



Center for Scientific Computing,
Theory and Data

Koopmans functionals

Baking localised charged excitation energies into DFT

Edward Linscott

CECAM Workshop on Excited States, 7 November 2024

Koopmans functionals: a correction to DFT tailored to improve spectral properties

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- Theory
 - what physical conditions motivate these functionals?
 - what approximations do we make?
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 - how can we make these functionals accessible?
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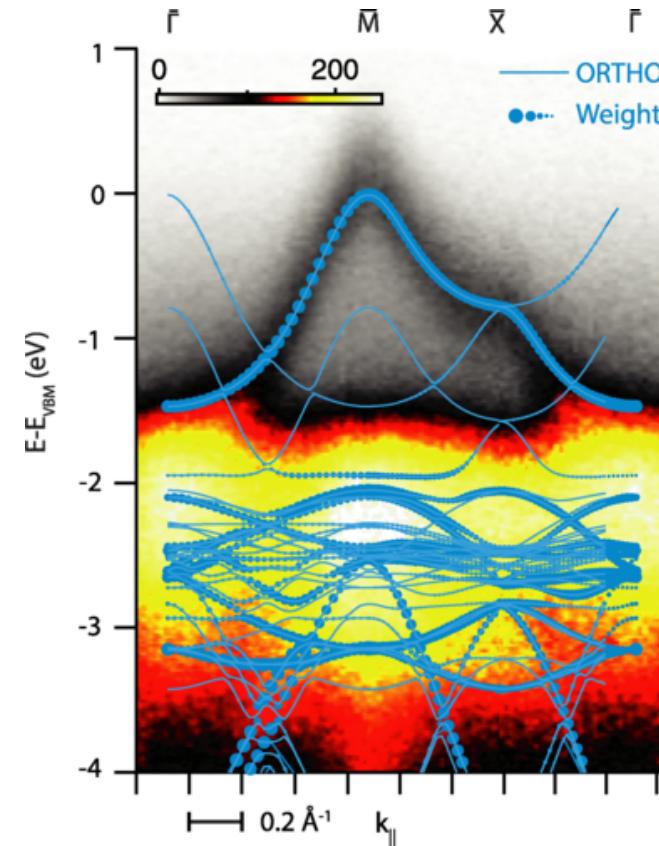
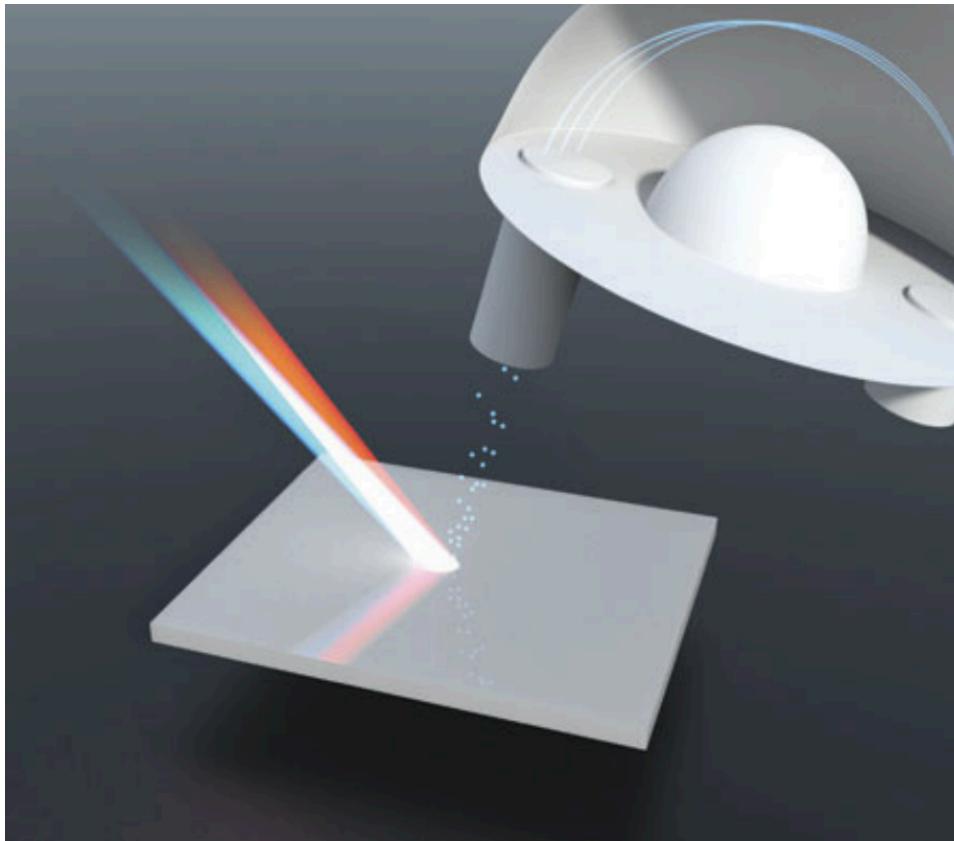
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 - what don't we understand?

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Theory

Spectral properties



... with a functional theory?



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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 equivalence to DFT and thereby improve its description of spectral properties

Theory



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

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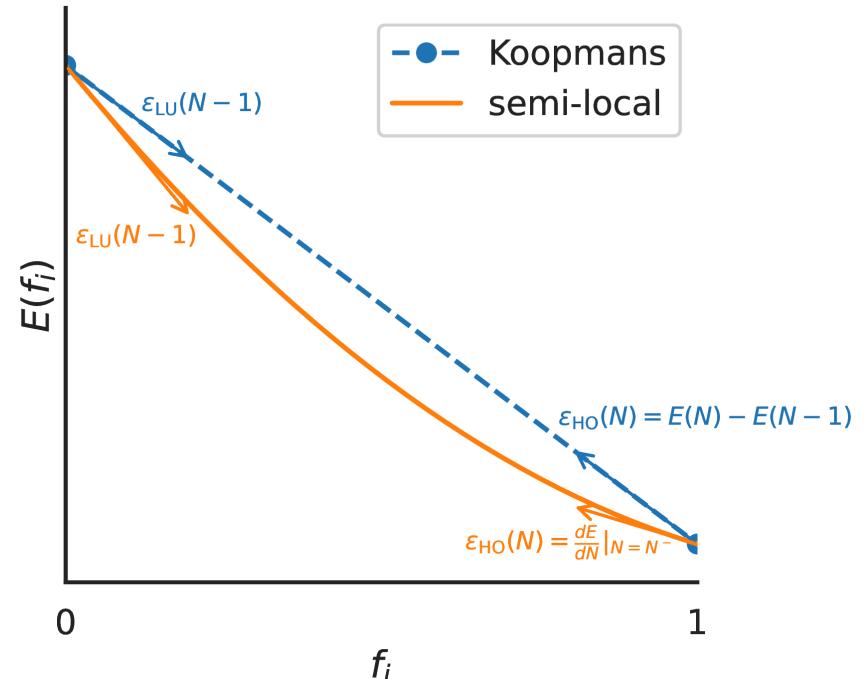
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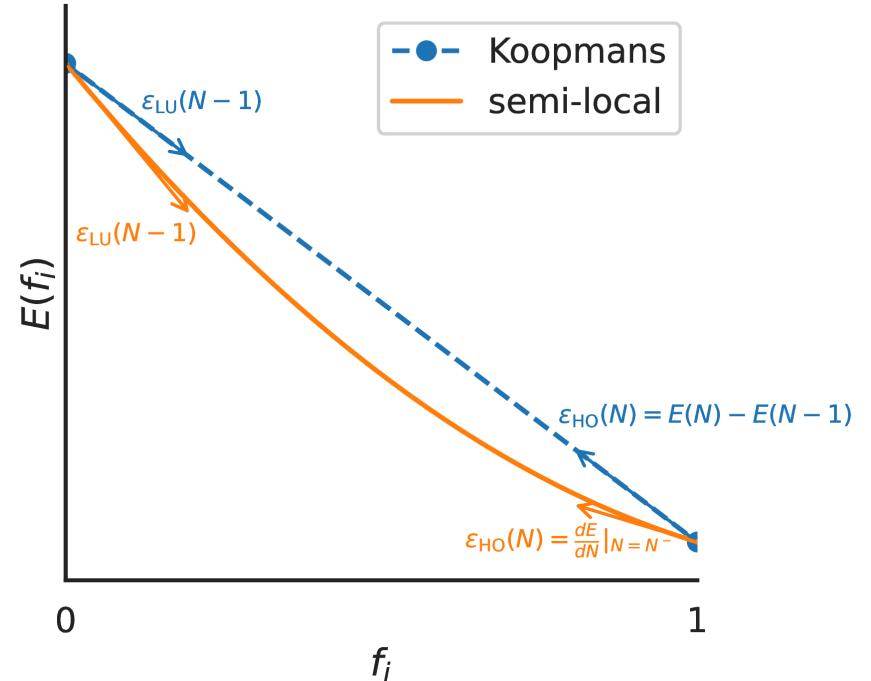


Theory

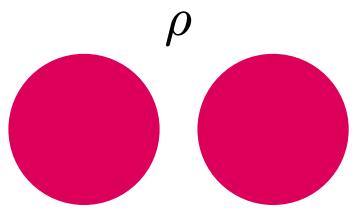
$$E^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

$$+ \sum_i \left\{ - \underbrace{\left(E^{\text{DFT}}[\rho] - E[\rho^{f_i \rightarrow 0}] \right)}_{\text{remove non-linear dependence}} \right. \\ \left. + f_i \underbrace{\left(E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}] \right)}_{\text{restore linear dependence}} \right\}$$

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

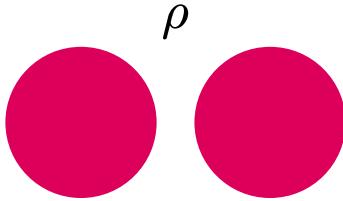


Theory

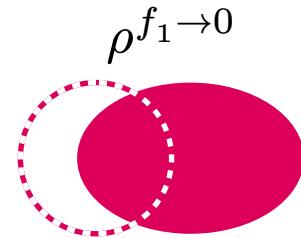


N -electron solution

Theory

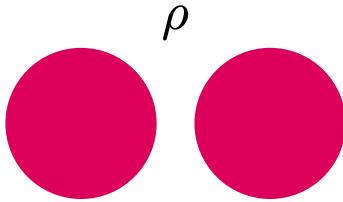


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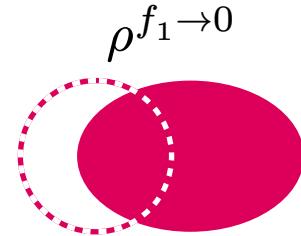


what appears in the
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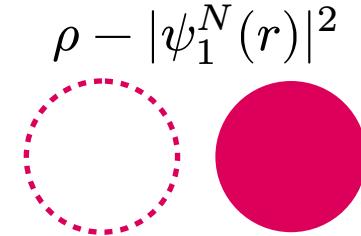
Theory



N -electron solution



what appears in the
functional



what we can quickly
evaluate

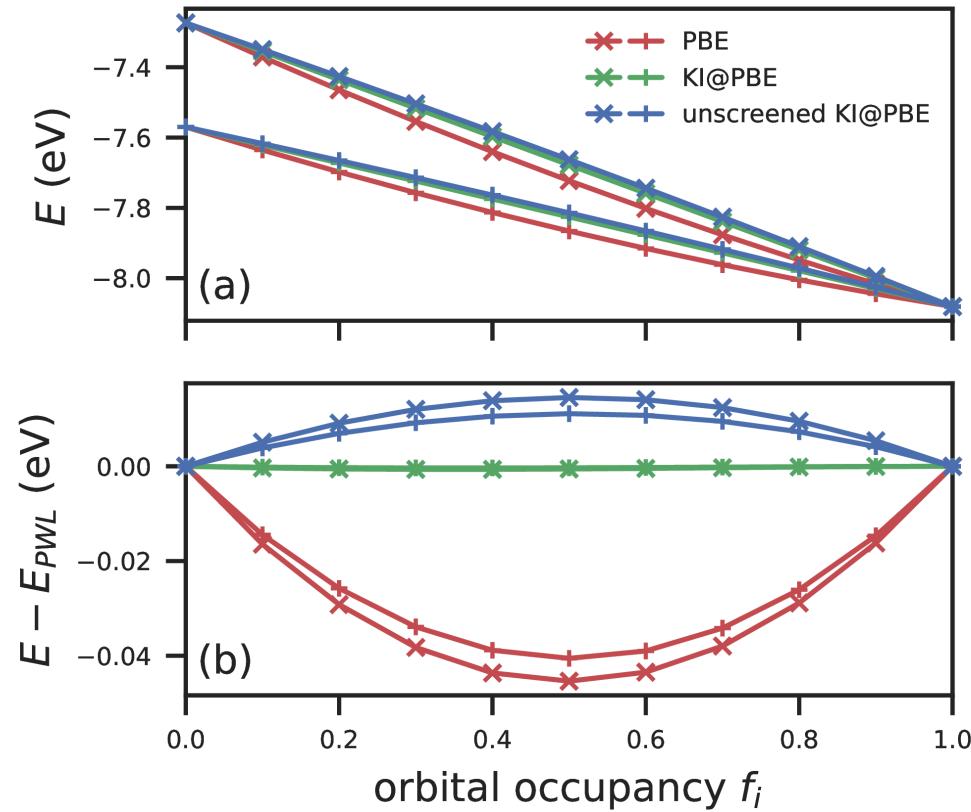
$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho]$$

