

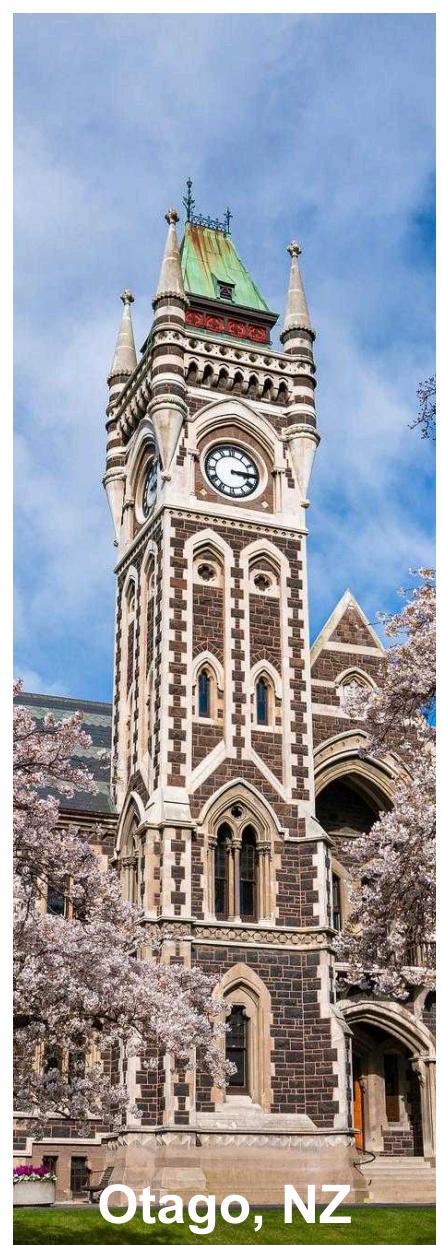
PSI

Center for Scientific Computing,
Theory and Data

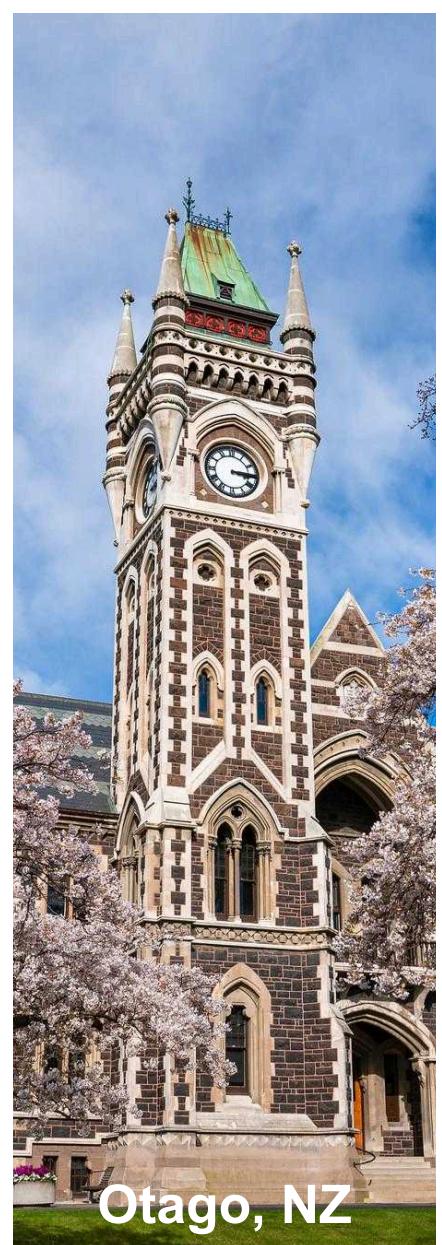
Correcting the failures of DFT Koopmans functionals, DFT+*U*, and more

Edward Linscott

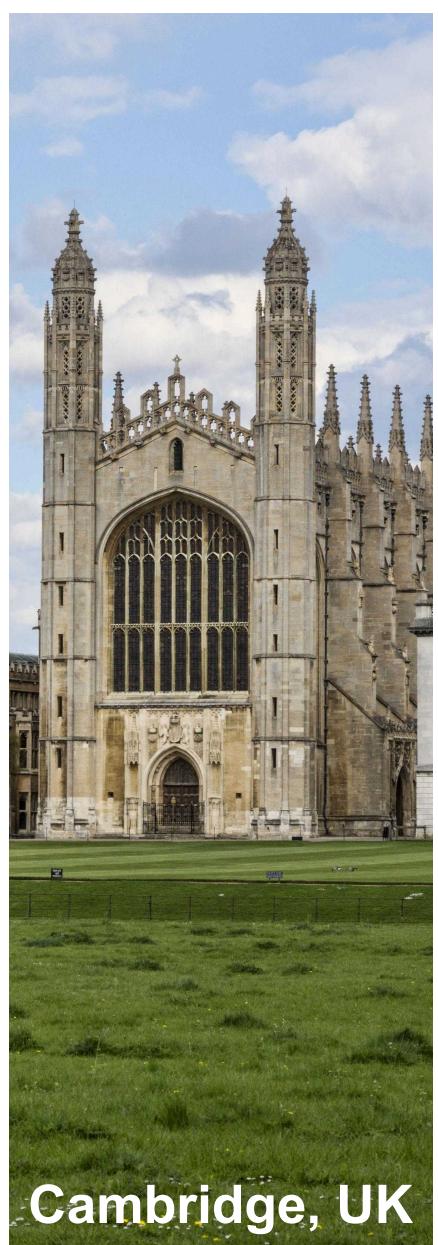
PsiQuantum, 30 October 2025



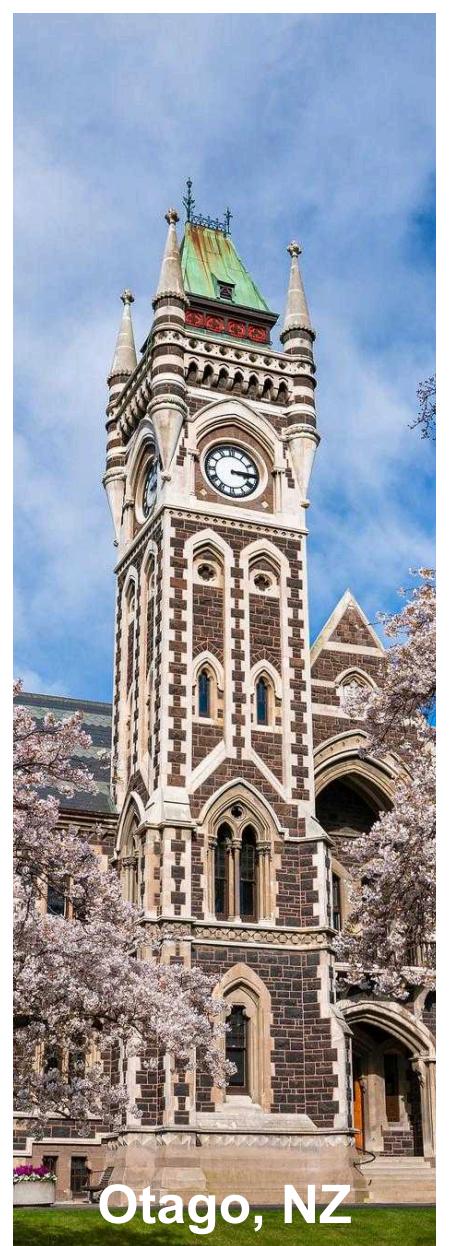
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Otago, NZ



