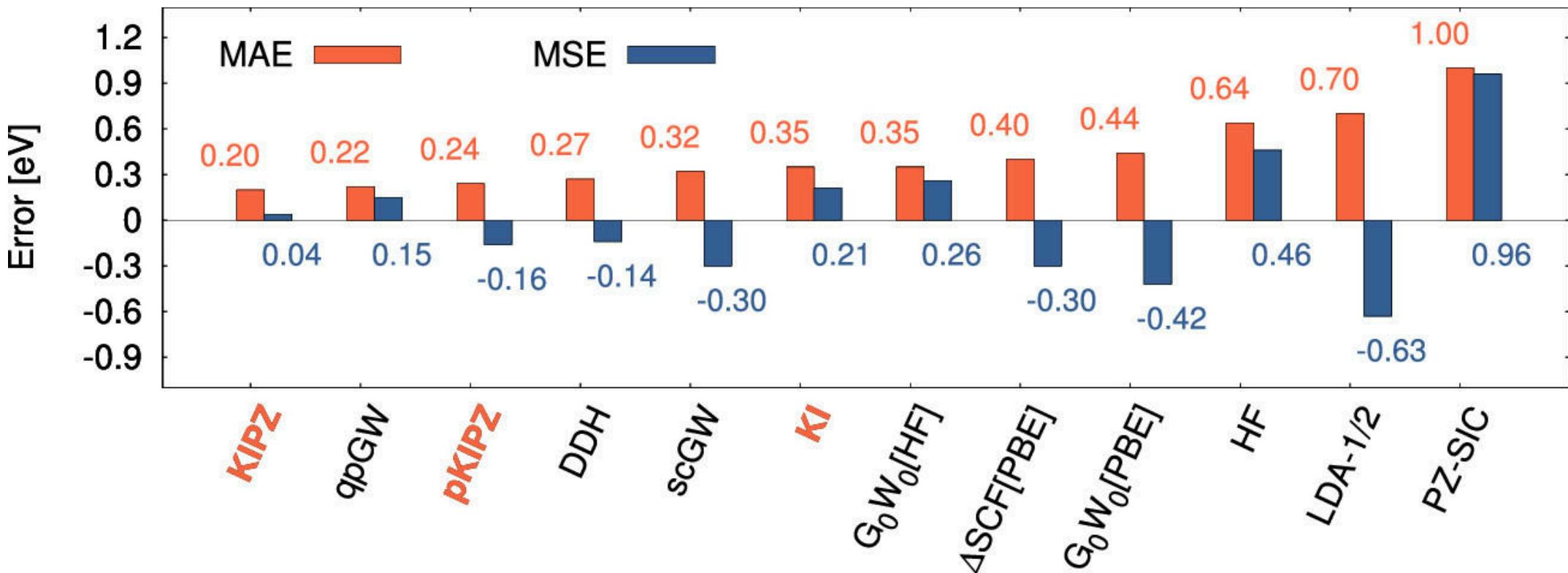
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| <i>orbitals defined by...</i> | Hubbard projectors (atom-centred, frozen, incomplete) | variational (localised) orbitals |
| <i>parametrised by...</i> | $\{U_I\}$ | $\{\alpha_i\}$ |

Results

Molecular systems

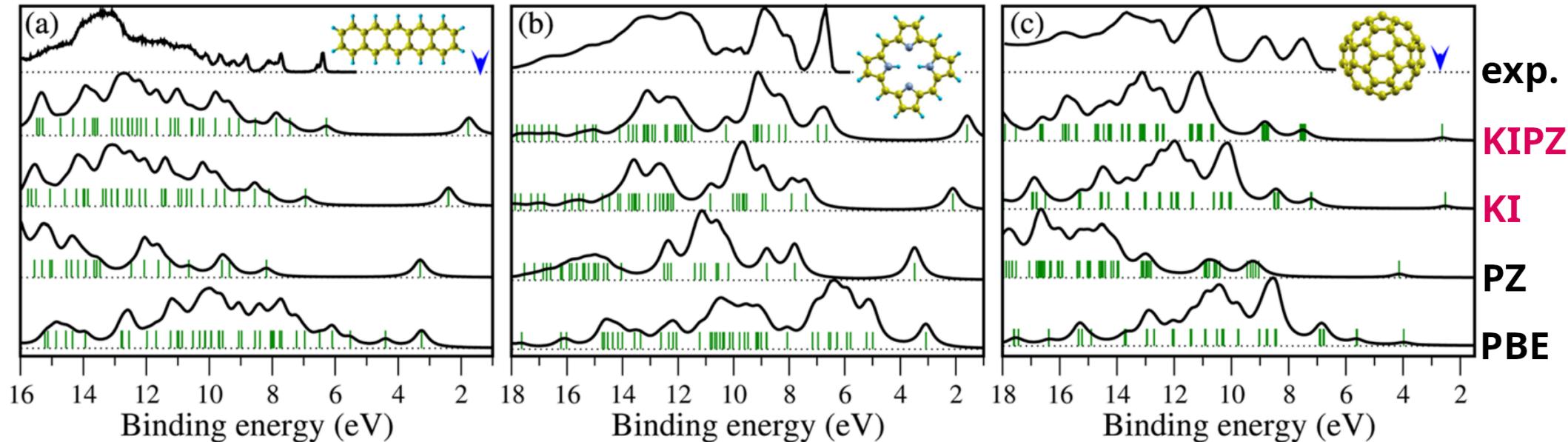
Ionisation potentials¹



¹N. Colonna et al. J. Chem. Theory Comput. **15**, 1905 (2019)

Molecular systems

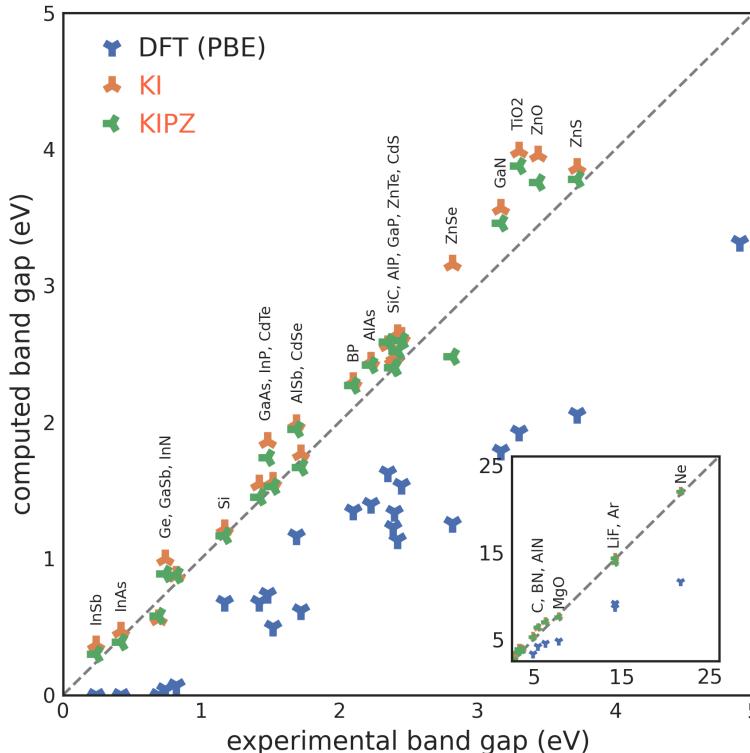
UV photoemission spectra¹



¹N. L. Nguyen *et al.* Phys. Rev. Lett. **114**, 166405 (2015)

Extended systems

Prototypical semiconductors and insulators¹

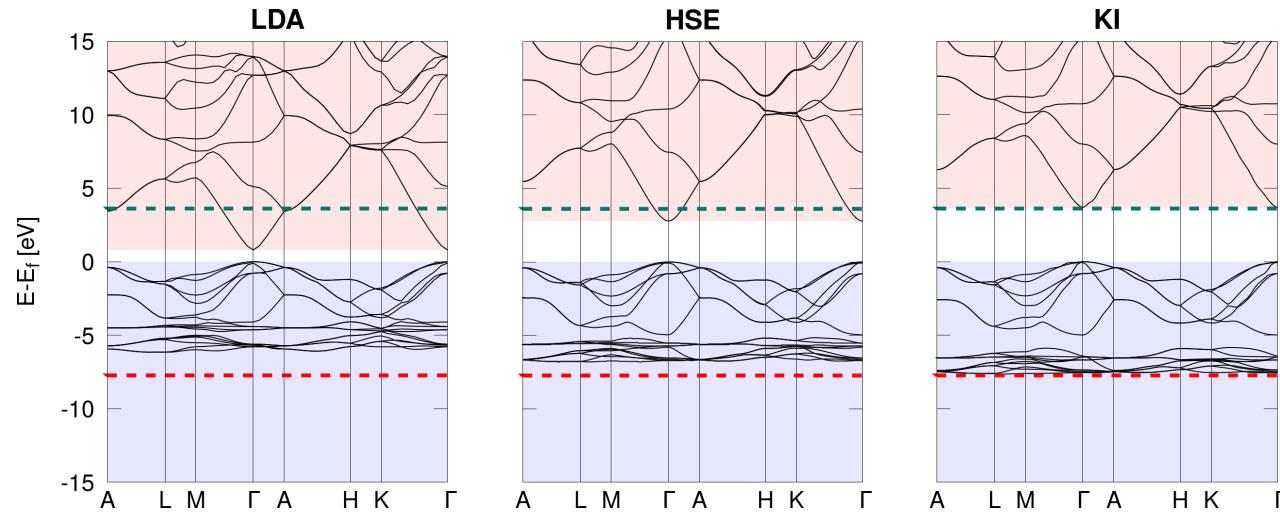


| | PBE | G_0W_0 | KI | KIPZ | $QSG\tilde{W}$ |
|------------------|------|----------|------|------|----------------|
| E_{gap} | 2.54 | 0.56 | 0.27 | 0.22 | 0.18 |
| IP | 1.09 | 0.39 | 0.19 | 0.21 | 0.49 |

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

Extended systems

ZnO¹

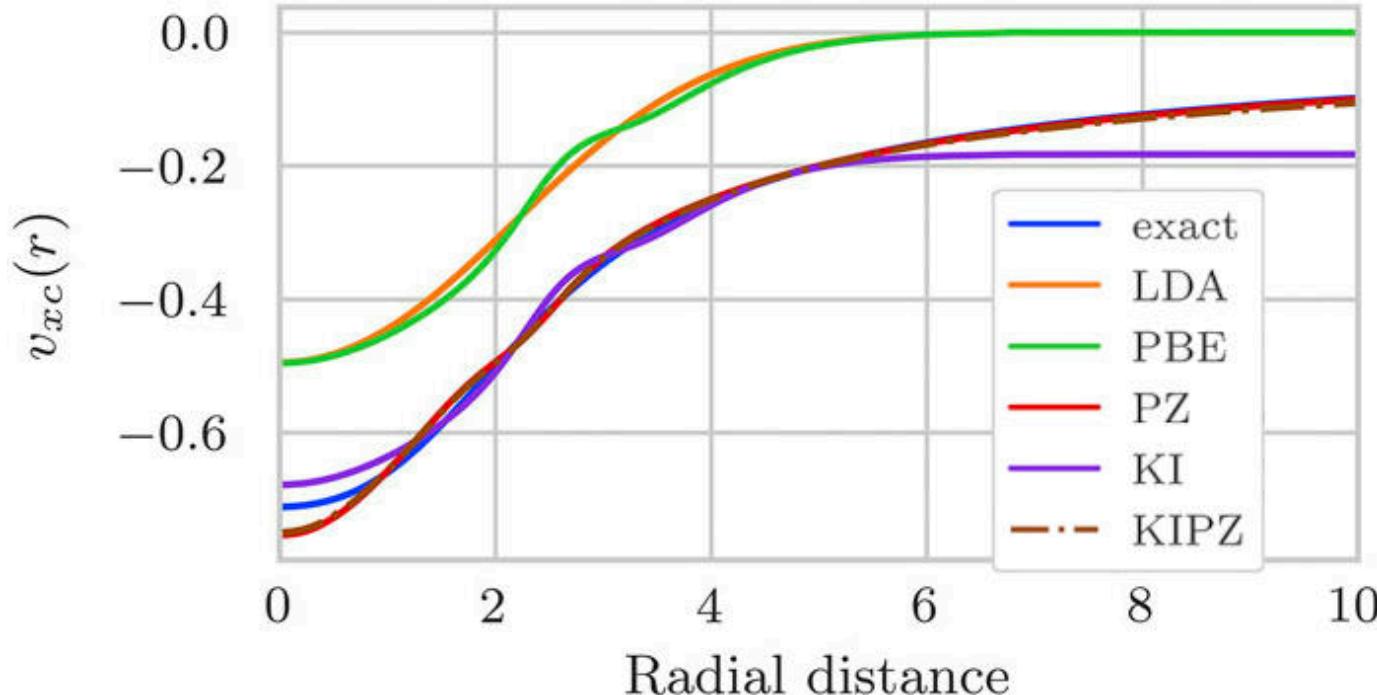


| | LDA | HSE | GW_0 | $scG\tilde{W}$ | KI | exp |
|---------------------------------|------|------|--------|----------------|--------------|---------------|
| E_{gap} | 0.79 | 2.79 | 3.0 | 3.2 | 3.68 | 3.60 |
| $\langle \varepsilon_d \rangle$ | -5.1 | -6.1 | -6.4 | -6.7 | -6.93 | -7.5 to -8.81 |
| Δ | 4.15 | | | | 4.99 | 5.3 |