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$$\approx E^{\text{DFT}}[\rho]$$

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

where $\rho_i(\mathbf{r}) = f_i |\varphi_i(\mathbf{r})|^2 = f_i n_i(\mathbf{r})$



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Screening

Construct α_i from explicit Δ SCF calculations¹

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

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

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

²N. Colonna *et al.* *Journal of Chemical Theory and Computation* **14**, 2549–2557 (2018)

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which can be efficiently computed via DFPT³ ... but is still the bulk of the computational cost (can use machine-learning)

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Orbital-density dependence

An orbital-density-dependent energy functional:

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... and an orbital-dependent potential:

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

Consequences of ODD

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-

¹N. Marzari *et al.* *Reviews of Modern Physics* **84**, 1419–1475 (2012)

²A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014)

Consequences of ODD

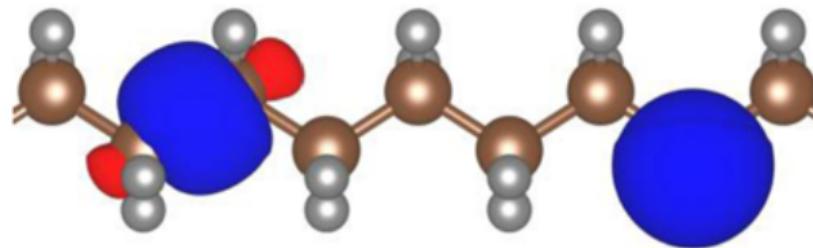
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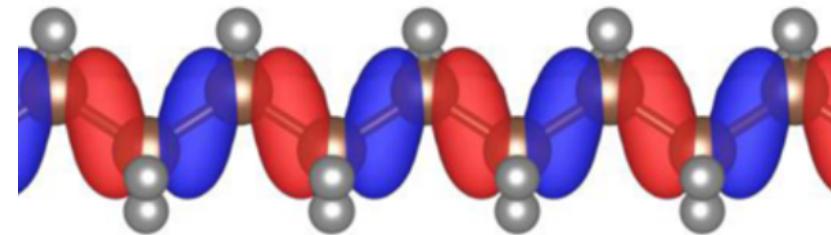
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Consequences of ODD

- loss of rotational invariance; minimisation of total energy is more complicated
- two sets of orbitals:



two variational orbitals



a canonical orbital

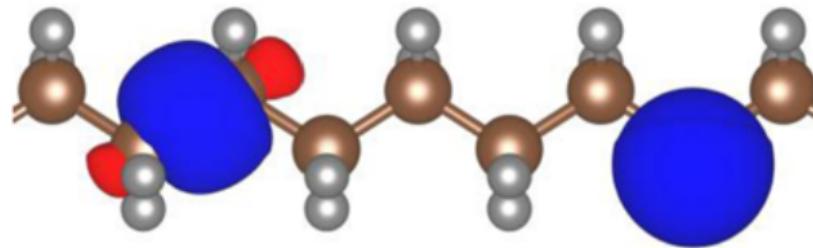
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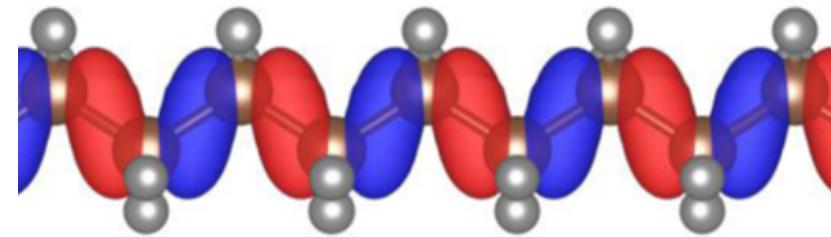
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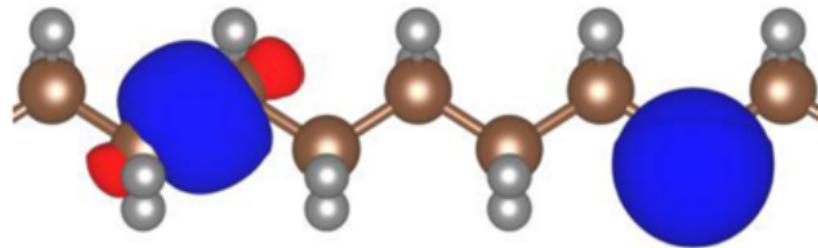
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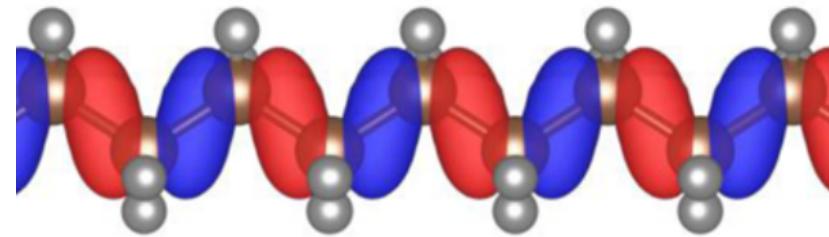
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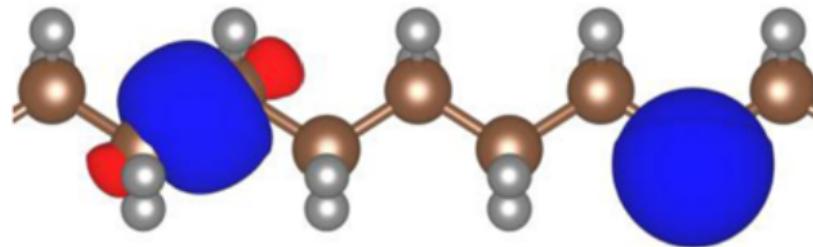
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- we know $\hat{H}|\varphi_i\rangle$ but we don't know \hat{H}
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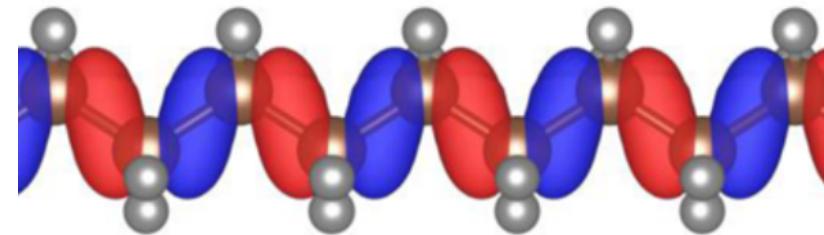
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- we can use MLWFs¹
- we know $\hat{H}|\varphi_i\rangle$ but we don't know \hat{H}
- a generalisation of DFT in the direction of spectral functional theory²

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²A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014)

A brief summary

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

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- an orbital-by-orbital correction to DFT
- localised charge excitations baked into derivatives
- screening parameters
- orbital-density-dependence
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A brief summary

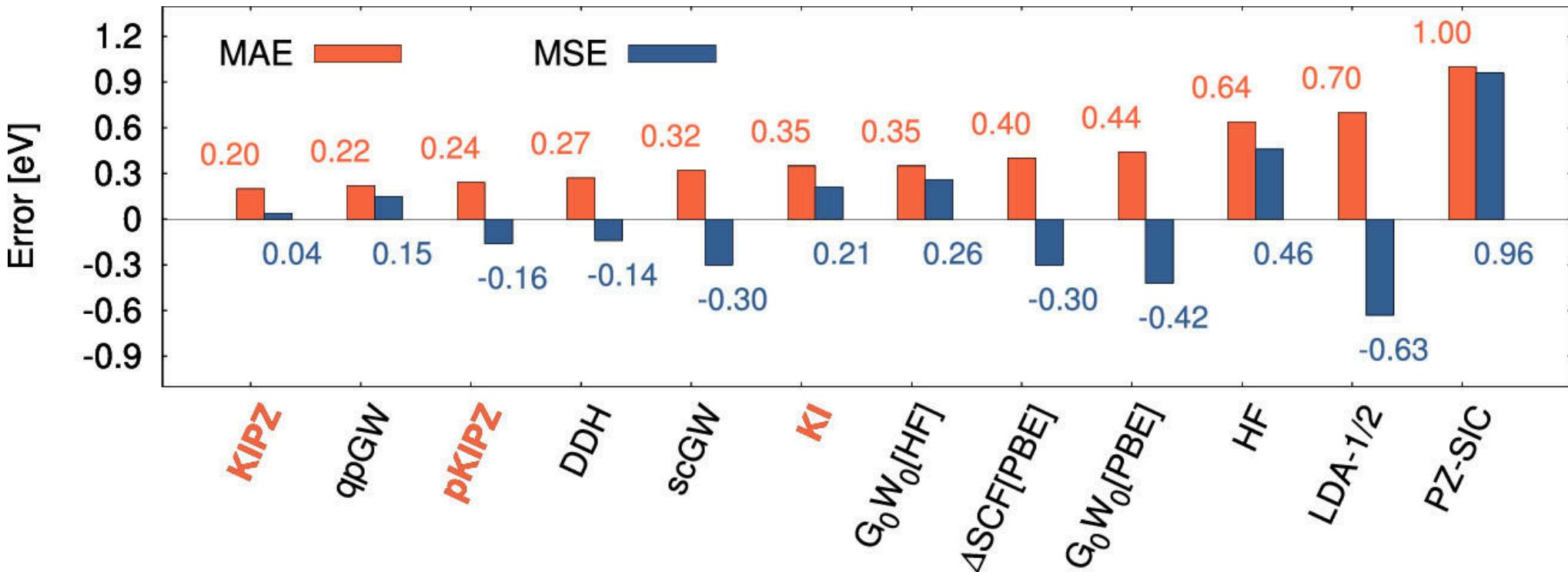
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- an orbital-by-orbital correction to DFT
- localised charge excitations baked into derivatives
- screening parameters
- orbital-density-dependence
- total energy unchanged!

Results

Molecular systems

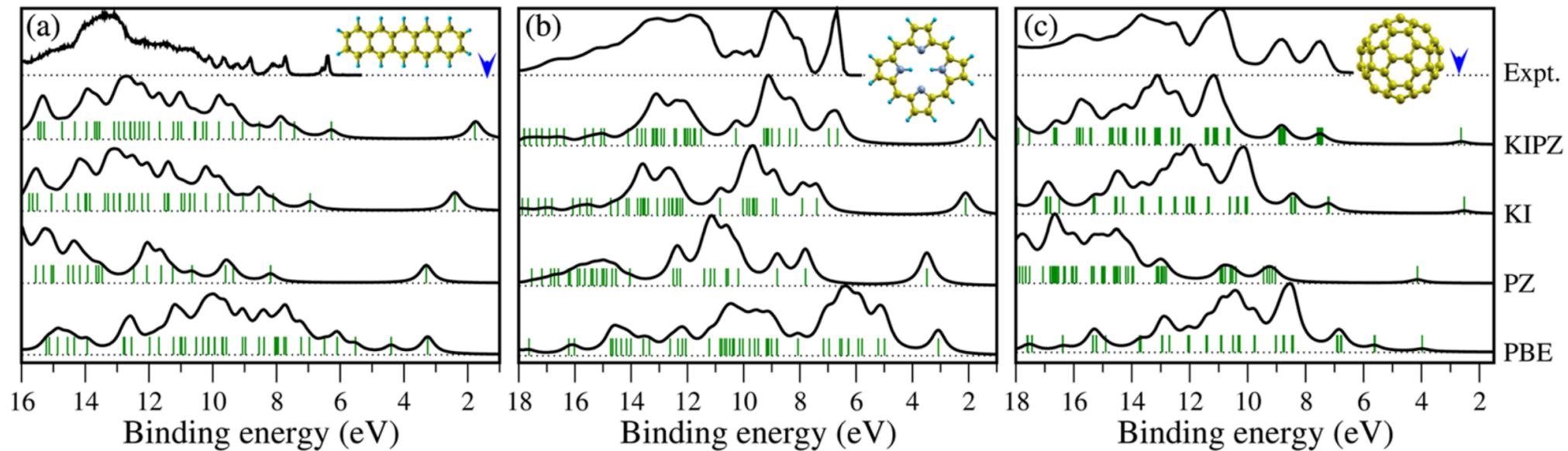
Ionisation potentials¹



¹N. Colonna et al. *Journal of Chemical Theory and Computation* **15**, 1905–1914 (2019)