Cambridge, UK



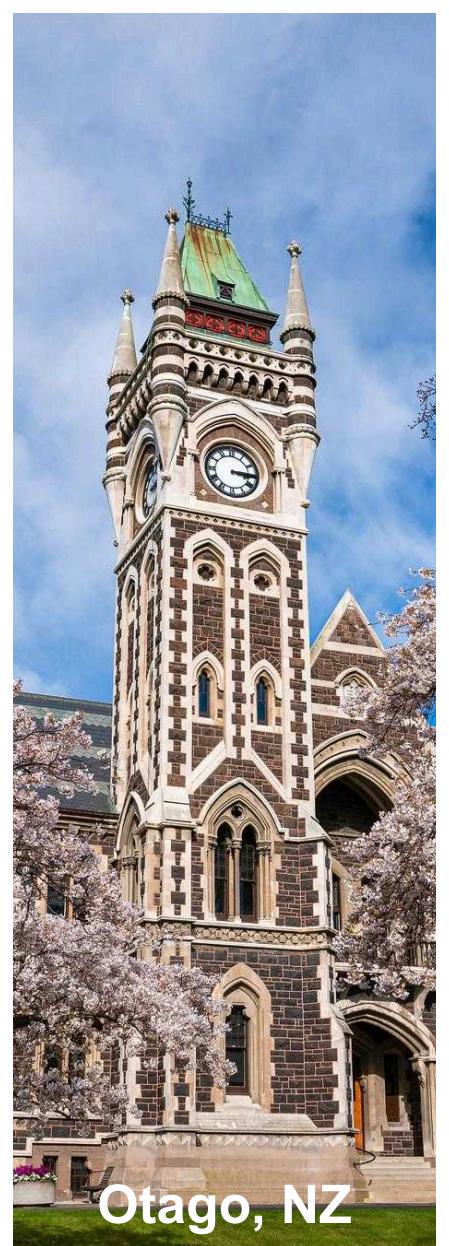
Otago, NZ



Cambridge, UK



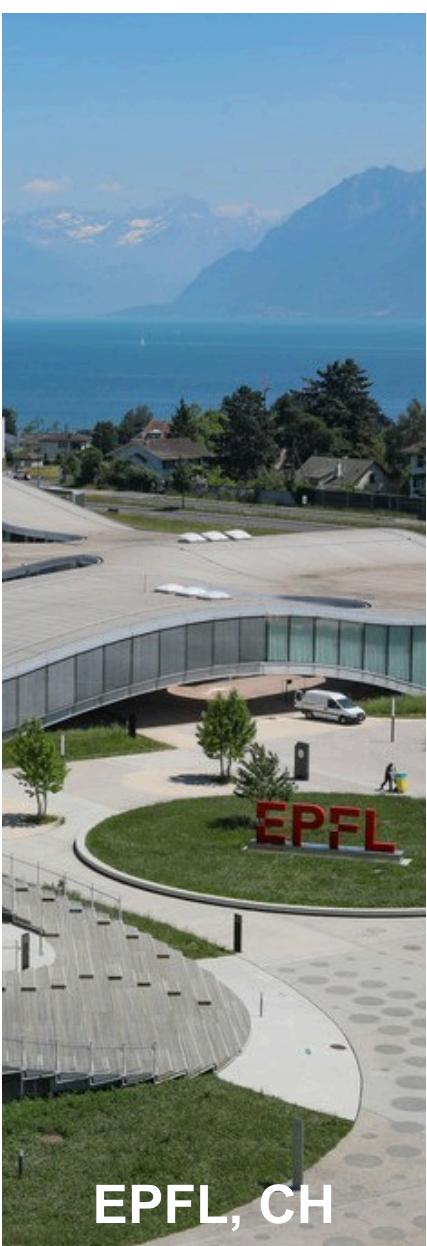
EPFL, CH



Otago, NZ



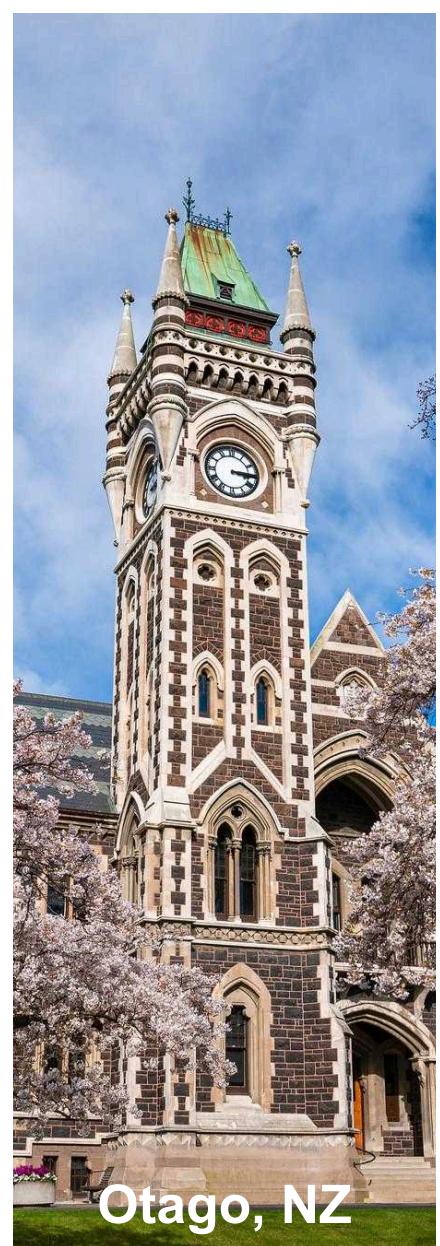
Cambridge, UK



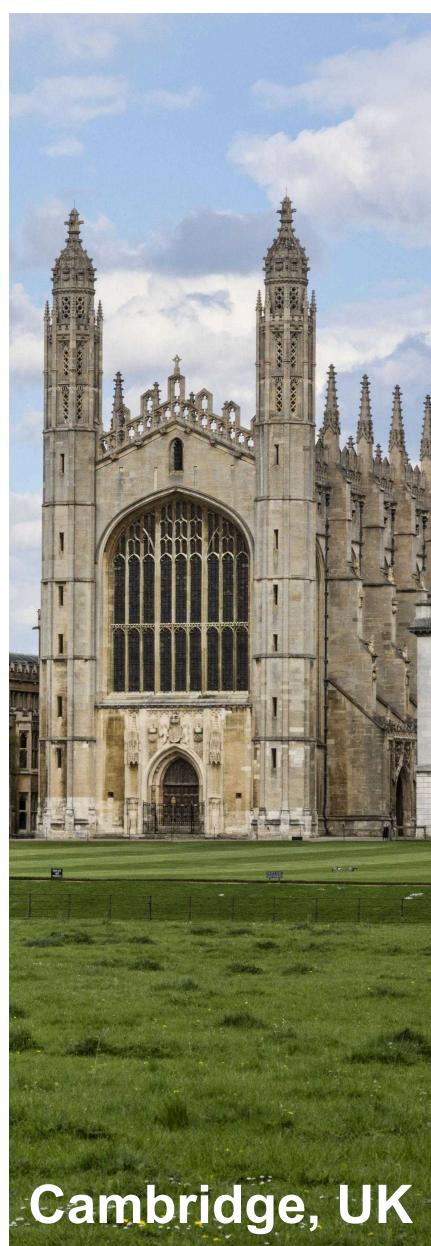
EPFL, CH



PSI, CH



Otago, NZ



Cambridge, UK



EPFL, CH



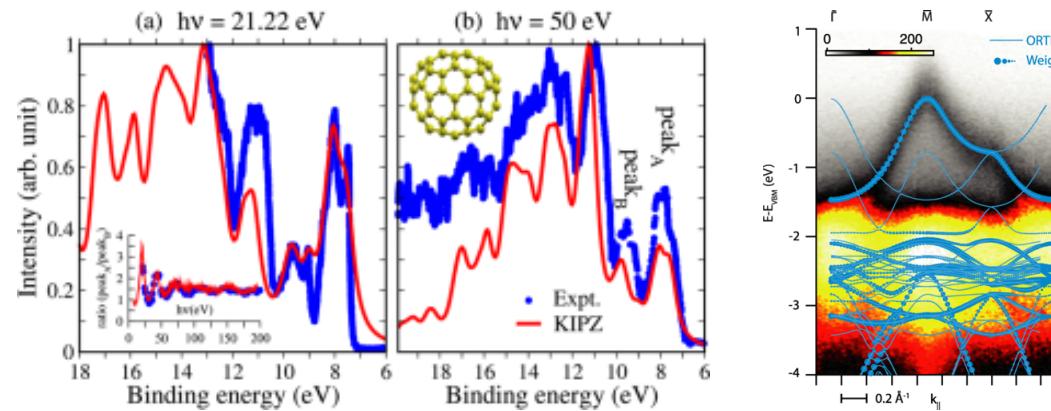
PSI, CH



... PsiQuantum
AU?

Predicting electronic excitations

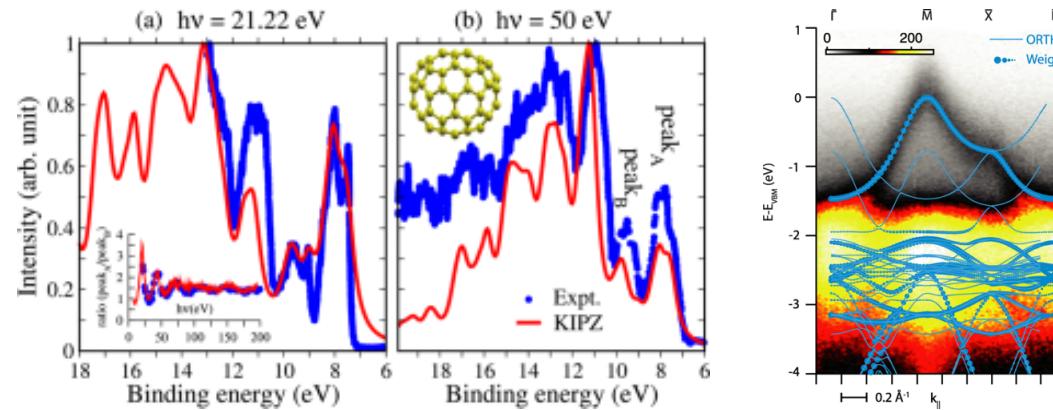
Spectral properties are fundamental to understanding molecules and materials...



¹N. L. Nguyen *et al.* *Phys. Rev. Lett.* 114, 166405 (2015), M. Puppin *et al.* *Phys. Rev. Lett.* 124, 206402 (2020)

Predicting electronic excitations

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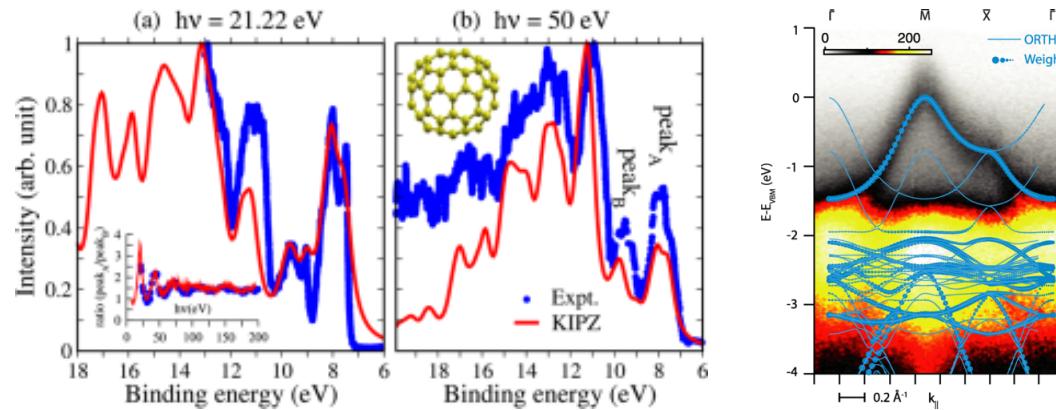


... but how can we routinely compute them?

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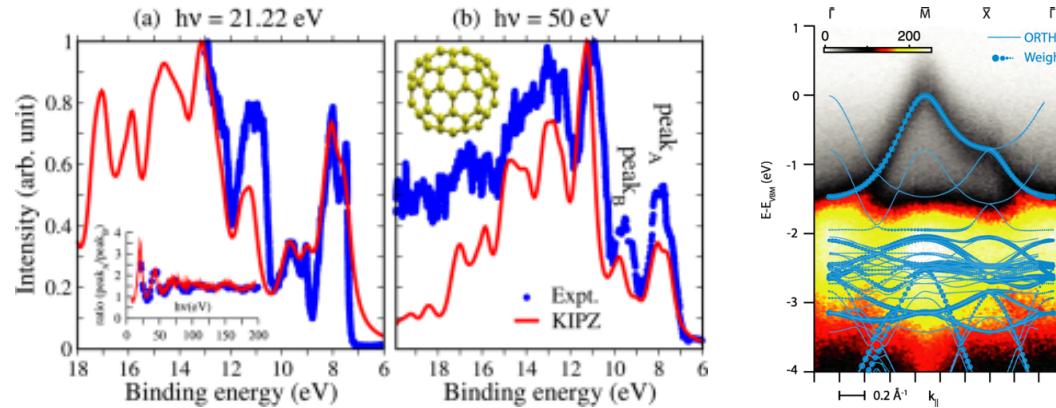
... but how can we routinely compute them?

- quantum chemistry: gold standard, but scales prohibitively (for now...)
- GW: accurate but expensive, often ill-behaved, diagrammatic
- DFT: plagued by intrinsic errors

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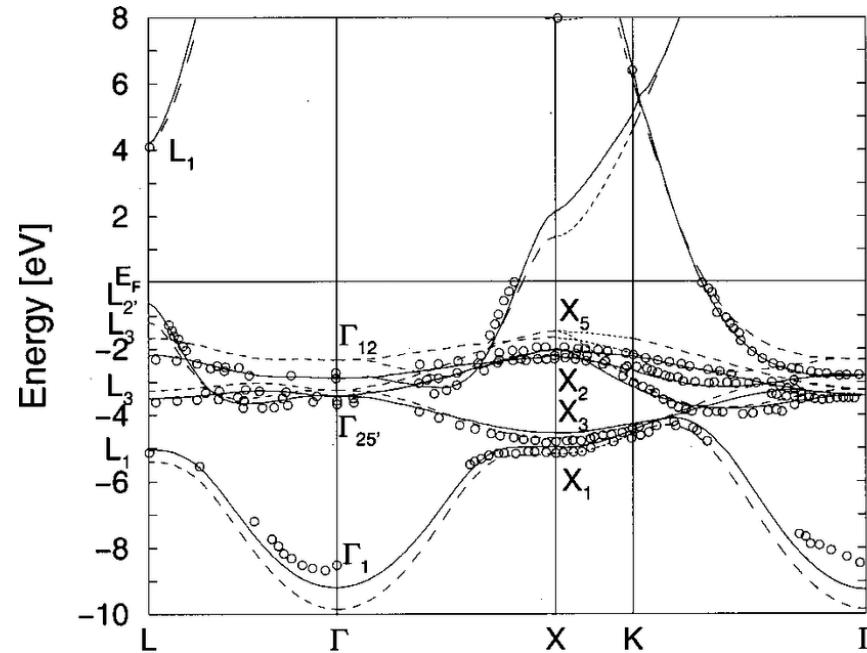
My work: understanding and correcting these intrinsic errors

¹N. L. Nguyen *et al.* *Phys. Rev. Lett.* 114, 166405 (2015), M. Puppin *et al.* *Phys. Rev. Lett.* 124, 206402 (2020)

