



PSI

Center for Scientific Computing,
Theory and Data

Koopmans functionals

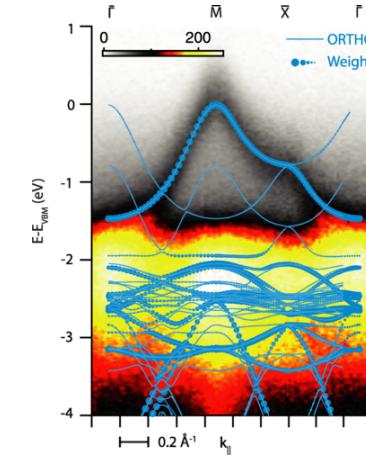
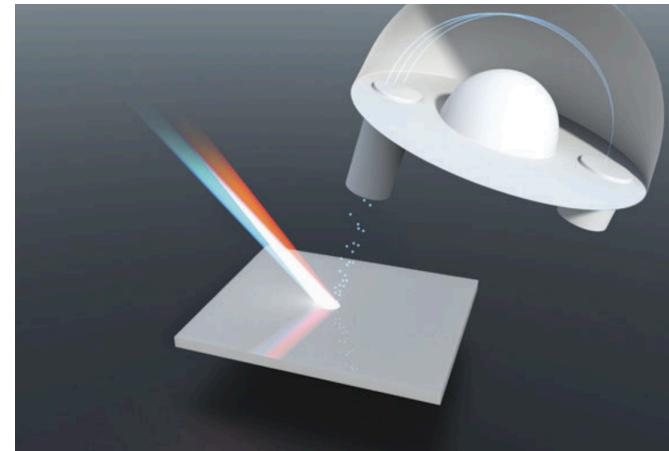
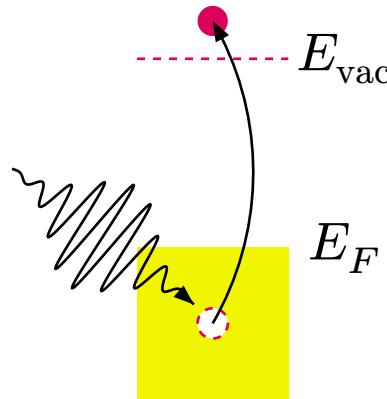
How satisfying piecewise linearity can yield reliable band structures

Edward Linscott

Psi-k, 27 August 2025

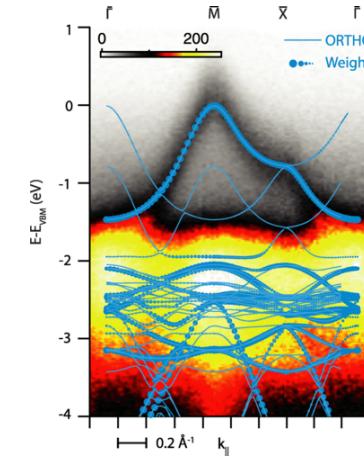
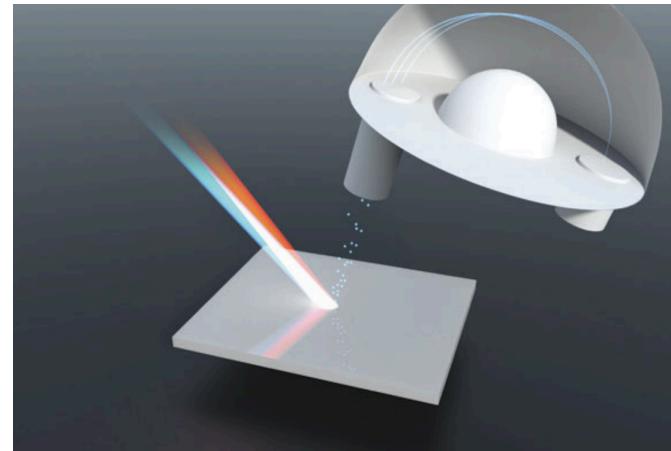
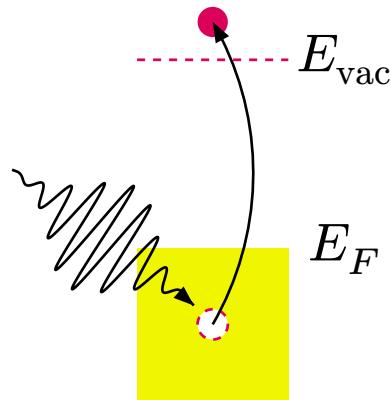
Predicting spectral properties

Spectral properties are fundamental to understanding materials...



Predicting spectral properties

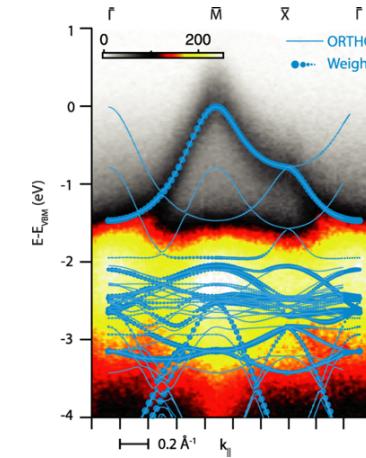
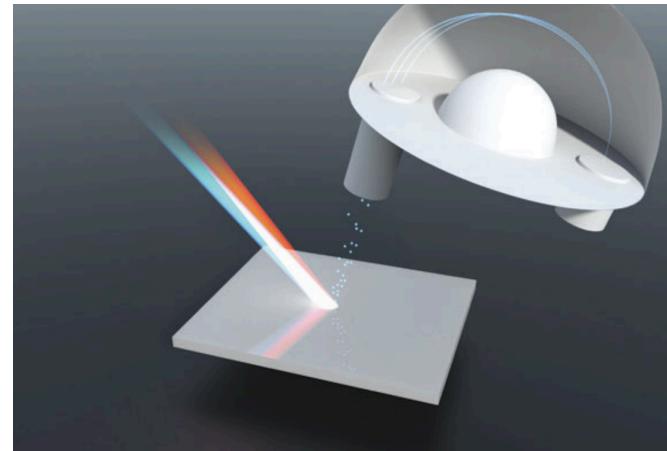
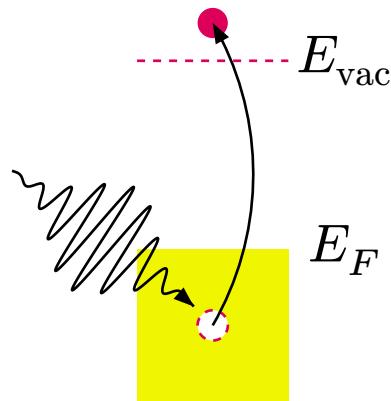
Spectral properties are fundamental to understanding materials...



... but how can we routinely compute them?

Predicting spectral properties

Spectral properties are fundamental to understanding materials...

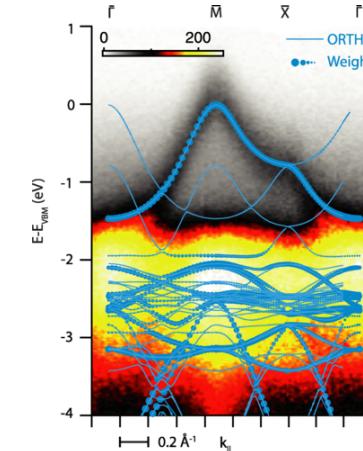
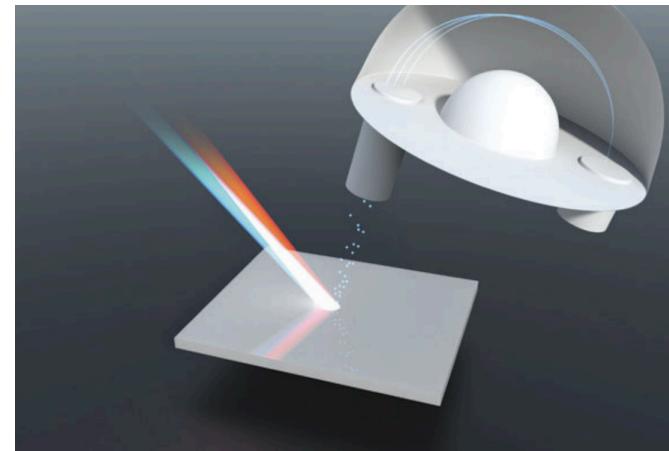
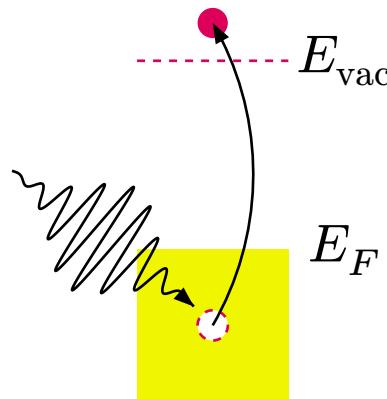


... but how can we routinely compute them?

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

Predicting spectral properties

Spectral properties are fundamental to understanding materials...



... but how can we routinely compute them?

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

 Koopmans functionals: cure systematic errors in DFT → a functional that can accurately predict single-particle excitations

Basic theory of Koopmans functionals

Total energy differences vs. eigenvalues

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

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

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

but DFT does *not*

**Core idea: impose this condition to DFT
to improve its description of spectral
properties**

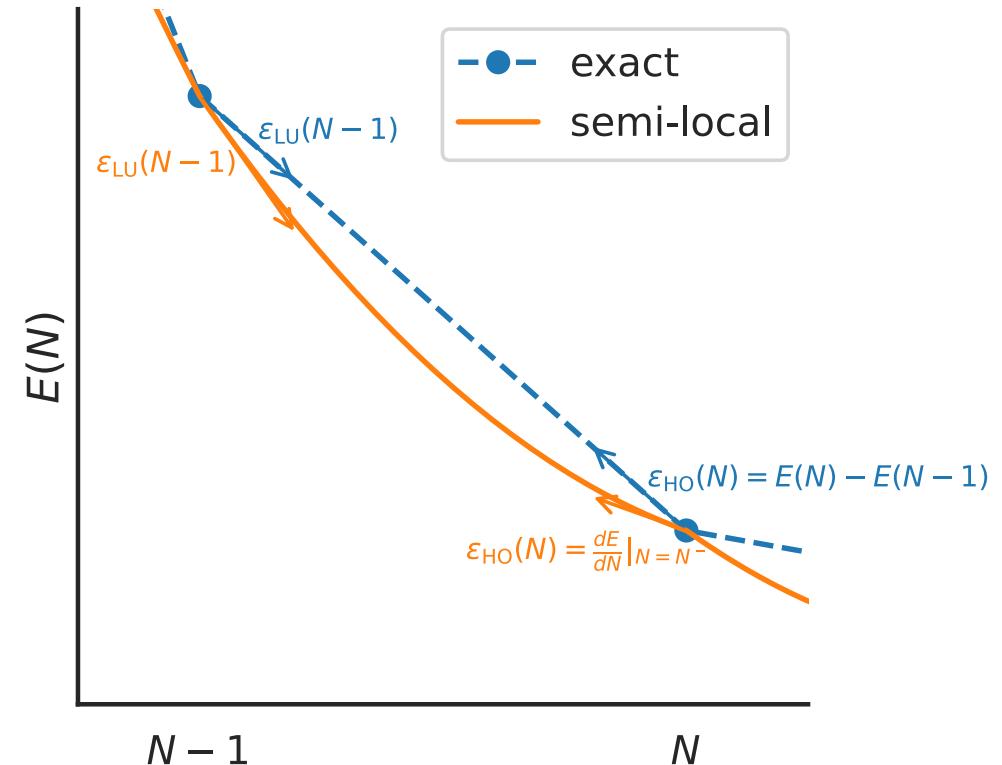
Imposing generalised piecewise linearity

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

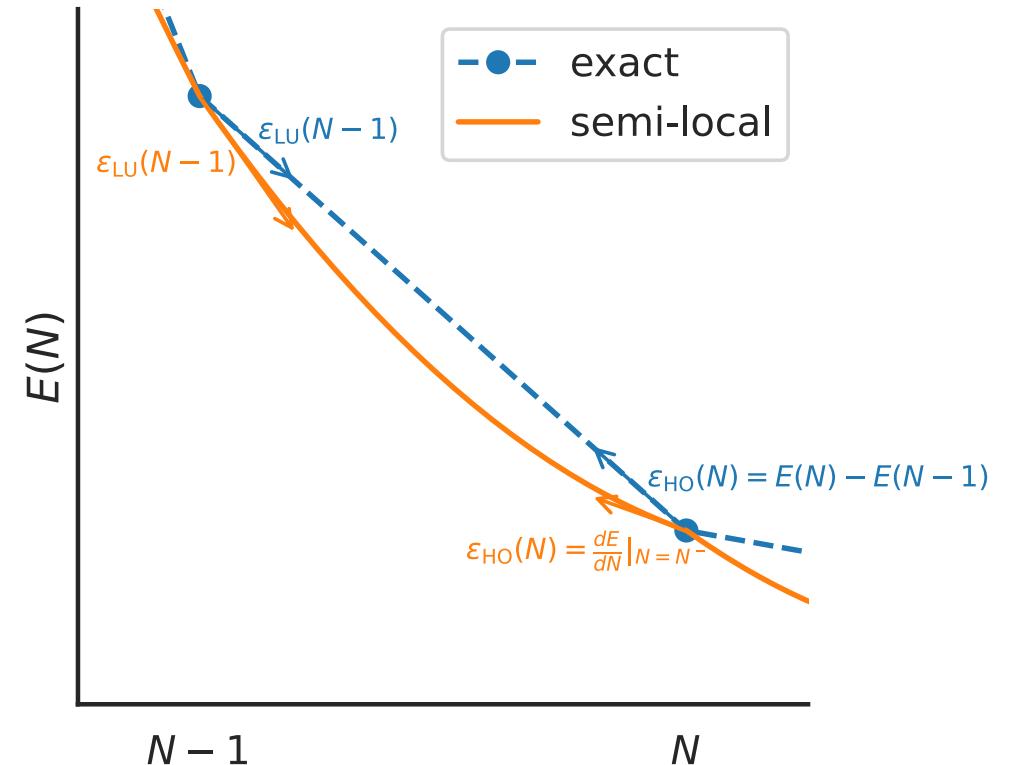
- independent of f_i
- equal to ΔE of explicit electron addition/
removal



Imposing generalised piecewise linearity

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

Bakes the total energy differences $E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]$ into the functional



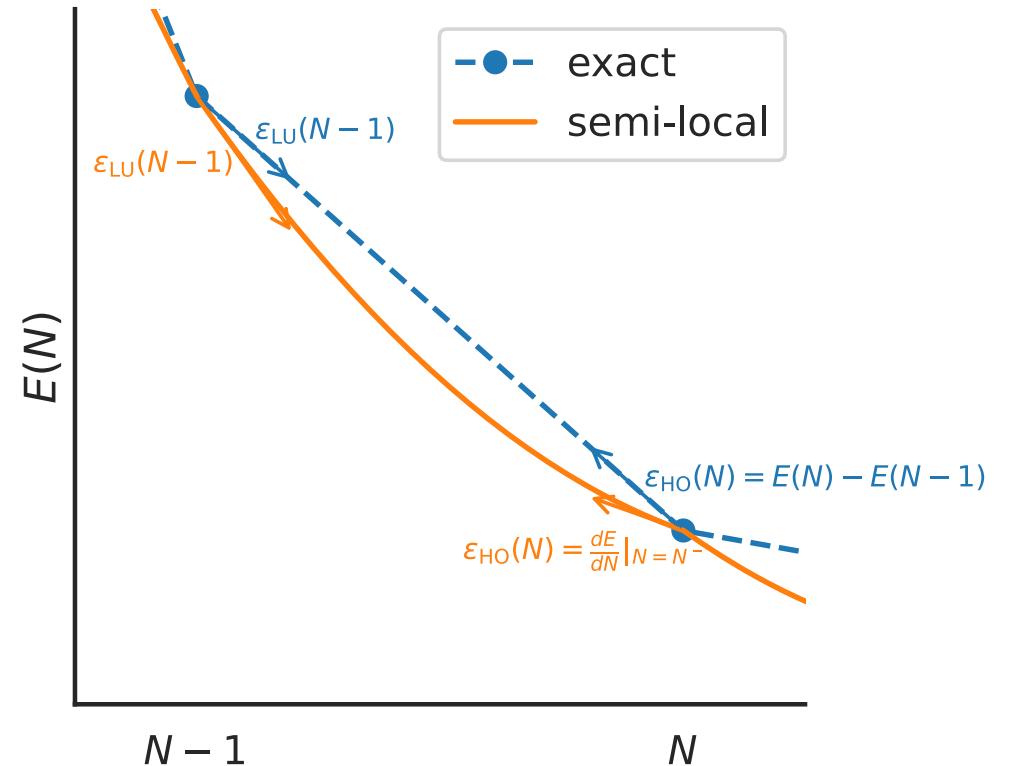
Imposing generalised piecewise linearity