Molecular systems

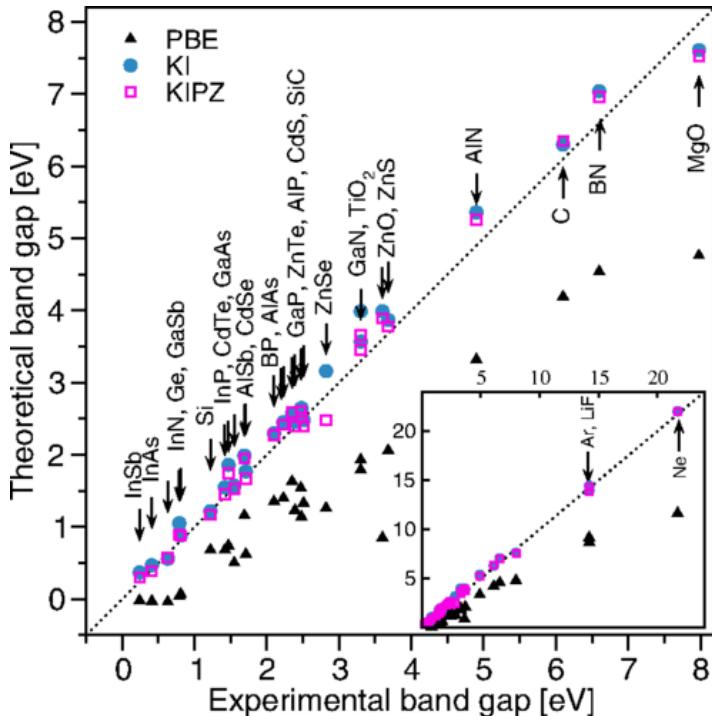
UV photoemission spectra²



²N. L. Nguyen et al. *Physical Review Letters* **114**, 166405 (2015)

Extended systems

Prototypical semiconductors and insulators¹

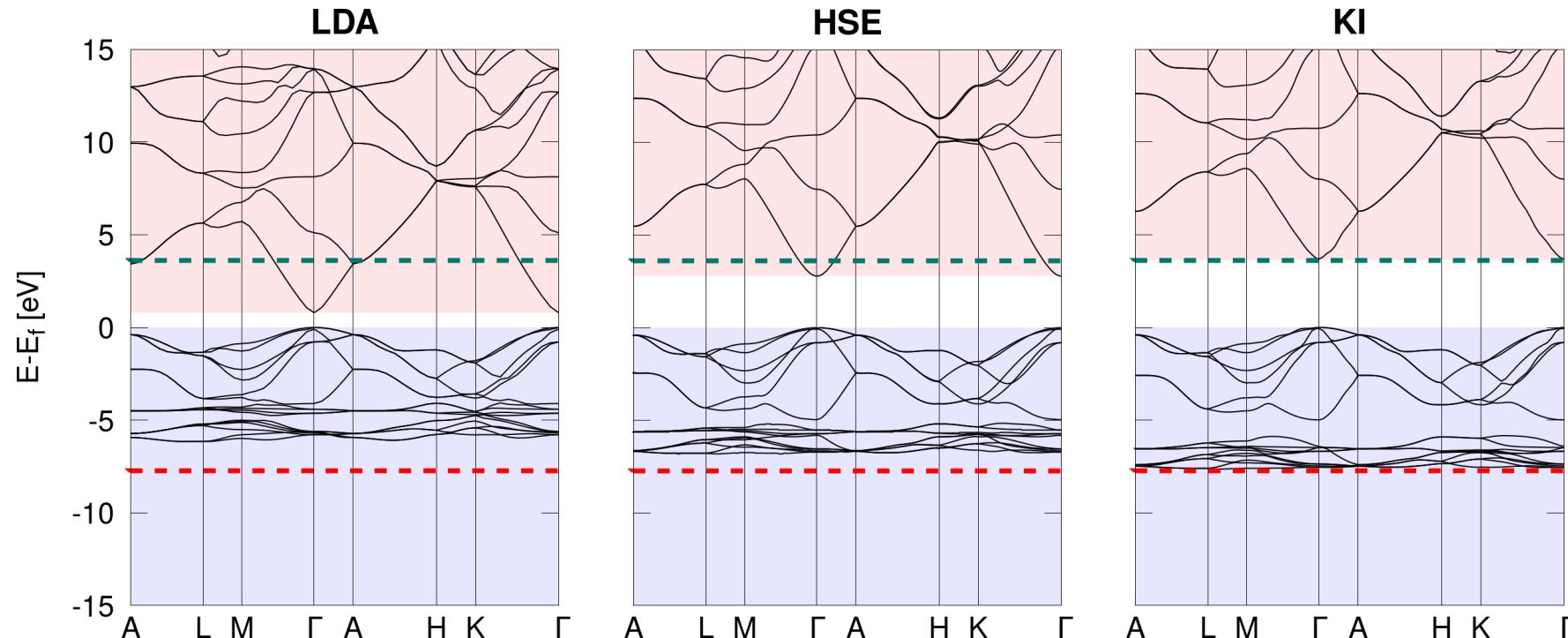


	PBE	G_0W_0	KI	KIPZ	$QS\tilde{G}W$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

¹N. L. Nguyen *et al.* *Physical Review X* **8**, 21051 (2018)

Extended systems

ZnO^1



¹N. Colonna et al. *Journal of Chemical Theory and Computation* **18**, 5435–5448 (2022)

Extended systems

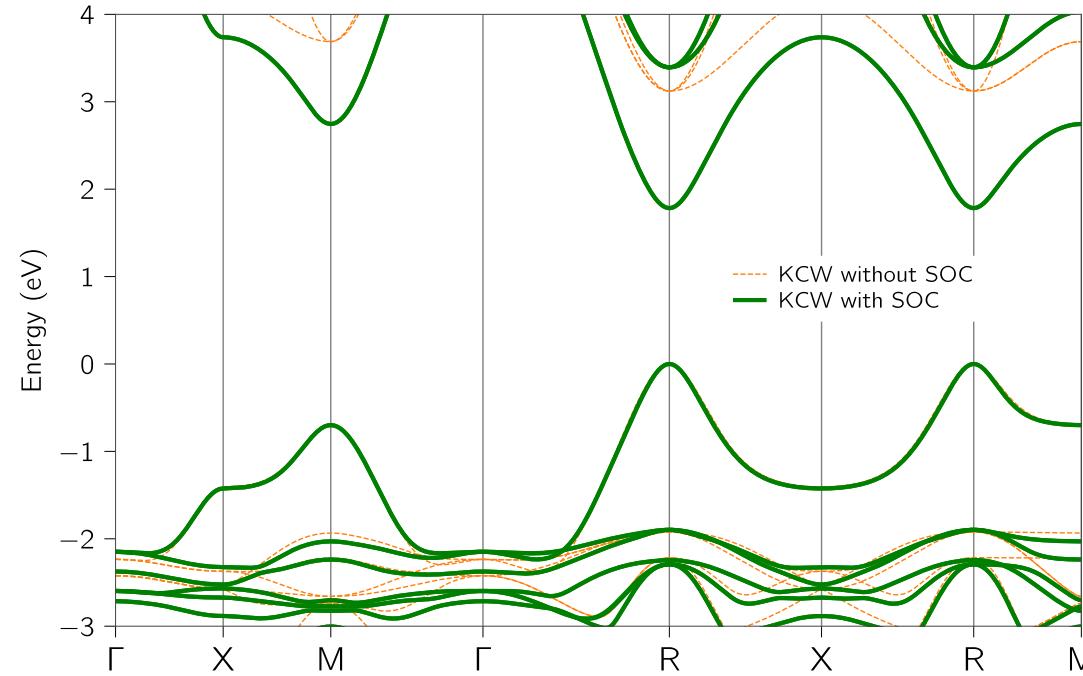
ZnO¹

	LDA	HSE	GW_0	sc $\tilde{\text{GW}}$	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	-6.9	-7.5 to -8.81
Δ	4.15				4.99	5.3

¹N. Colonna *et al.* *Journal of Chemical Theory and Computation* **18**, 5435–5448 (2022)

Extended systems

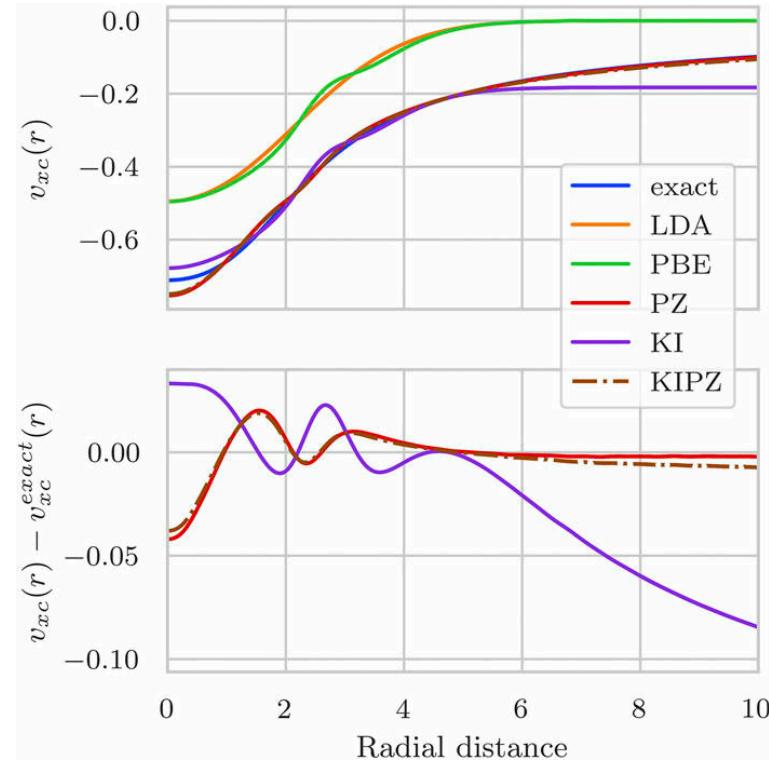
Spin-orbit coupling¹



¹A. Marrazzo *et al.* (2024) doi:10.48550/arXiv.2402.14575

Model systems

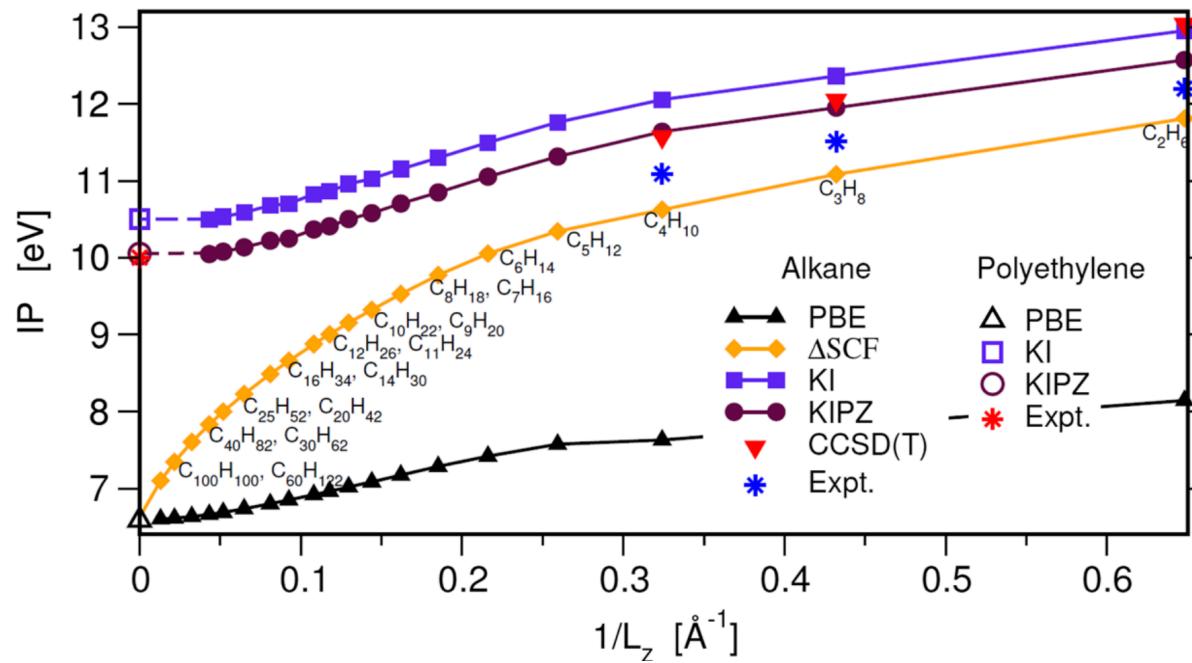
Hooke's atom¹



¹Y. Schubert et al. *The Journal of Chemical Physics* **158**, 144113 (2023)