¹N. Colonna et al. *J. Chem. Theory Comput.* **18**, 5435 (2022)

Model systems

Hooke's atom¹



¹Y. Schubert *et al.* *J. Chem. Phys.* **158**, 144113 (2023)

Caveats

Limitations

- only valid for systems with $E_{\text{gap}} > 0$

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- empty state localisation in the bulk limit

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- empty state localisation in the bulk limit
- can break crystal point group symmetry

Resonance with other efforts

- Wannier transition state method of Anisimov and Kozhevnikov¹
- Optimally-tuned range-separated hybrid functionals of Kronik, Pasquarello, and others²
- Ensemble DFT of Kraisler and Kronik³
- Koopmans-Wannier method of Wang and co-workers⁴
- Dielectric-dependent hybrid functionals of Galli and co-workers⁵
- Scaling corrections of Yang and co-workers⁶

¹V. I. Anisimov *et al.* *Phys. Rev. B* **72**, 75125 (2005)

²L. Kronik *et al.* *J. Chem. Theory Comput.* **8**, 1515–1531 (2012), D. Wing *et al.* *Proc. Natl. Acad. Sci.* **118**, e2104556118 (2021)

³E. Kraisler *et al.* *Phys. Rev. Lett.* **110**, 126403 (2013)

⁴J. Ma *et al.* *Sci. Rep.* **6**, 24924 (2016)

⁵J. H. Skone *et al.* *Phys. Rev. B* **93**, 235106 (2016)

⁶C. Li *et al.* *Natl. Sci. Rev.* **5**, 203–215 (2018)

Extensions

Non-collinear spin

Non-collinear spin

$$\rho_i(\mathbf{r})$$

¹A. Marrazzo *et al.* *Phys. Rev. Res.* **6**, 33085 (2024)

Non-collinear spin

$$\rho_i(\mathbf{r}) \rightarrow \boldsymbol{\rho}_i(\mathbf{r}) = (\rho_i(\mathbf{r}), m_i^x(\mathbf{r}), m_i^y(\mathbf{r}), m_i^z(\mathbf{r}))$$

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e.g. for the corrective potential

$$v_i^{\text{qKI}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_i(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \rho_i(\mathbf{r}') + (1 - f_i) \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \rho_i(\mathbf{r}')$$

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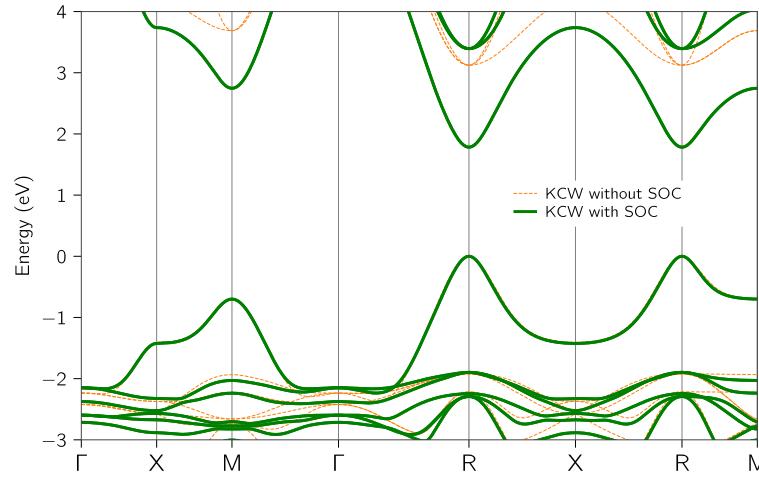
↓

$$v_i^{\text{qKI}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \boldsymbol{\rho}_i(\mathbf{r}) \mathbb{F}_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\rho}_i(\mathbf{r}') \sigma_0 + (1 - f_i) \sum_{\alpha} \int d\mathbf{r}' [\mathbb{F}_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\rho}_i(\mathbf{r}')]_{\alpha} \sigma_{\alpha}$$

¹A. Marrazzo *et al.* *Phys. Rev. Res.* **6**, 33085 (2024)

Non-collinear spin

CsPbBr₃



| | LDA | HSE | G ₀ W ₀ | scG \tilde{W} | KI | exp |
|-----------------|------|------|-------------------------------|-----------------|-------------|------|
| with SOC | 0.18 | 0.78 | 0.94 | 1.53 | 1.78 | 1.85 |
| without SOC | 1.40 | 2.09 | 2.56 | 3.15 | 3.12 | |

¹A. Marrazzo *et al.* Phys. Rev. Res. **6**, 33085 (2024)

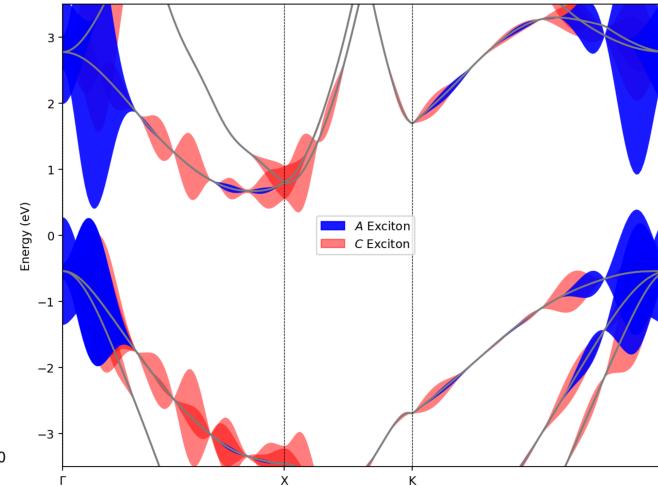
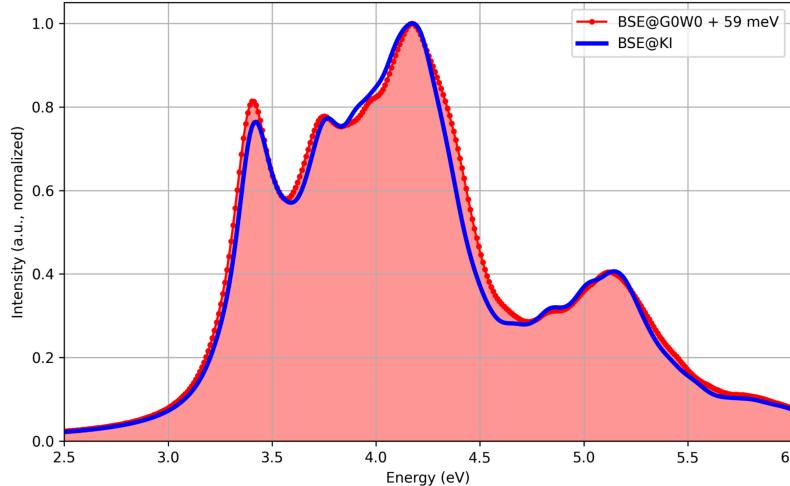
Optical spectra

Optical spectra

Solve the BSE, using Koopmans eigenvalues in lieu of GW

Optical spectra

Solve the BSE, using Koopmans eigenvalues in lieu of GW



| silicon | indirect gap | direct gap | first excitonic peak | excitonic binding energy |
|---------------|--------------|------------|----------------------|--------------------------|
| qKI+BSE | 1.12 | 3.31 | 3.42 | 0.09 |
| G_0W_0 +BSE | 1.17 | 3.25 | 3.34 | 0.09 |

Computational cost and scaling

Computational cost and scaling

The vast majority of the computational cost: determining screening parameters

$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

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 - ΔSCF¹: embarrassingly parallel steps which each cost $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$

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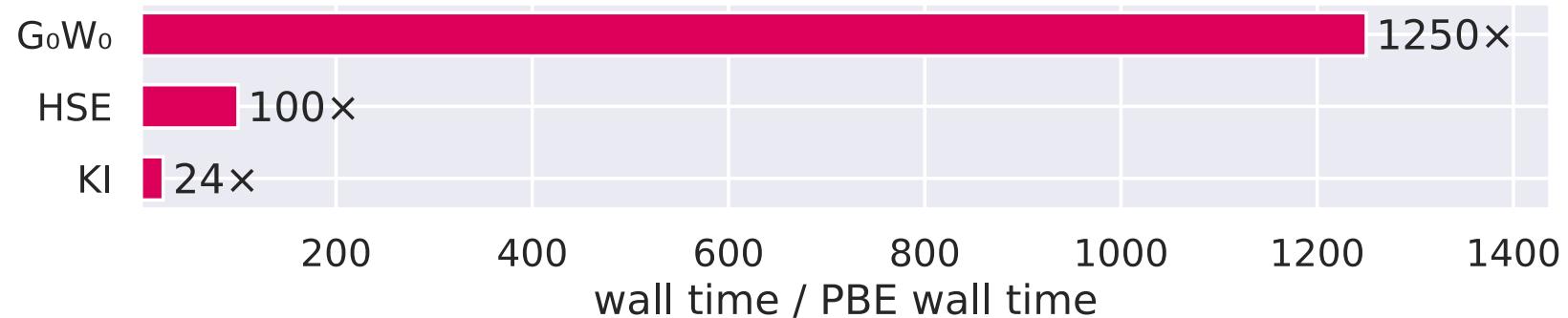
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 - DFPT²: $\mathcal{O}(N_{\mathbf{k}}^2 N^3)$

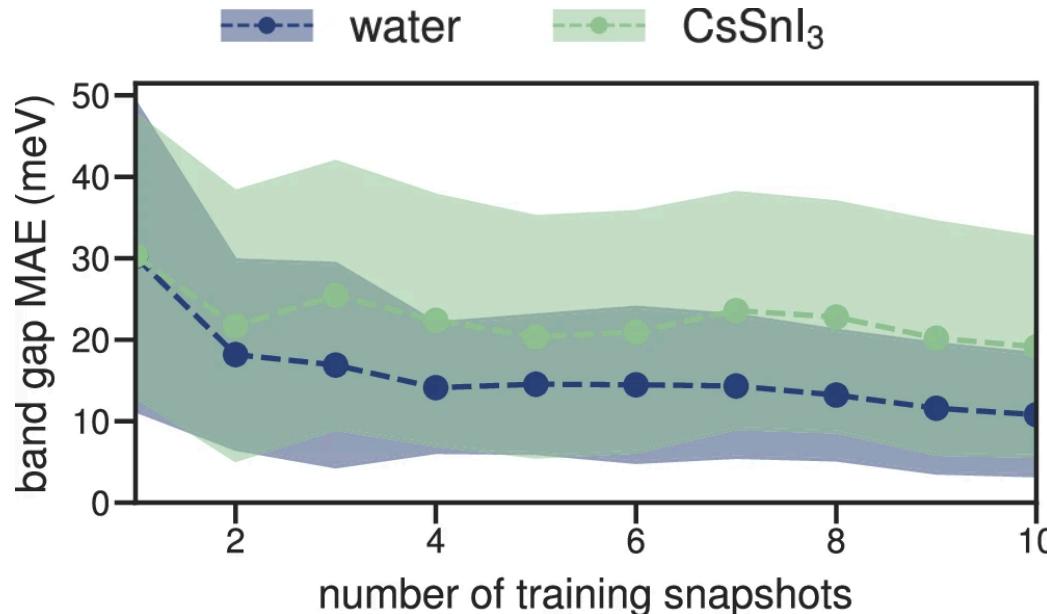
¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

²N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022), N. Colonna *et al.* *J. Chem. Theory Comput.* **14**, 2549 (2018)