$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

$$+ \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df + f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

removes non-linear dependence on f_i

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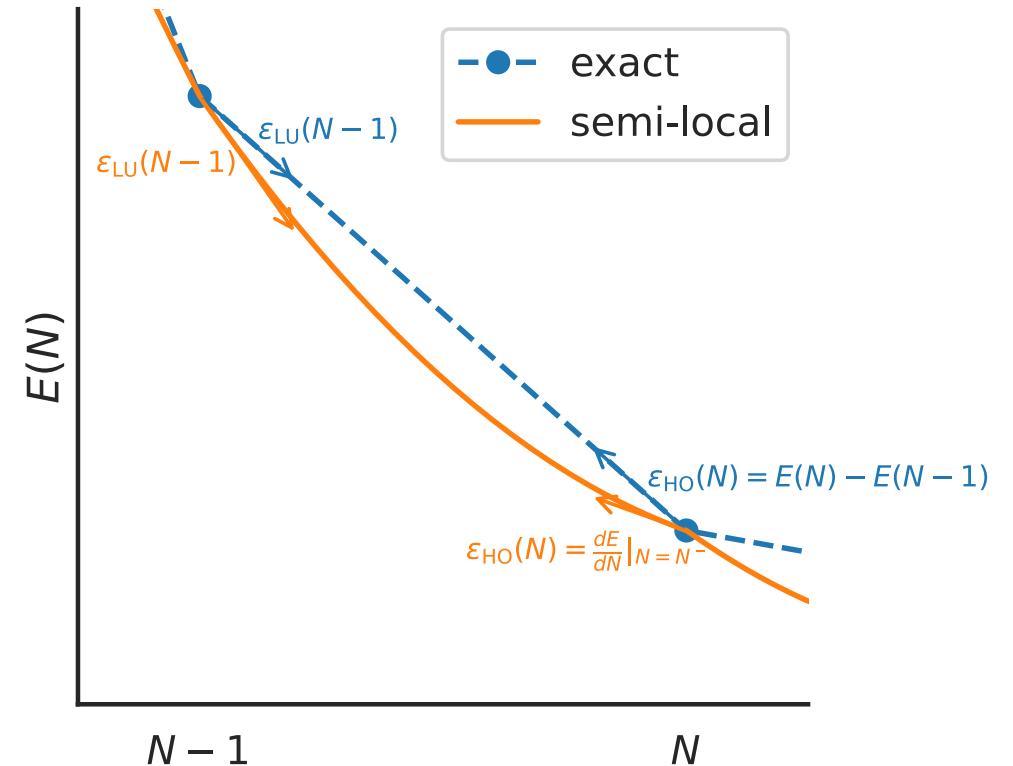
removes non-linear dependence on f_i

$$+ f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

restores linear dependence on f_i

Bakes the total energy differences

$E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]$ into the functional



Comparison with DFT+*U* (and BLOR)

DFT+*U*

designed to
correct...

by
construction...

correction
applied to...

orbitals defined
by...

parametrised
by...

Koopmans

Comparison with DFT+*U* (and BLOR)

| DFT+ <i>U</i> | Koopmans |
|--------------------------|---|
| designed to correct... | erroneous global curvature in total energies w.r.t. N |
| by construction... | |
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Comparison with DFT+ U (and BLOR)

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Comparison with DFT+ U (and BLOR)

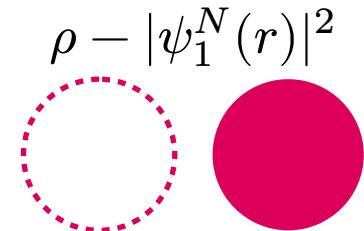
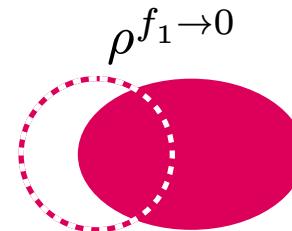
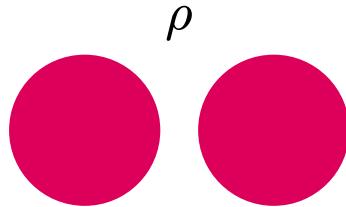
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| by construction... | corrects local curvature in total energies (BLOR does so more faithfully) | removes dependence of ε_i on f_i and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$ |
| correction applied to... | | |
| orbitals defined by... | | |
| parametrised by... | | |

Making the functional tractable

$E[\rho^{f_i \rightarrow f}]$ cannot be directly evaluated

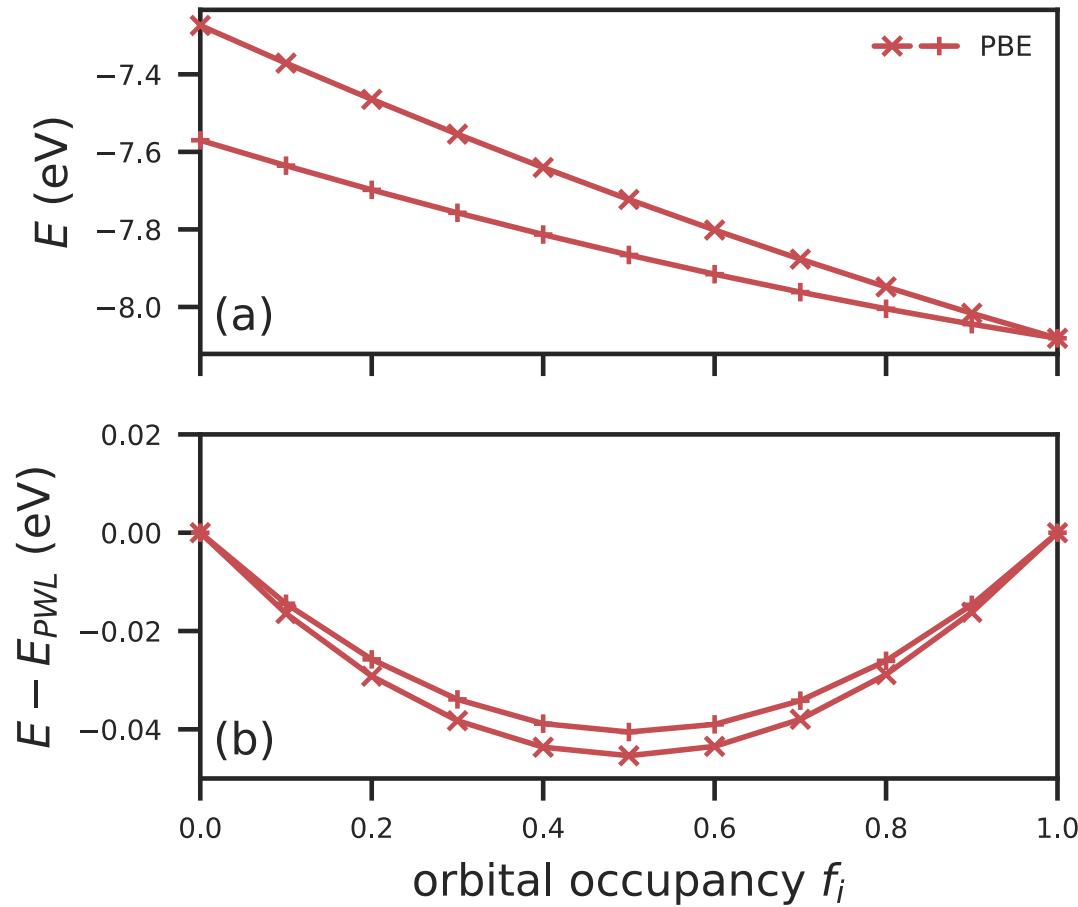


N -electron solution

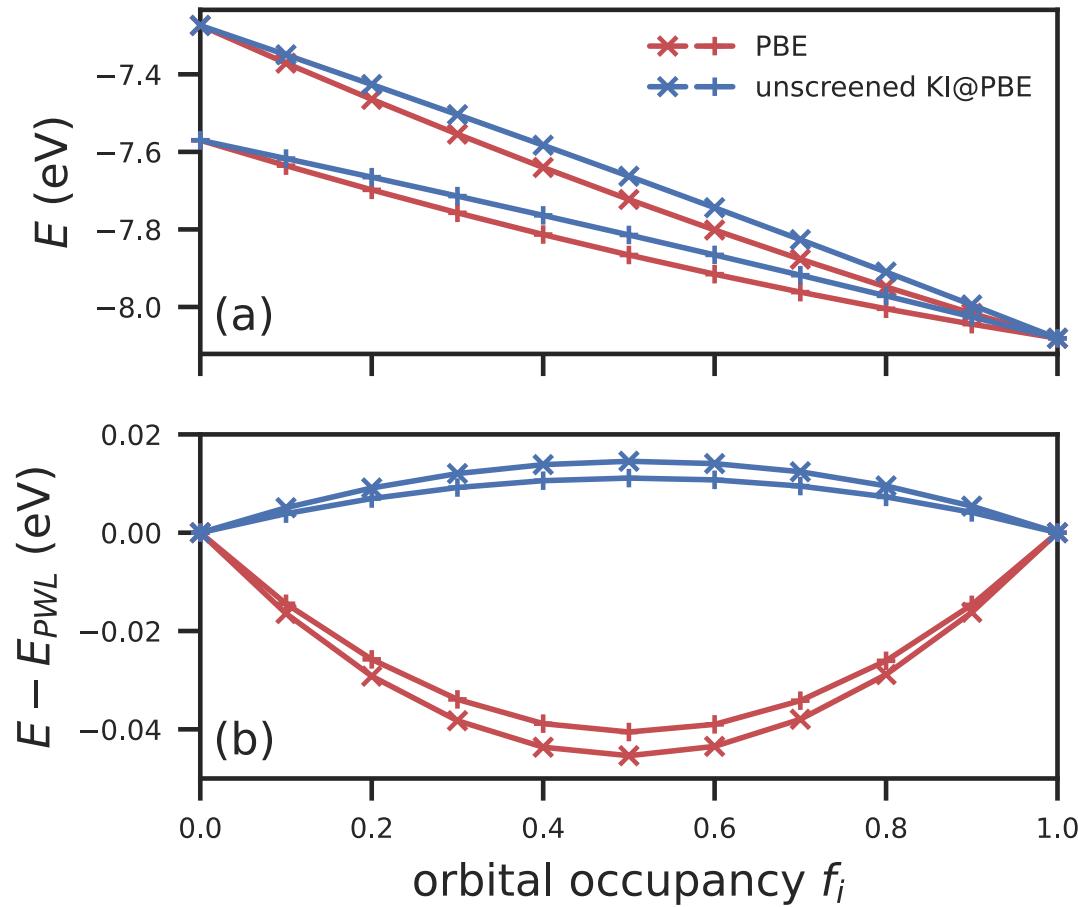
what we'd like to evaluate

what we can quickly evaluate

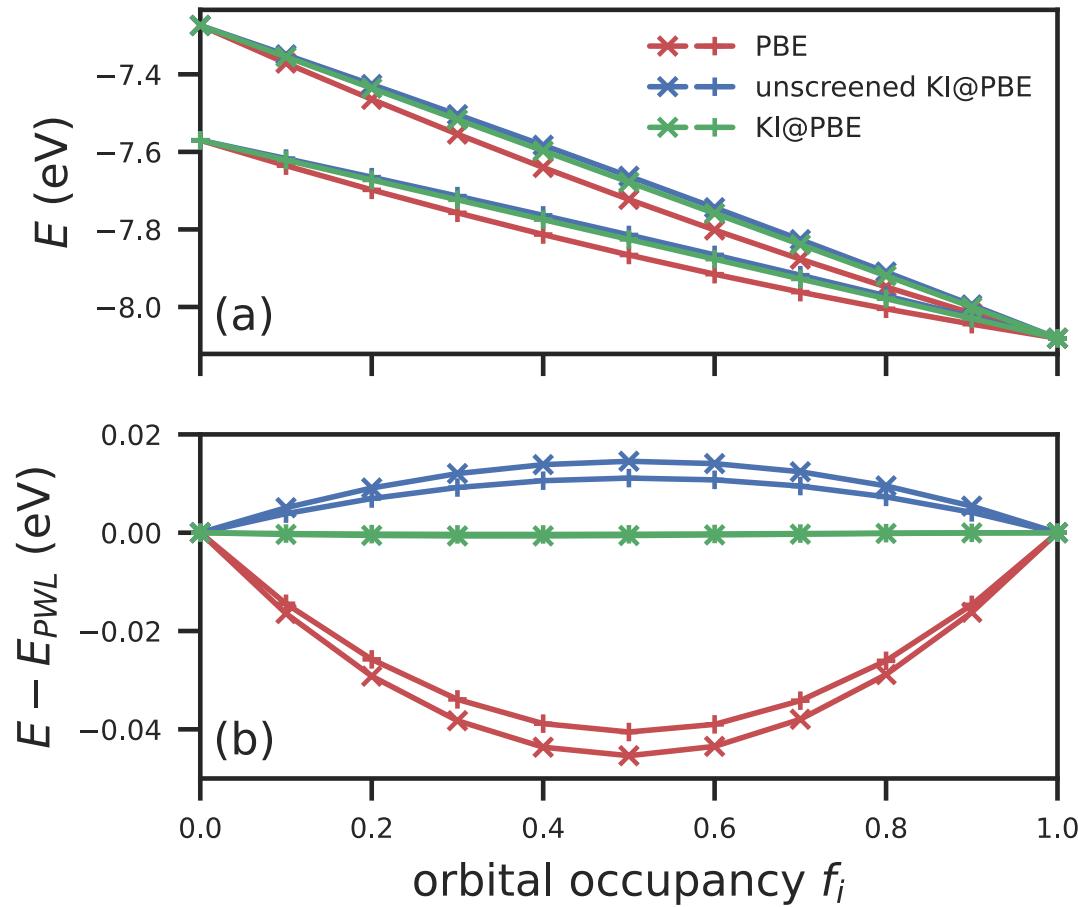
Making the functional tractable



Making the functional tractable



Making the functional tractable



Making the functional tractable

So instead of...

$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \left\{ -\left(E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right) + f_i \left(E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right) \right\}$$

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cannot evaluate directly cannot evaluate directly cannot evaluate directly

Making the functional tractable

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we can instead evaluate...

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

Making the functional tractable

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uses frozen orbitals uses frozen orbitals uses frozen orbitals

Making the functional tractable

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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

Making the functional tractable

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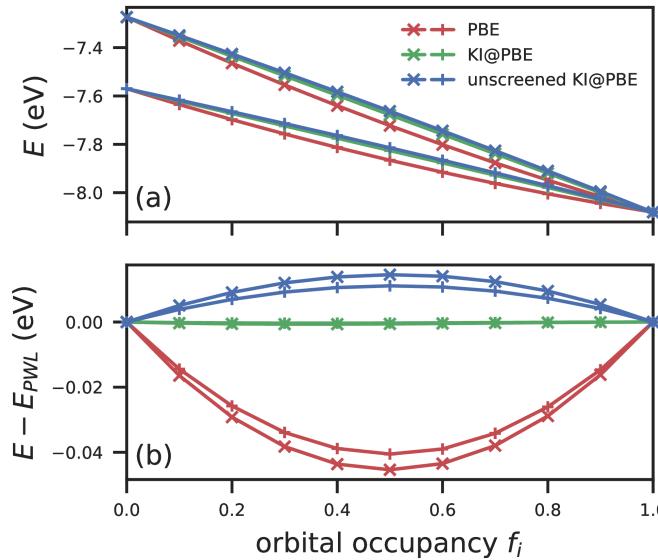
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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

which is easy to evaluate e.g.