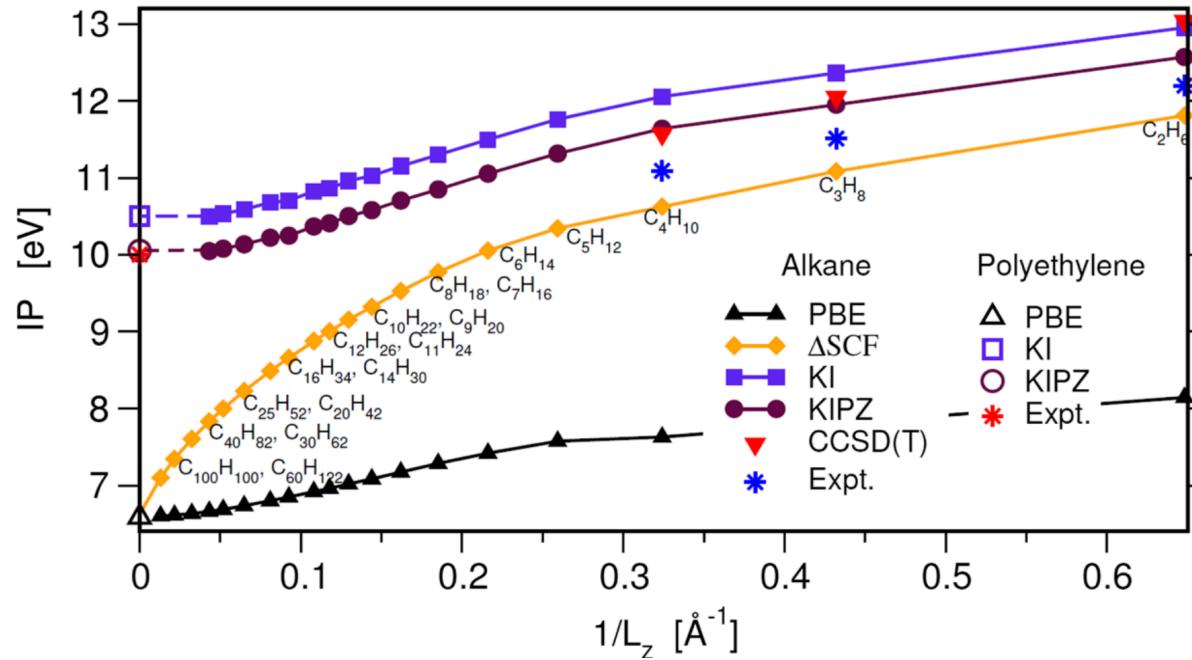
Caveats

Issues with extended systems



¹N. L. Nguyen et al. *Physical Review X* **8**, 21051 (2018)

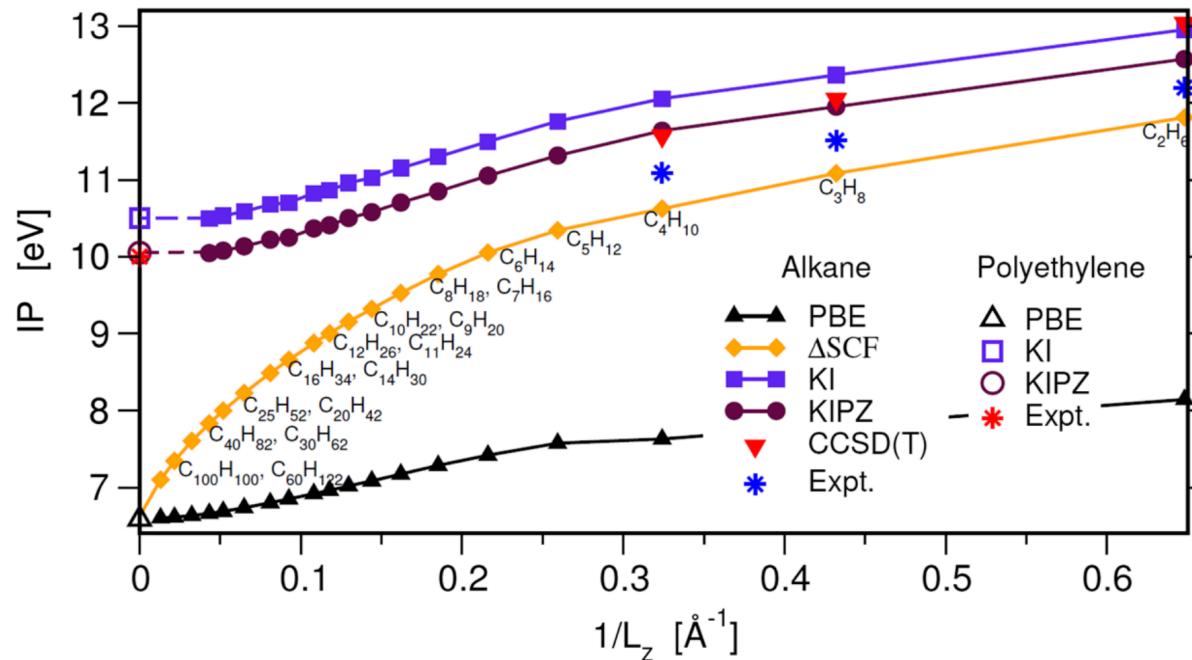
Issues with extended systems



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

¹N. L. Nguyen et al. *Physical Review X* **8**, 21051 (2018)

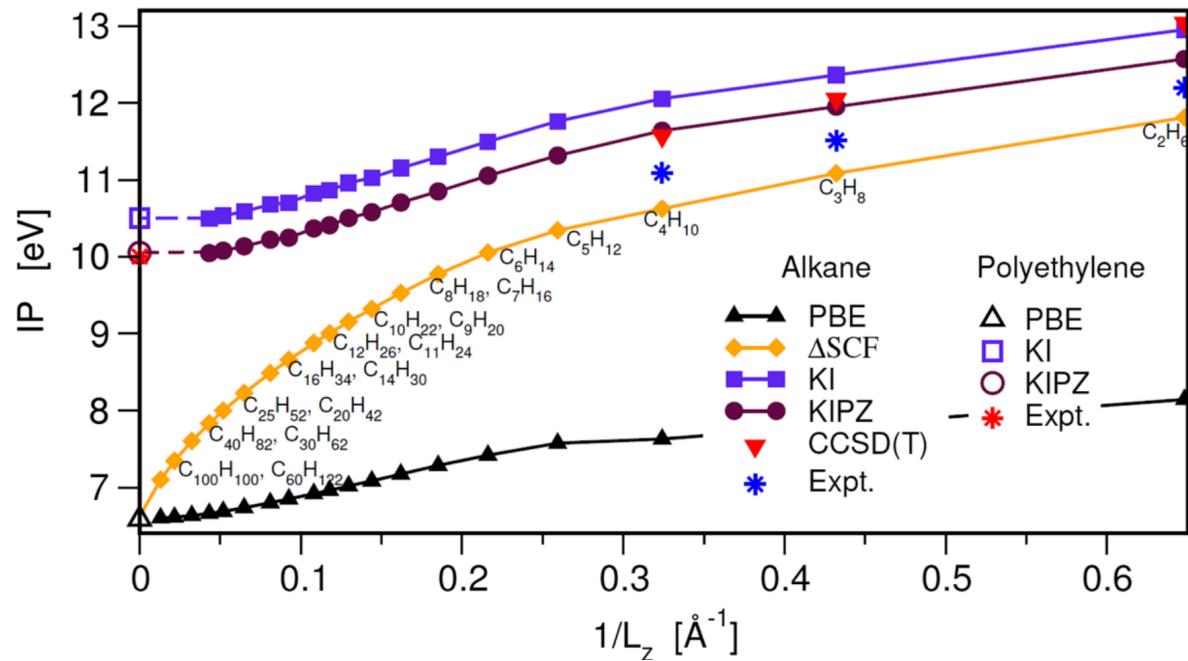
Issues with extended systems



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

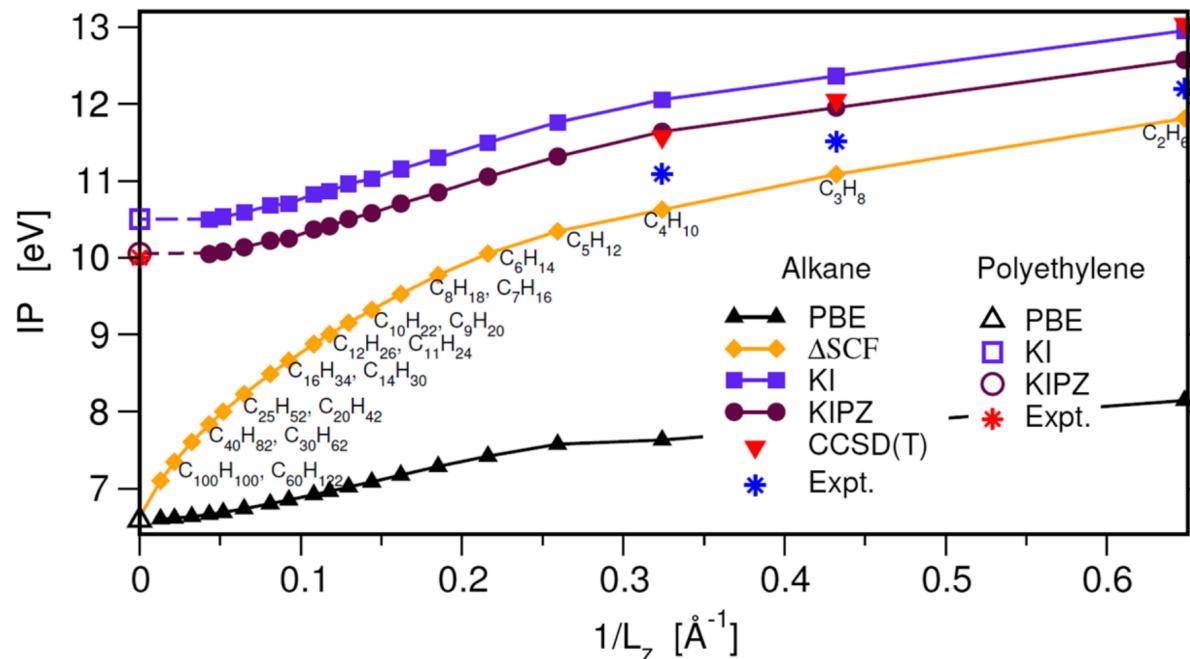
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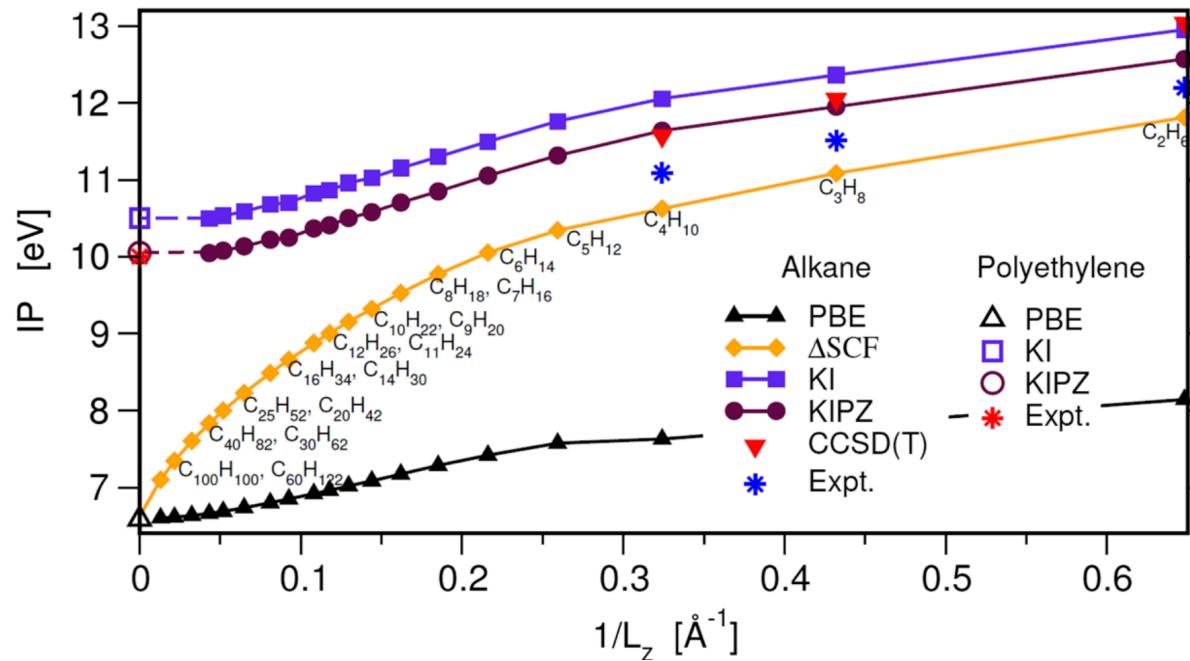
Two options:

Issues with extended systems



Two options: 1. use a more advanced functional

Issues with extended systems



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

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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Limitations

- 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.* *Physical Review B* **72**, 75125 (2005)

²L. Kronik *et al.* *Journal of Chemical Theory and Computation* **8**, 1515–1531 (2012), D. Wing *et al.* *Proceedings of the National Academy of Sciences* **118**, e2104556118 (2021)

³E. Kraisler *et al.* *Physical Review Letters* **110**, 126403 (2013)

⁴J. Ma *et al.* *Scientific Reports* **6**, 24924 (2016)

⁵J. H. Skone *et al.* *Physical Review B* **93**, 235106 (2016)

⁶C. Li *et al.* *National Science Review* **5**, 203–215 (2018)

Electronic screening via machine learning

Electronic screening via machine learning



A key ingredient of Koopmans functional calculations are the 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.* *Physical Review X* **8**, 21051 (2018), R. De Gennaro *et al.* *Physical Review B* **106**, 35106 (2022)

²N. Colonna *et al.* *Journal of Chemical Theory and Computation* **14**, 2549–2557 (2018), N. Colonna *et al.* *Journal of Chemical Theory and Computation* **18**, 5435–5448 (2022)