The failures of DFT

Learning nothing from Icarus

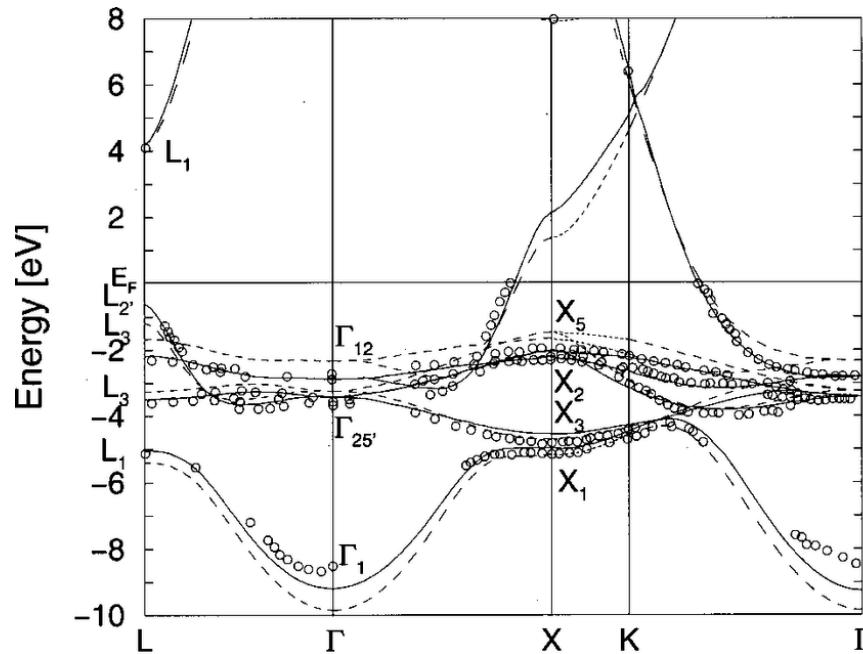
From the auxiliary, non-interacting system:



¹G. Onida *et al.* Rev. Mod. Phys. 74, 601 (2002)

Learning nothing from Icarus

From the auxiliary, non-interacting system:



... the temptation is too much!

¹G. Onida *et al.* Rev. Mod. Phys. 74, 601 (2002)

Learning nothing from Icarus

But single-particle excitation energies can be related to total energy differences

$$-\varepsilon_{\text{HOMO}} = I = E(N-1) - E(N)$$

... and even to the long-range decay of the density

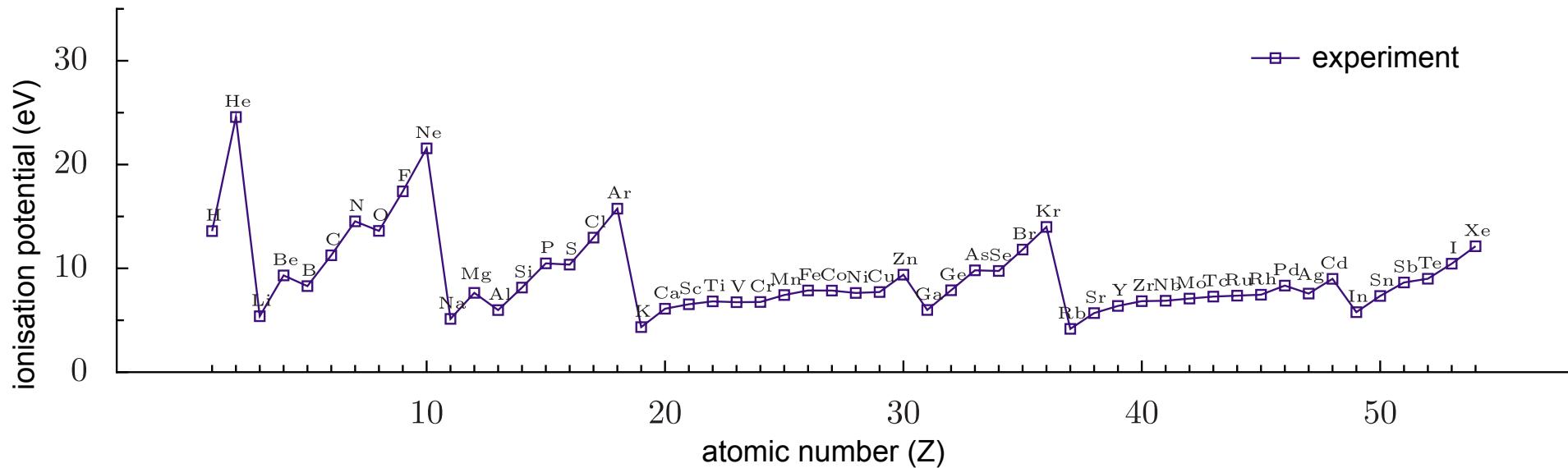
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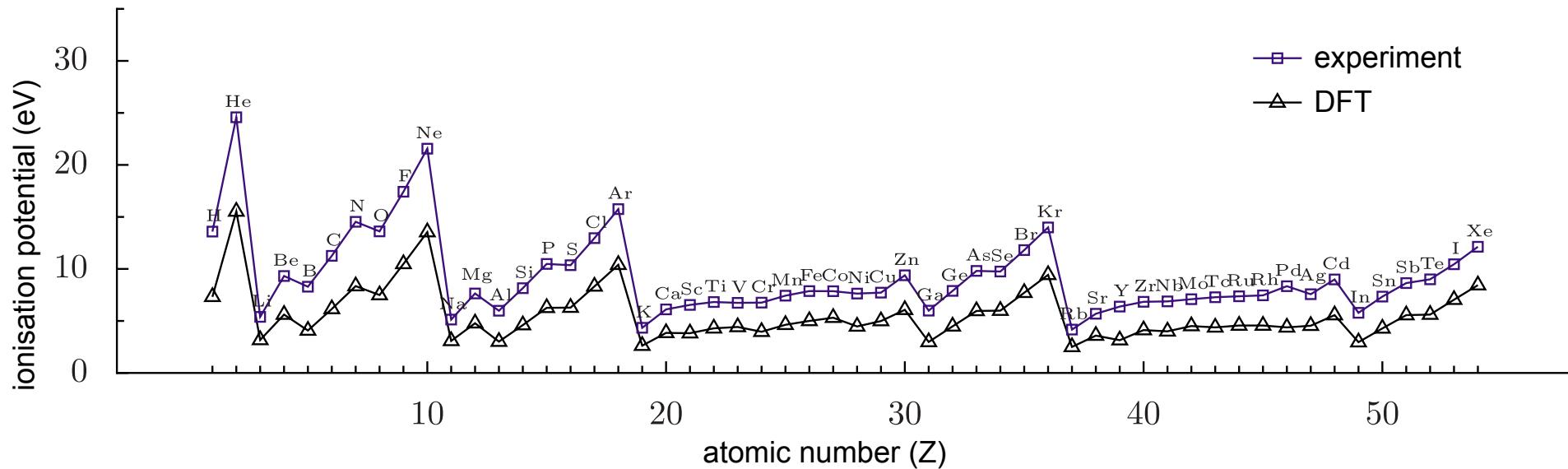
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What's going wrong?

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

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cf. Janak's theorem:

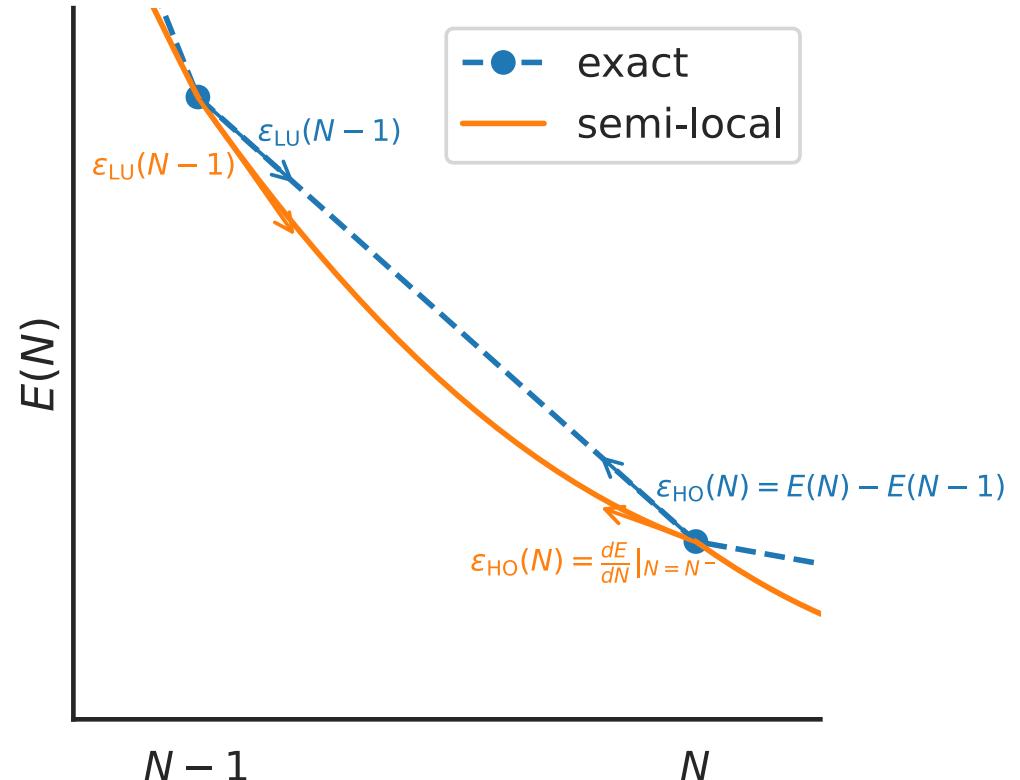
$$\varepsilon_i^{\text{DFT}} = \frac{dE^{\text{DFT}}}{df_i}$$

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Aside: piecewise linearity

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¹J. P. Perdew *et al.* *Phys. Rev. Lett.* 49, 1691–1694 (1982)

²W. Yang *et al.* *Phys. Rev. Lett.* 84, 5172–5175 (2000)

³A. C. Burgess *et al.* *J. Chem. Phys.* 159, 211102 (2023)

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$$2E(N) \leq E(N + 1) + E(N - 1)$$

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- ... and that similar reasoning can be applied to magnetisation⁴