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

Screening

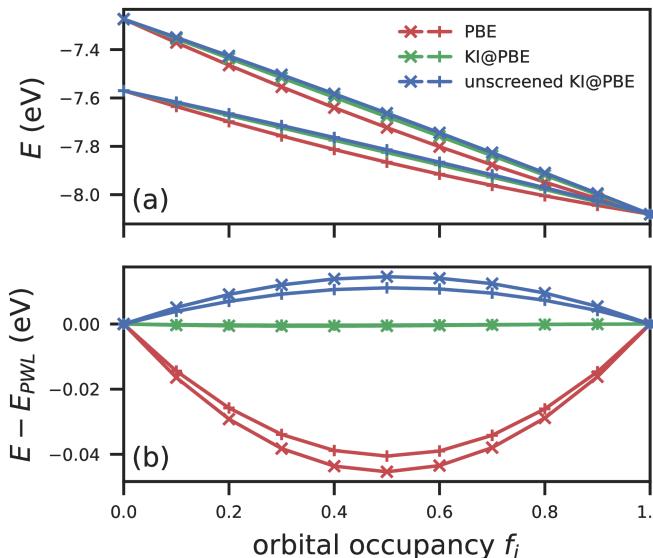


¹N. L. Nguyen *et al.* *Phys. Rev. X* **8**, 21051 (2018), R. De Gennaro *et al.* *Phys. Rev. B* **106**, 35106 (2022)

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

³N. Colonna *et al.* *J. Chem. Theory Comput.* **18**, 5435 (2022)

Screening



Construct α_i from explicit Δ SCF calculations¹

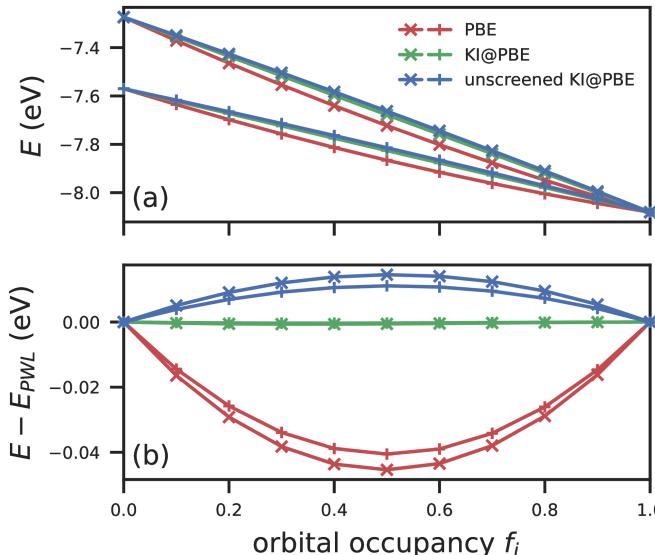
$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)} \text{ where } \lambda_{ii}(\alpha) = \langle \varphi_i | \hat{h}^{\text{DFT}} + \alpha \hat{v}_i^{\text{KI}} | \varphi_i \rangle$$

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Recast via linear response²:

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

which can be efficiently computed via DFPT³

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Orbital-density dependence

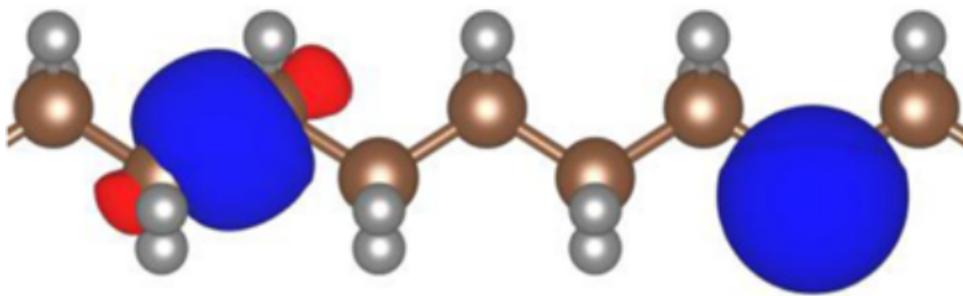
The potential is orbital-dependent!

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

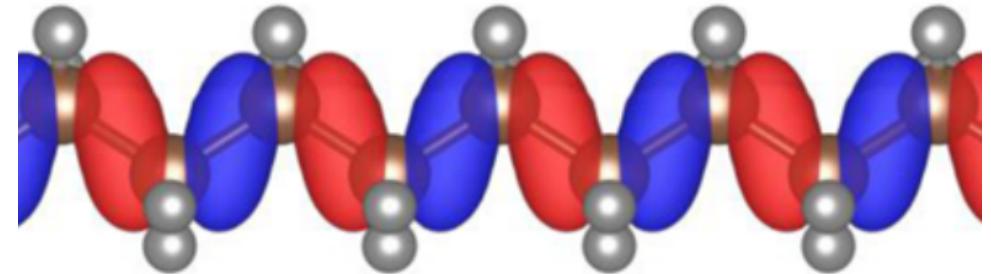
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two variational orbitals



a canonical orbital

Orbital-density dependence

Because we have an ODD...

¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Phys. Rev. B* **89**, 195134 (2014)

Orbital-density dependence

Because we have an ODD...

- minimisation gives localised orbitals, so we can use MLWFs¹

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

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Orbital-density dependence

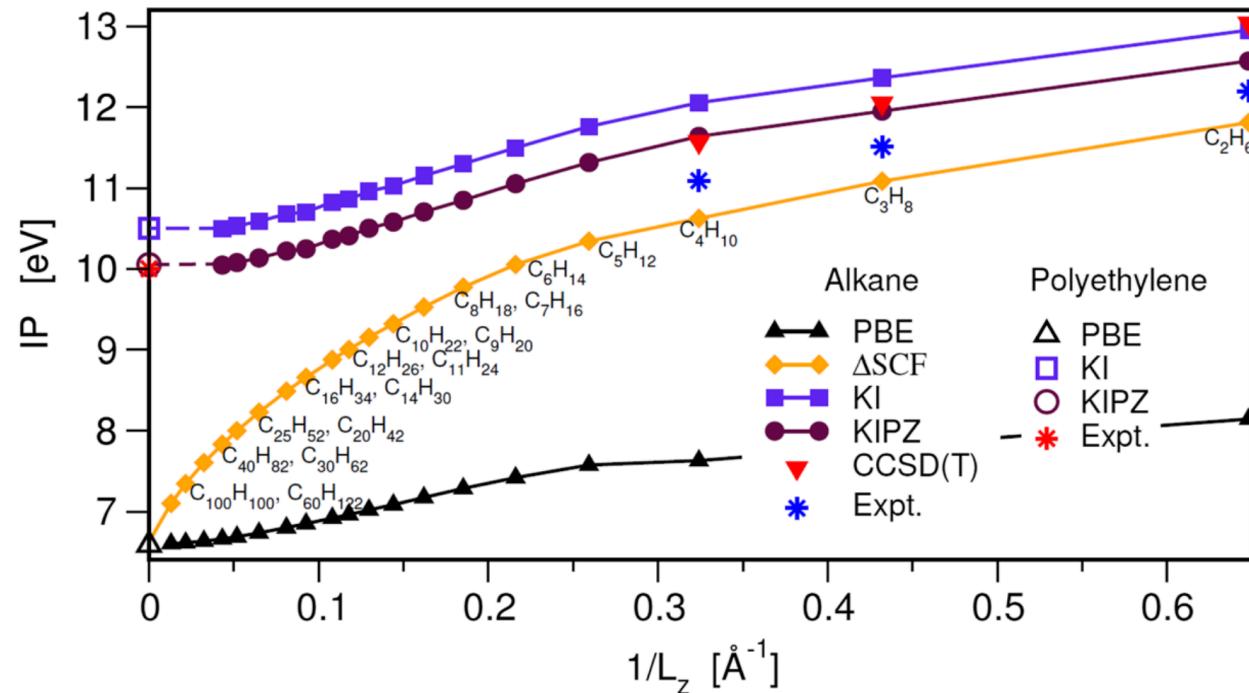
Because we have an ODD...

- minimisation gives localised orbitals, so we can use MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}
- we have a natural generalisation of DFT towards spectral functional theory²

¹N. Marzari *et al.* *Rev. Mod. Phys.* **84**, 1419–1475 (2012)

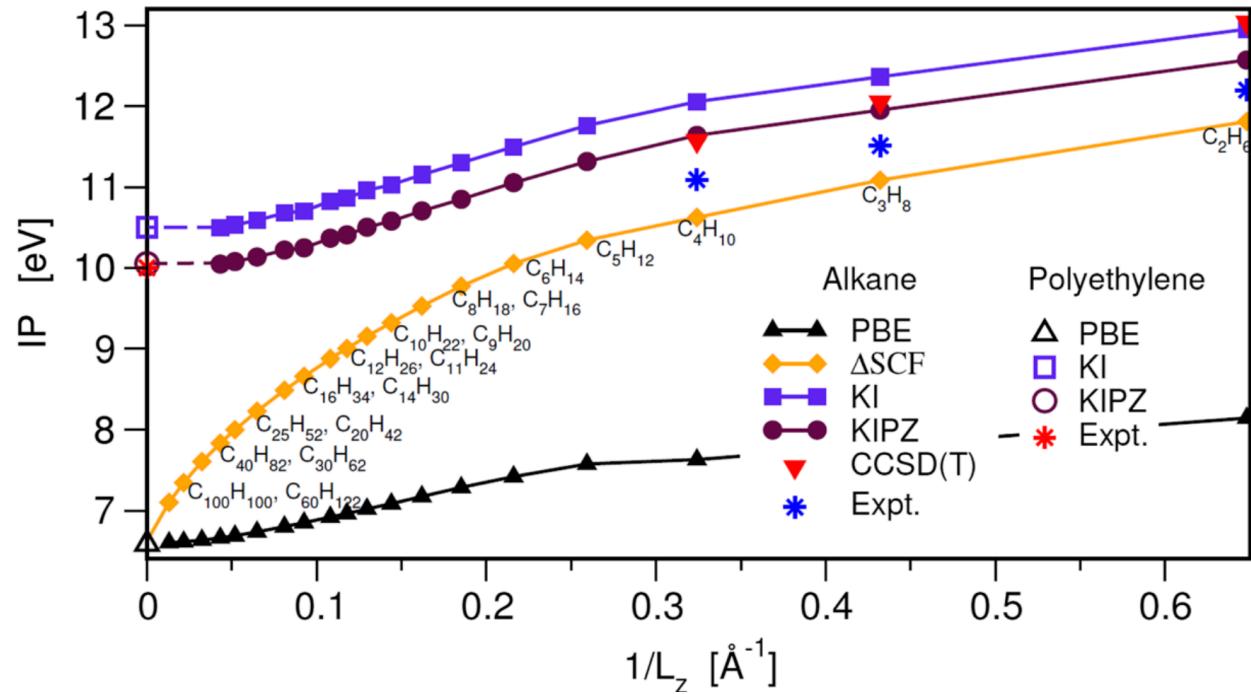
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Issues with extended systems



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

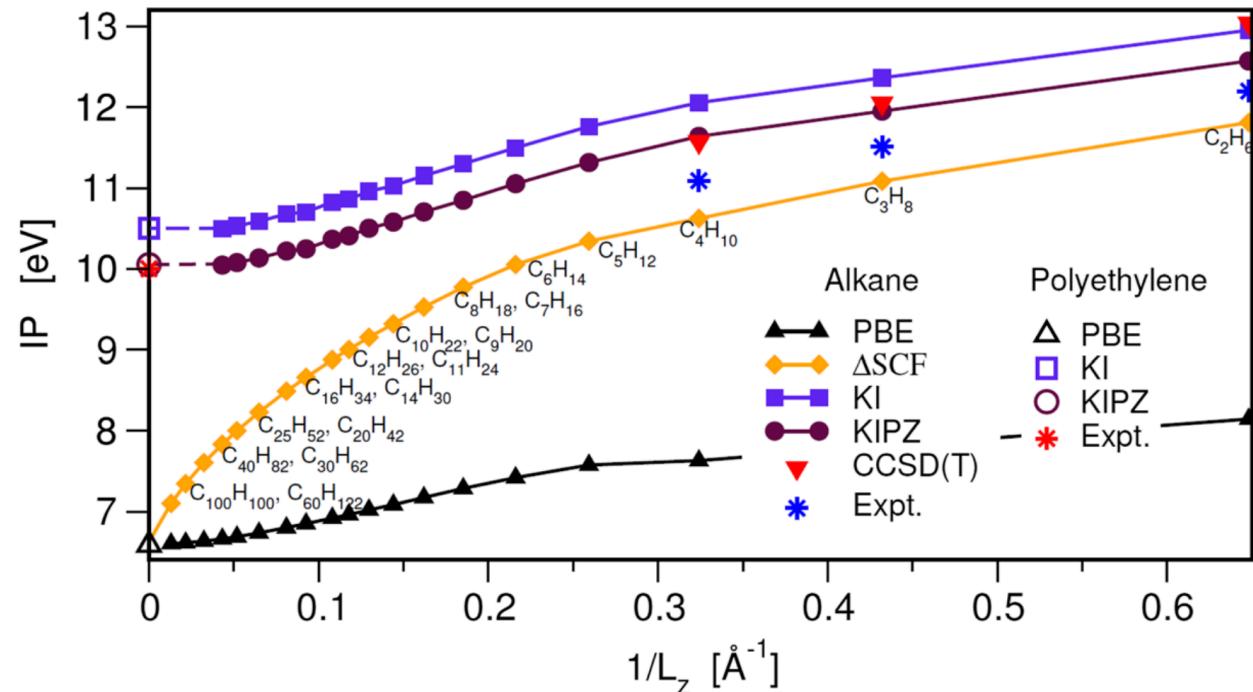
Issues with extended systems



One cell: $E(N + \delta N) - E(N)$

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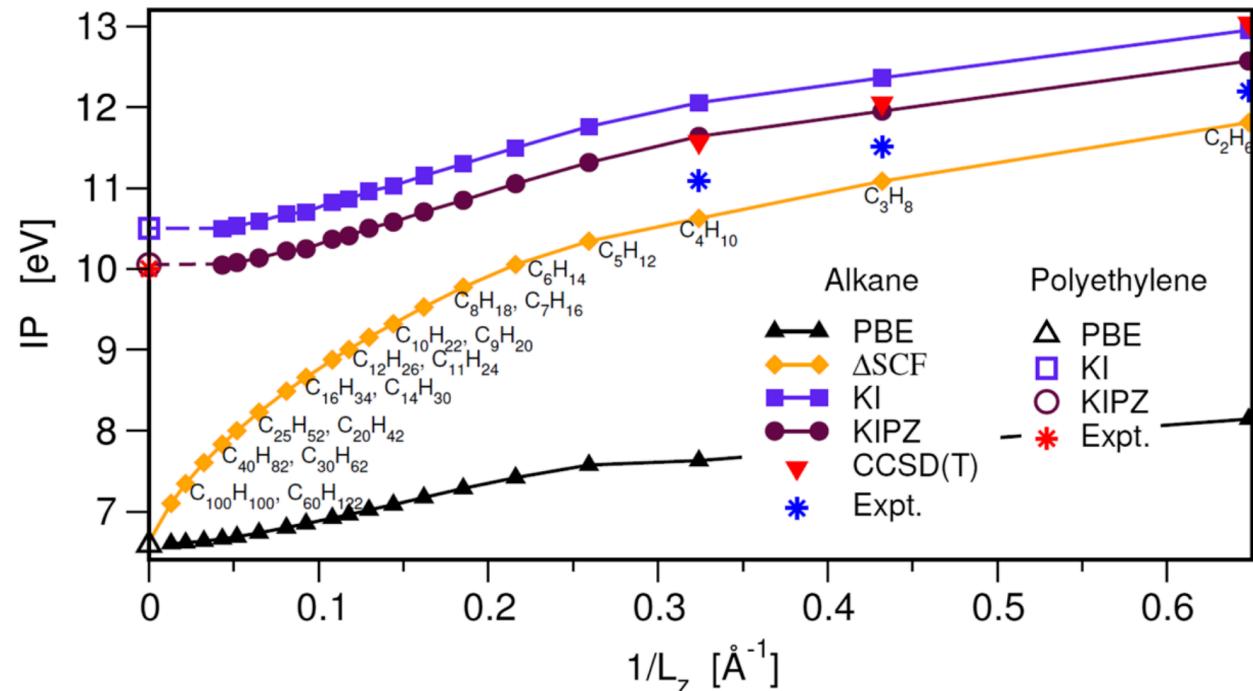
Issues with extended systems