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- a local measure of the degree by which electronic interactions are screened
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- must be computed *ab initio* via ΔSCF ¹ or DFPT²
-

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Electronic screening via machine learning



A key ingredient of Koopmans functional calculations are the screening parameters:

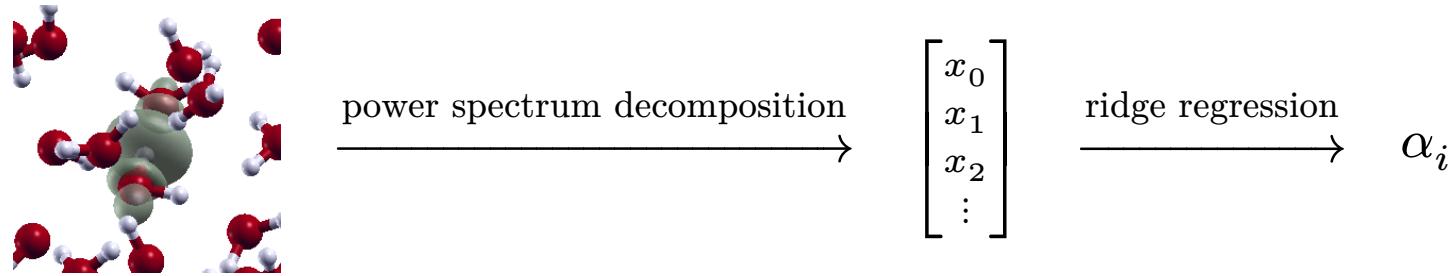
$$\alpha_i = \frac{\langle n_i | \varepsilon^{-1} f_{\text{Hxc}} | n_i \rangle}{\langle n_i | f_{\text{Hxc}} | n_i \rangle}$$

- a local measure of the degree by which electronic interactions are screened
- one screening parameter per (non-equivalent) orbital
- must be computed *ab initio* via ΔSCF ¹ or DFPT²
- corresponds to the vast majority of the computational cost of Koopmans functional calculation

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

²N. Colonna *et al.* *Journal of Chemical Theory and Computation* **14**, 2549–2557 (2018), N. Colonna *et al.* *Journal of Chemical Theory and Computation* **18**, 5435–5448 (2022)

The machine-learning framework

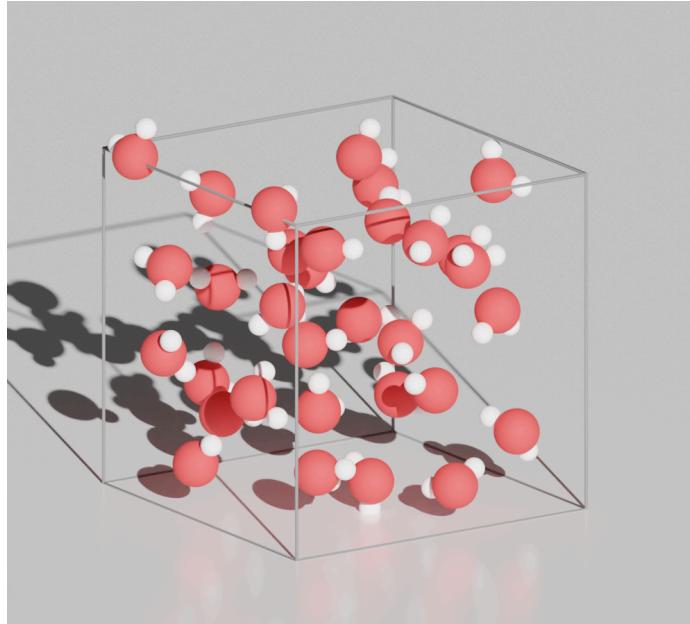


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

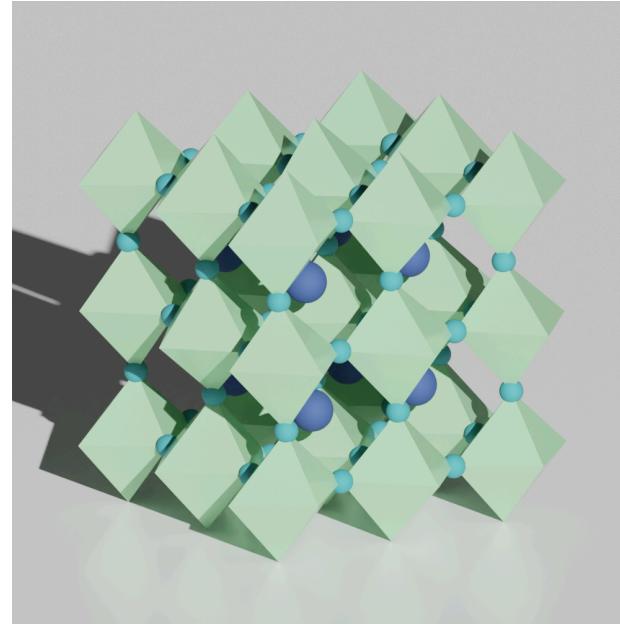
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

Two test systems



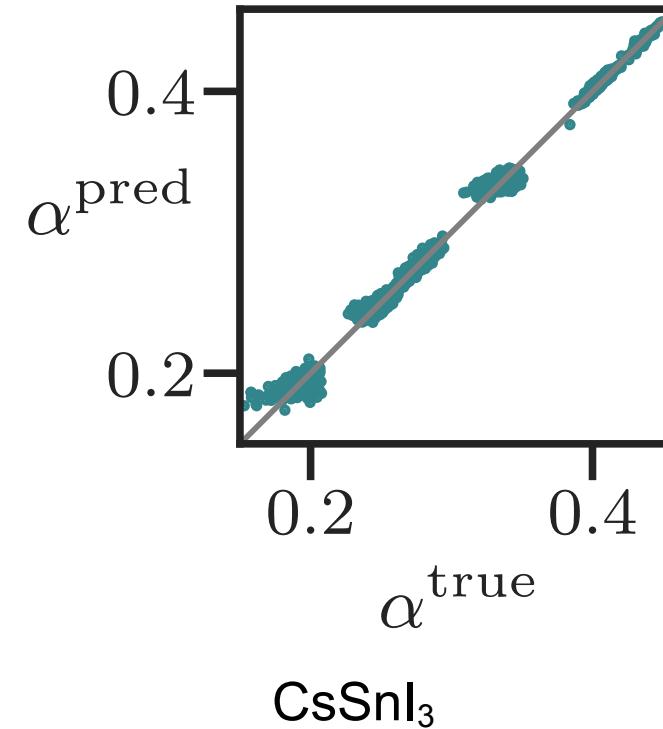
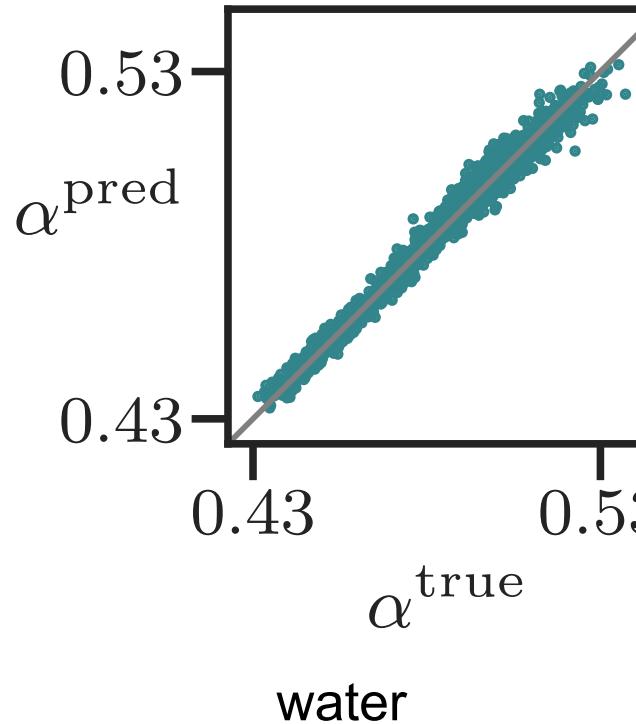
water



CsSnI₃

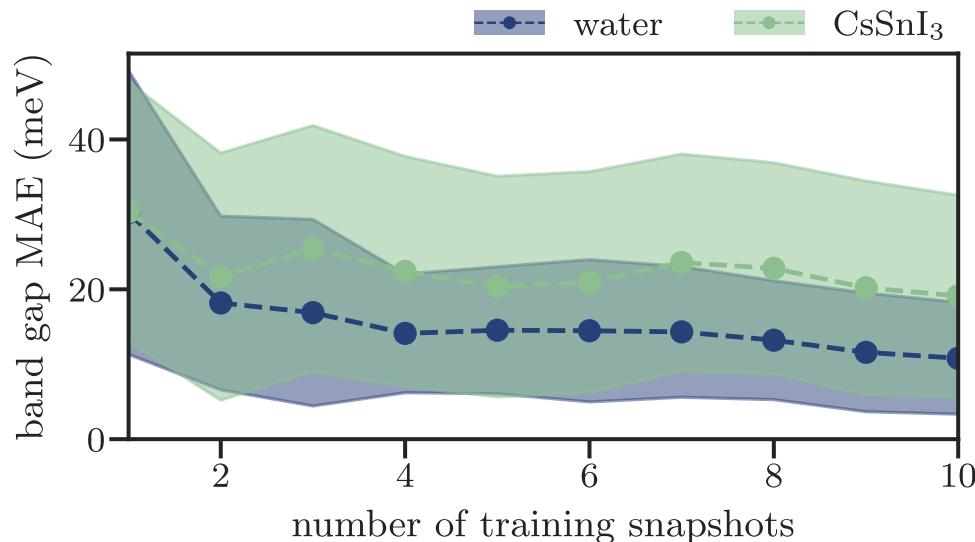
¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

Results: screening parameters

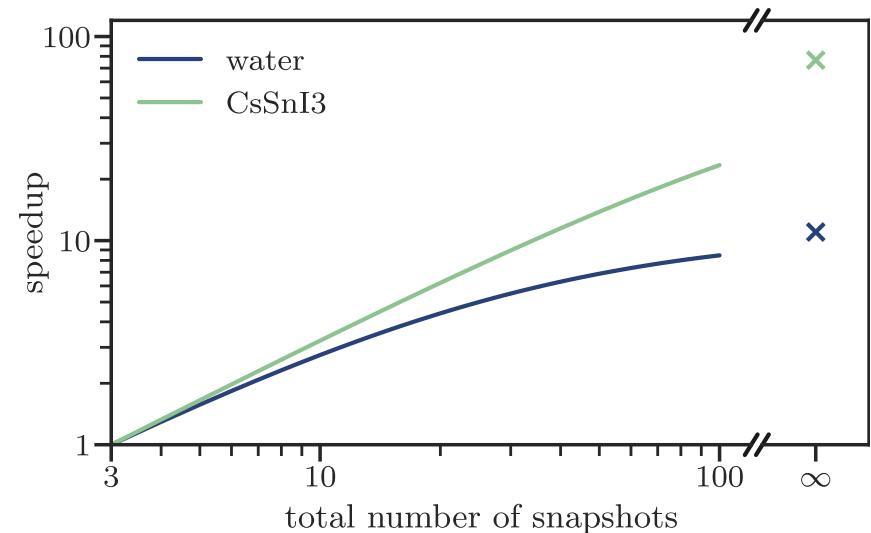


¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

Results: balancing accuracy and speedup



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



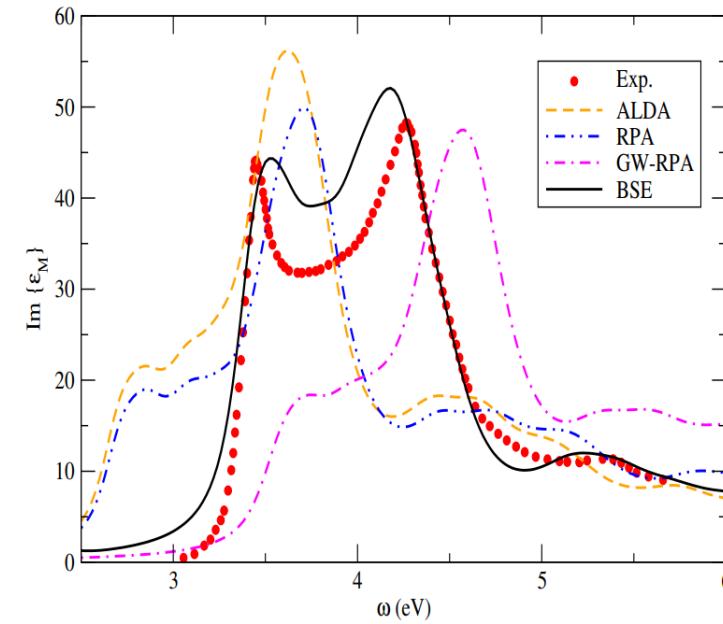
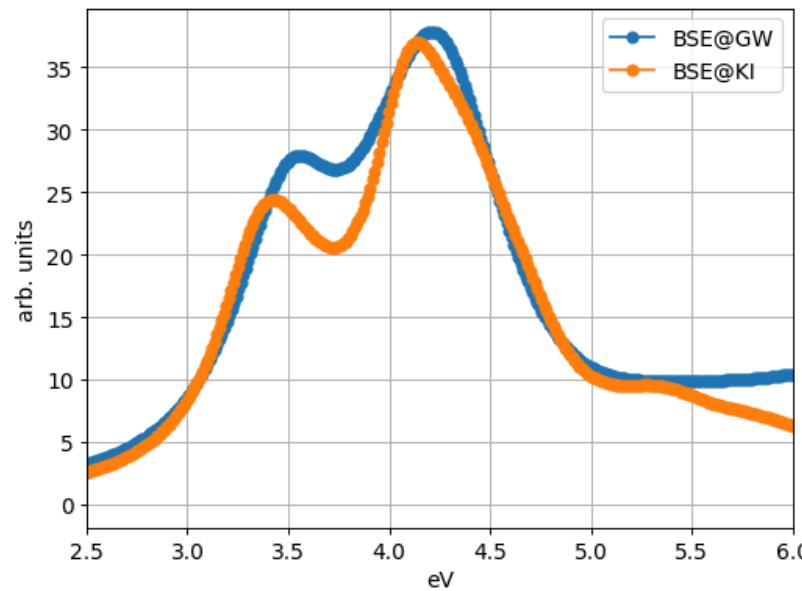
speedup of $\mathcal{O}(10)$ to $\mathcal{O}(100)$

¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

Takeaway: predicting electronic response can be done efficiently with frozen-orbital approximations and machine learning

Going beyond single-particle excitations (preliminary)

The idea: solve the BSE, skipping GW and instead using Koopmans eigenvalues¹

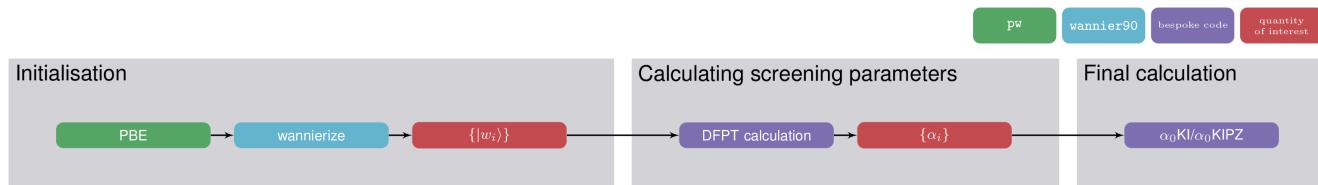
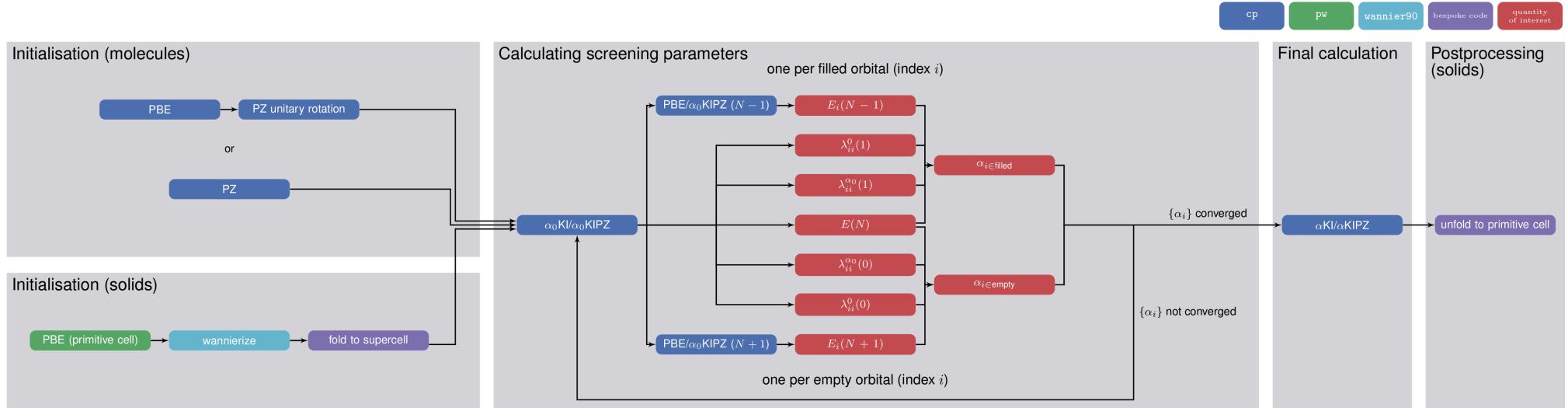


N.B. using DFT response

¹P. Lautenschlager *et al.* *Physical Review B* **36**, 4821–4830 (1987), F. Sottile. (École Polytechnique, 2003).

Making Koopmans functionals accessible

The general workflow



Because we have...

- bespoke code
- complicated workflows

then...

- there is lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Koopmans

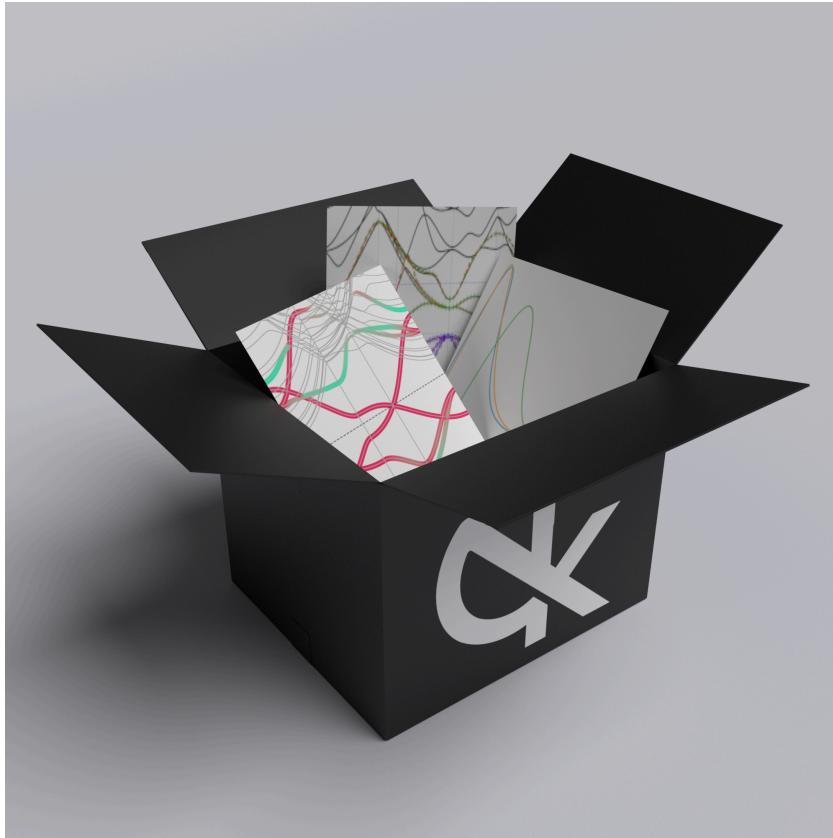
An ongoing effort to make Koopmans functional calculations straightforward for non-experts¹

- easy installation
- automated workflows
- minimal input required of the user

For more details, go to koopmans-functionals.org

¹E. B. Linscott *et al.* *Journal of Chemical Theory and Computation* **19**, 7097–7111 (2023)

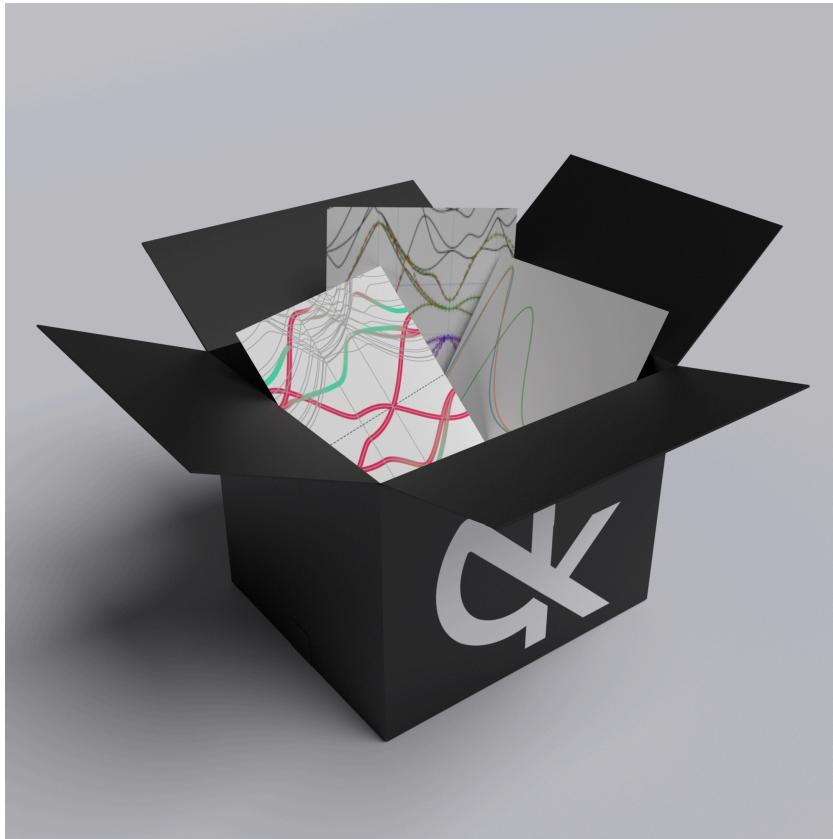
Making Koopmans functionals accessible



1. scriptable with python
- 2.
- 3.

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

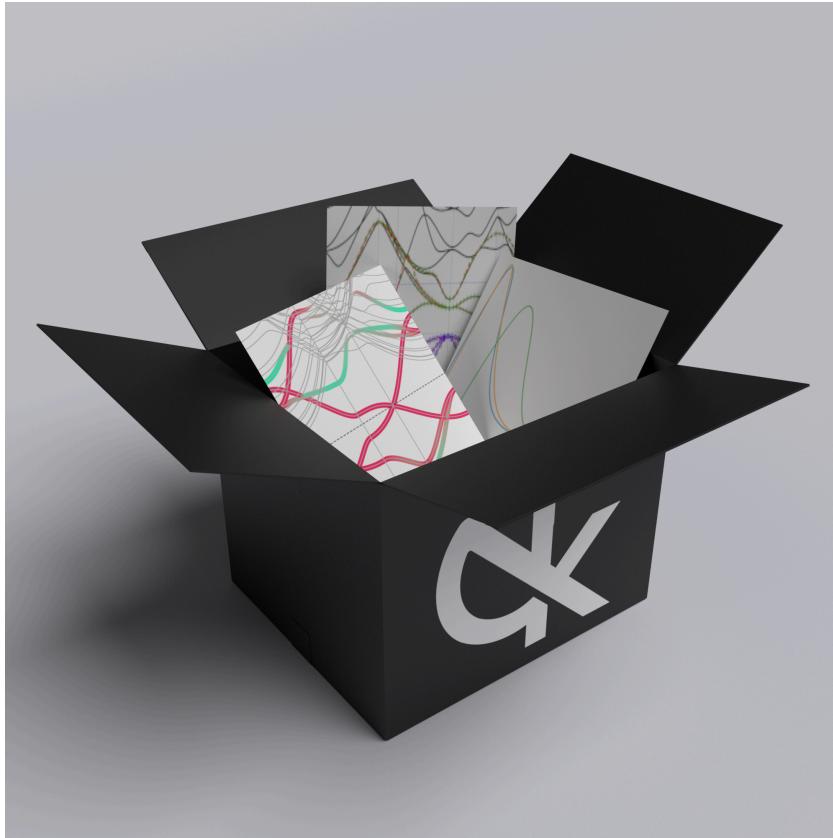
Making Koopmans functionals accessible



1. scriptable with python
2. automated Wannerisation
- 3.

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Making Koopmans functionals accessible

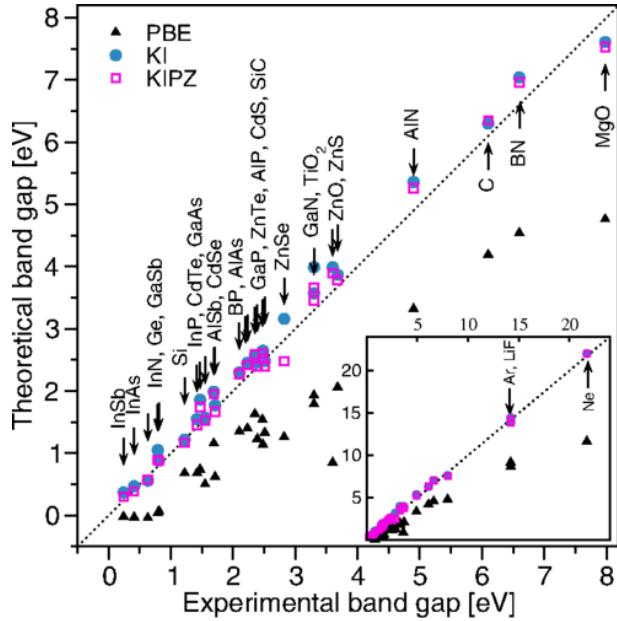


1. scriptable with python
2. automated Wannerisation
3. integration with AiIDA¹

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

Summary

Summary



Koopmans functionals...