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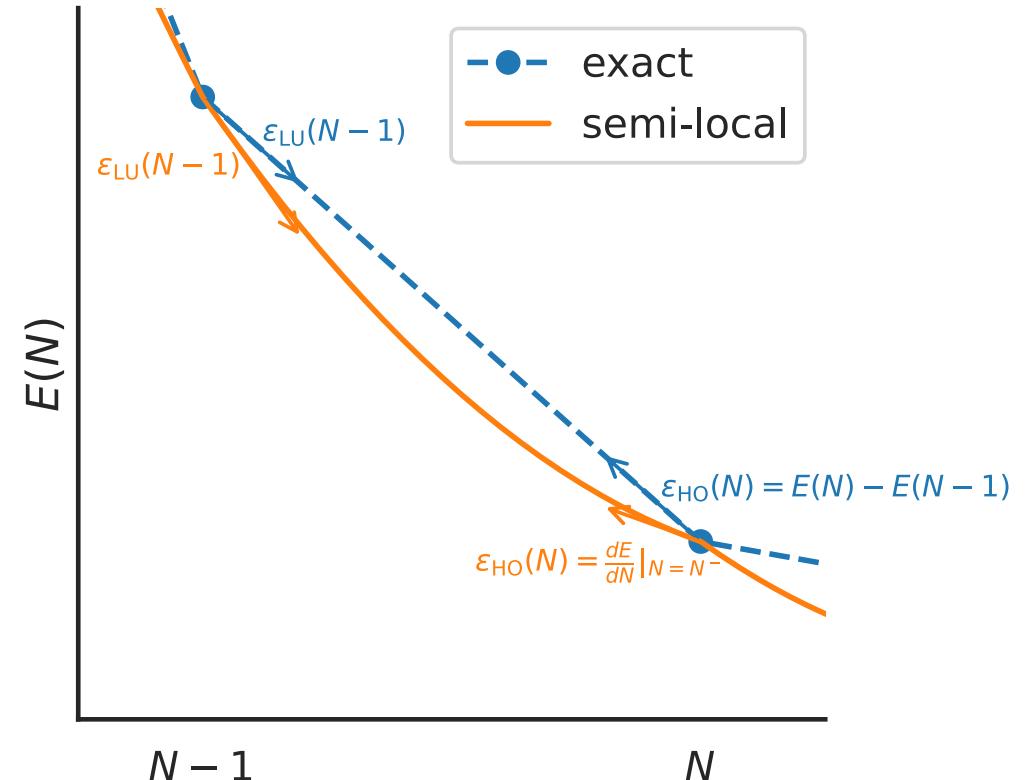
⁴A. C. Burgess *et al.* *Phys. Rev. Lett.* 133, 26404 (2024)

Core idea: enforce piecewise linearity

Imposing generalised piecewise linearity

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

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

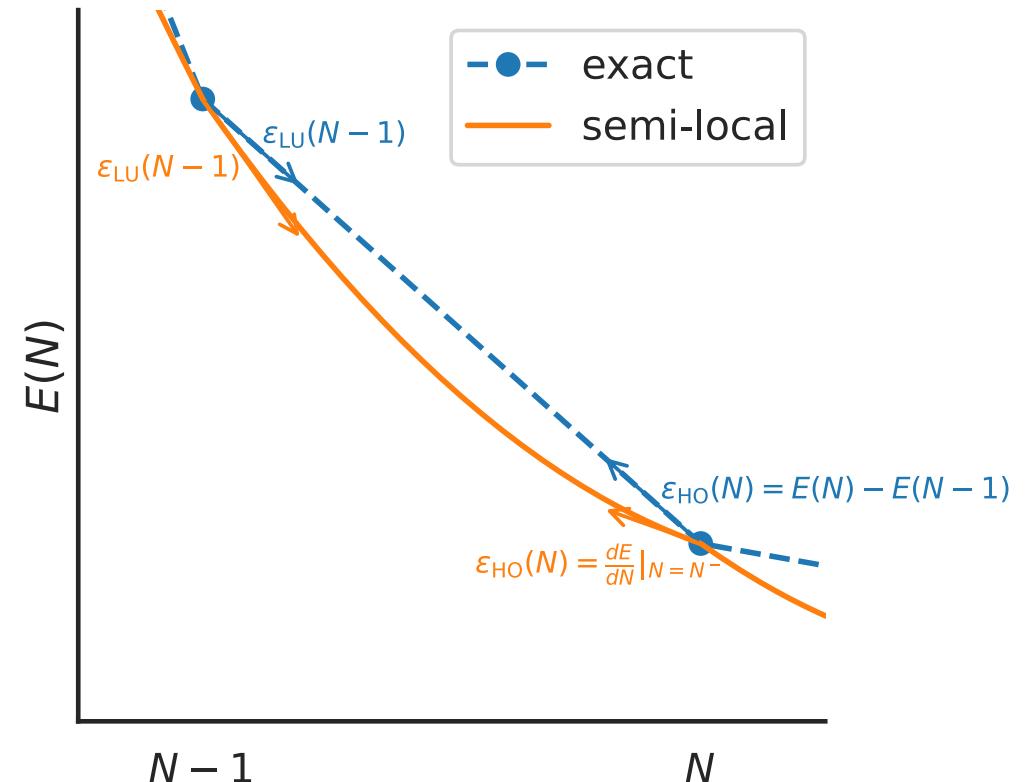


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removes dependence on f_i



Imposing generalised piecewise linearity

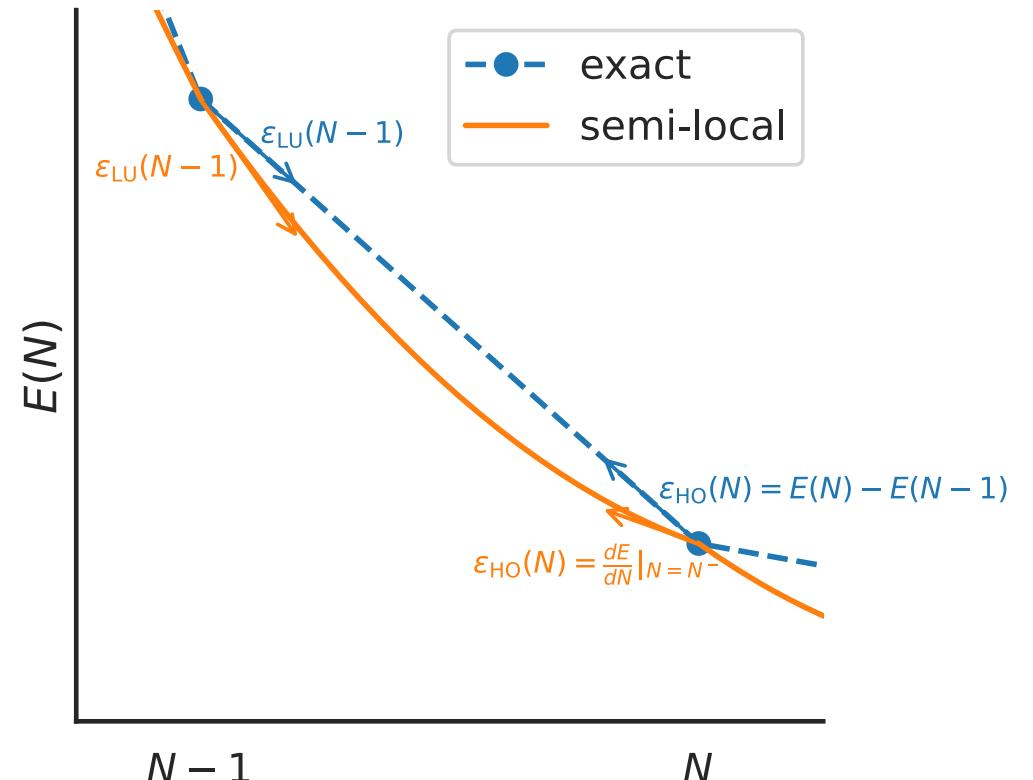
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$$+ \sum_i \left(- \int_0^{f_i} \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

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

removes dependence on f_i

restores linear dependence on f_i

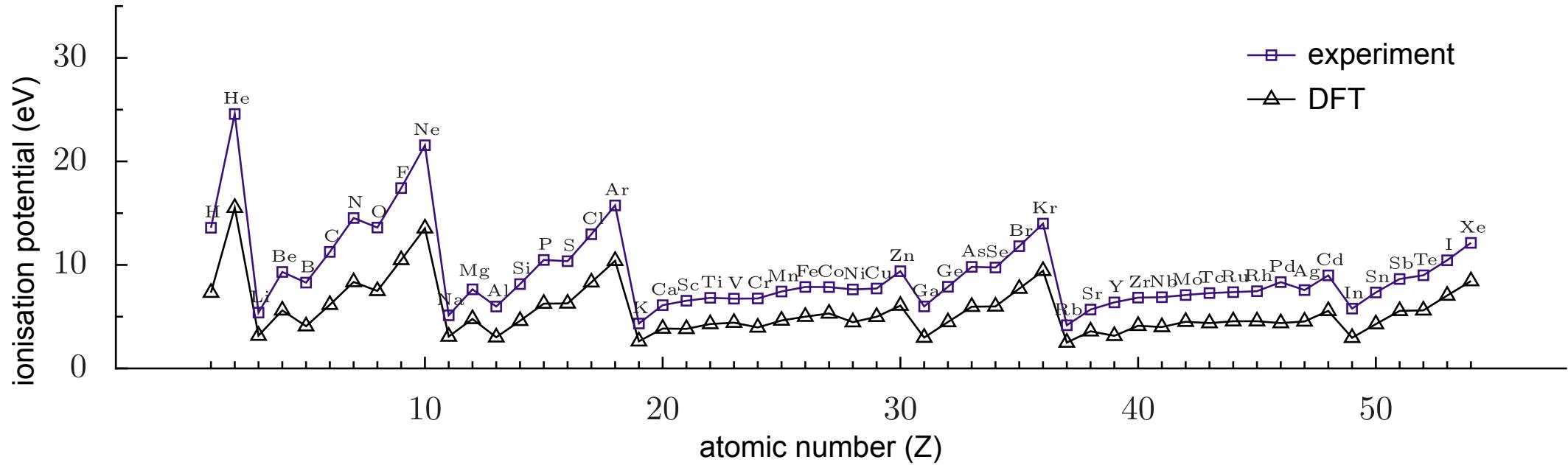


Details for the experts

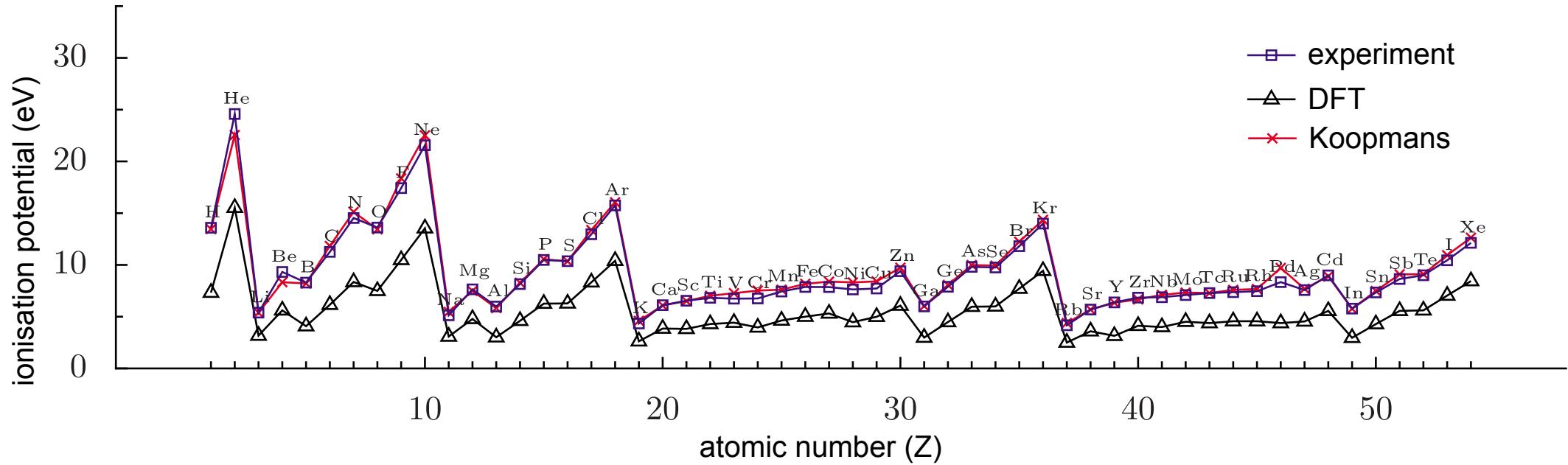
$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) \right. \\ \left. + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

- orbital-density-dependence
- screening parameters
- total energy at integer occupations unchanged!