One cell: $E(N + \delta N) - E(N)$ all cells: $\Delta E = \frac{1}{\delta N}(E(N + \delta N) - E(N)) = \frac{dE}{dN} = -\varepsilon_{HO}$ ¹

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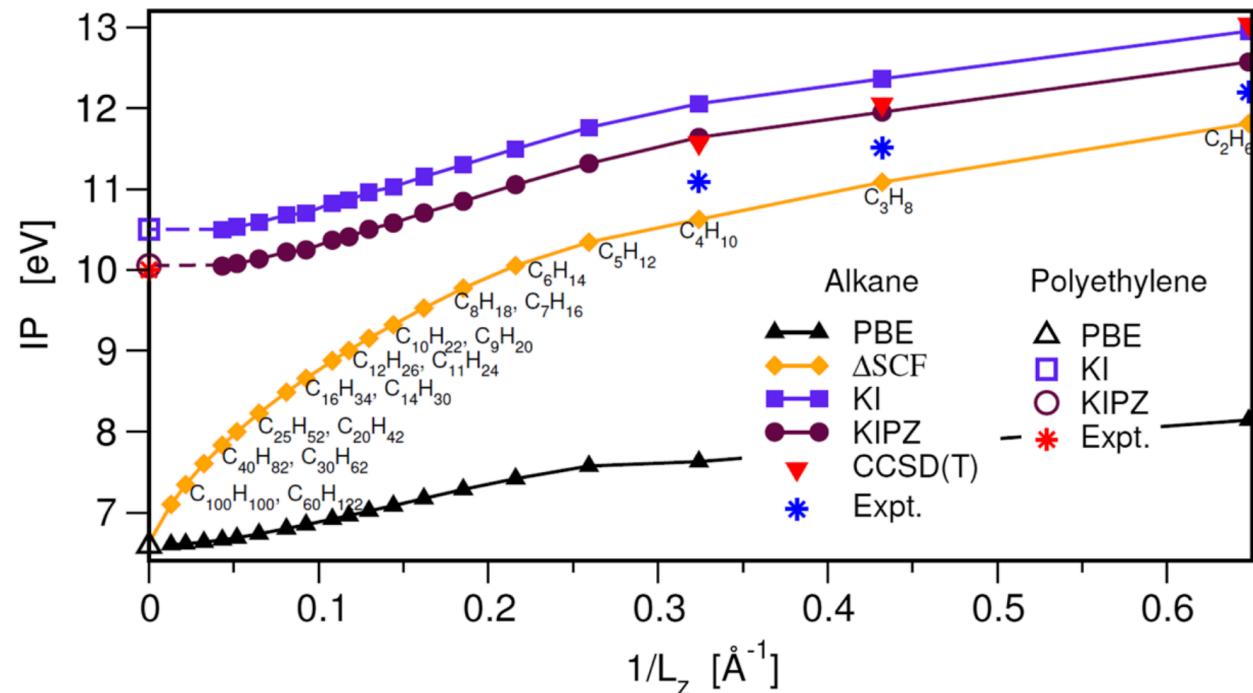
Issues with extended systems



Two options:

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

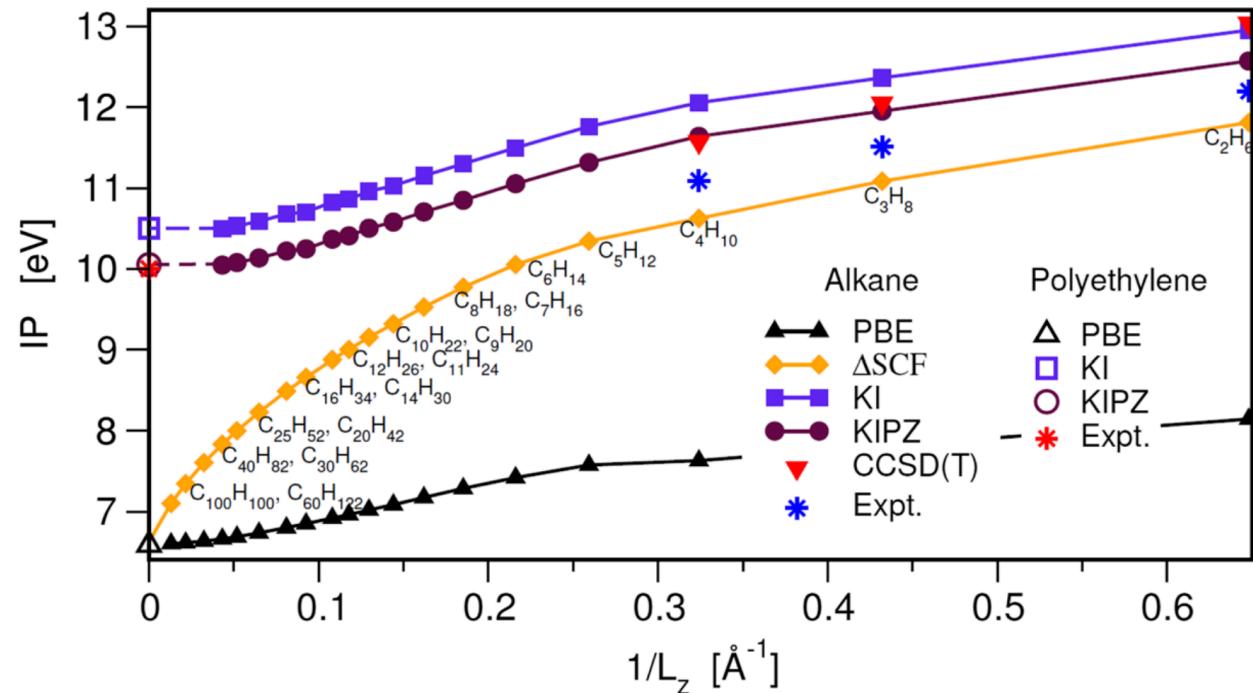
Issues with extended systems



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)

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
- localised charge excitations baked into derivatives
- total energy unchanged!
- screening parameters
- orbital-density-dependence

Comparison with DFT+ U (and BLOR)

| | DFT+ U | Koopmans |
|---------------------------------|---|---|
| <i>designed 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>by construction...</i> | corrects local curvature in total energies (BLOR does so more faithfully) | removes dependence of ε_i on orbital occupations and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$ |
| <i>correction applied to...</i> | | |
| <i>orbitals defined by...</i> | | |
| <i>parametrised by...</i> | | |

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| <i>correction applied to...</i> | selected subspaces (e.g. 3d orbitals) | |
| <i>orbitals defined by...</i> | | |
| <i>parametrised by...</i> | | |

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| <i>by construction...</i> | corrects local curvature in total energies (BLOR does so more faithfully) | removes dependence of ε_i on 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> | | |
| <i>parametrised by...</i> | | |

Comparison with DFT+ U (and BLOR)

| | DFT+ U | Koopmans |
|---------------------------------|---|---|
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| | DFT+ U | Koopmans |
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| <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> | | |

Comparison with DFT+*U* (and BLOR)

| | DFT+ <i>U</i> | Koopmans |
|---------------------------------|---|--|
| <i>designed to correct...</i> | erroneous global curvature in total energies w.r.t. N | erroneous global curvature in total energies w.r.t. canonical orbital occupancies |
| <i>by construction...</i> | corrects local curvature in total energies (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> | | |

Comparison with DFT+U (and BLOR)

| | DFT+U | Koopmans |
|---------------------------------|---|--|
| <i>designed to correct...</i> | erroneous global curvature in total energies w.r.t. N | erroneous global curvature in total energies w.r.t. canonical orbital occupancies |
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| <i>orbitals defined by...</i> | Hubbard projectors (atom-centred, frozen, incomplete) | variational (localised) orbitals |
| <i>parametrised by...</i> | $\{U_i\}$, defined w.r.t. charge-neutral excitations if using LR | |

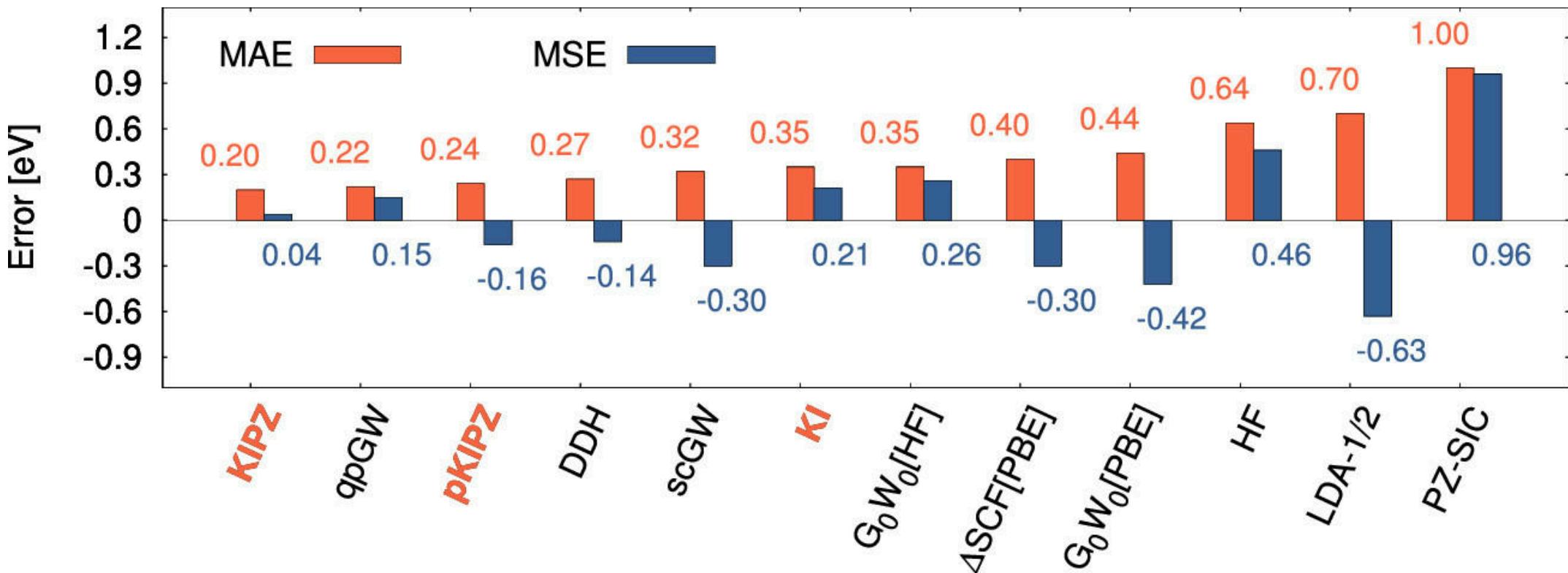
Comparison with DFT+U (and BLOR)

| | DFT+U | Koopmans |
|---------------------------------|---|--|
| <i>designed to correct...</i> | erroneous global curvature in total energies w.r.t. N | erroneous global curvature in total energies w.r.t. canonical orbital occupancies |
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| <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> | $\{U_i\}$, defined w.r.t. charge-neutral excitations if using LR | $\{\alpha_i\}$, defined w.r.t. charged excitations |