- bake localised charged excitation energies into DFT

•

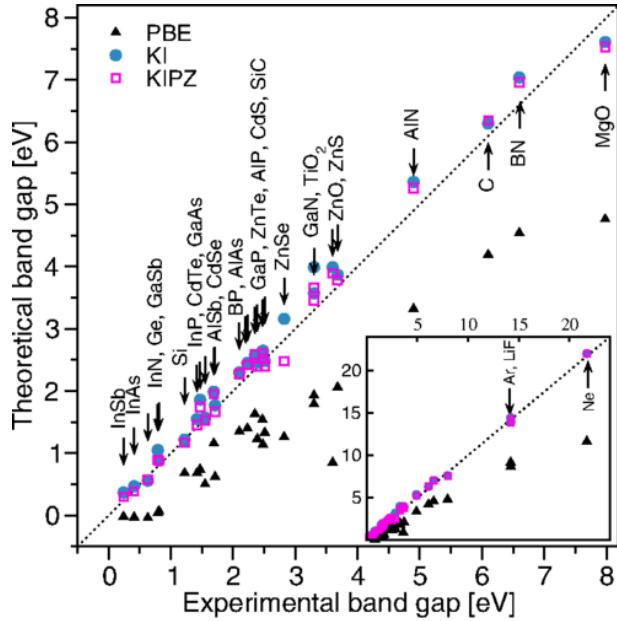
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¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

Summary

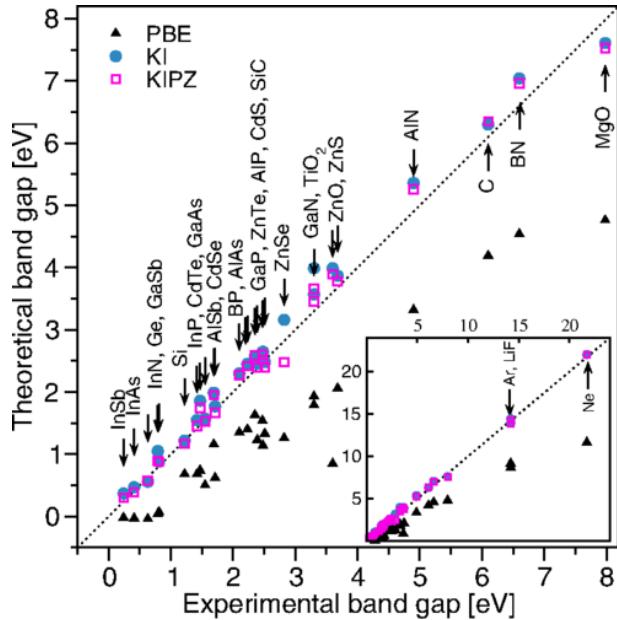


Koopmans functionals...

- bake localised charged excitation energies into DFT
- give band structures with comparable accuracy to state-of-the-art GW
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Summary

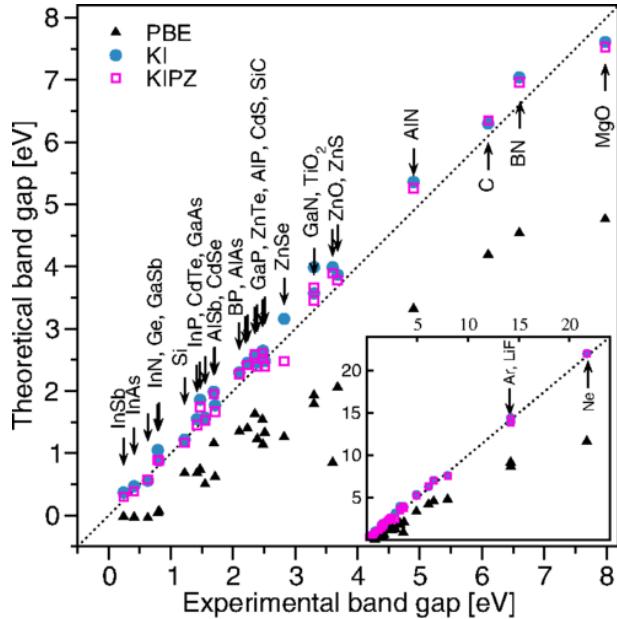


Koopmans functionals...

- bake localised charged excitation energies into DFT
- give band structures with comparable accuracy to state-of-the-art GW
- machine learning can be used to calculate the screening parameters¹
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Summary

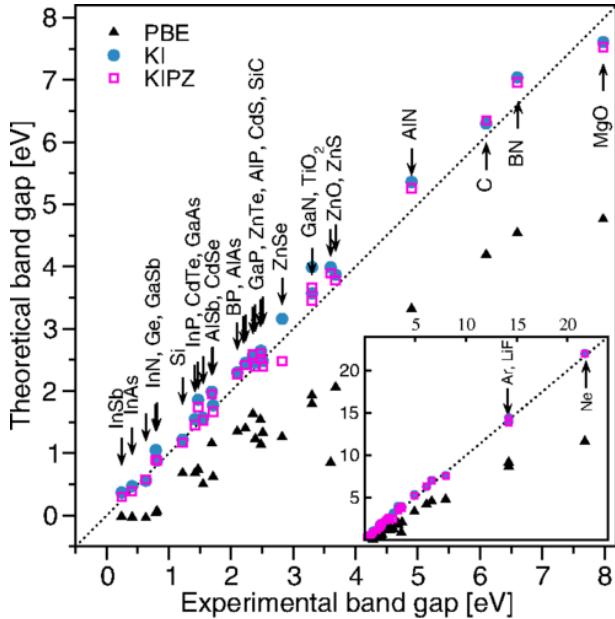


Koopmans functionals...

- bake localised charged excitation energies into DFT
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- machine learning can be used to calculate the screening parameters¹
- can be used in place of GW in BSE calculation of excitons
-

¹Y. Schubert *et al.* <http://arxiv.org/abs/2406.15205> (2024)

Summary



Koopmans functionals...

- bake localised charged excitation energies into DFT
- give band structures with comparable accuracy to state-of-the-art GW
- machine learning can be used to calculate the screening parameters¹
- can be used in place of GW in BSE calculation of excitons
- is available in the easy-to-use package koopmans

¹Y. Schubert et al. <http://arxiv.org/abs/2406.15205> (2024)

Open questions

- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they take?
- how to extend to metallic systems?
- can we provide a formal basis for the Koopmans correction?
 - ▶ GKS
 - ▶ spectral functional theory¹
 - ▶ ensemble DFT
 - ▶ RDMFT

¹A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014)

Acknowledgements



Nicola Marzari



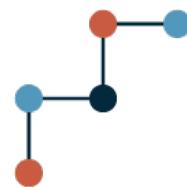
Nicola Colonna



Yannick Schubert



Miki Bonacci

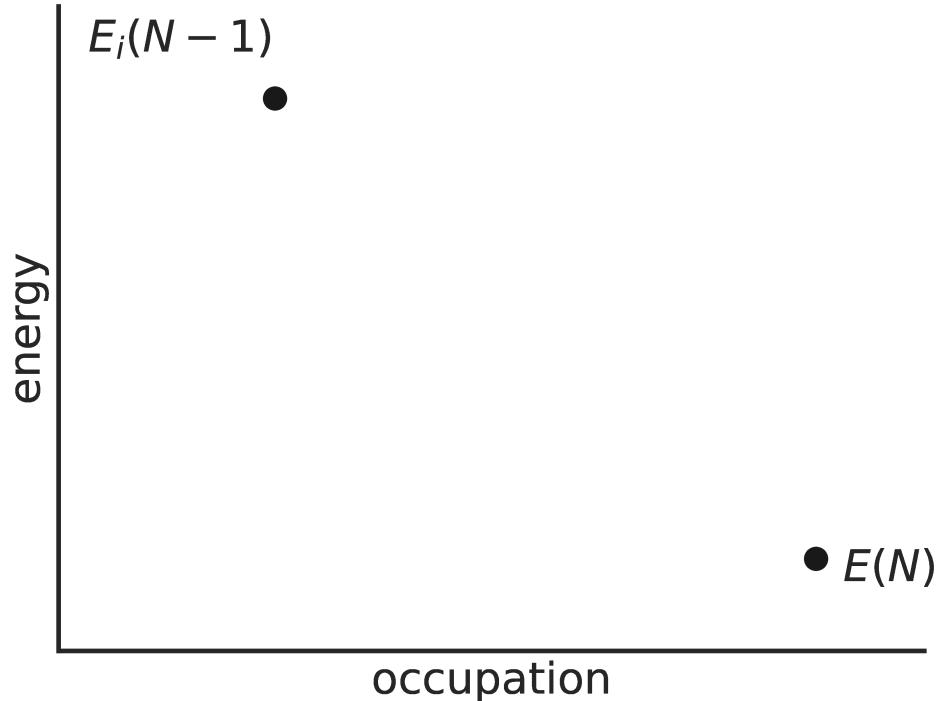


**Swiss National
Science Foundation**

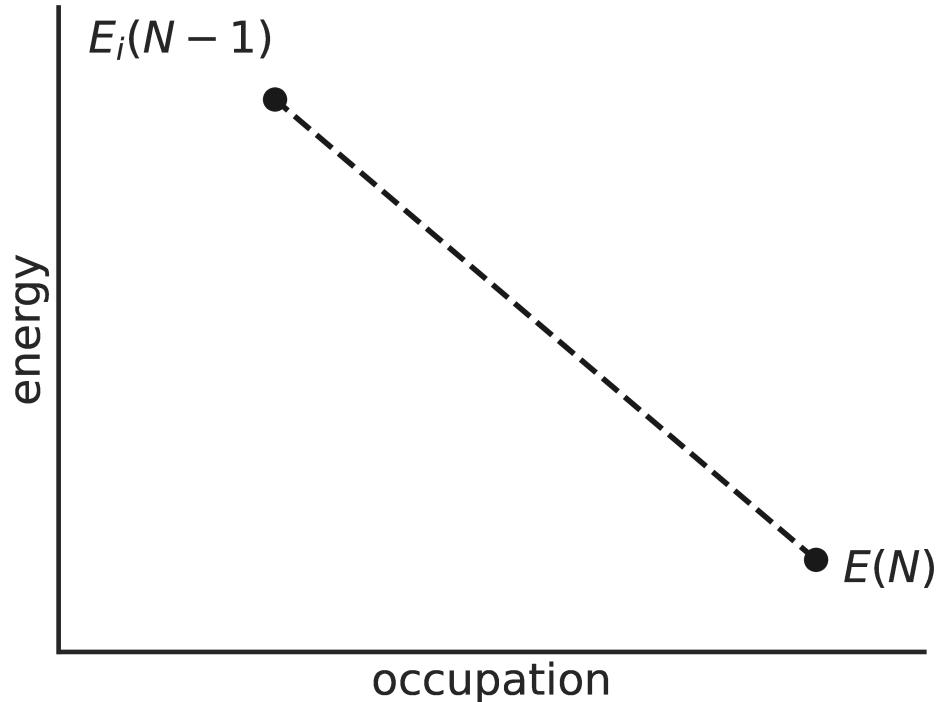
MARVEL
The MARVEL logo features the word "MARVEL" in a bold, sans-serif font above four red hexagons arranged horizontally. The first hexagon is outlined in red, while the others are solid red with black outlines.