Results



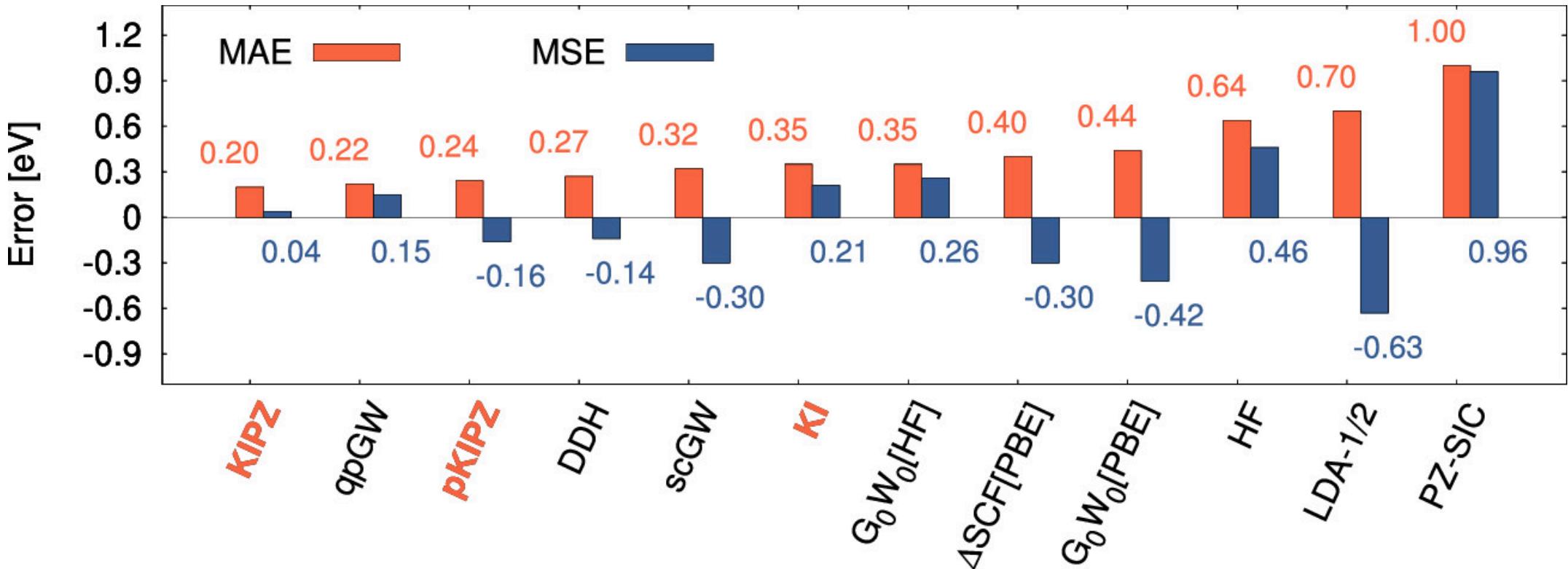
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Molecules

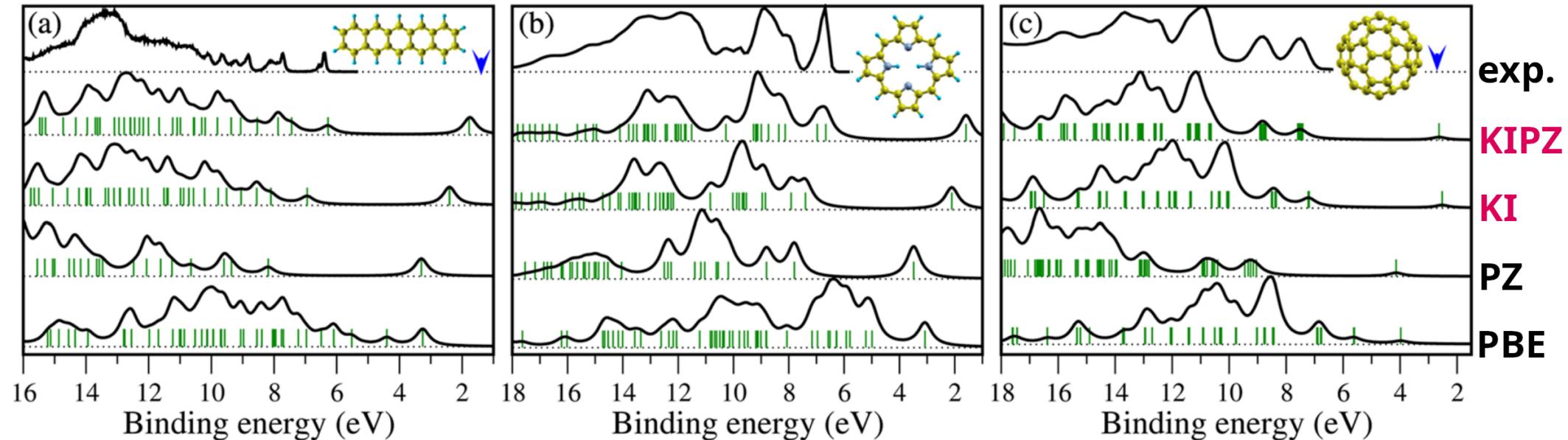
Ionisation potentials¹



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

Molecules

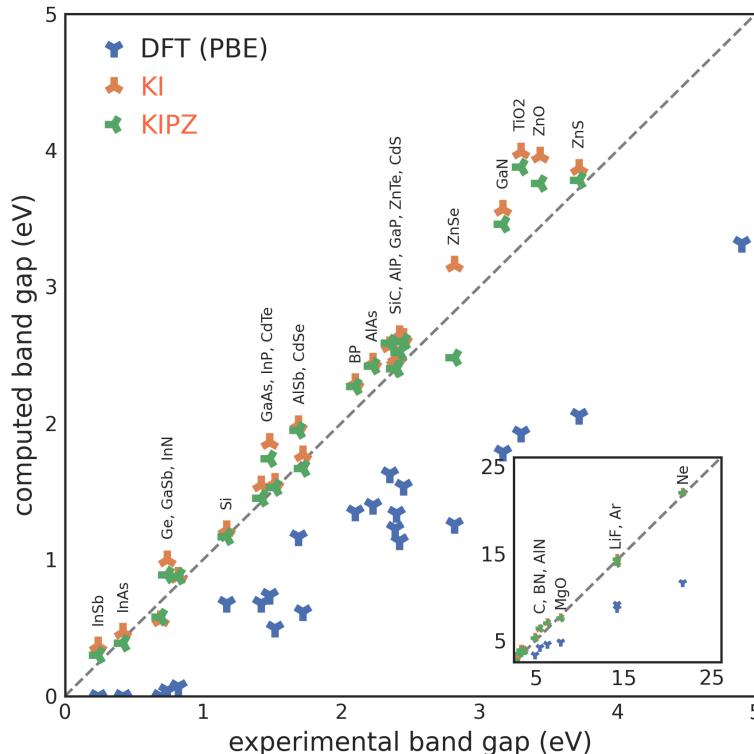
UV photoemission spectra¹



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

Materials

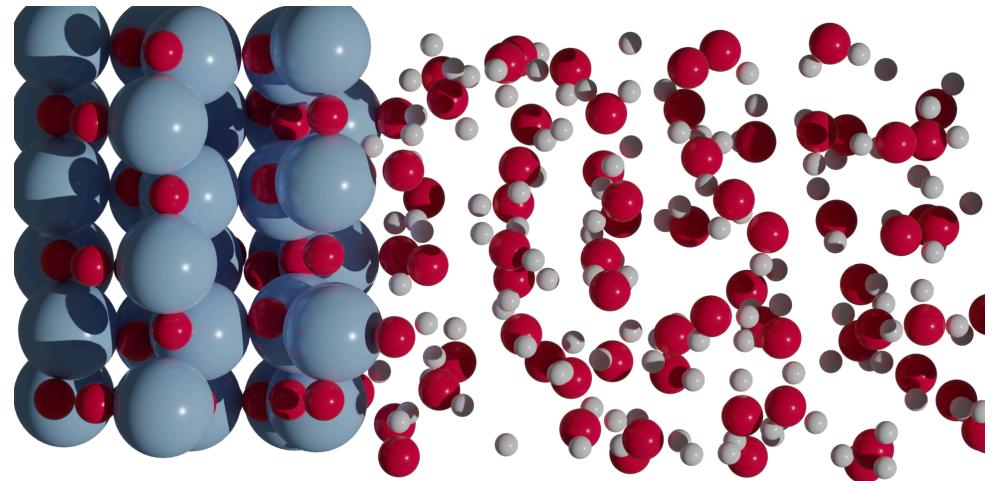
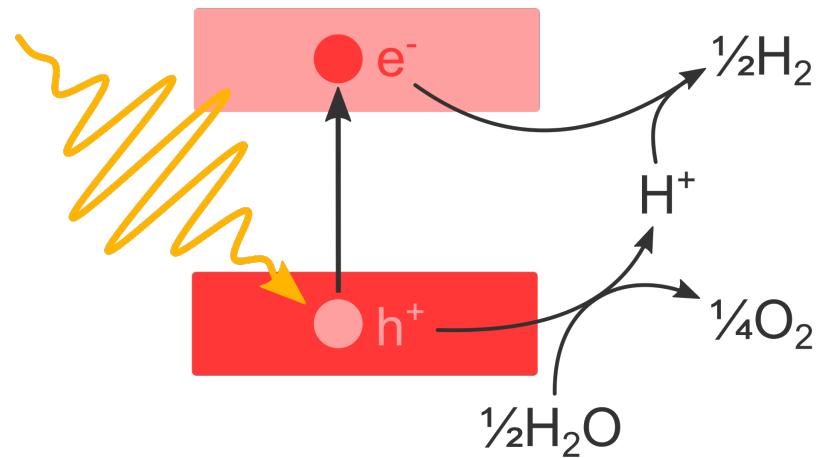
Prototypical semiconductors and insulators¹



	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

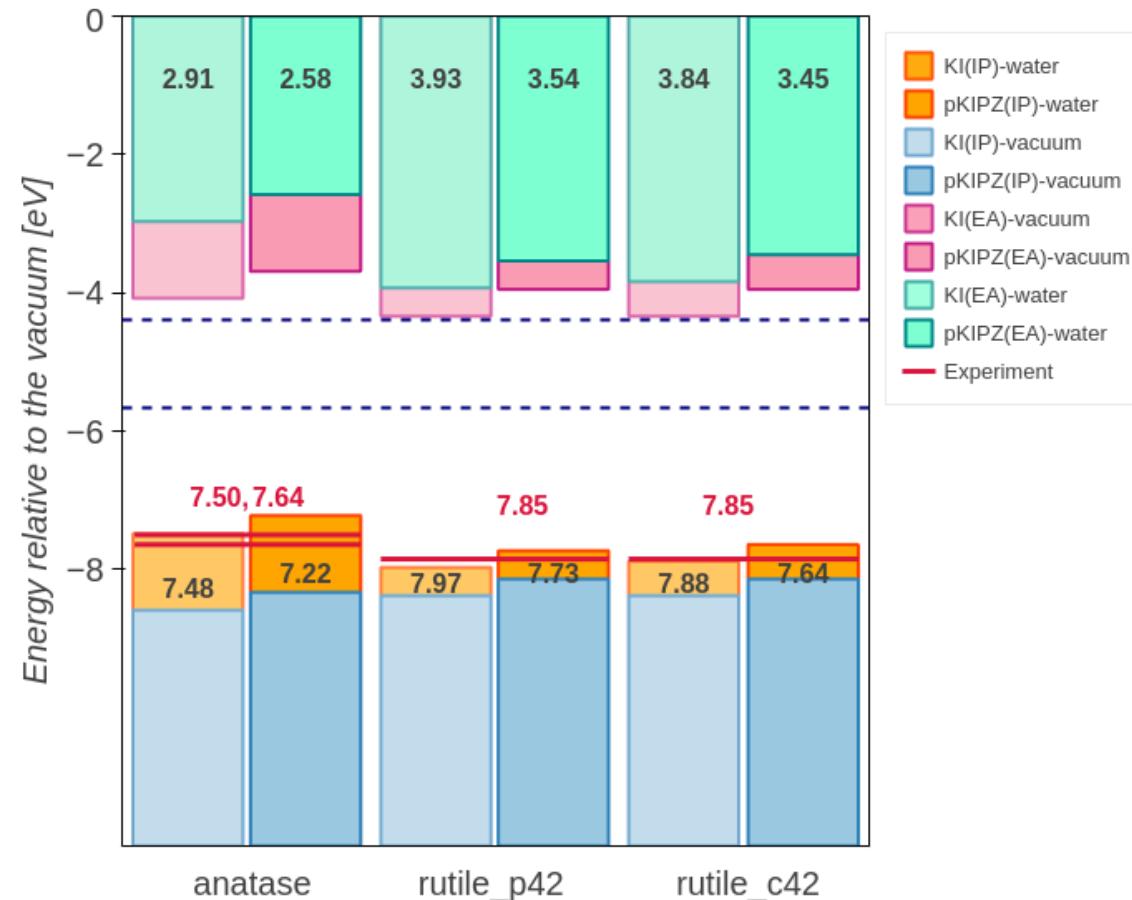
¹N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