Results

Molecular systems

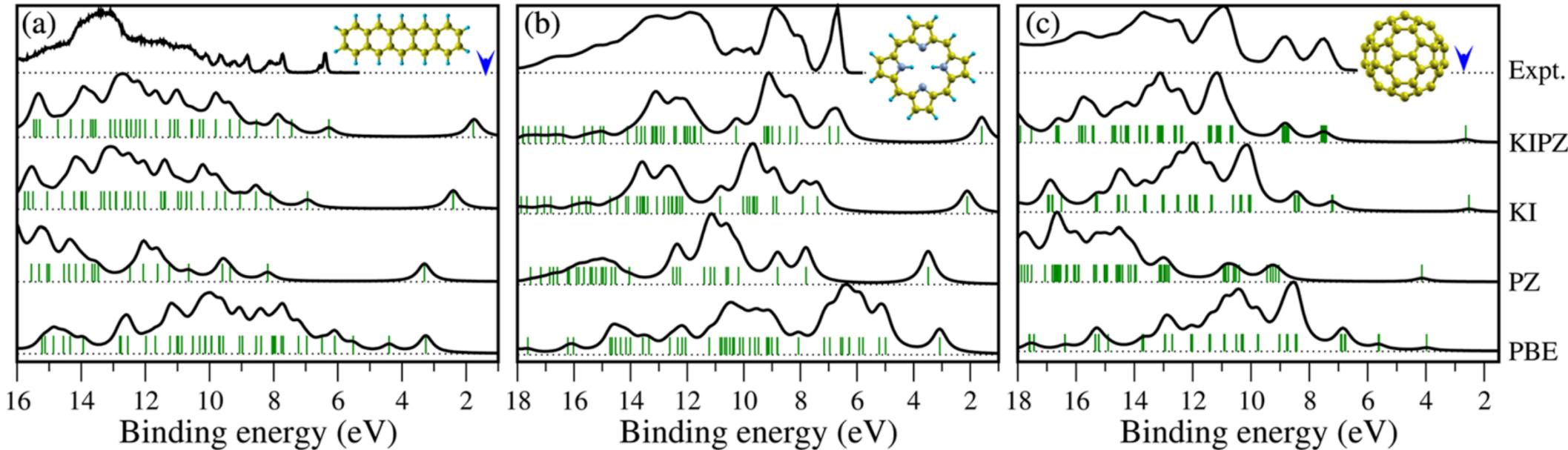
Ionisation potentials¹



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

Molecular systems

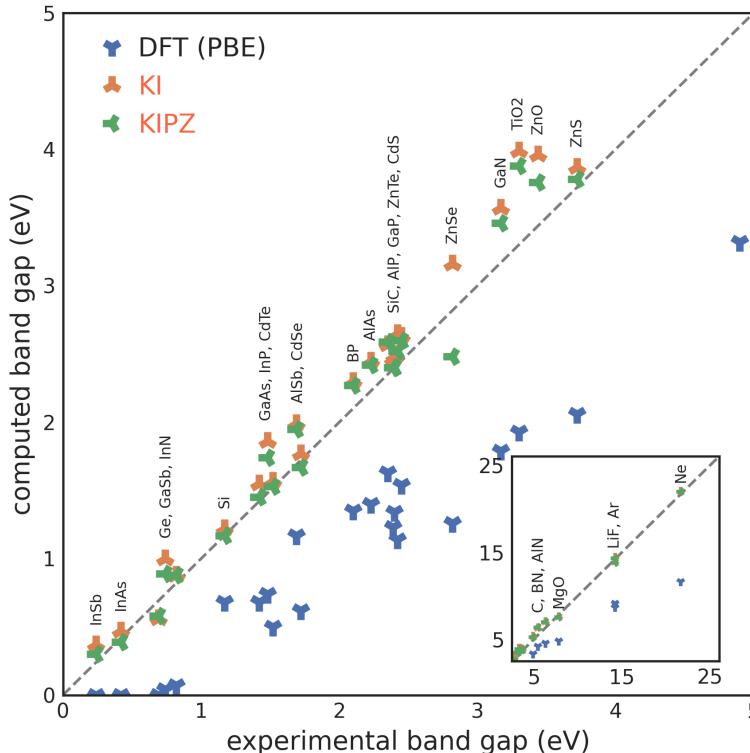
UV photoemission spectra¹



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

Extended systems

Prototypical semiconductors and insulators¹

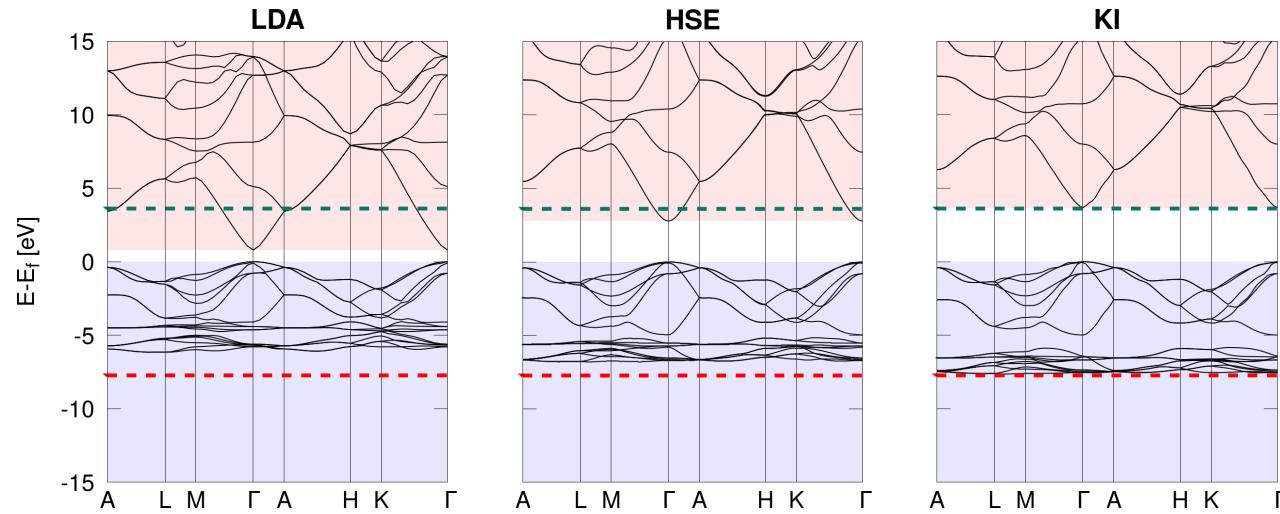


| | PBE | G_0W_0 | KI | KIPZ | $QSG\tilde{W}$ |
|------------------|------|----------|------|------|----------------|
| E_{gap} | 2.54 | 0.56 | 0.27 | 0.22 | 0.18 |
| IP | 1.09 | 0.39 | 0.19 | 0.21 | 0.49 |

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

Extended systems

ZnO¹

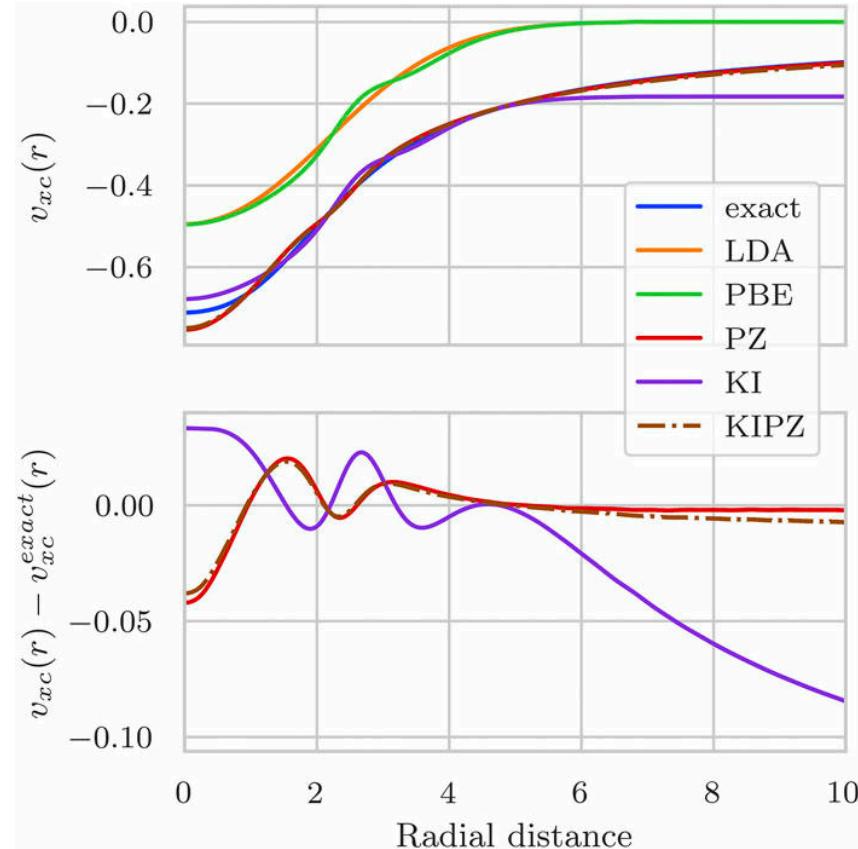


| | LDA | HSE | GW_0 | $scG\tilde{W}$ | KI | exp |
|---------------------------------|------|------|--------|----------------|--------------|---------------|
| E_{gap} | 0.79 | 2.79 | 3.0 | 3.2 | 3.52 | 3.52 |
| $\langle \varepsilon_d \rangle$ | -5.1 | -6.1 | -6.4 | -6.7 | -6.93 | -7.5 to -8.81 |
| Δ | 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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- only valid for systems with $E_{\text{gap}} > 0$
- 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

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

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

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e.g. for the corrective potential

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

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

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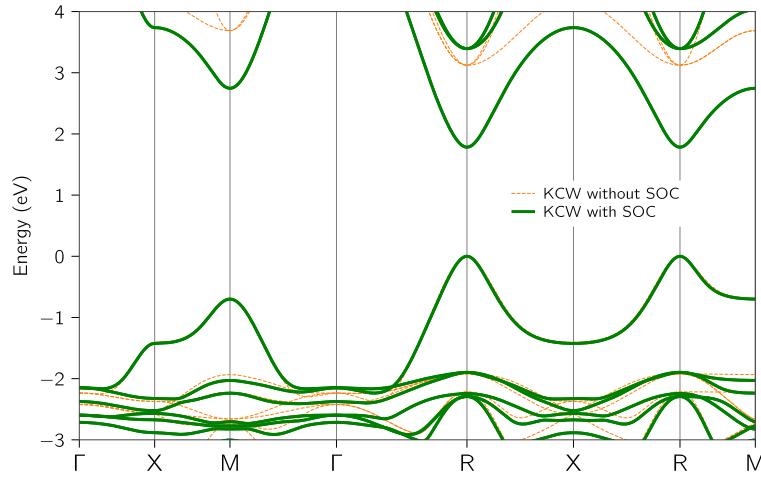
↓

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

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

Non-collinear spin

CsPbBr₃



| | LDA | HSE | G_0W_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)

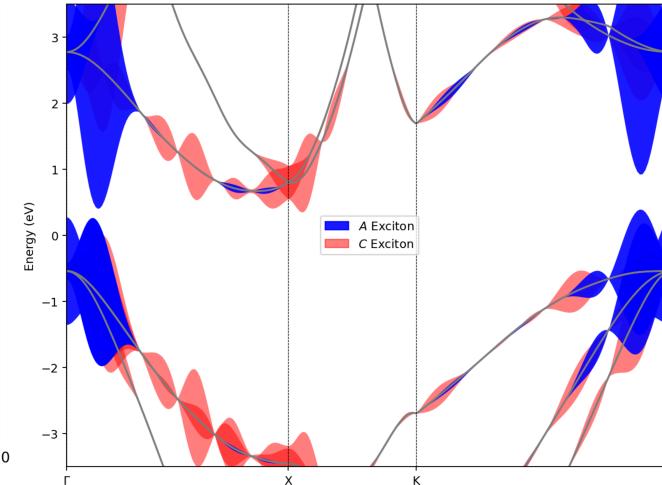
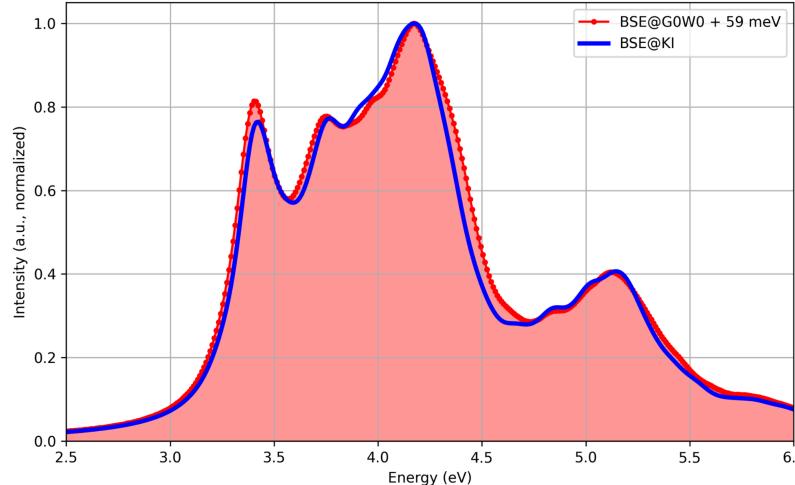
Optical spectra

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

Scaling

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

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- a local measure of screening of electronic interactions

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- one screening parameter per orbital

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 - ΔSCF^1 : embarrassingly parallel steps which each cost $\mathcal{O}(N_{\text{SC}}^3) \sim \mathcal{O}(N_{\mathbf{k}}^3 N^3)$

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

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

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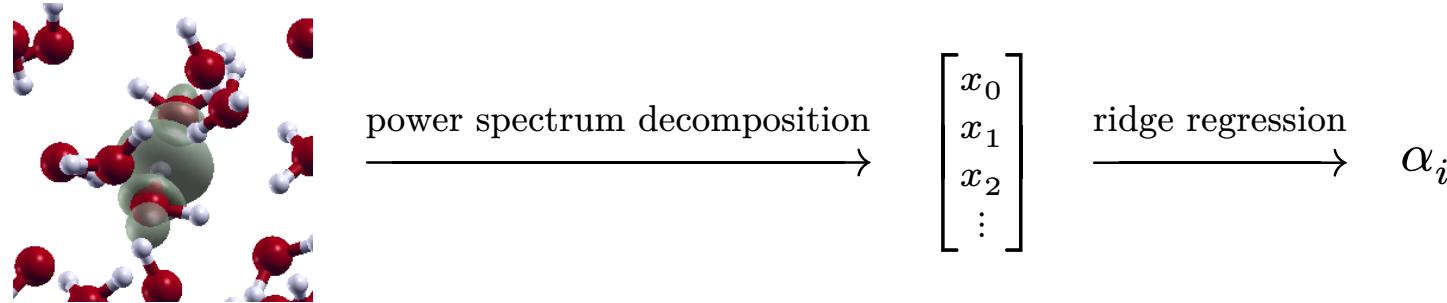
... can we do even better?

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

Machine-learned electronic screening

Machine-learned electronic screening

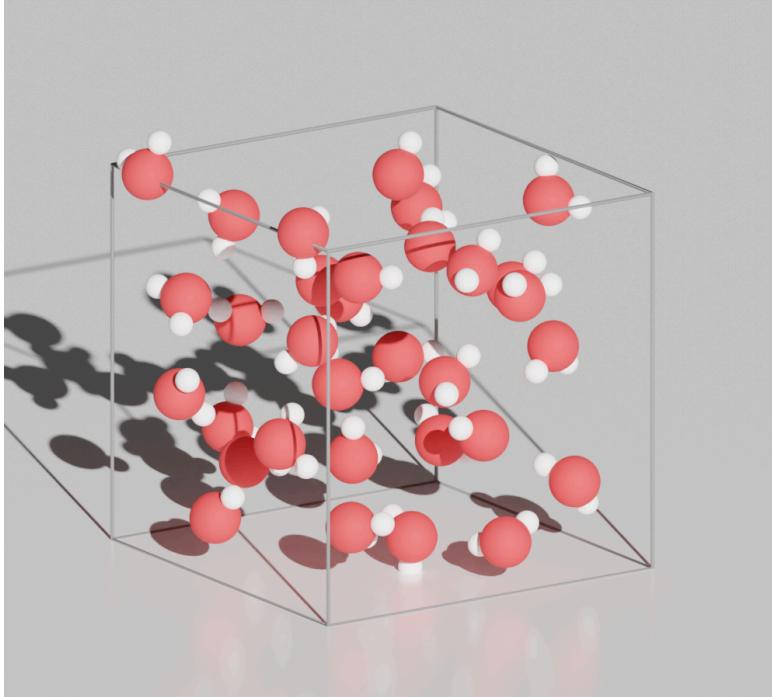


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

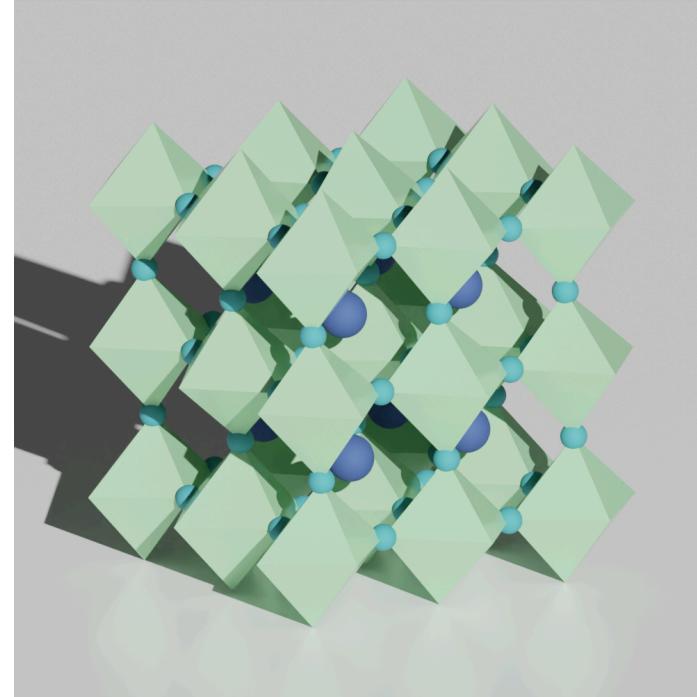
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