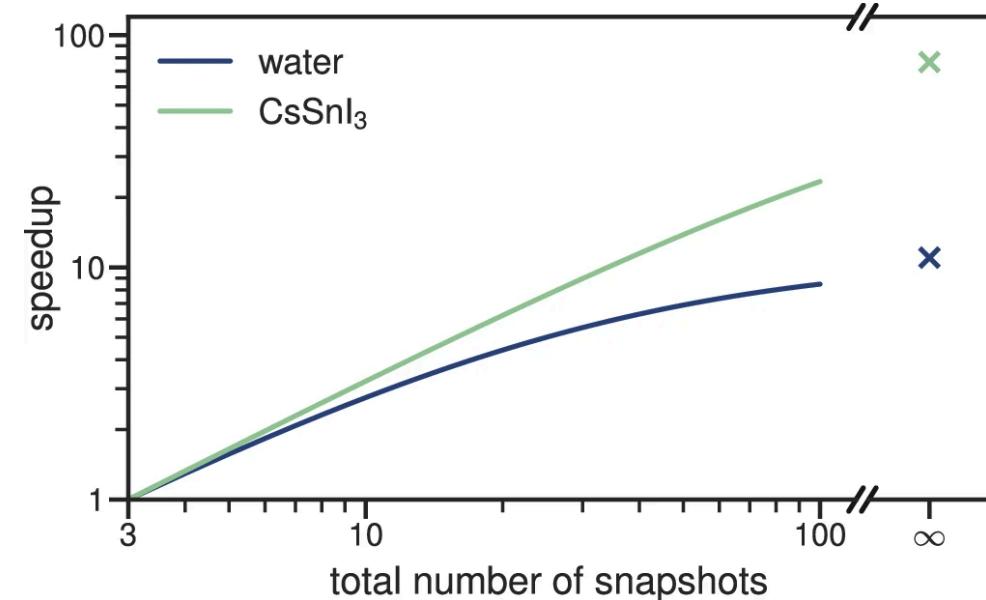
Computational cost and scaling



Machine-learned electronic screening



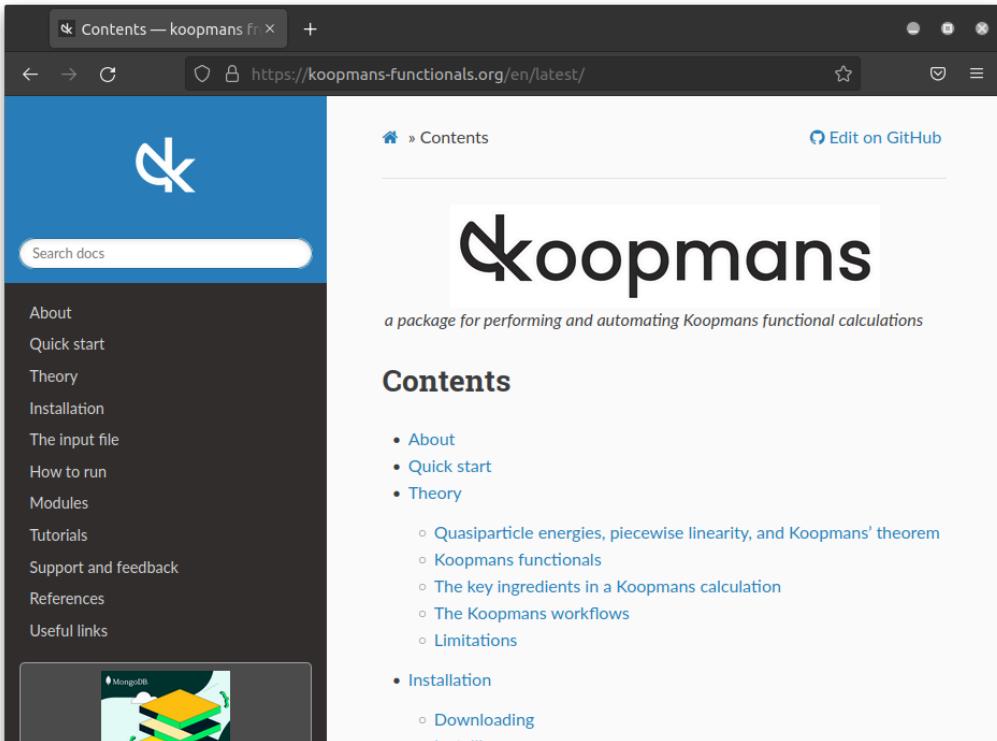
accurate to within $\mathcal{O}(10 \text{ meV})$ cf. typical
band gap accuracy of $\mathcal{O}(100 \text{ meV})$



speedup of $\mathcal{O}(10)$ to $\mathcal{O}(100)$

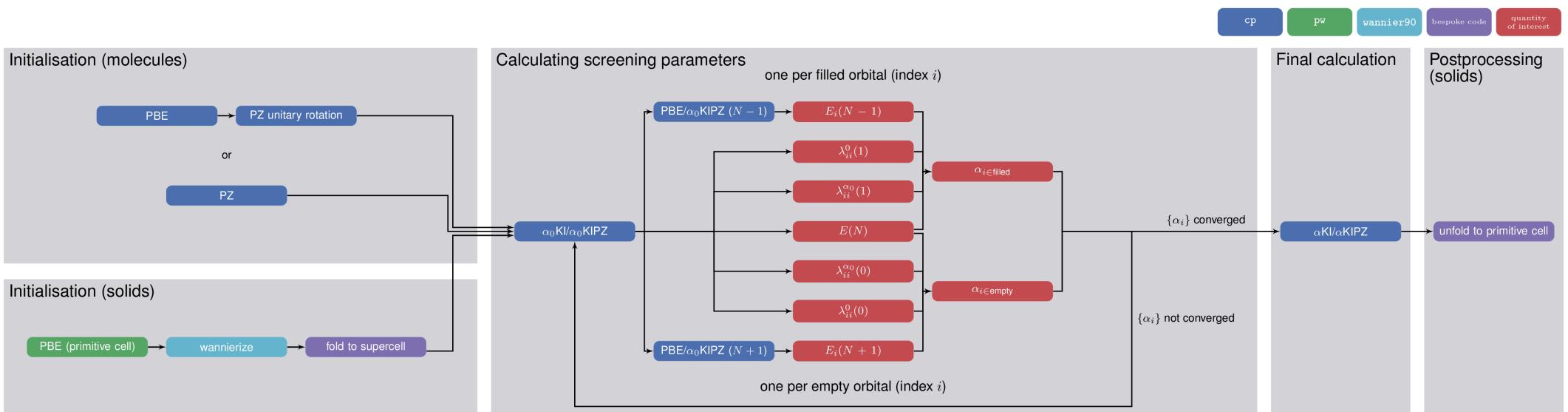
¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

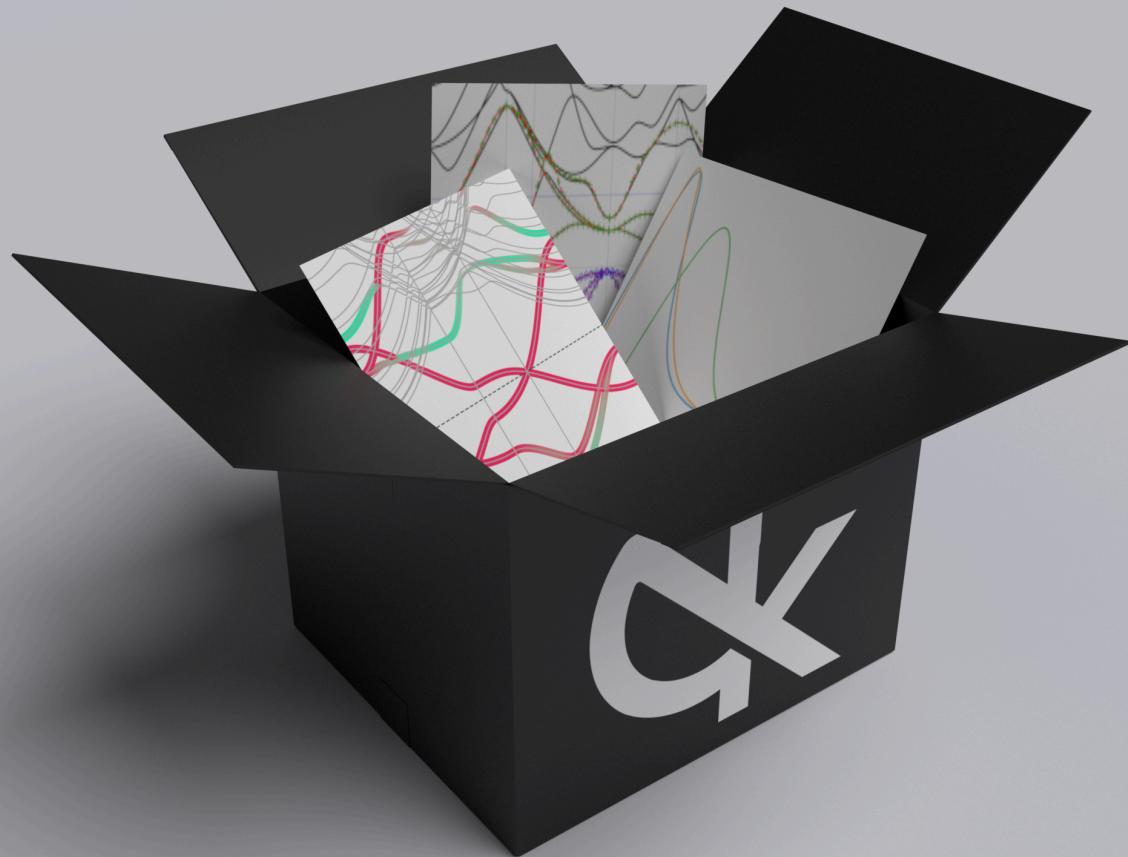
koopmans



- automated workflows
- Quantum ESPRESSO backend
- easy installation
- python API

See koopmans-functionals.org





Our goal:

1. accurate
2. robust
3. minimal input
4. fast

Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

- to initialise the minimising orbitals, or
- in place of the minimising orbitals entirely

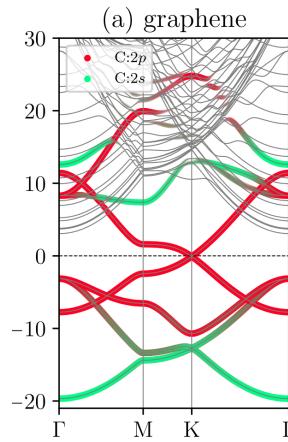
¹J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

²J. Qiao *et al.* *npj Comput Mater* **9**, 206 (2023)

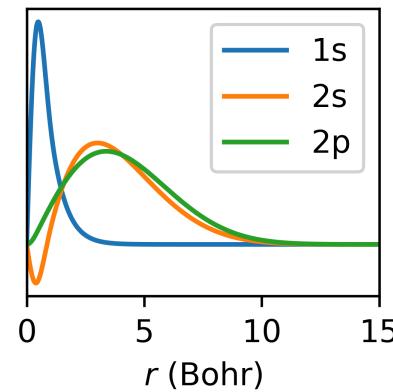
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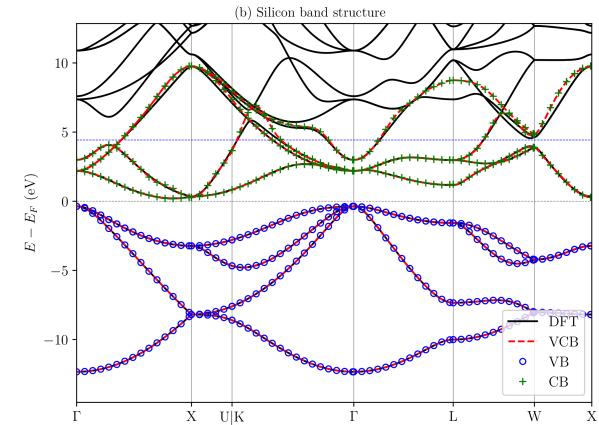
- to initialise the minimising orbitals, or
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projectability-based
disentanglement¹



use PAOs found in
pseudopotentials



parallel transport to separate
manifolds²

¹J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

²J. Qiao *et al.* *npj Comput Mater* **9**, 206 (2023)

koopmans

AiiDA

¹S. P. Huber *et al.* *Sci Data* **7**, 300 (2020)



```
$ koopmans run tio2.json
```

¹S. P. Huber *et al.* *Sci Data* **7**, 300 (2020)



```
$ koopmans run tio2.json → $ koopmans run --engine=aiida tio2.json
```

remote compute, parallel step execution, provenance-tracking, (requires configuration,
WIP...)