Photocatalysis



¹M. Stojkovic *et al.* (2024) doi:10.48550/arXiv.2412.17488

Photocatalysis



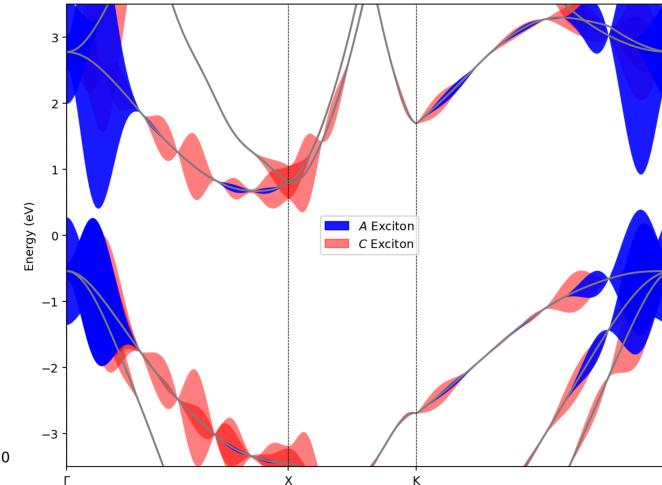
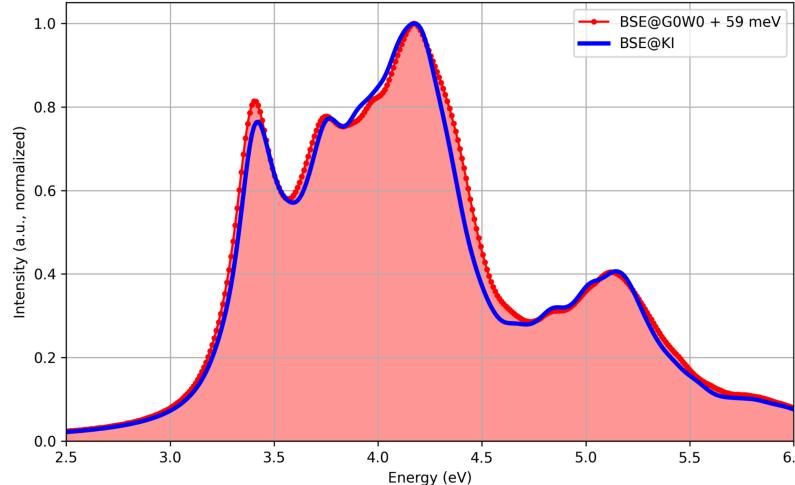
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Optical spectra

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

G₀W₀+BSE

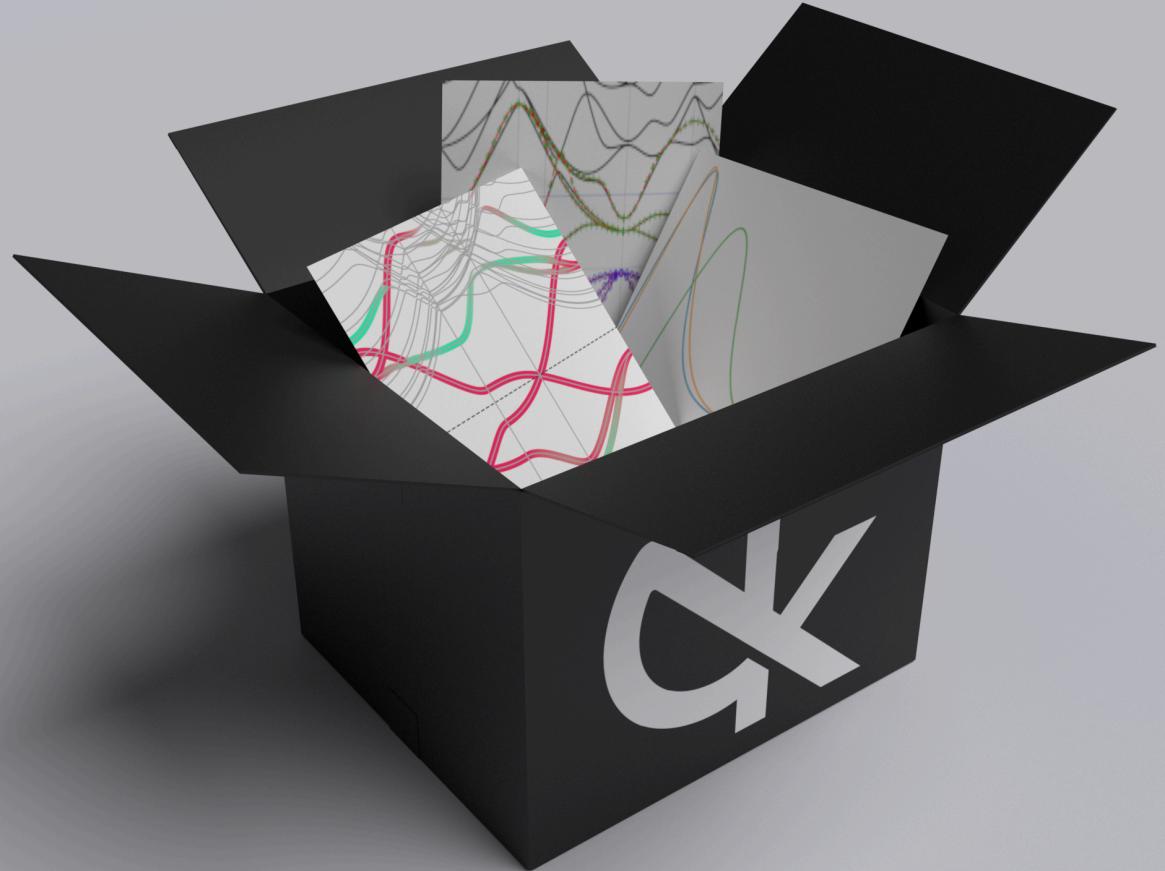
1.17

3.25

3.34

0.09

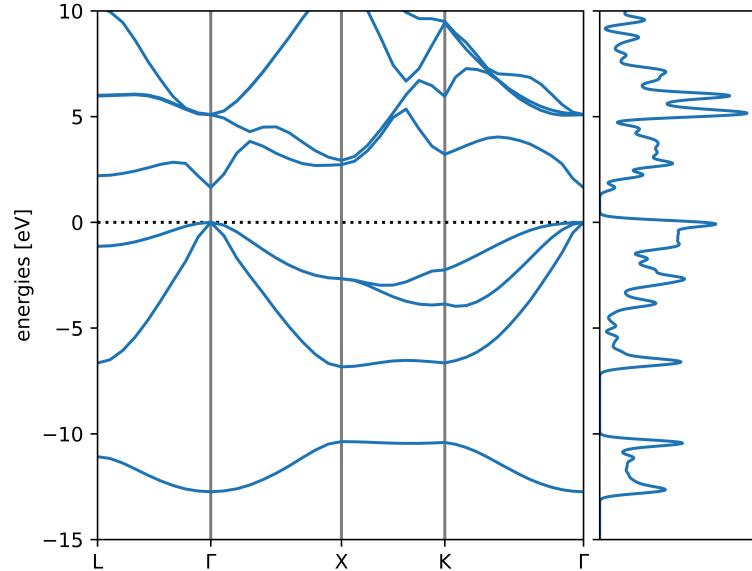
koopmans



Our goal:

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

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	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



- used by a Fortune Global 500 company
- two schools (online and then in Pavia, IT)

See koopmans-functionals.org

¹E. B. Linscott *et al.* *J. Chem. Theory Comput.* 19, 7097 (2023)

An alternative approach: DFT + U

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[n^{I\sigma}(1 - n^{I\sigma})]$$

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[n^{I\sigma}(1 - n^{I\sigma})]$$

site and spin indices

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

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site and spin indices
 local occupation matrix

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

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site and spin indices local occupation matrix

$$n_{mm'}^{I\sigma} = \langle \varphi_m^I | \hat{\rho}^\sigma | \varphi_{m'}^I \rangle = \sum_i \langle \varphi_m^I | \psi_i \rangle f_i \langle \psi_i | \varphi_{m'}^I \rangle$$

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

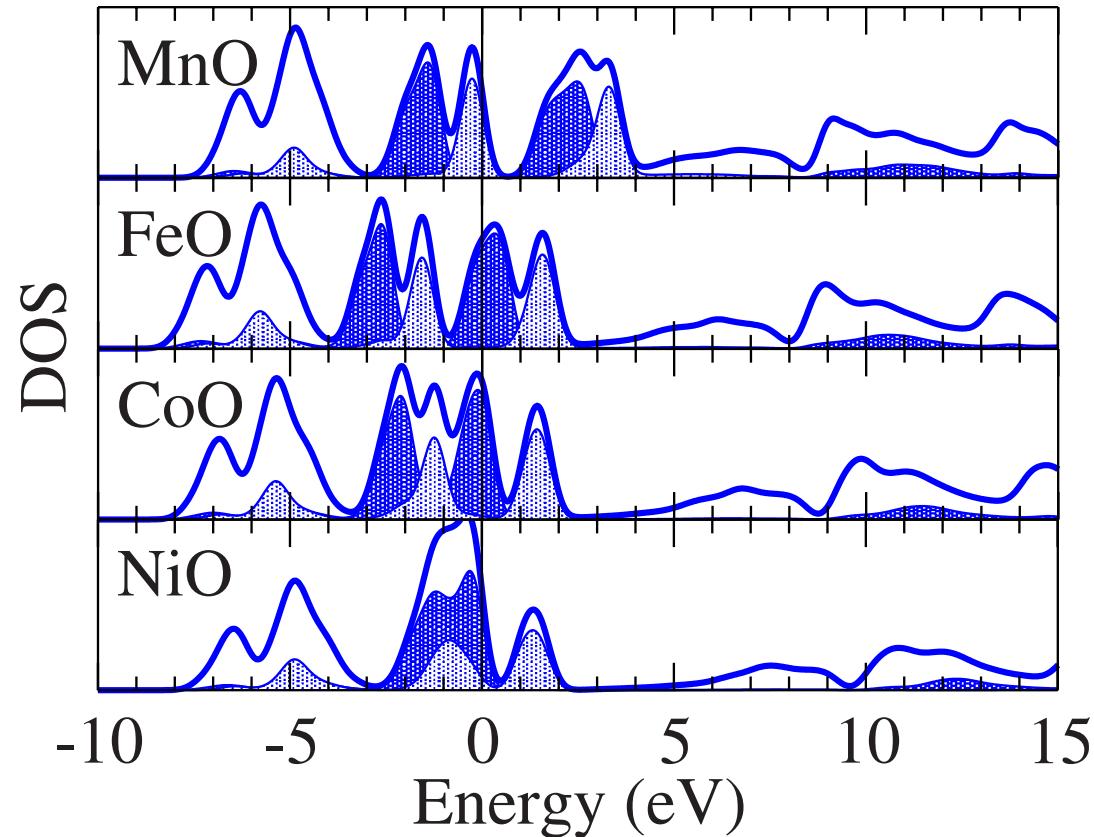
$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\mathbf{n}^{I\sigma} (1 - \mathbf{n}^{I\sigma})]$$