Machine-learned electronic screening



water

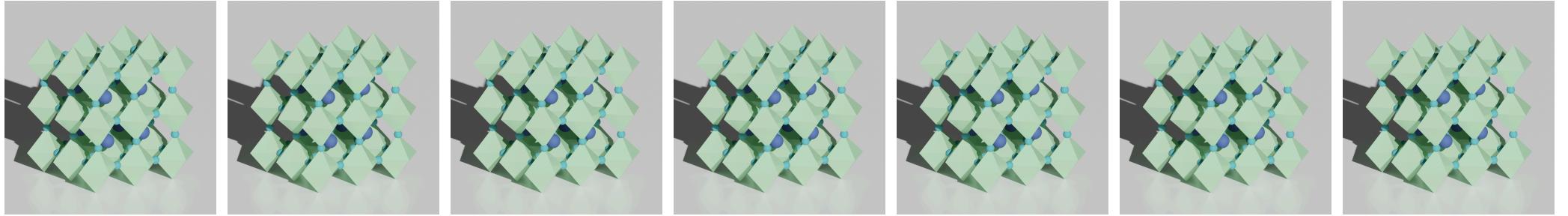


CsSnI₃

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

Machine-learned electronic screening

The use-case

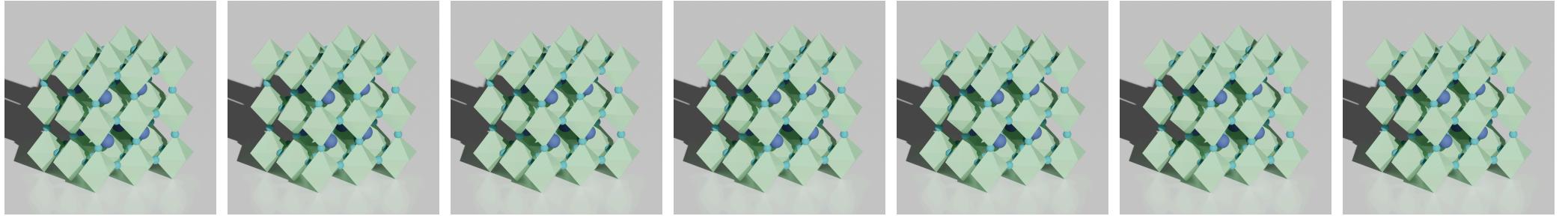


train

predict

Machine-learned electronic screening

The use-case

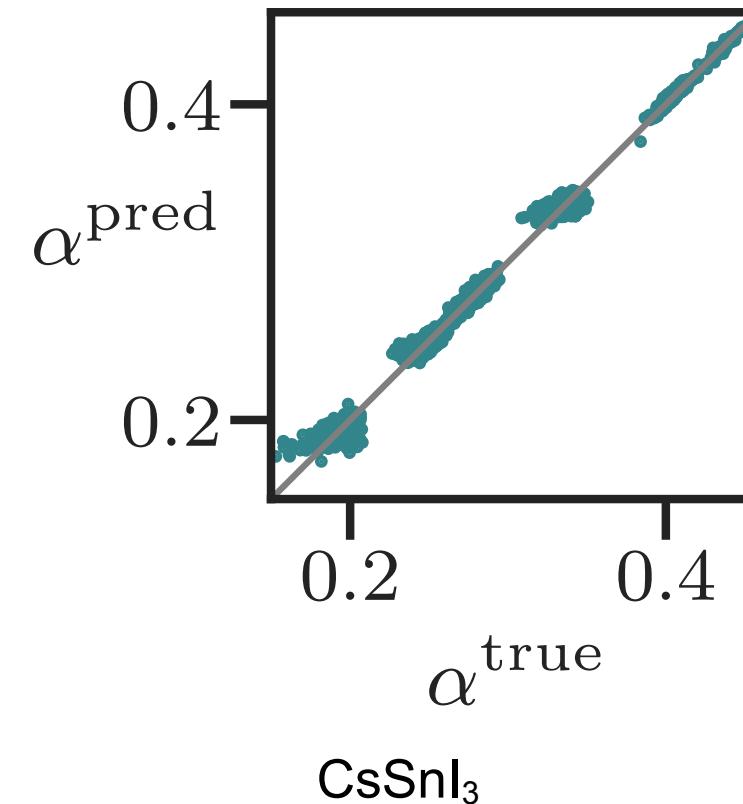
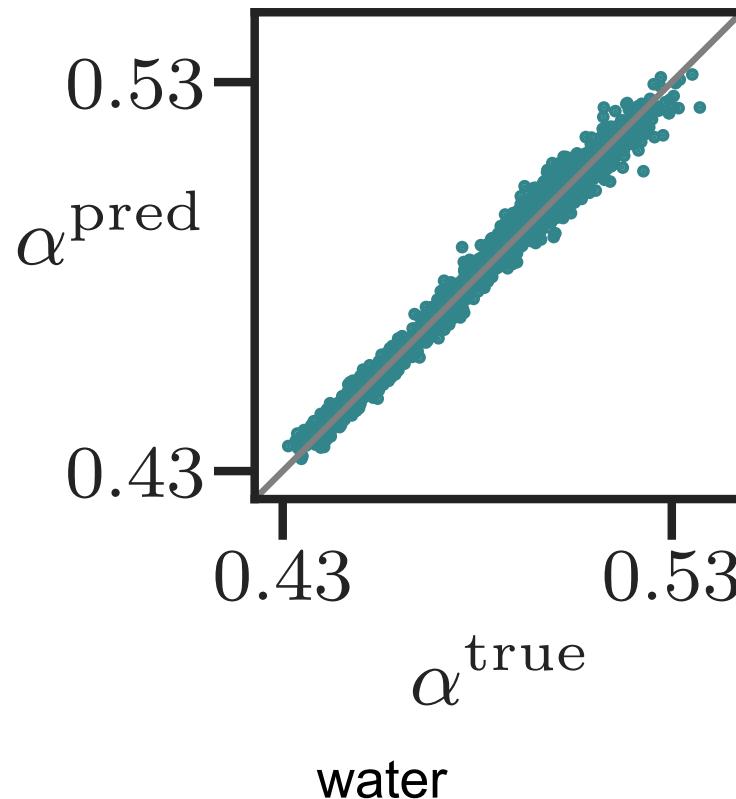


train

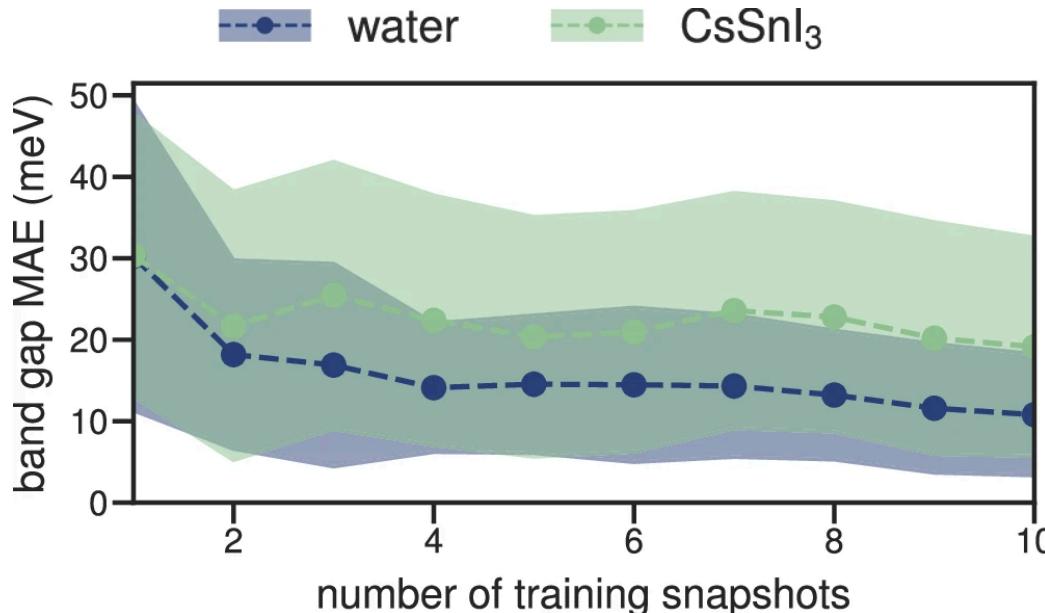
predict

N.B. not a general model

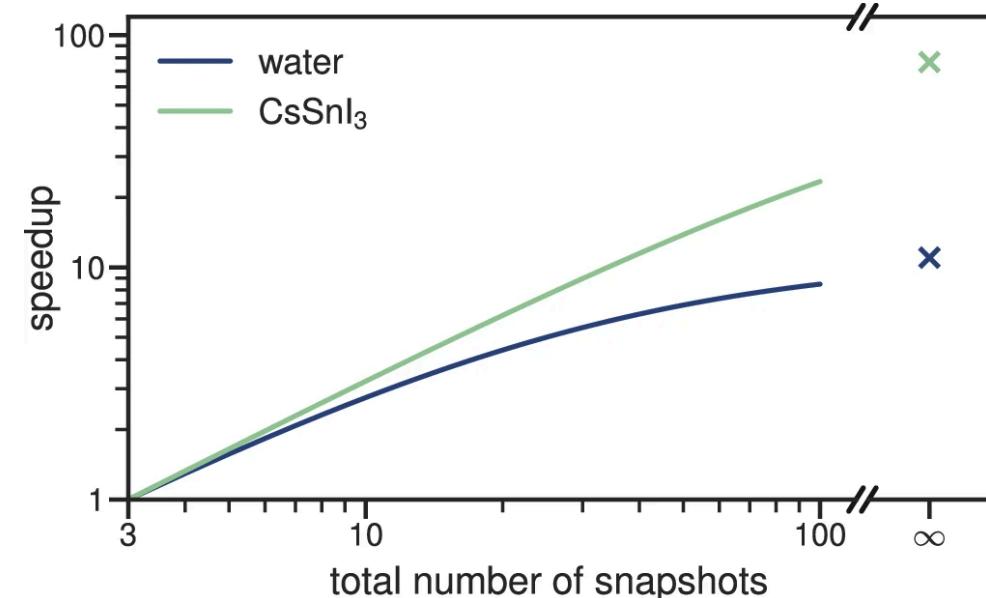
Machine-learned electronic screening



Machine-learned electronic screening



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

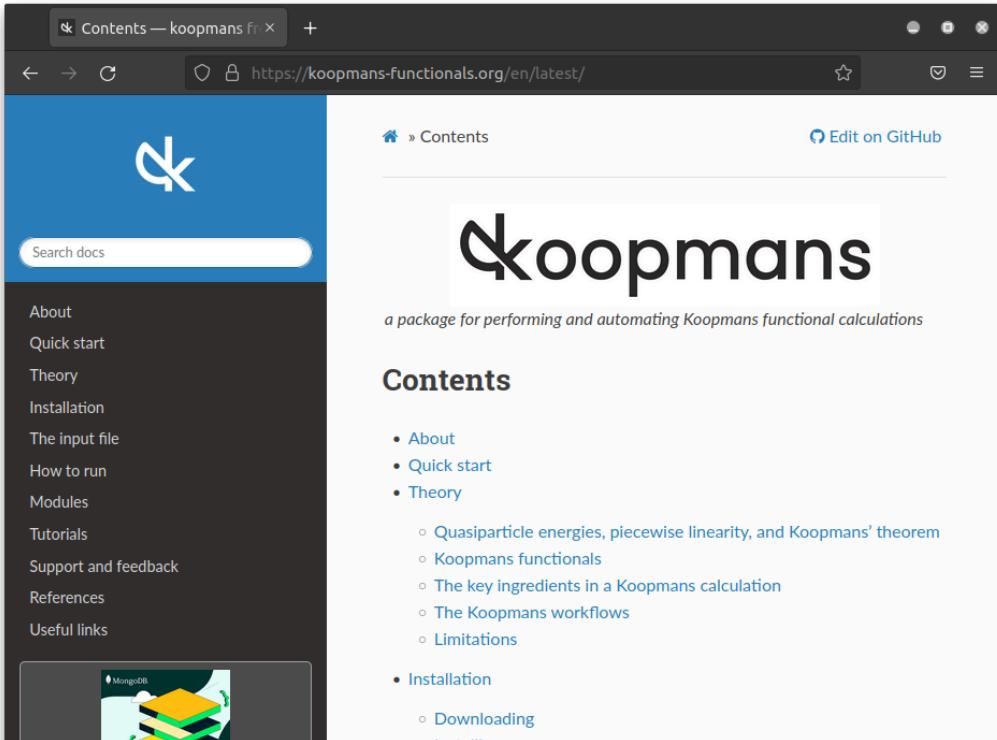


speedup of $\mathcal{O}(10)$ to $\mathcal{O}(100)$

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

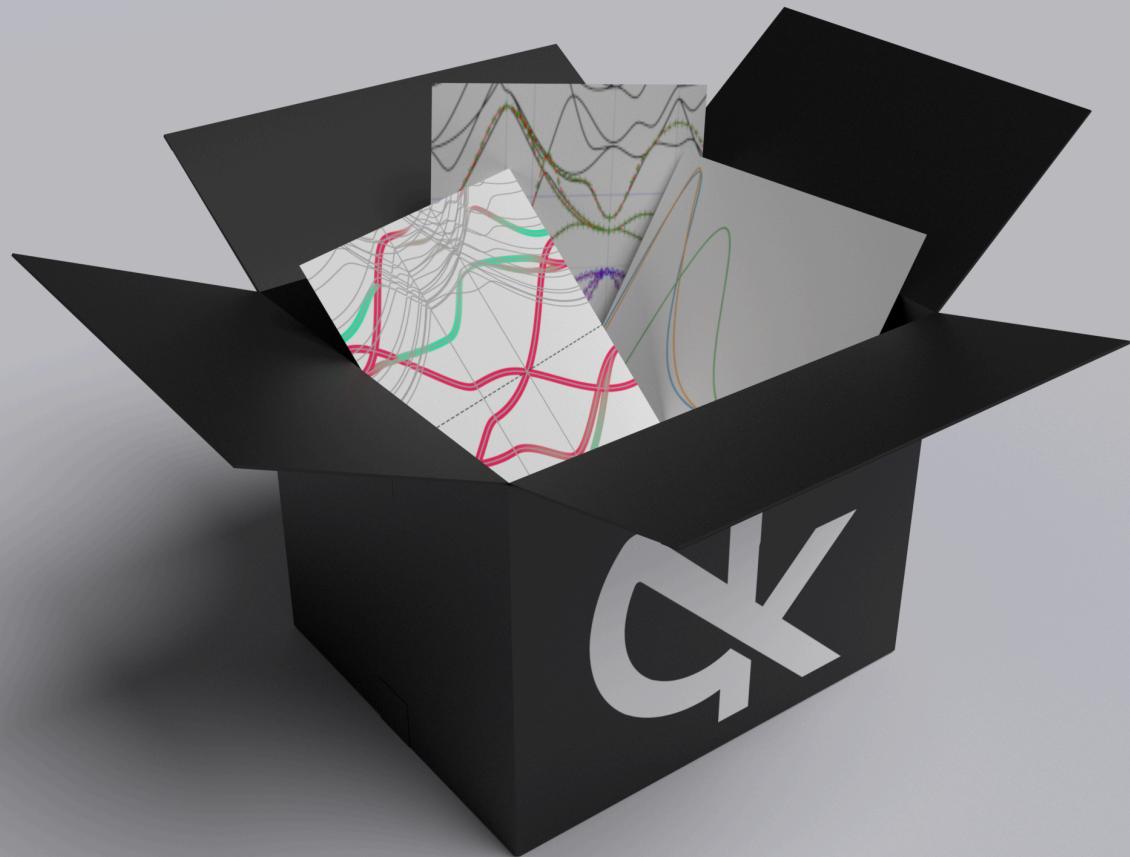
How can I run these calculations?

koopmans



- automated workflows
- Quantum ESPRESSO backend
- easy installation
- minimal technical knowledge required
- python API

See koopmans-functionals.org



Our goal:

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

```
{  
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```

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    },  
    "ui": {  
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    }  
}
```

Towards black-box: automated Wannierisation

Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

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

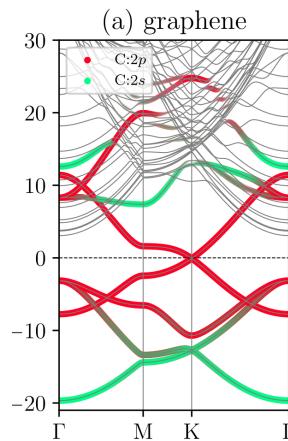
¹J. Qiao *et al.* *npj Comput Mater* **9**, 208 (2023)

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

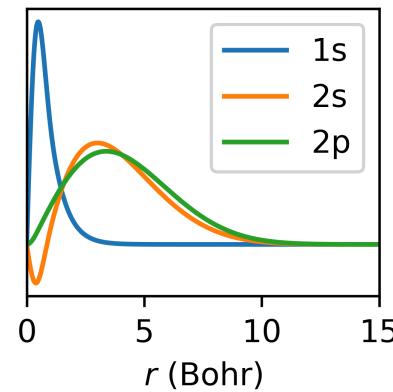
Automated Wannierisation

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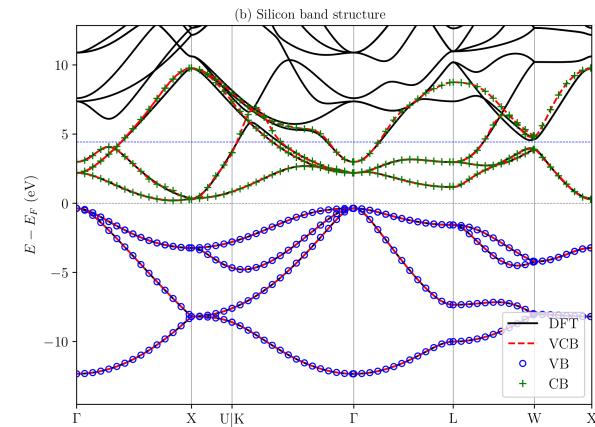
- to initialise the minimising orbitals, or
- in place of the minimising orbitals entirely