¹S. P. Huber *et al.* *Sci Data* **7**, 300 (2020)

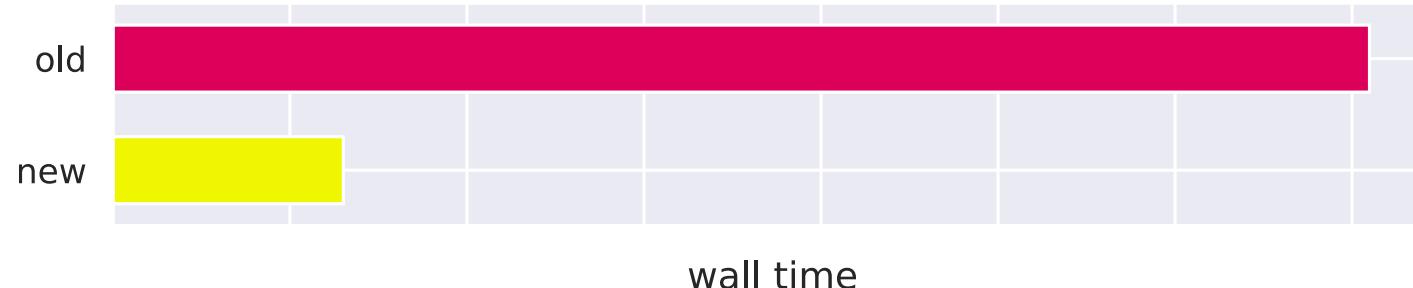
koopmans

AiiDA

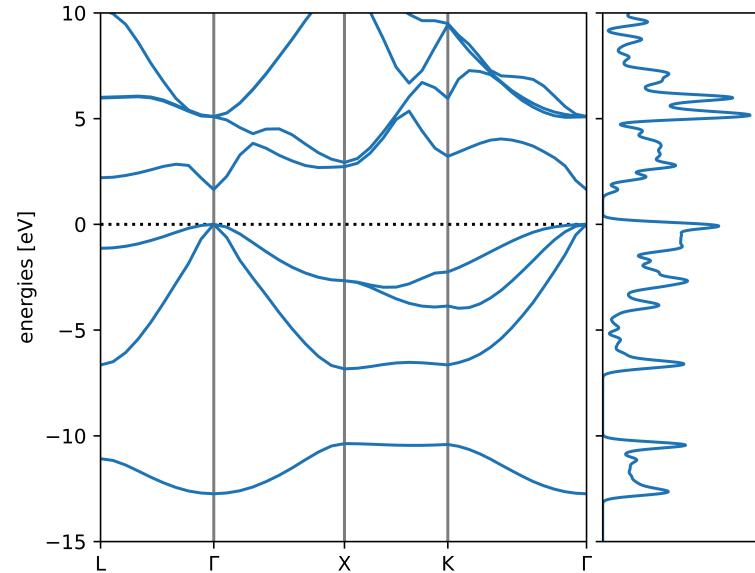
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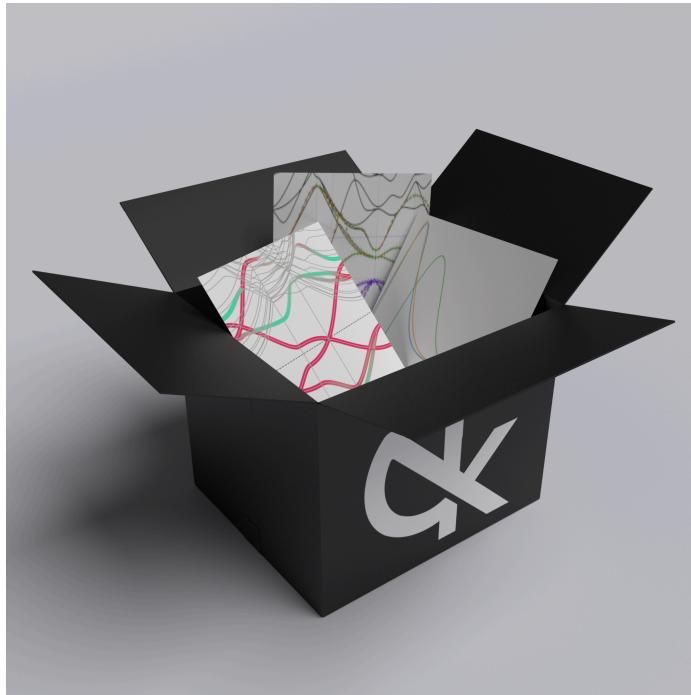
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    "orbital_groups_spread_tol": 0.05
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      "positions": [[{"Ga": 0.0, 0.0, 0.0}, {"As": 0.25, 0.25, 0.25}]]
    }
  },
  "kpoints": {
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  },
  "calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
      "dis_proj_max": 0.8,
      "auto_projections": true
    },
    "ui": {
      "smooth_int_factor": 2
    }
  }
}
```



| | LDA | HSE | GW_0 | scG \tilde{W} | KI | exp |
|---------------------------------|-------|-------|--------|-----------------|--------------|-------|
| E_{gap} | 0.26 | 1.28 | 1.55 | 1.62 | 1.54 | 1.55 |
| $\langle \varepsilon_d \rangle$ | -14.9 | -15.6 | -17.3 | -17.6 | -17.9 | -18.9 |
| Δ | 12.8 | 13.9 | | | 12.7 | 13.1 |

Summary

Summary



Koopmans functionals...

- impose generalised piecewise linearity condition to DFT
- give band structures with comparable accuracy to state-of-the-art GW
- can be used in place of GW in BSE calculation of excitons, for systems with strong SOC, ...