Spare slides

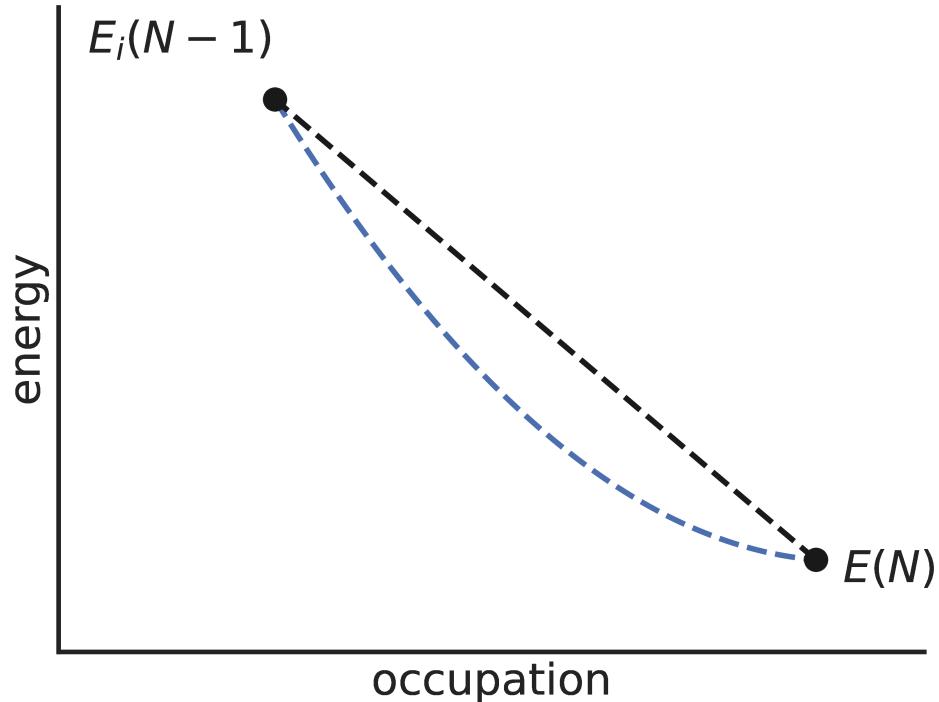
Calculating screening parameters via SCF



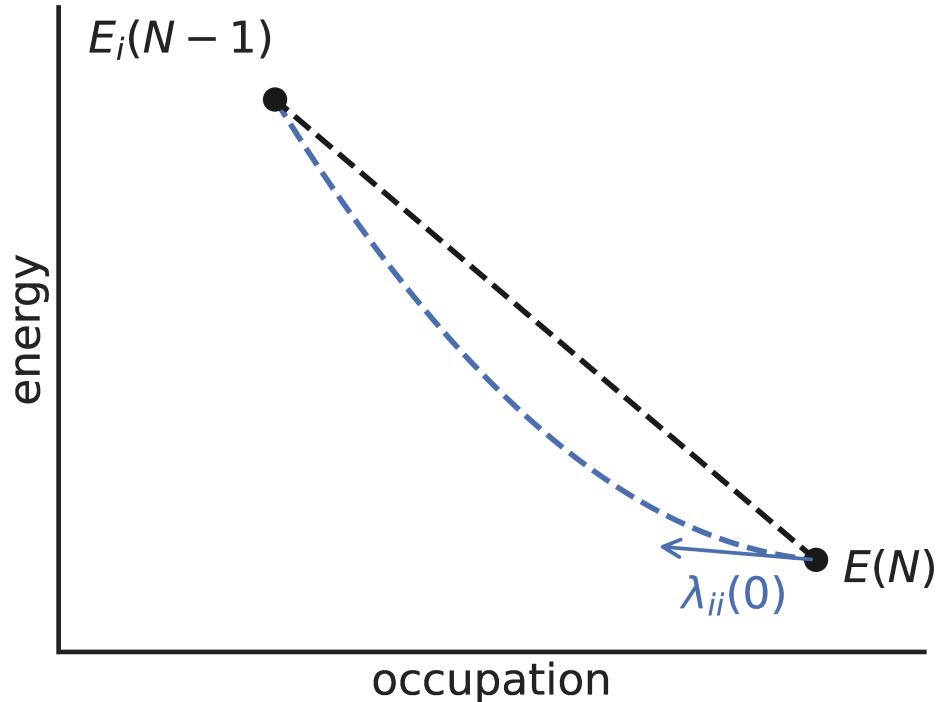
Calculating screening parameters via SCF



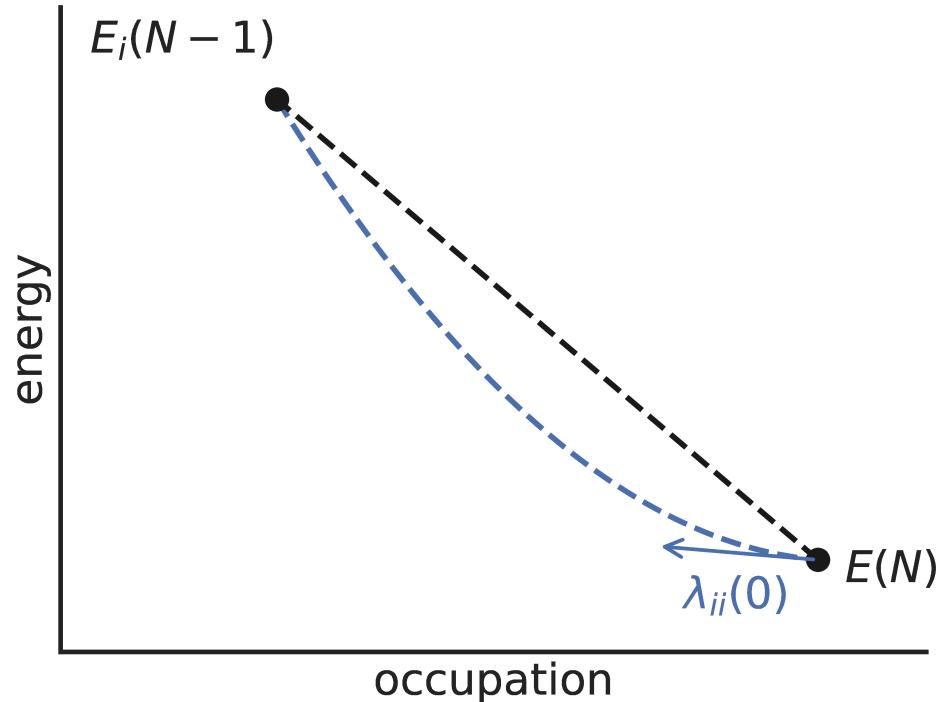
Calculating screening parameters via SCF



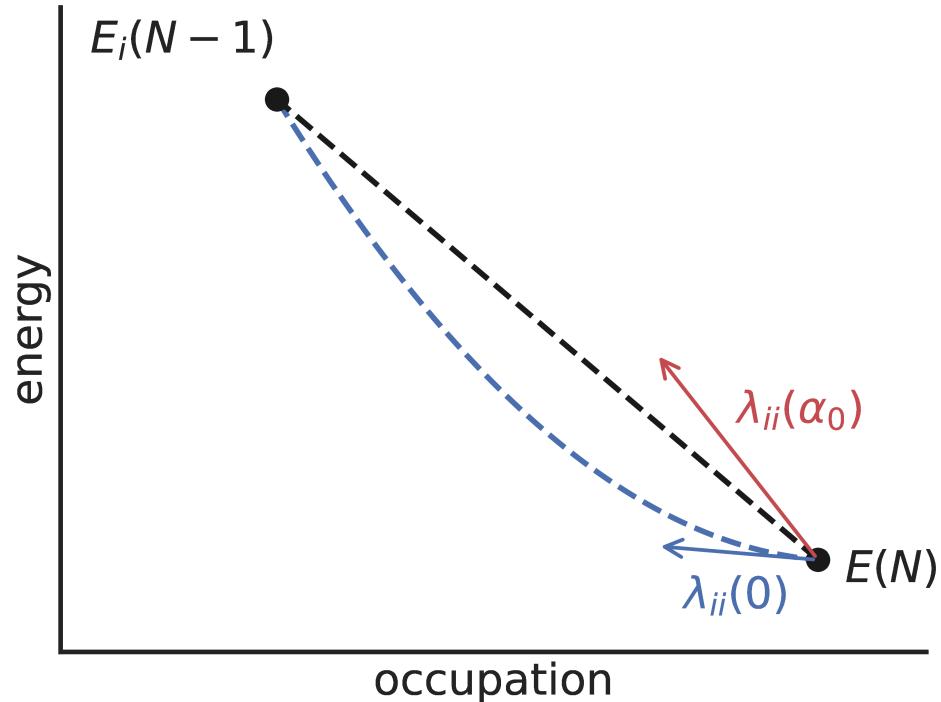
Calculating screening parameters via SCF



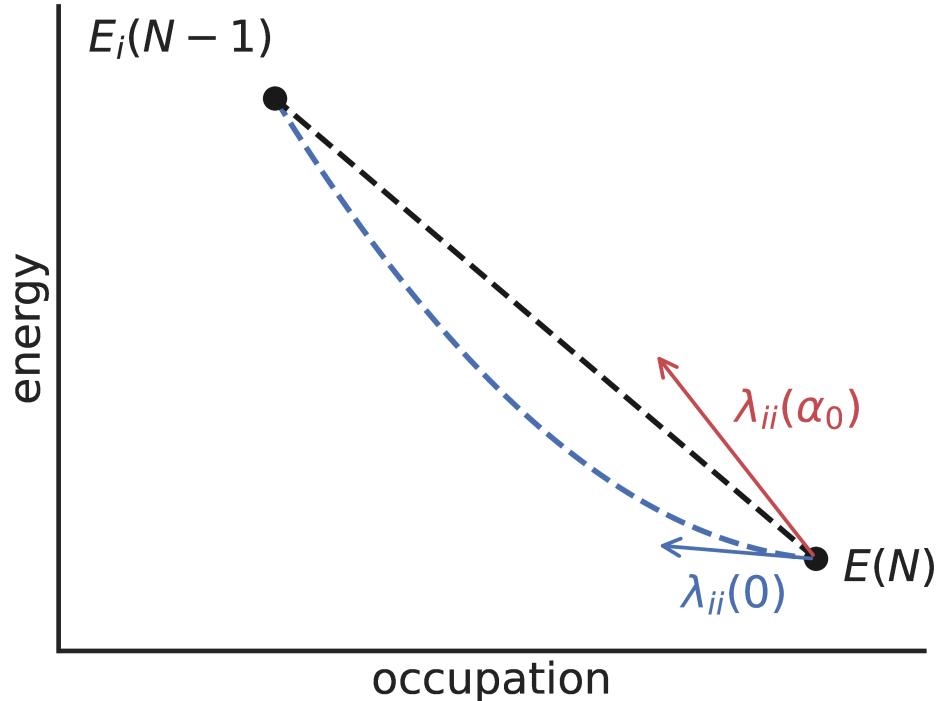
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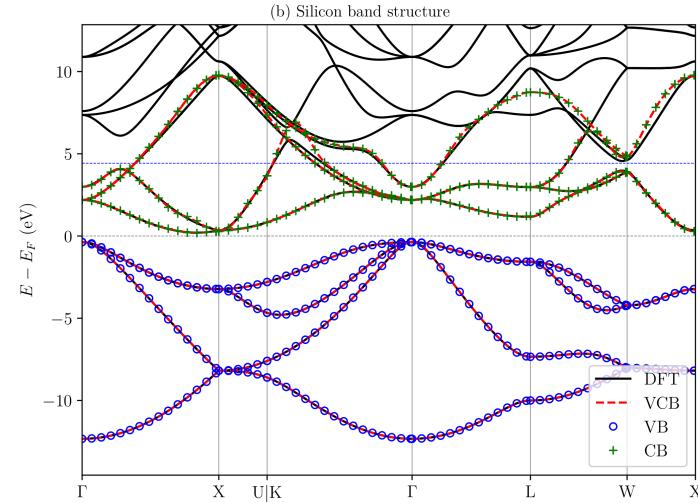
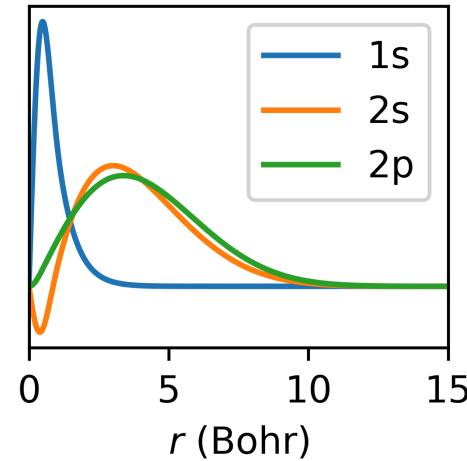
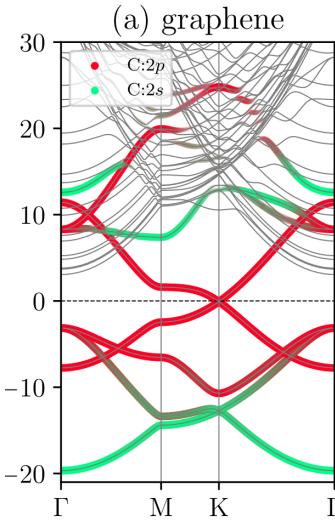
Calculating screening parameters via SCF



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

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

The key ingredients of automated Wannierisation



projectability-based
disentanglement¹

use PAOs found in
pseudopotentials

parallel transport to separate
manifolds²

¹J. Qiao *et al.* *npj Computational Materials* **9**, 208 (2023)

²J. Qiao *et al.* *npj Computational Materials* **9**, 206 (2023)

Connections with approximate self-energies³

Orbital-density functional theory:

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

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

³A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014), N. Colonna *et al.* *Journal of Chemical Theory and Computation* **15**, 1905–1914 (2019)

Connections with approximate self-energies²



Orbital-density functional theory:

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

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

cf. Green's function theory:

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

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

Connections with approximate self-energies¹



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

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

¹A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014), N. Colonna *et al.* *Journal of Chemical Theory and Computation* **15**, 1905–1914 (2019)

Connections with approximate self-energies²

Screened exchange plus Coulomb hole (COHSEX)

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

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

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

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

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

¹A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014), N. Colonna *et al.* *Journal of Chemical Theory and Computation* **15**, 1905–1914 (2019)

Connections with approximate self-energies²

Static $GW\Gamma_{xc}$ — local (DFT-based) vertex corrections²

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

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

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

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

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

¹A. Ferretti *et al.* *Physical Review B* **89**, 195134 (2014), N. Colonna *et al.* *Journal of Chemical Theory and Computation* **15**, 1905–1914 (2019)

²M. 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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