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)

Automated Wannierisation

```
{  
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        "method": "dfpt",  
        "init_orbitals": "mlwfs",  
        "pseudo_library": "PseudoDojo/0.4/LDA/SR/standard/upf",  
        "block_wannierization_threshold": 5.0,  
        "orbital_groups_spread_tol": 0.05  
    },  
    "atoms": {  
        "cell_parameters": {  
            "periodic": true,  
            "ibrav": 2,  
            "celldms": {"1": 10.68374}  
        },  
        "atomic_positions": {  
            "units": "crystal",  
            "positions": [[{"Ga": 0.00, 0.00, 0.00},  
                          {"As": 0.25, 0.25, 0.25}]]  
        }  
    },  
},
```

Automated Wannierisation

```
"kpoints": {  
    "grid": [6, 6, 6]  
},  
"calculator_parameters": {  
    "ecutwfc": 60.0,  
    "w90": {  
        "dis_proj_max": 0.8,  
        "auto_projections": true  
    },  
    "ui": {  
        "smooth_int_factor": 2  
    }  
}
```

Towards black-box: taking advantage of symmetries

Taking advantage of symmetries

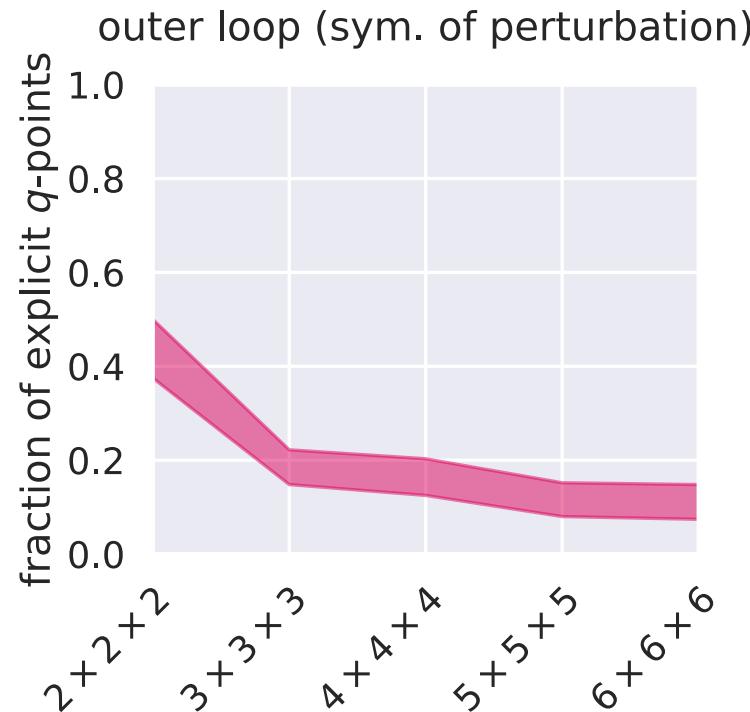
To compute screening parameters via DFPT...

```

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

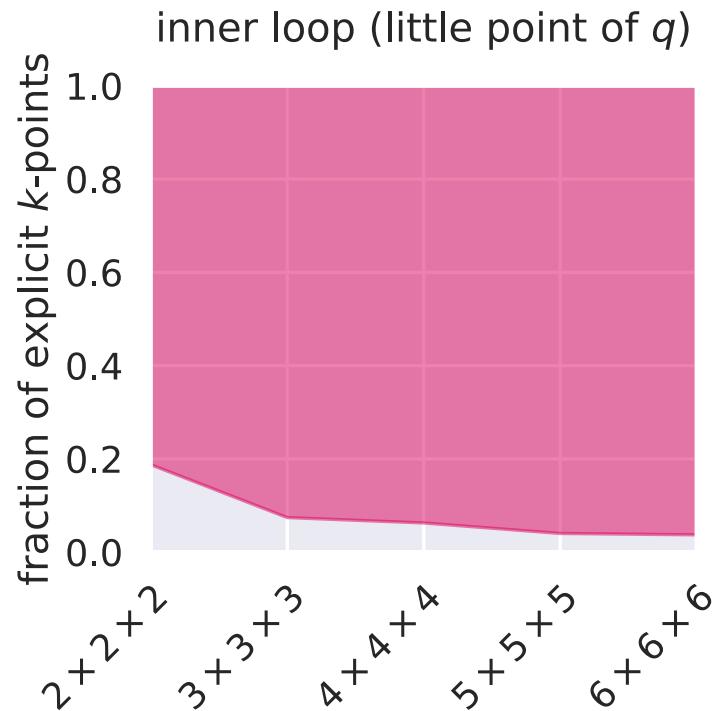
```

Taking advantage of symmetries



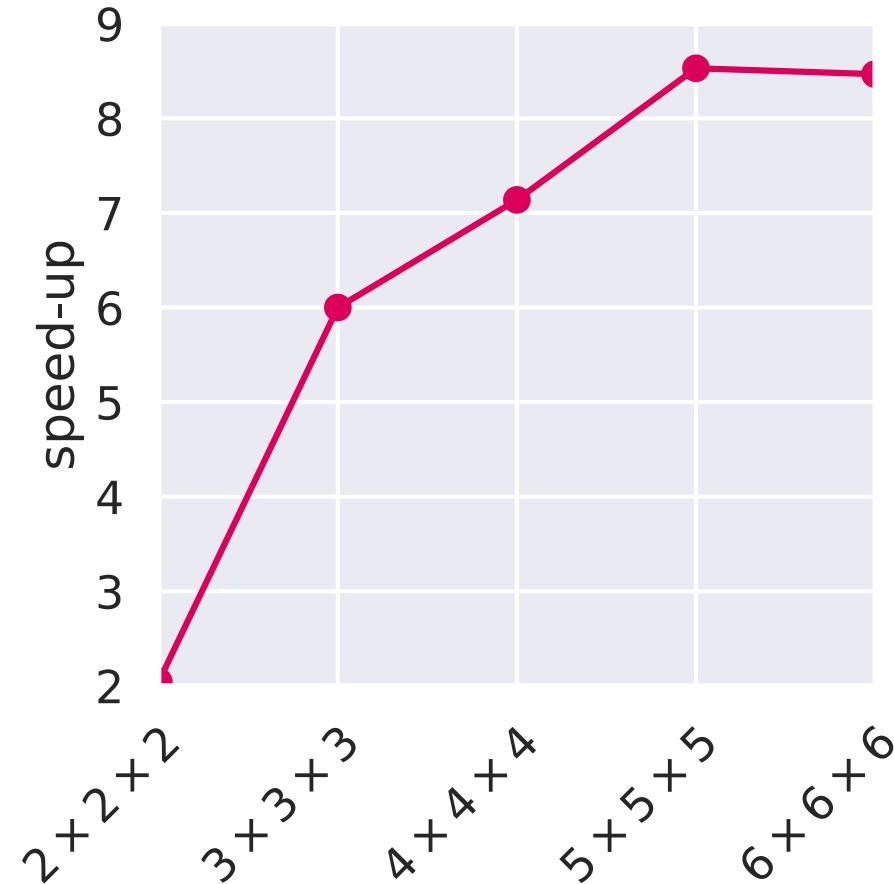
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$ (the symmetry of the perturbation; lower than that of the primitive cell)