- are increasingly black-box

Open questions

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?

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 - GKS
 - spectral functional theory¹
 - ensemble DFT
 - RDMFT

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Want to find out more?



Nicola Marzari
Monday

spectral theories



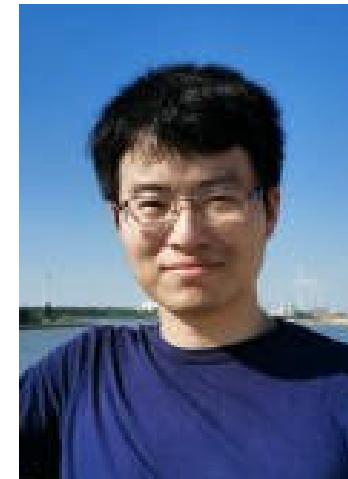
Marija Stojkovic
Monday

band alignment for
photocatalysis



Nicola Colonna
Tuesday

non-collinear spin



Junfeng Qiao
Poster B4.16
today!

automated
Wannierisation



Aleksandr Poliukhin
Thu 1000 Room C

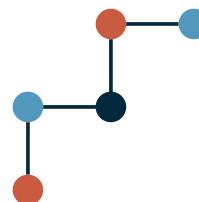
electron-phonon

... or go to koopmans-functionals.org

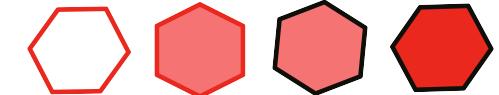
Acknowledgements



Nicola Colonna Miki Bonacci Aleksandr Poliukhin Marija Stojkovic Giovanni Cistaro Julian Geiger Junfeng Qiao Yannick Schubert Nicola Marzari



**Swiss National
Science Foundation**

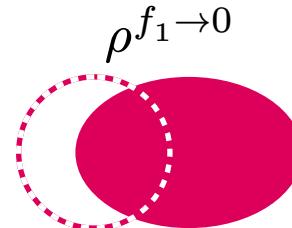
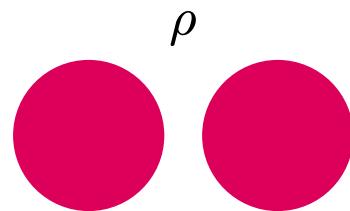
MARVEL


Thank you!

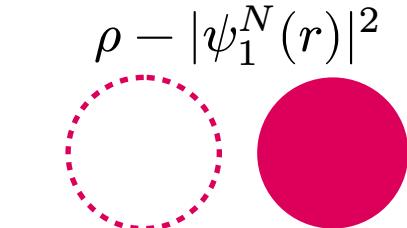
these slides are available at  [*elinscott-talks*](https://github.com/elinscott-talks)

spare slides

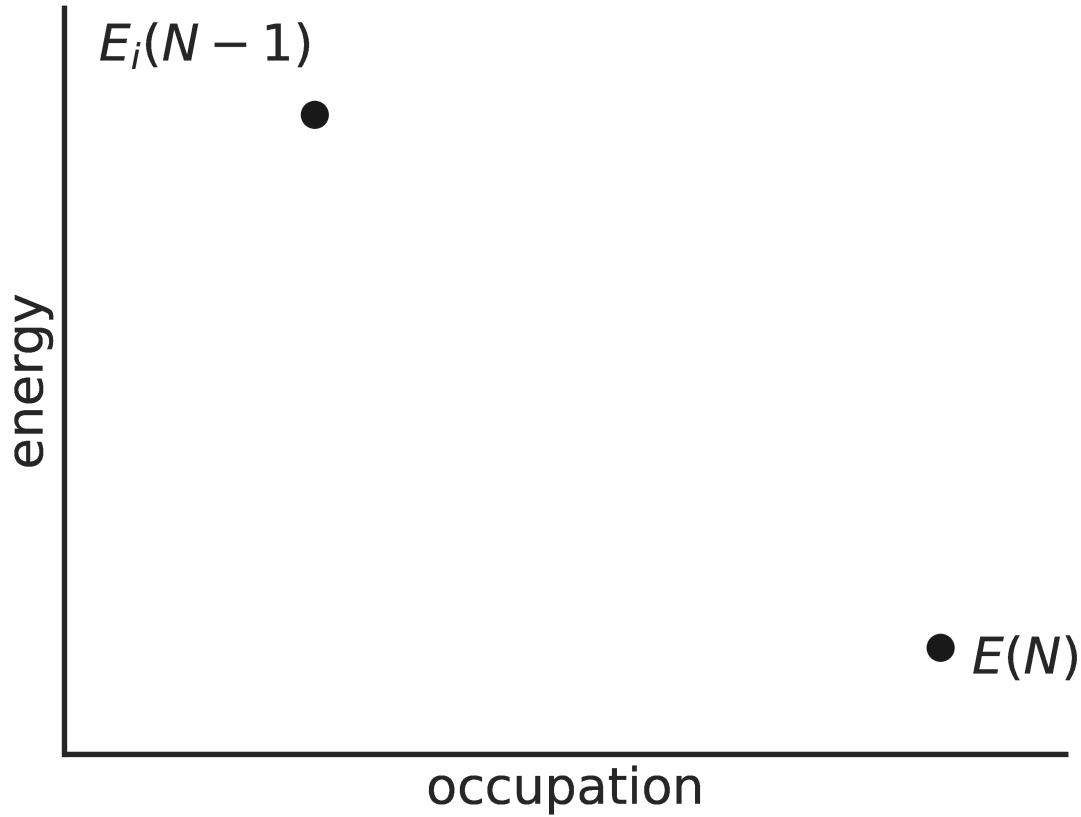
Frozen orbital approximation

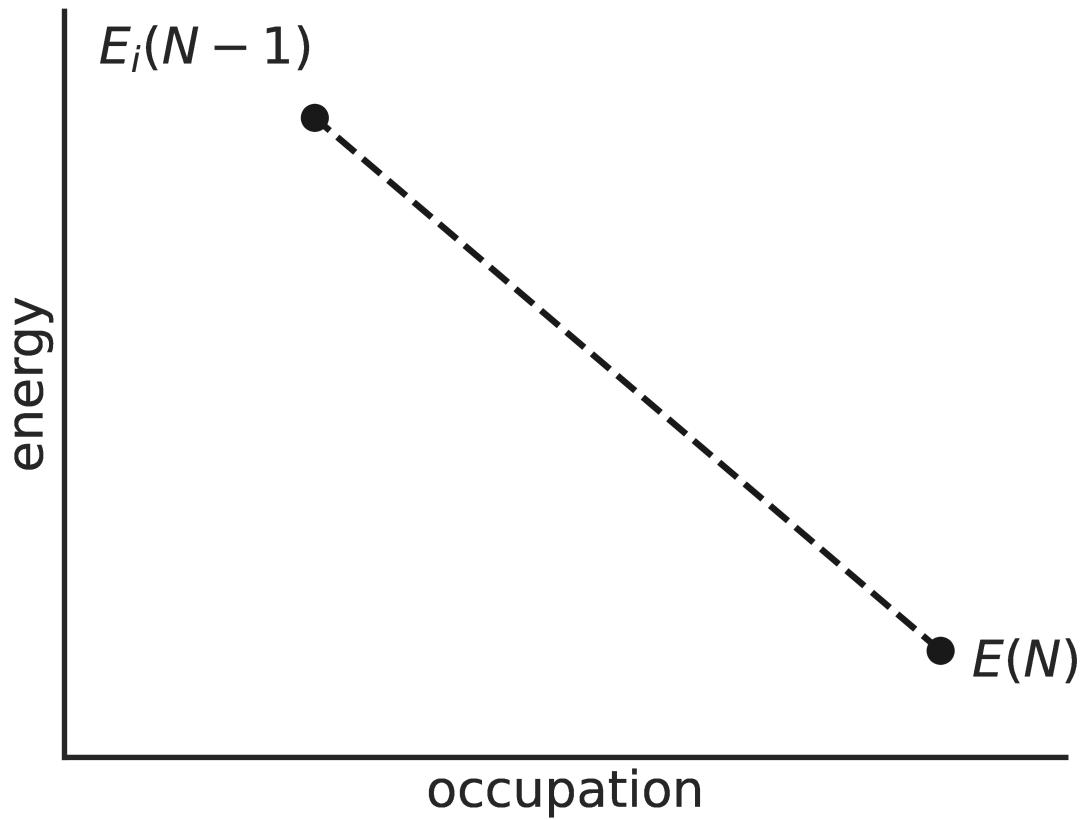


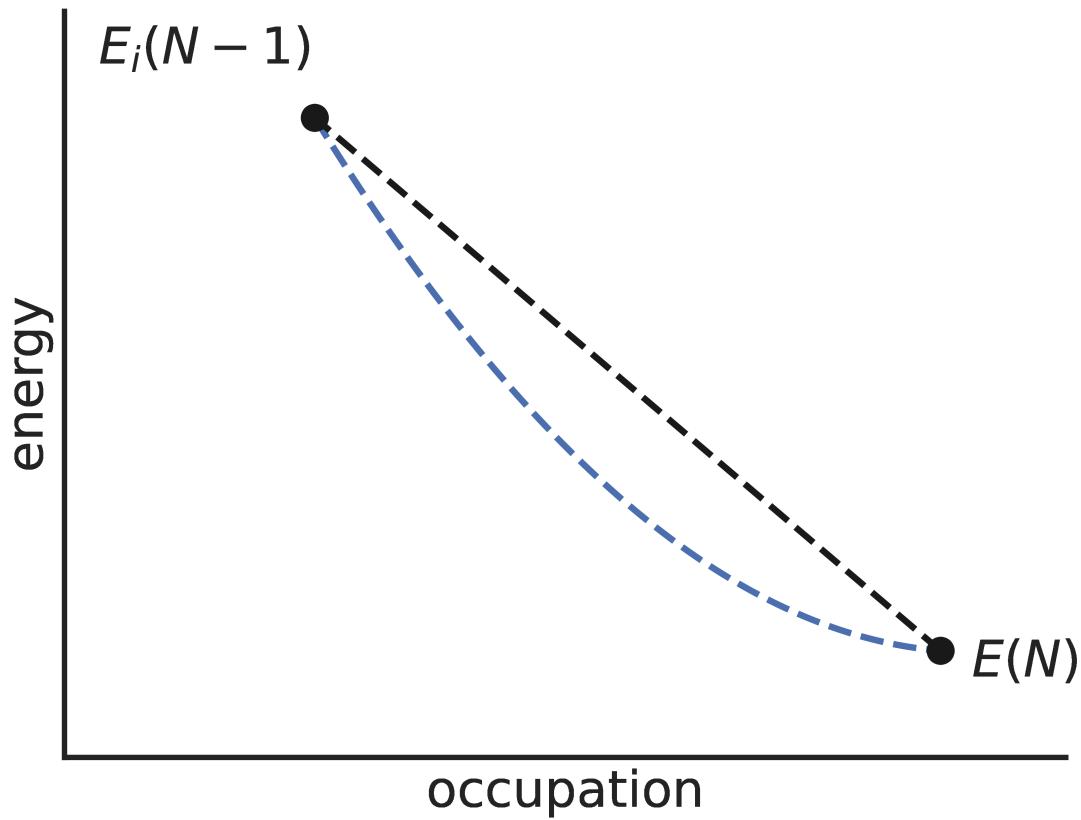