Hubbard parameter
 site and spin indices
 local occupation matrix

$$n_{mm'}^{I\sigma} = \langle \varphi_m^I | \hat{\rho}^\sigma | \varphi_{m'}^I \rangle = \sum_i \langle \varphi_m^I | \psi_i \rangle f_i \langle \psi_i | \varphi_{m'}^I \rangle$$

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

The historical derivation of DFT+ U (+ J)



The historical derivation of DFT+U(+J)

Let a correlated subspace be defined by a set of basis orbitals (known as *Hubbard projectors*). Within this subspace, the operator associated with electron-electron interactions is

$$\hat{U} = \sum_{mnm'n'} \sum_{\sigma\sigma'} U_{mnm'n'} \hat{c}_{m\sigma}^\dagger \hat{c}_{n\sigma'}^\dagger \hat{c}_{m'\sigma'} \hat{c}_{n'\sigma}, \quad (1)$$

where (m, n, m', n') are Hubbard projector labels and $\{\sigma\}$ are spin indices, and $\hat{c}_{m\sigma}^\dagger$ are the associated creation operators. One can show that

$$\begin{aligned} E_{\text{Hub}} = \langle \hat{U} \rangle &= \frac{1}{2} \sum_{\substack{mnm'n'\sigma \\ m \neq n, m' \neq n'}} (U_{mnm'n'} - U_{mnn'm'}) \langle n', \sigma; m', \sigma | \hat{\rho}_2 | n, \sigma; m, \sigma \rangle \\ &\quad + \frac{1}{2} \sum_{mnm'n'\sigma} U_{mnm'n'} \langle n', \sigma; m', -\sigma | \hat{\rho}_2 | n, -\sigma; m, \sigma \rangle - U_{mnn'm'} \langle n', -\sigma; m', \sigma | \hat{\rho}_2 | n, -\sigma; m, \sigma \rangle \end{aligned} \quad (2)$$

Hartree-Fock approximation

where $\hat{\rho}_2$ is the two-body density matrix. Adopting the ansatz that the many-body wavefunction is a Slater determinant of single-particle states, the two-body density matrices $\hat{\rho}_2$ can be decomposed as determinants of single-body density.¹ In this case

$$E_{\text{Hub}} = \frac{1}{2} \sum_{\substack{mnm'n'\sigma \\ m \neq n, m' \neq n'}} (U_{mnn'm'} - U_{mnm'n'}) n_{mm'}^\sigma n_{nn'}^\sigma + \frac{1}{2} \sum_{mnm'n'\sigma} U_{mnm'n'} n_{mn}^\sigma n_{nm'}^{-\sigma}, \quad (3)$$

where $n_{mm'}^\sigma = \langle m | \hat{\rho}^\sigma | m' \rangle$. At this stage the only approximation that has been introduced is the assertion that the state corresponds to a Slater determinant. If $U_{mnm'n'}$ is obtained using the unscreened Coulomb potential, then Equation 3 is equivalent to a Hartree-Fock treatment of the system.

two-site terms only

Now, all but two-site terms are ignored. Due to the symmetries of $U_{mnm'n'}$, this leaves only two types of terms: U_{mnnm} and U_{mnmm} . These are then averaged over the Hubbard projectors to yield two scalars:

$$U = \frac{1}{(2l+1)^2} \sum_{mn} U_{mnnm}; J = \frac{1}{(2l+1)^2} \sum_{mn} U_{mnmm}. \quad (4)$$

Using these average values in place of the tensorial terms simplifies Equation 3 to

¹R. G. Parr *et al.* (Oxford University Press, Oxford, 1989).

The historical derivation of DFT+U(+J)

$$E_{\text{Hub}} = \frac{1}{2} \sum_{mn\sigma} U(n_{mm}^\sigma n_{nn}^\sigma - n_{mn}^\sigma n_{nm}^\sigma + n_{mm}^\sigma n_{nn}^{-\sigma}) + \frac{1}{2} \sum_{mn\sigma} J(n_{mn}^\sigma n_{nm}^\sigma - n_{mm}^\sigma n_{nn}^\sigma + n_{mn}^\sigma n_{nm}^{-\sigma}) = \sum_\sigma \frac{U}{2} ((n^\sigma)^2 + n^\sigma n^{-\sigma} - \text{Tr}(n^\sigma n^\sigma)) + \frac{J}{2} (\text{Tr}(n^\sigma n^\sigma + n^\sigma n^{-\sigma}) - (n^\sigma)^2) \quad (5)$$

where $n^\sigma = \text{Tr}(n^\sigma)$. If at this stage Equation 5 was to be incorporated directly into the DFT formalism, interactions associated with the subsystems that are already being handled by the conventional exchange-correlation functional would be double-counted. To avoid this, the **fully localised limit**¹ is considered, where all correlated subspaces have integer occupancy. In this approximation

adopt some double-counting term

$$\text{Tr}(n^\sigma n^\sigma) \rightarrow n^\sigma; \text{Tr}(n^\sigma n^{-\sigma}) \rightarrow n^{\sigma_{\min}}, \quad (6)$$

where σ_{\min} denotes the minority spin. Thus in the fully localised limit, the double counting term becomes

$$E_{\text{DC}} = \frac{U}{2} n(n-1) - \frac{J}{2} \sum_\sigma n^{\sigma(n^\sigma-1)} + J n^{\sigma_{\min}} \quad (7)$$

where $n = \sum_\sigma n^\sigma$. Hence

$$E_{\text{Hub}} - E_{\text{DC}} = \sum_{I\sigma} \frac{U^I - J^I}{2} \text{Tr}(n^{I\sigma}(1 - n^{I\sigma})) + \sum_{I\sigma} \frac{J^I}{2} (\text{Tr}(n^{I\sigma} n^{I-\sigma}) - 2\delta_{\sigma\sigma_{\min}} n^{I\sigma}). \quad (8)$$

Note that the entire expression has now been generalised to allow for the possibility of multiple sites (labelled with the index I), to each of which a correction term is applied. As a final approximation, **terms arising from interaction between opposite spin (those contained in the second sum) are neglected**. This leaves

neglect J

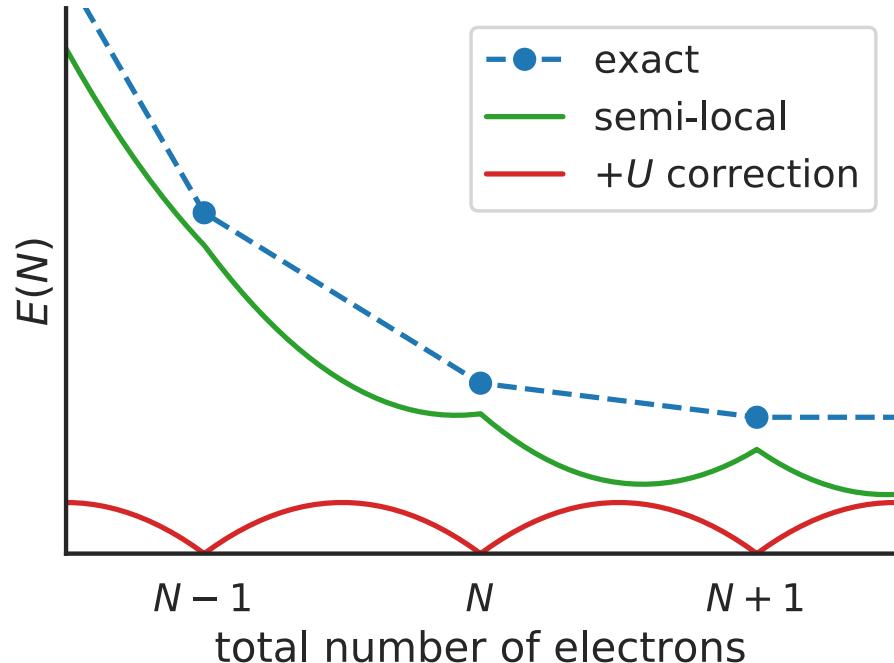
$$E_U = E_{\text{Hub}} - E_{\text{DC}} = \sum_{I\sigma} \frac{U_{\text{eff}}^I}{2} \text{Tr}(n^{I\sigma}(1 - n^{I\sigma})), \quad (9)$$

where the on-site Coulomb repulsion parameter U^I has been effectively reduced by J^I to U_{eff}^I . The DFT+U correction to the KS potential is given by

$$\hat{V}_U = \sum_{I\sigma mn} U^I |m\rangle \left(\frac{1}{2} - n_{mn}^{I\sigma} \right) \langle n|. \quad (10)$$

¹A. G. Petukhov *et al.* *Phys. Rev. B* 67, 153106 (2003)

The modern interpretation

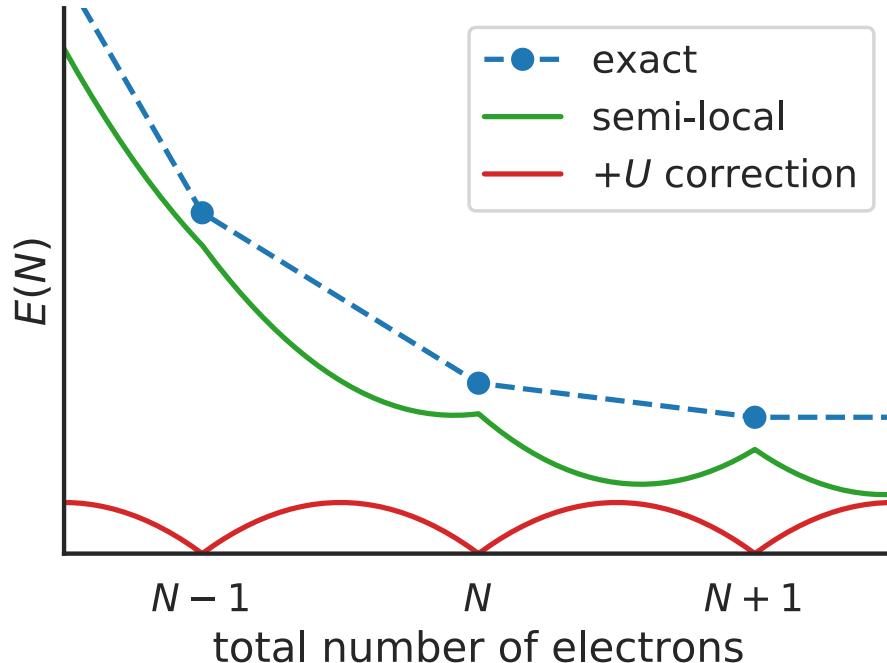


In a basis such that $n_{ij}^{I\sigma} = \lambda_i^{I\sigma} \delta_{ij}$,

$$E_U = \sum_{I\sigma} \frac{U^I}{2} \sum_i \lambda_i^{I\sigma} (1 - \lambda_i^{I\sigma})$$