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



Towards black-box: AiIDA integration



```
$ 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, outputs stored in a database, provenance-tracking, (requires configuration, WIP...)

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

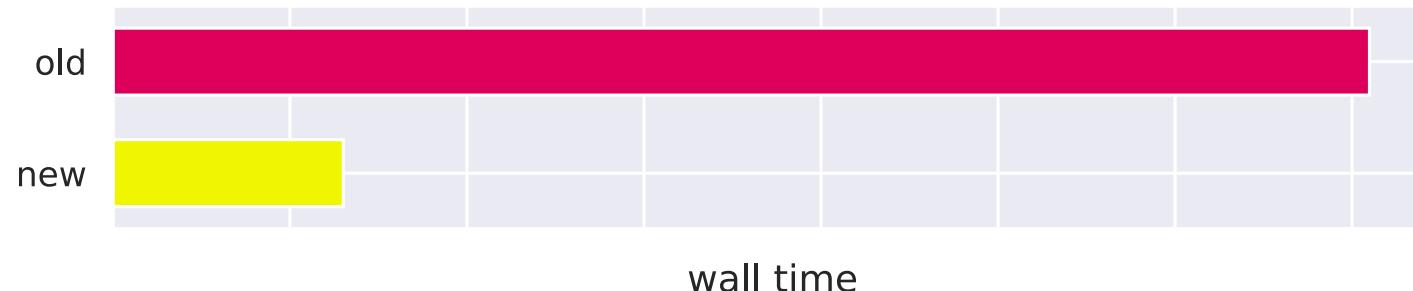
koopmans

 🤝 

AiiDA

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

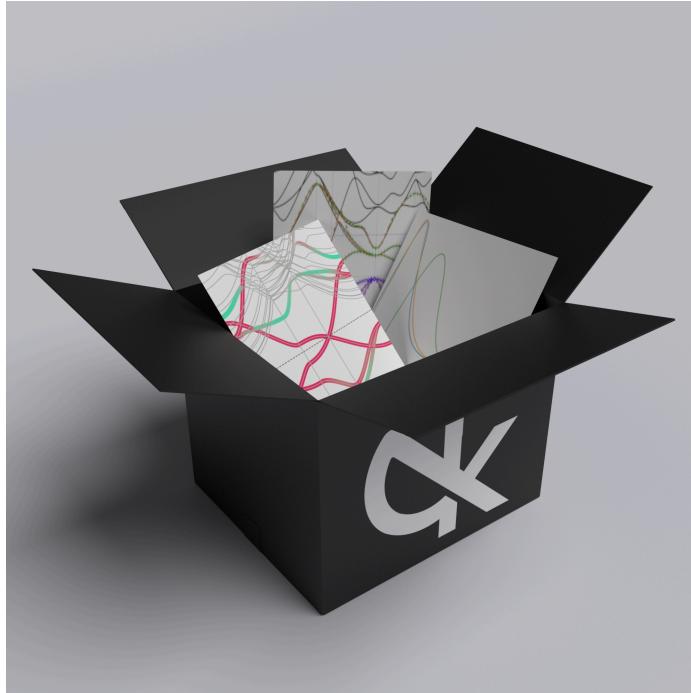
remote compute, parallel step execution, outputs stored in a database, provenance-tracking, (requires configuration, WIP...)



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

Summary

Summary



Koopmans functionals...

- bake localised charged excitation energies into 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
- are increasingly black-box
 - ▶ aiida-koopmans release coming soon!

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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- can we provide a formal basis for the Koopmans correction?
 - 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



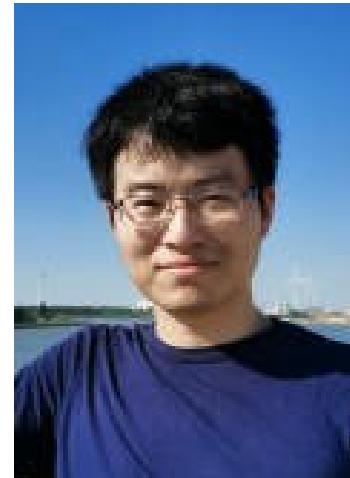
Marija Stojkovic
Monday

band alignment for
photocatalysis



Nicola Colonna
Tuesday

non-collinear spin



Junfeng Qiao
Poster B4.16
today!

automated
Wannierisation



Aleksandr Poliukhin
Thu 1000 Room C

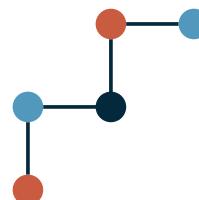
phonons

... or go to koopmans-functionals.org

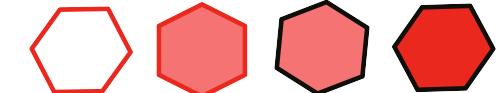
Acknowledgements



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



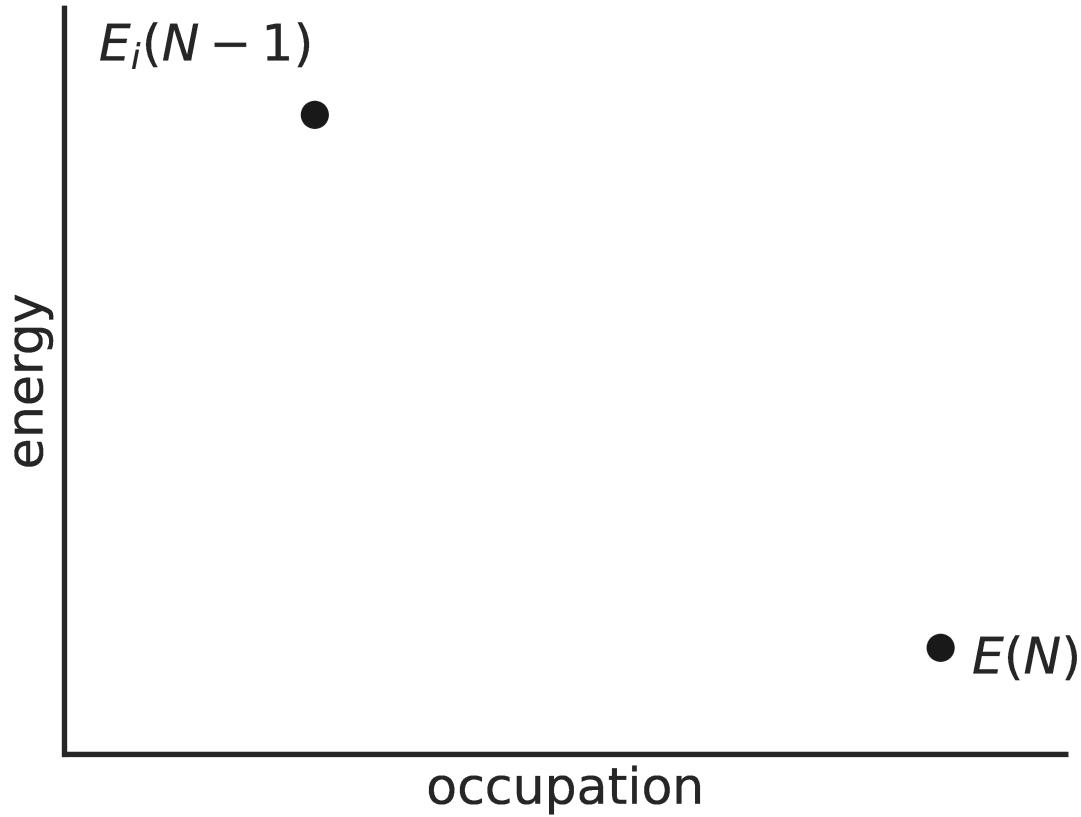
**Swiss National
Science Foundation**

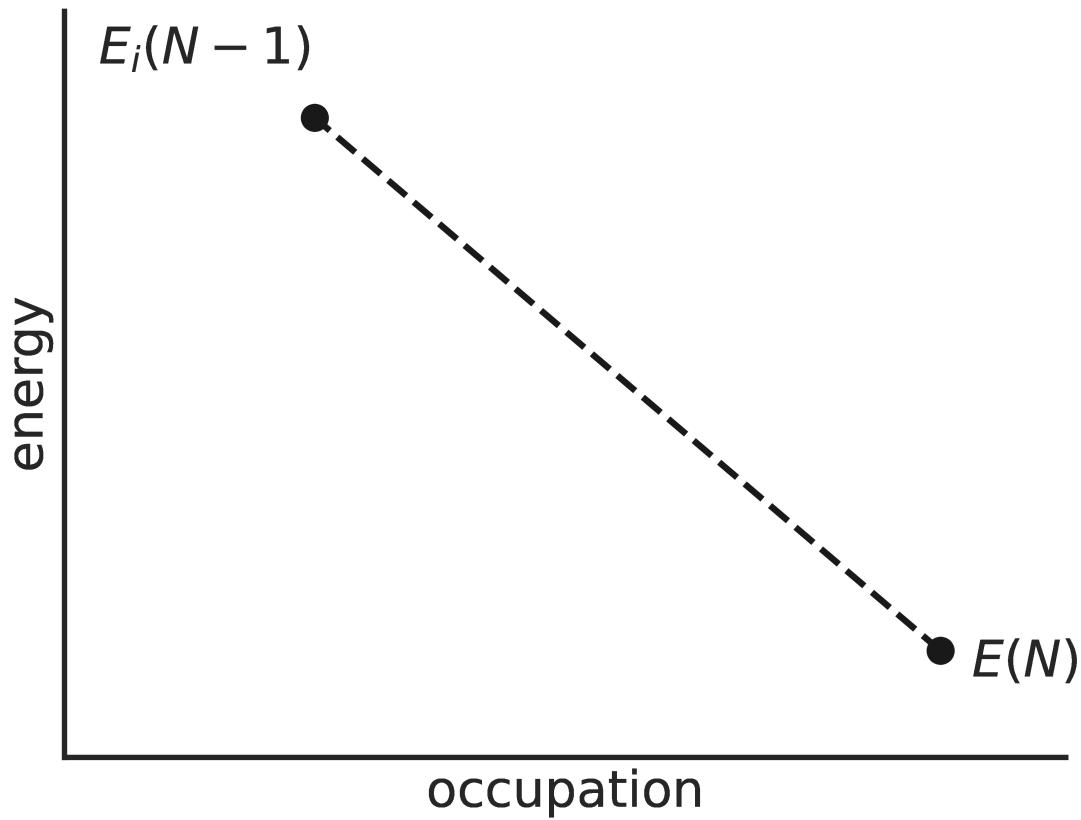
MARVEL


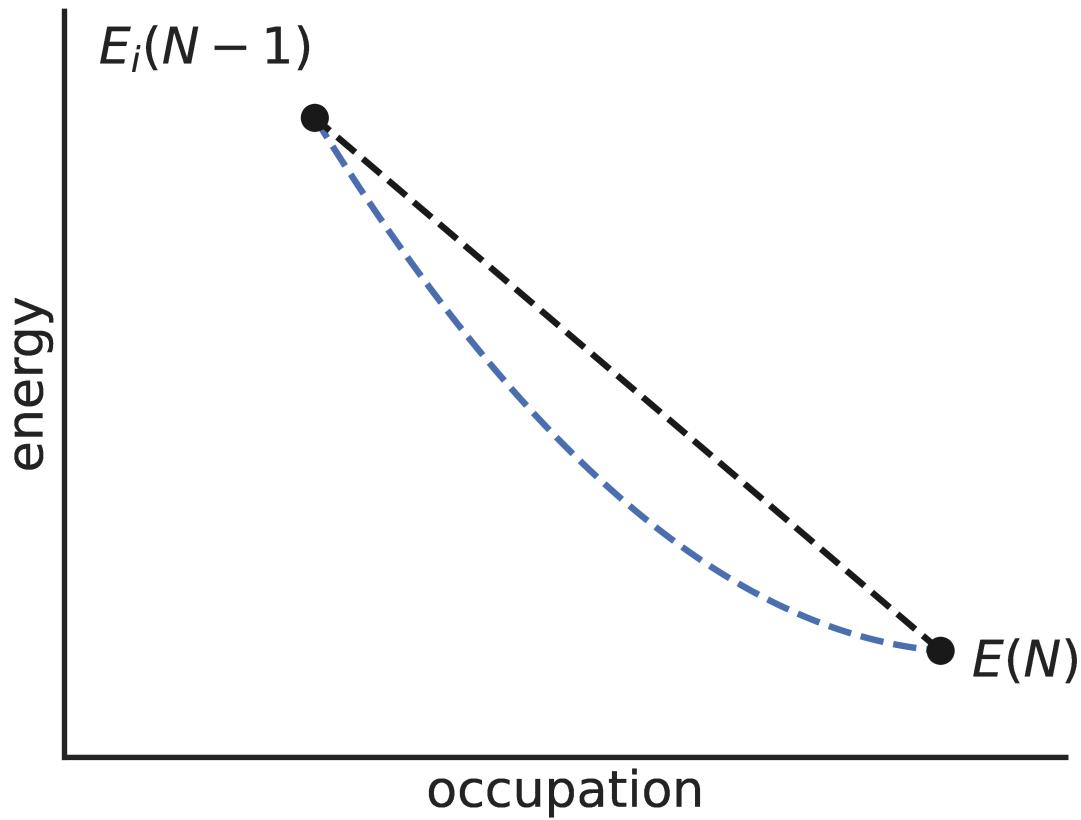
Thank you!

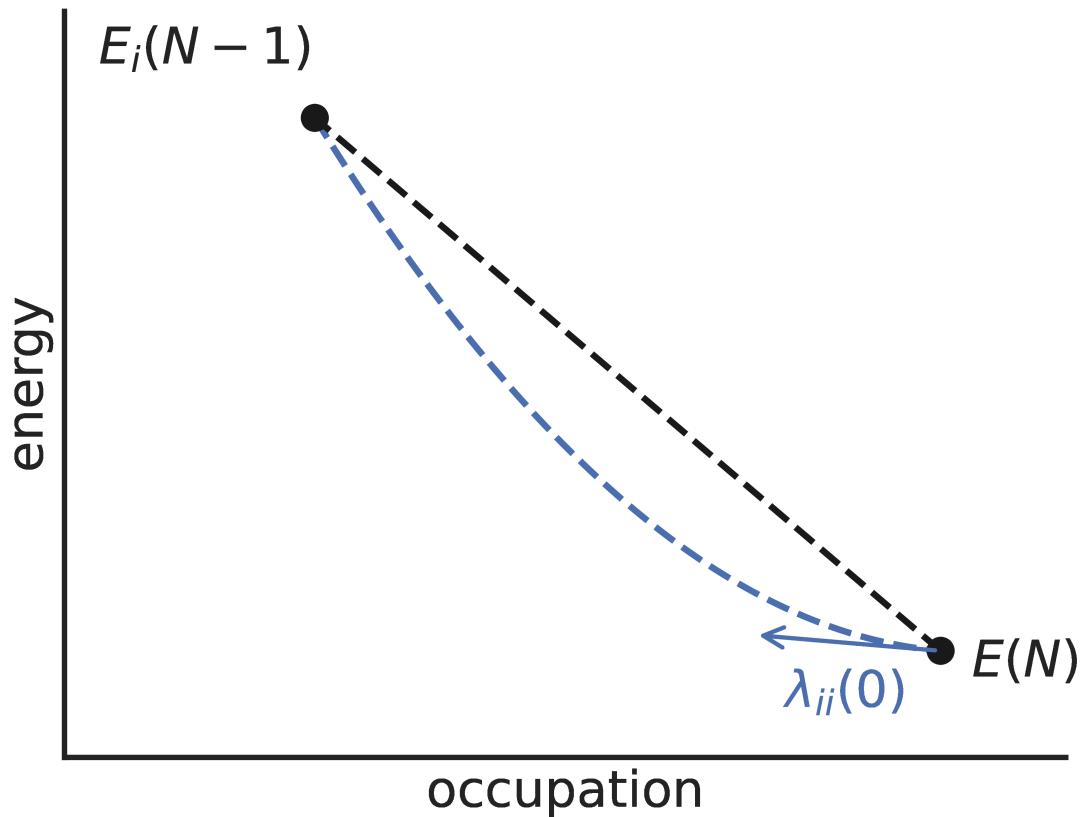
these slides are available at  [elinscott-talks](https://github.com/elinscott-talks)

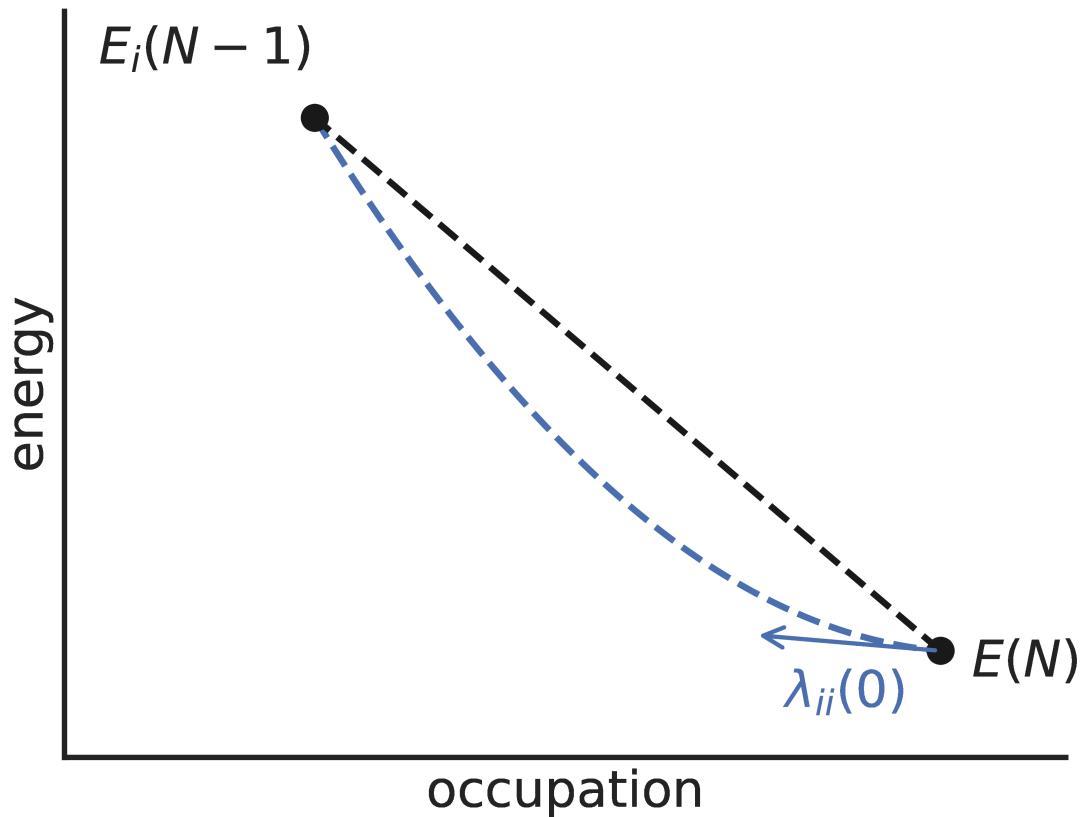
spare slides

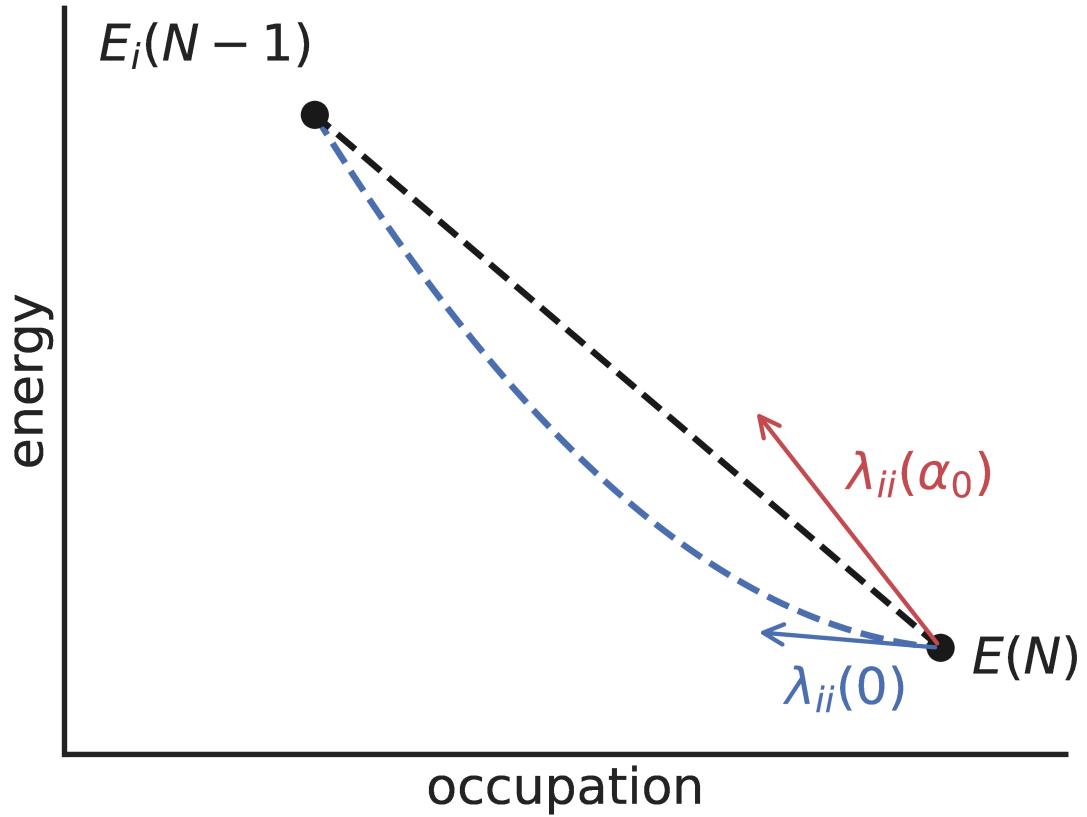


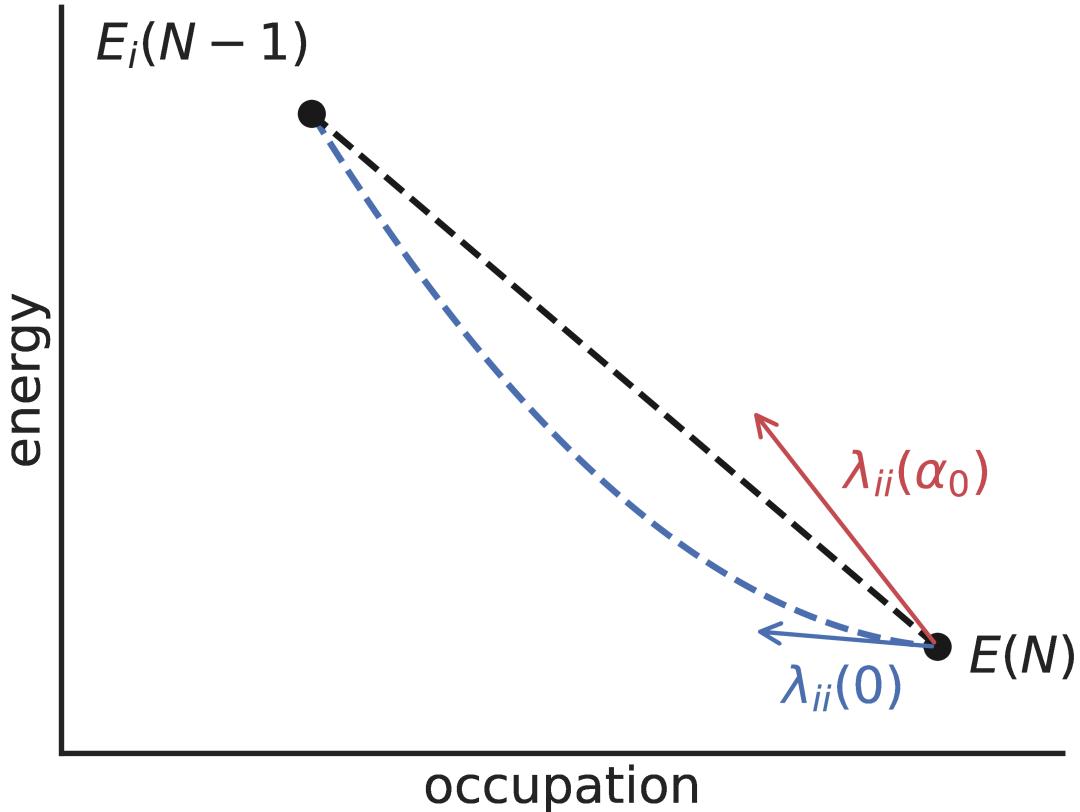












$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

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

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)

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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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