2-electron solution

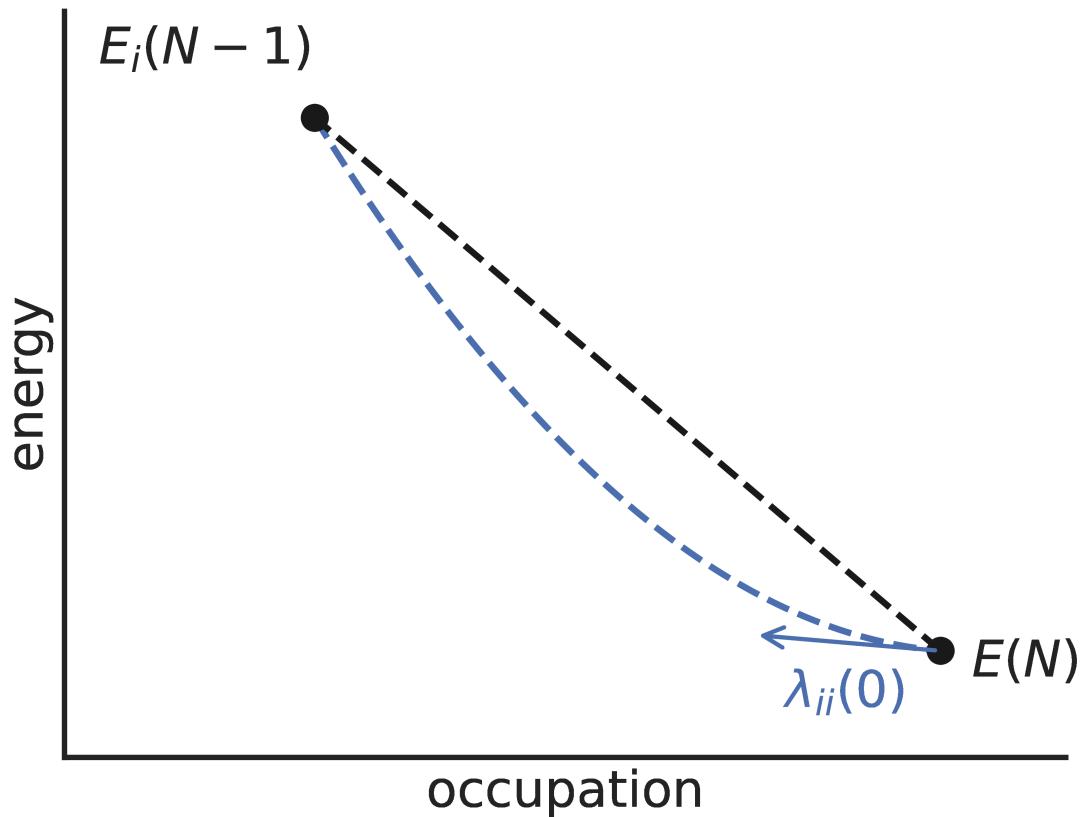


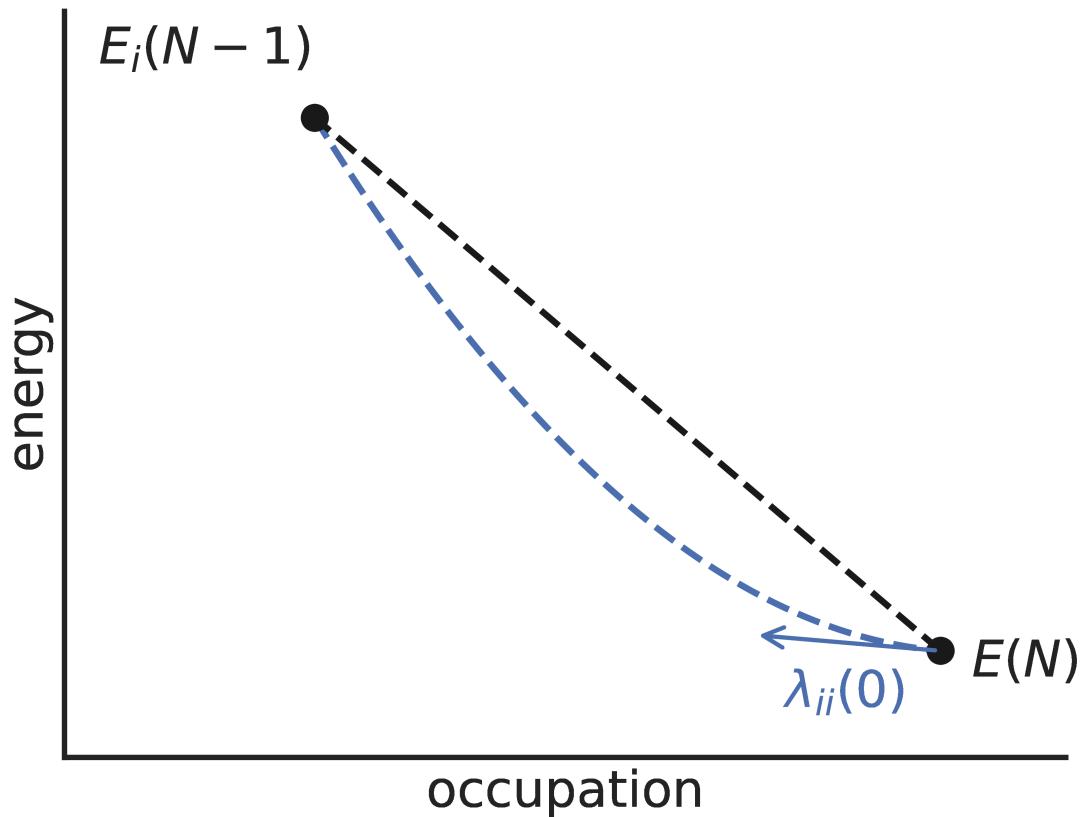
what we can quickly evaluate

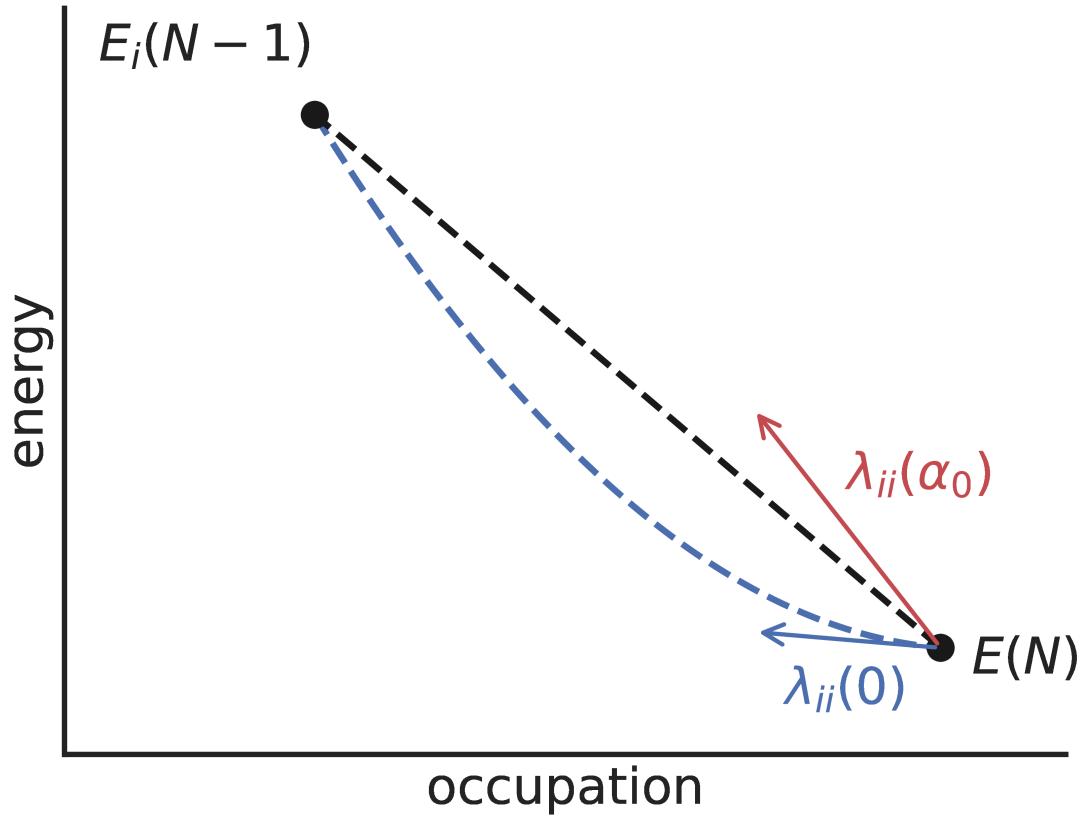


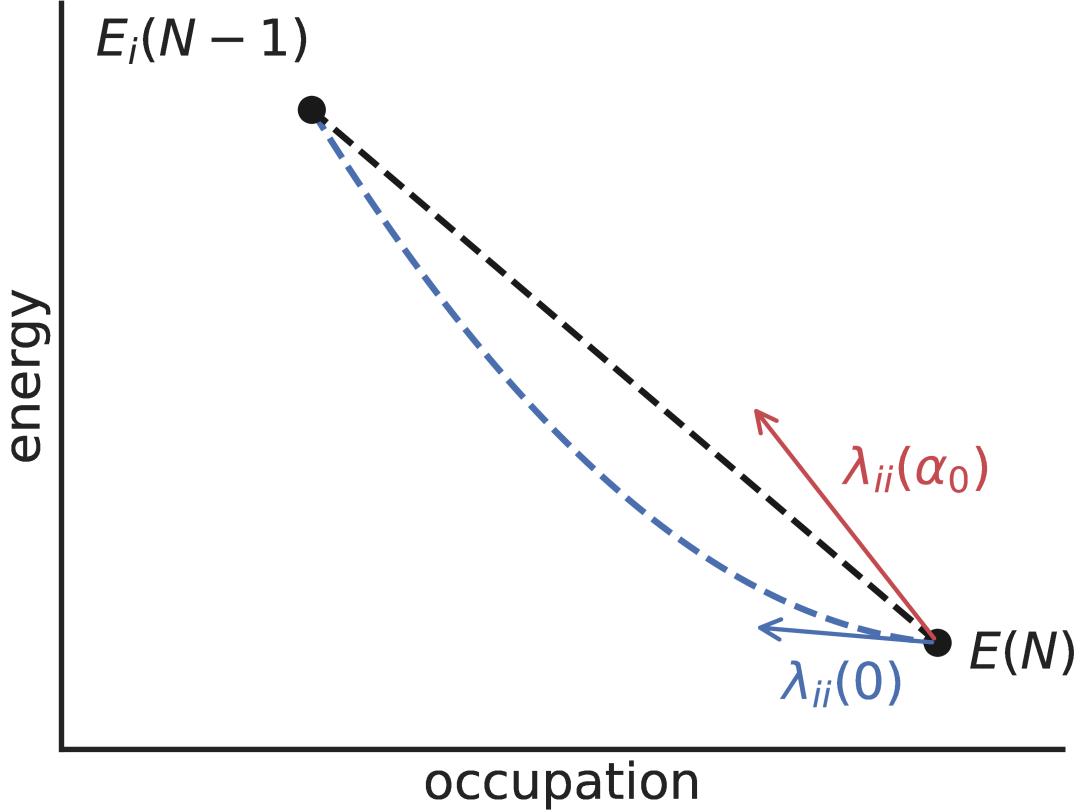








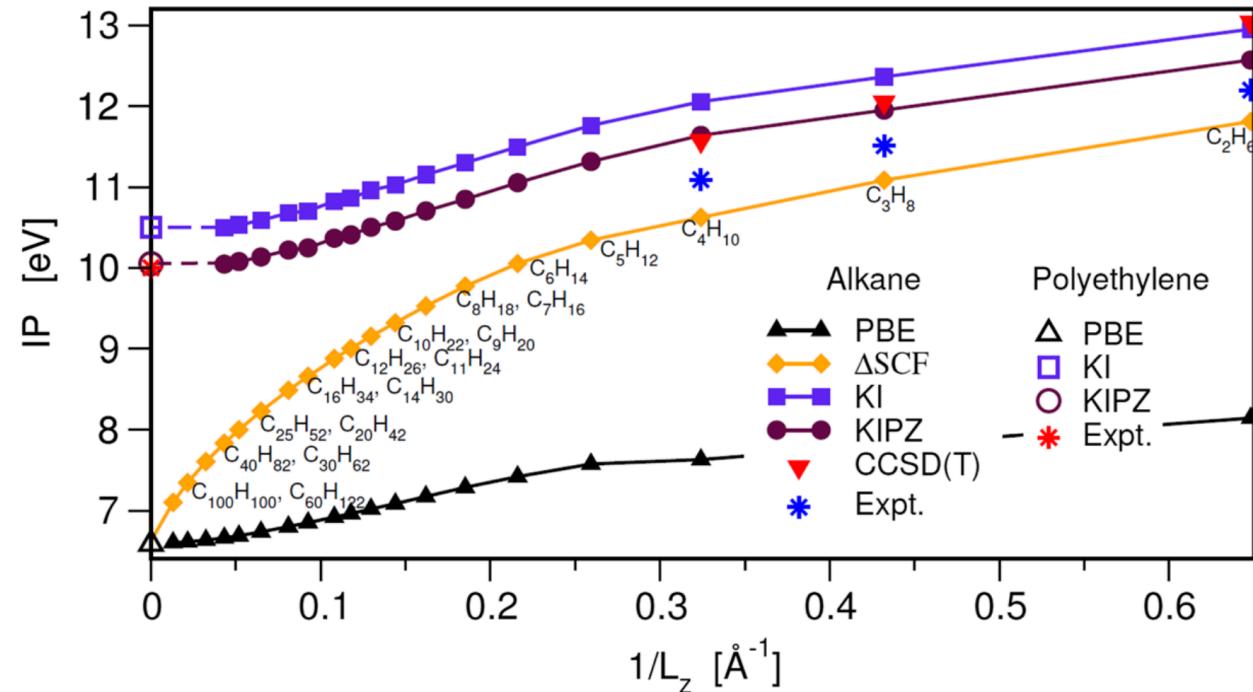




$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

$$\lambda_{ii}(\alpha) = \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}_i^{\text{KI}} | \varphi_i \rangle$$

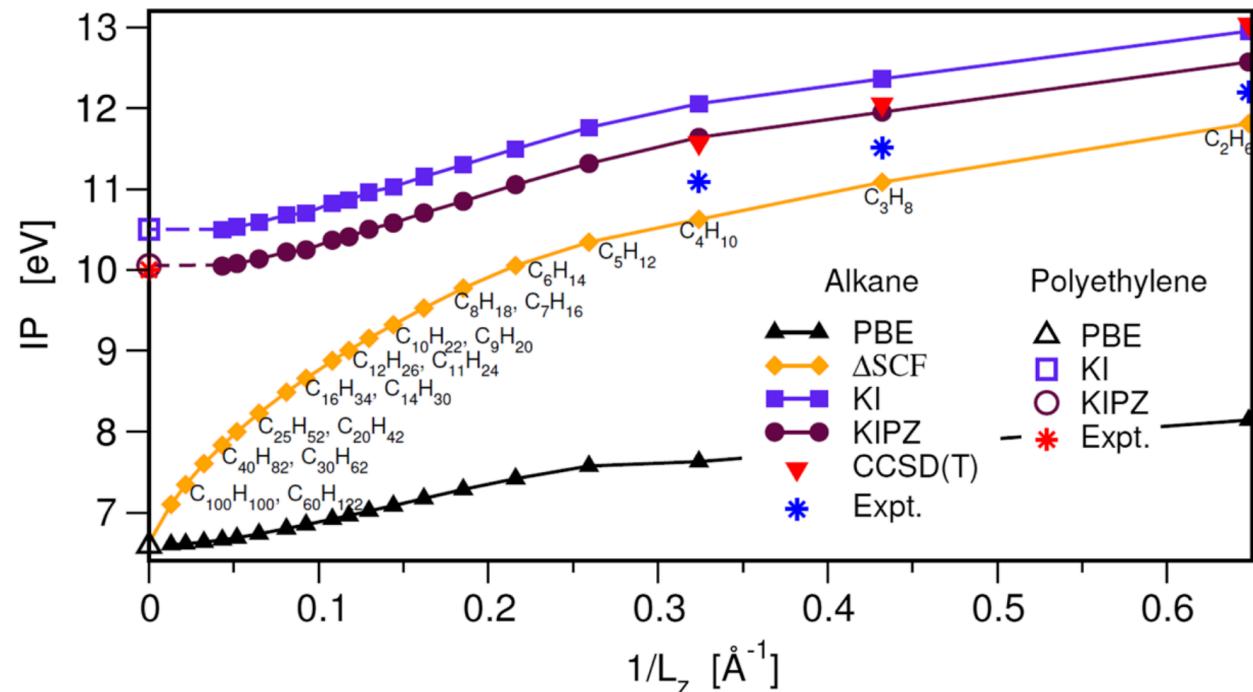
Issues with extended systems



Two options:

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

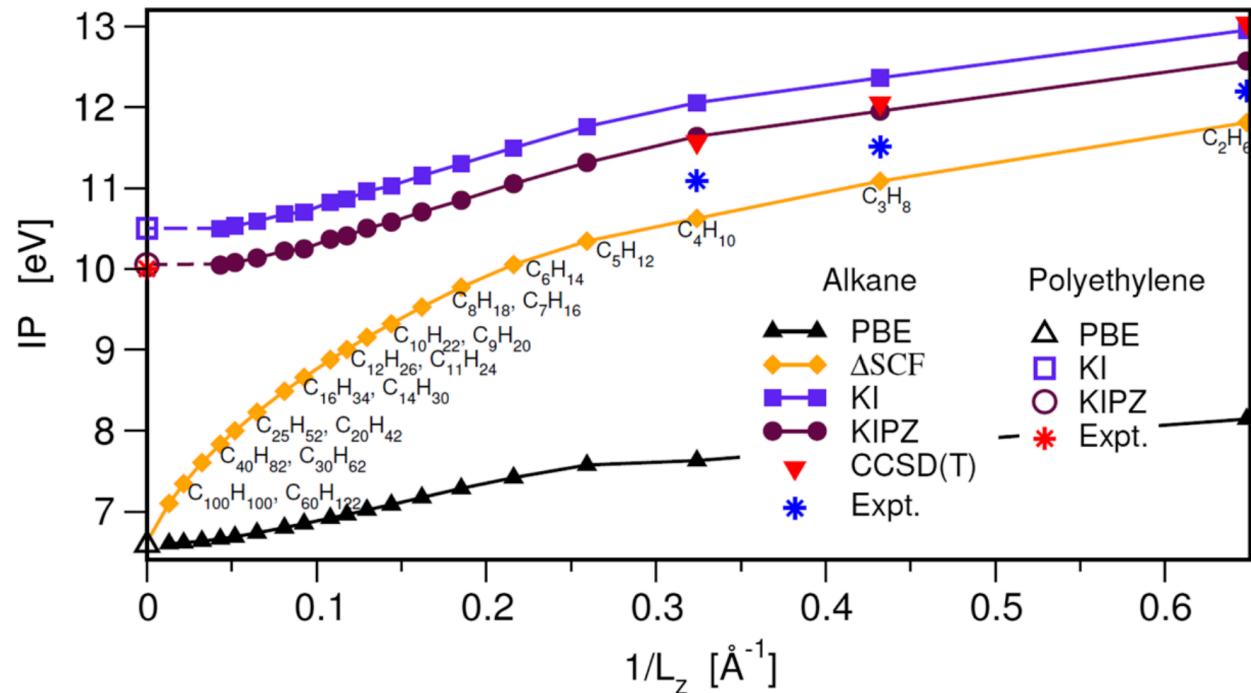
Issues with extended systems



Two options: 1. use a more advanced functional

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

Issues with extended systems



Two options: 1. use a more advanced functional, or 2. stay in the “safe” region

¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

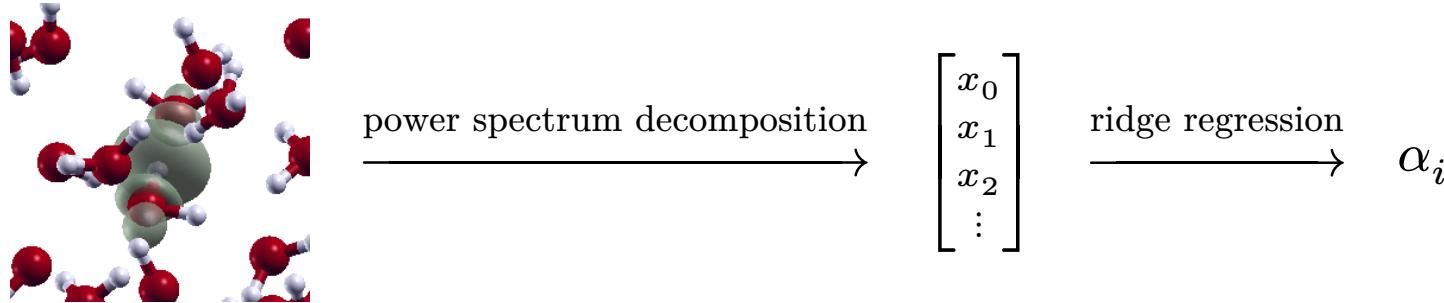
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    },  
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    }  
  },  
},
```

```

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            ],
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            "dis_win_max": 18.6
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    }
}

```

Machine-learned electronic screening

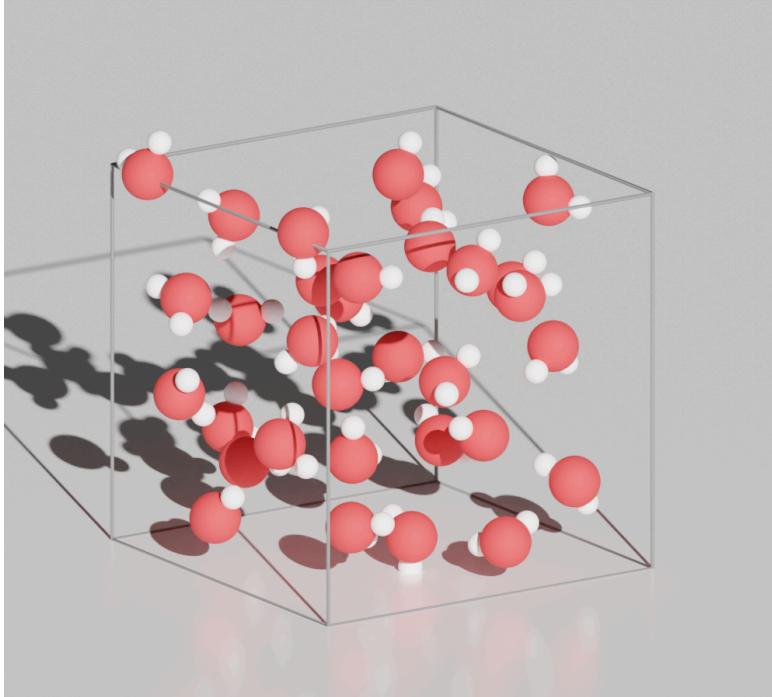


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

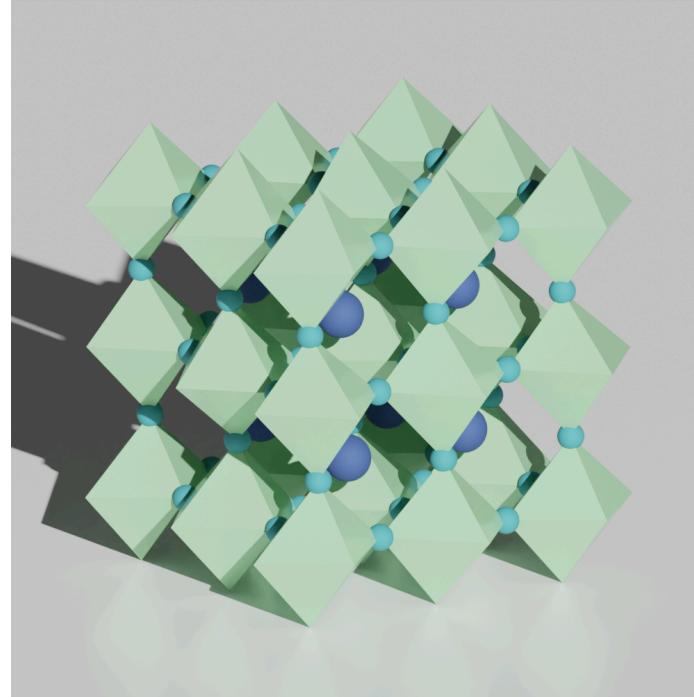
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

Machine-learned electronic screening



water

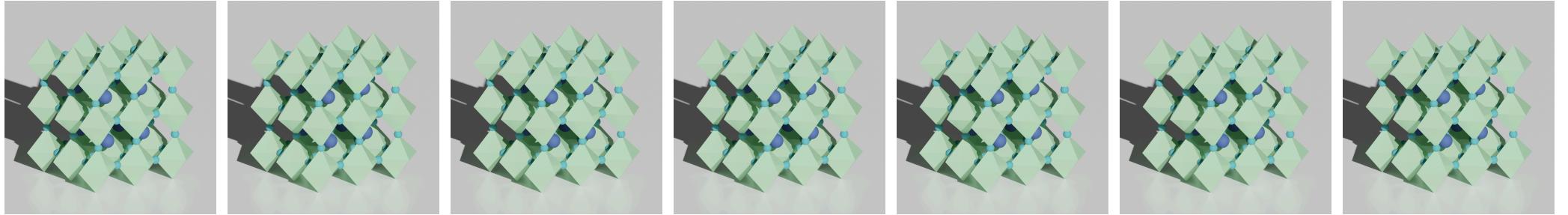


CsSnI₃

¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

Machine-learned electronic screening

The use-case

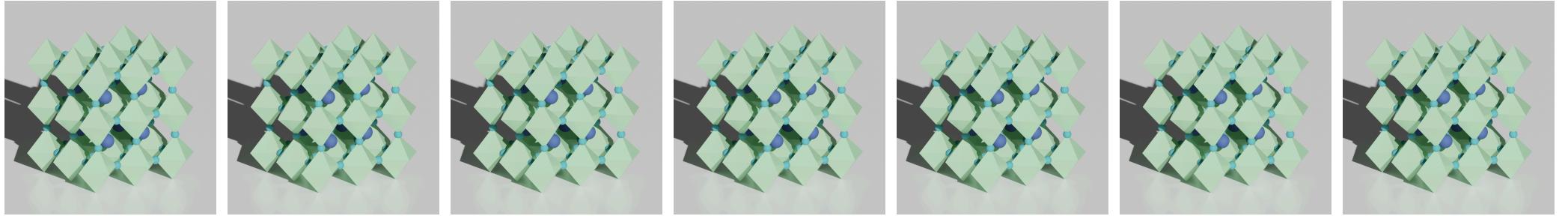


train

predict

Machine-learned electronic screening

The use-case

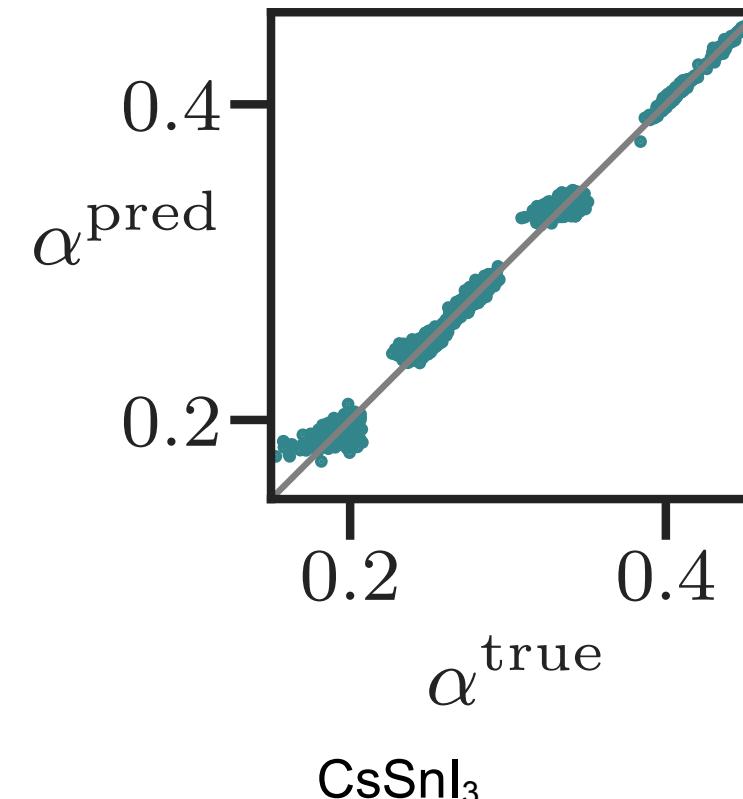
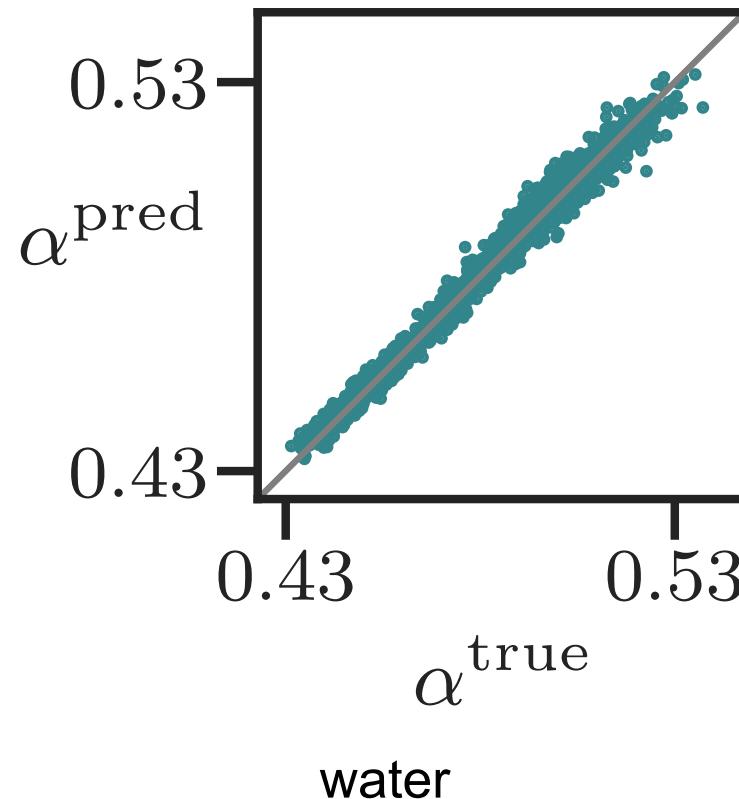


train

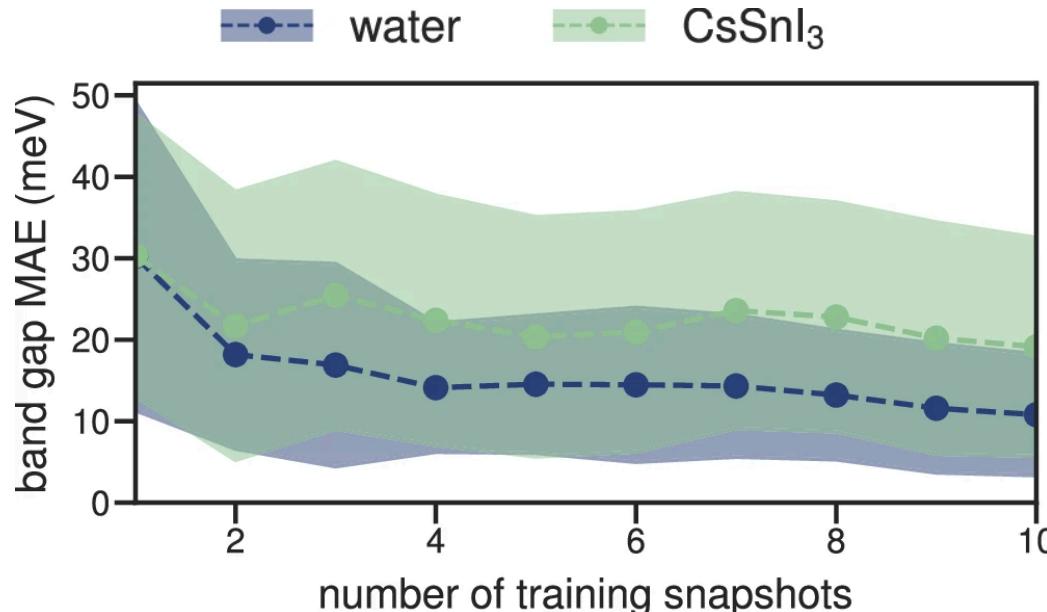
predict

N.B. not a general model

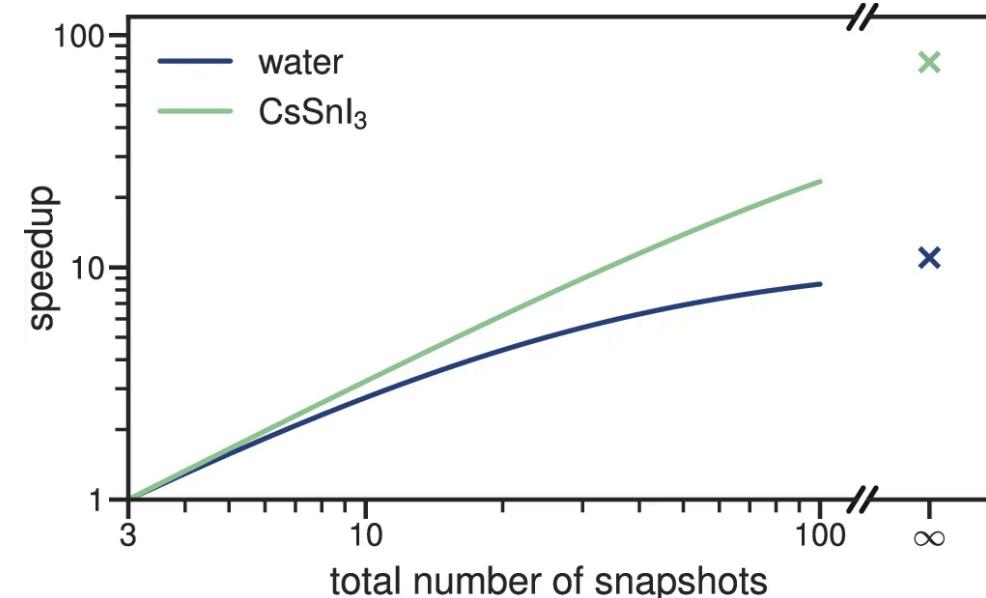
Machine-learned electronic screening



Machine-learned electronic screening



accurate to within $\mathcal{O}(10 \text{ meV})$ cf. typical
band gap accuracy of $\mathcal{O}(100 \text{ meV})$



speedup of $\mathcal{O}(10)$ to $\mathcal{O}(100)$

¹Y. Schubert *et al.* *npj Comput Mater* **10**, 1–12 (2024)

Taking advantage of symmetries

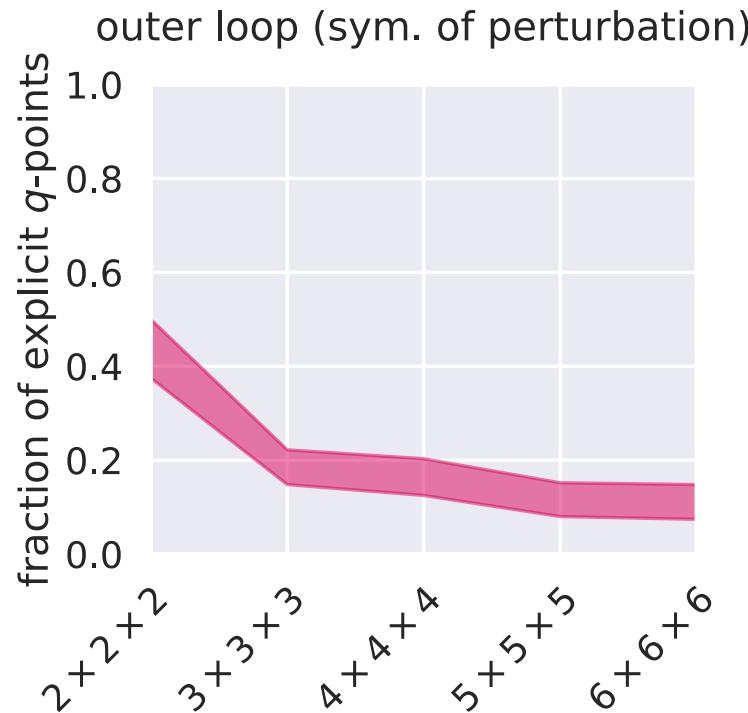
To compute screening parameters via DFPT...

```

1:function CalculateAlpha( $n$ )
2:   for  $q \in \text{BZ}$  do
3:     for  $k \in \text{BZ}$  do
4:       ▷ Linear system  $Ax = b$  to obtain  $\Delta\psi_{\mathbf{k}+\mathbf{q},v}(\mathbf{r})$ 
5:     end
6:      $\Delta\rho_q^{0n} \leftarrow \sum_{\mathbf{k}\mathbf{v}} \psi_{\mathbf{k}\mathbf{v}}^*(\mathbf{r}) \Delta\psi_{\mathbf{k}+\mathbf{q},v}(\mathbf{r}) + c.c.$ 
7:      $\Pi_{0n,\mathbf{q}}^{(r)} \leftarrow \langle \Delta\rho_q^{0n} | f_{\text{Hxc}} | \rho_{\mathbf{q}}^{0n} \rangle$ 
8:      $\Pi_{0n,\mathbf{q}}^{(u)} \leftarrow \langle \rho_{\mathbf{q}}^{0n} | f_{\text{Hxc}} | \rho_{\mathbf{q}}^{0n} \rangle$ 
9:   end
10:  return  $1 + \sum_{\mathbf{q}} \Pi_{0n,\mathbf{q}}^{(r)} / \sum_{\mathbf{q}} \Pi_{0n,\mathbf{q}}^{(u)}$ 
11end

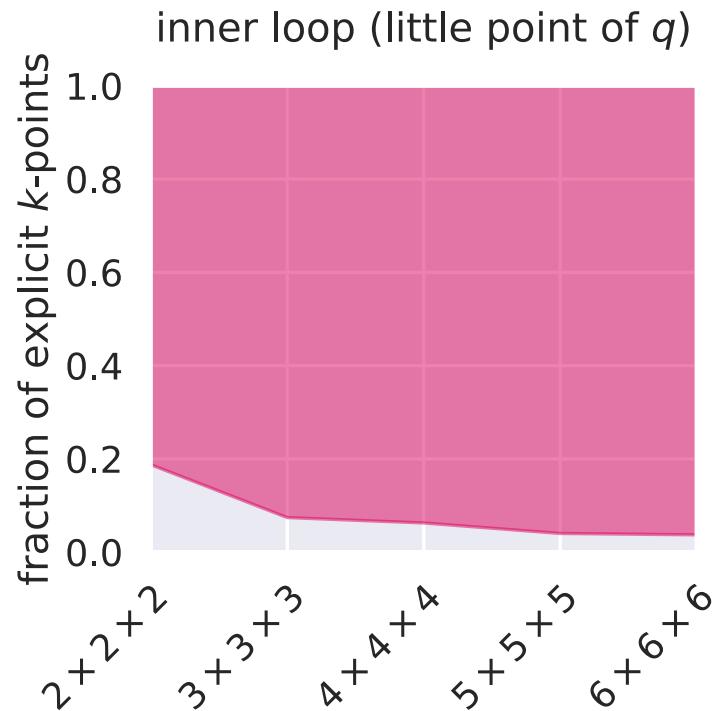
```

Taking advantage of symmetries



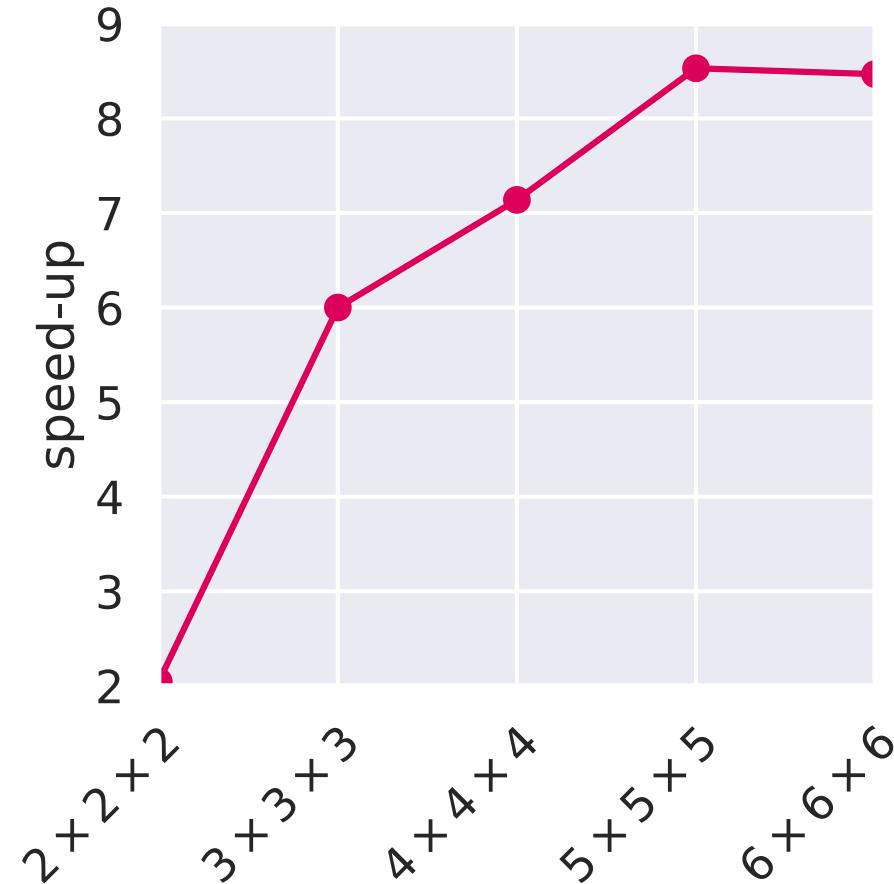
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$ (the symmetry of the perturbation; lower than that of the primitive cell)

Taking advantage of symmetries



$k \in \text{BZ} \rightarrow k \in \text{IBZ}(q)$ (can only use symmetries that leave q invariant)

Taking advantage of symmetries



Connections with approx. self-energies

Orbital-density functional theory:

$$(h + \alpha_i v_i^{KI}) |\psi_i\rangle = \lambda_i |\psi_i\rangle$$

$v_i^{KI}(\mathbf{r})$ is real, local, and state-dependent

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014), N. Colonna *et al.* *J. Chem. Theory Comput.* **15**, 1905 (2019)

Connections with approx. self-energies

Orbital-density functional theory:

$$(h + \alpha_i v_i^{KI}) |\psi_i\rangle = \lambda_i |\psi_i\rangle$$

$v_i^{KI}(\mathbf{r})$ is real, local, and state-dependent

cf. Green's function theory:

$$(h + \Sigma_i) |\psi_i\rangle = z_i |\psi_i\rangle$$

$\Sigma_i(\mathbf{r}, \mathbf{r}')$ is complex, non-local, and state-dependent

¹A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014), N. Colonna *et al.* *J. Chem. Theory Comput.* **15**, 1905 (2019)

Connections with approx. self-energies

Hartree-Fock self-energy in localized representation

$$\begin{aligned}\Sigma_x(\mathbf{r}, \mathbf{r}') &= -\sum_{k\sigma}^{\text{occ}} \psi_{k\sigma}(\mathbf{r}) f_H(\mathbf{r}, \mathbf{r}') \psi_{k\sigma}^*(\mathbf{r}') \\ &\implies \langle \varphi_{i\sigma} | \Sigma_x | \varphi_{j\sigma'} \rangle \approx -\langle \varphi_{i\sigma} | v_H[n_{i\sigma}] | \varphi_{i\sigma} \rangle \delta_{ij} \delta_{\sigma\sigma'}\end{aligned}$$

Unscreened KIPZ@ Hartree ($v_{\text{xc}} \rightarrow 0$; $f_{\text{Hxc}} \rightarrow f_H$; $\varepsilon^{-1} \rightarrow 1$)

$$\langle \varphi_{i\sigma} | v_{j\sigma', \text{xc}}^{\text{KIPZ}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | f_H | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \approx -\langle \varphi_{i\sigma} | v_H[n_{i\sigma}] | \varphi_{i\sigma} \rangle \delta_{ij} \delta_{\sigma\sigma'}$$

Connections with approx. self-energies

Screened exchange plus Coulomb hole (COHSEX)

$$\Sigma_{\text{xc}}^{\text{SEX}}(s, s') = - \sum_{k\sigma}^{\text{occ}} \psi_{k\sigma}(\mathbf{r}) \psi_{k\sigma}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}')$$

$$\Sigma_{\text{xc}}^{\text{COH}}(s, s') = \frac{1}{2} \delta(s, s') \{W(\mathbf{r}, \mathbf{r}') - f_H(\mathbf{r}, \mathbf{r}')\}$$

$$\Rightarrow \langle \varphi_{i\sigma} | \Sigma_{\text{xc}}^{\text{COHSEX}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | W | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

KIPZ@ Hartree with RPA screening ($v_{\text{xc}} \rightarrow 0$; $f_{\text{Hxc}} \rightarrow f_H$; $\varepsilon^{-1} \rightarrow \text{RPA}$)

$$\langle \varphi_{i\sigma} | v_{j\sigma', \text{xc}}^{\text{KIPZ}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | W | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

Connections with approx. self-energies

Static $\text{GW}\Gamma_{\text{xc}}$ — local (DFT-based) vertex corrections¹

$$\Sigma_{\text{xc}(1,2)}^{G\text{W}\Gamma_{\text{xc}}} = iG(1,2)W_{t-e}(1,2)$$

$$W_{t-e} = (1 - f_{\text{Hxc}}\chi_0)^{-1}f_H$$

$$\Rightarrow \langle \varphi_{i\sigma} | \Sigma_{\text{xc}}^{G\text{W}\Gamma_{\text{xc}}} | \varphi_{j\sigma'} \rangle \approx \left\{ \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | W_{t-e} | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

KIPZ@ DFT ($v_{\text{xc}} \rightarrow \text{DFT}$; $f_{\text{Hxc}} \rightarrow \text{DFT}$; $\varepsilon^{-1} \rightarrow \text{DFT}$)

$$\langle \varphi_{i\sigma} | v_{j\sigma',\text{xc}}^{\text{KIPZ}} | \varphi_{j\sigma'} \rangle \approx \left\{ \langle \varphi_{i\sigma} | v_{\sigma,\text{xc}}^{\text{DFT}} | \varphi_{i\sigma} \rangle + \left(\frac{1}{2} - f_{i\sigma} \right) \langle n_{i\sigma} | \varepsilon_{t-e}^{-1} f_{\text{Hxc}} | n_{i\sigma} \rangle - E_H[n_{i\sigma}] \right\} \delta_{ij} \delta_{\sigma\sigma'}$$

¹M. S. Hybertsen *et al.* *Phys. Rev. B* **35**, 5585–5601 (1987), R. Del Sole *et al.* *Phys. Rev. B* **49**, 8024–8028 (1994)

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