¹M. Cococcioni *et al.* Phys. Rev. B 71, 35105 (2005)

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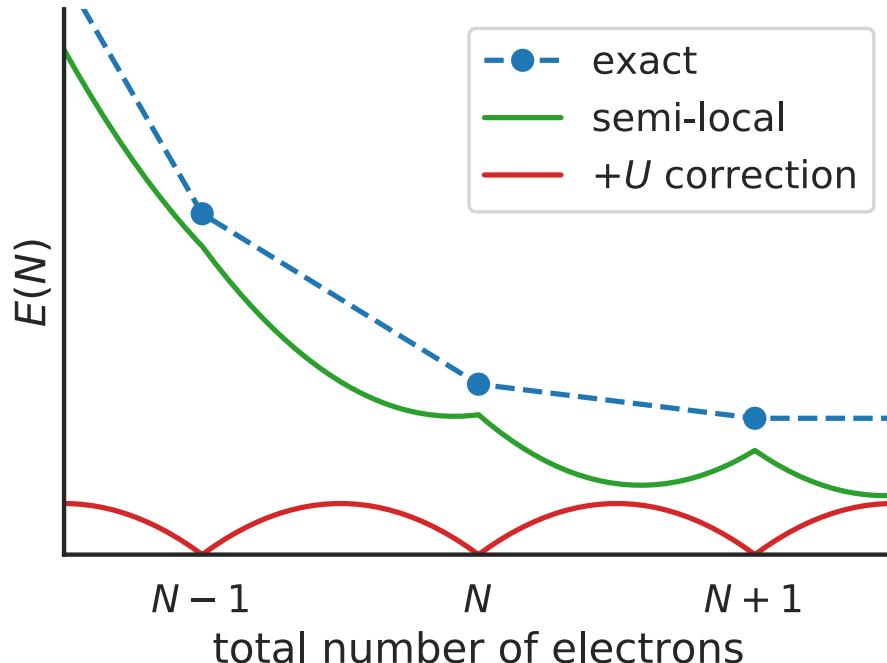
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U can be measured by linear response¹ –
critical for predictive calculations

¹M. Cococcioni *et al.* Phys. Rev. B 71, 35105 (2005)

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\mathbf{n}^{I\sigma}(1 - \mathbf{n}^{I\sigma})] \quad U^I = [\chi_0^{-1} - \chi^{-1}]_{II}$$

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

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functional treats spin channels
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LR treats them together

¹E. B. Linscott *et al.* *Phys. Rev. B* 98, 235157 (2018)

Role of spin in the calculation of Hubbard U and Hund's J parameters from first principles

Edward B. Linscott,^{1,*} Daniel J. Cole,² Michael C. Payne,¹ and David D. O'Regan^{3,†}

¹*Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom*

²*School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom*

³*School of Physics, CRANN and AMBER, Trinity College Dublin, Dublin 2, Ireland*



(Received 25 February 2018; revised manuscript received 19 November 2018; published 26 December 2018)

The density functional theory (DFT) + U method is a pragmatic and effective approach for calculating the ground-state properties of strongly correlated systems, and linear-response calculations are widely used to determine the requisite Hubbard parameters from first principles. We provide a detailed treatment of spin within the linear-response framework, demonstrating that the conventional Hubbard U formula, unlike the conventional DFT + U corrective functional, incorporates interactions that are off-diagonal in the spin indices and places greater weight on one spin channel over the other. We construct alternative definitions for Hubbard and Hund's parameters that are consistent with the contemporary DFT + U functional, expanding upon the minimum-tracking linear-response method. This approach allows Hund's J and spin-dependent U parameters to be calculated with the same ease as for the standard Hubbard U . Our methods accurately reproduce the

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→

$$U^{I\sigma} = ???$$

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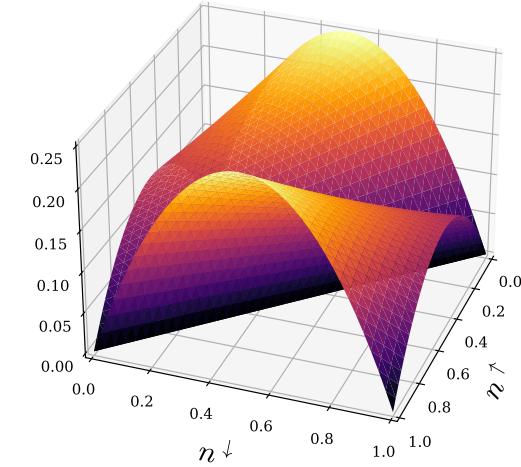
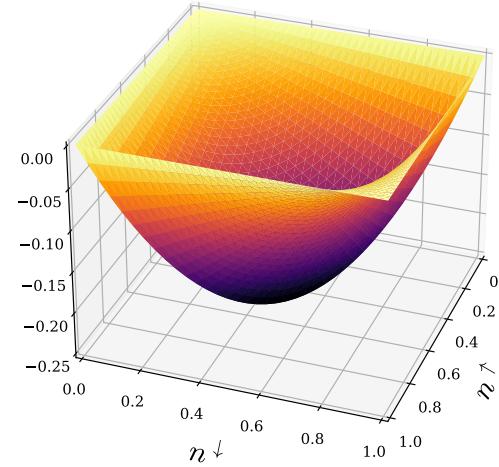
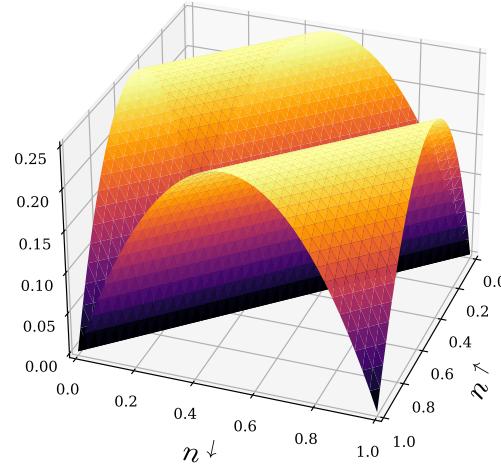
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- can recover the conventional linear response results
- J is “free”
- easily implemented

Now used in Materials Project!

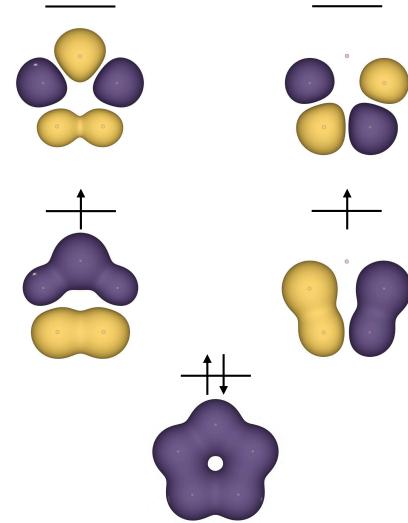
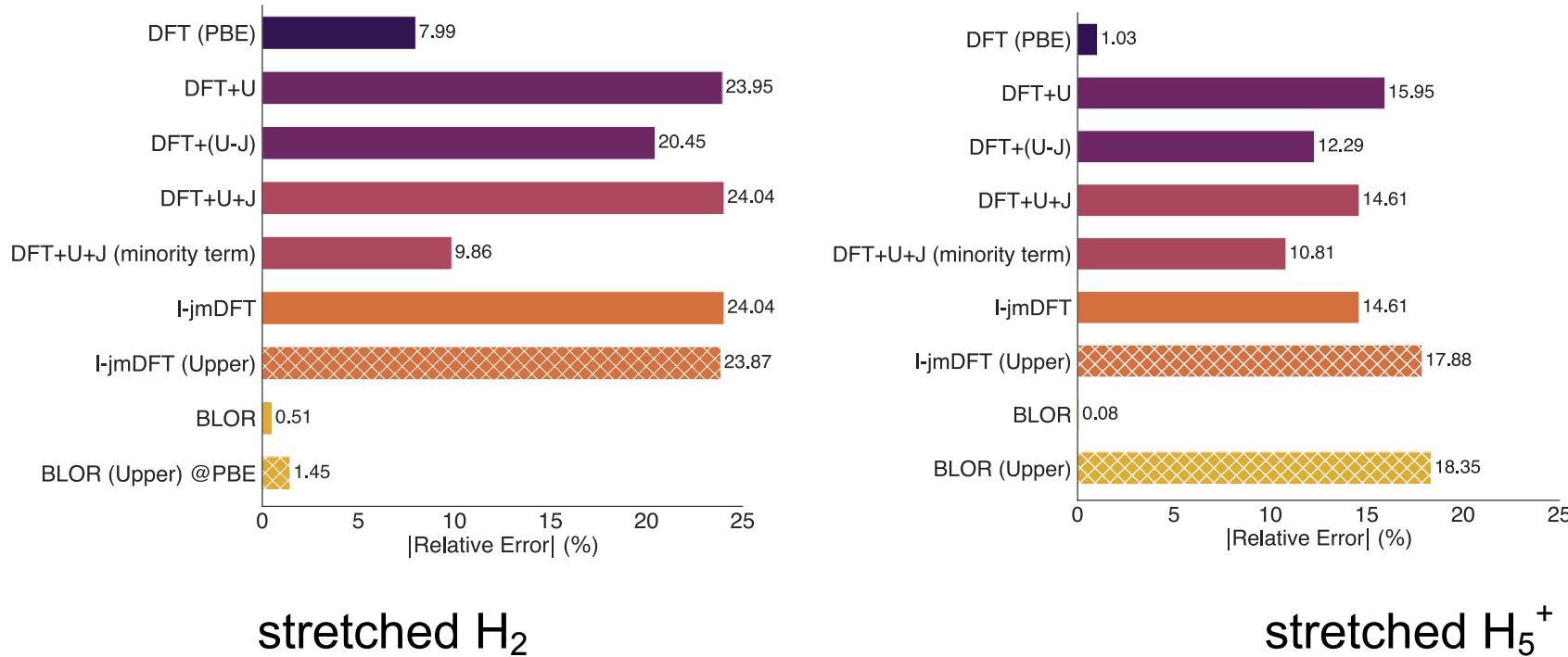


¹G. C. Moore et al. *Phys. Rev. Mater.* 8, 14409 (2024)



BLOR: a DFT+ U type functional that...

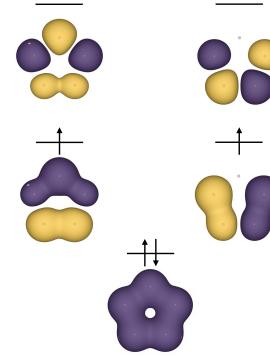
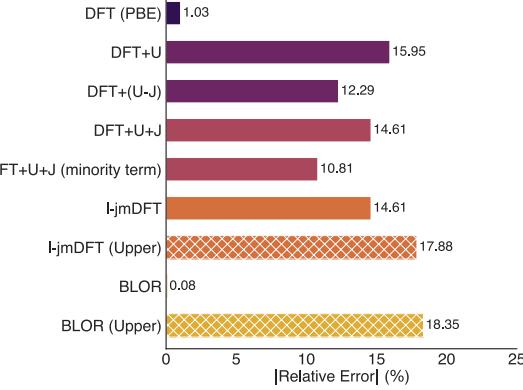
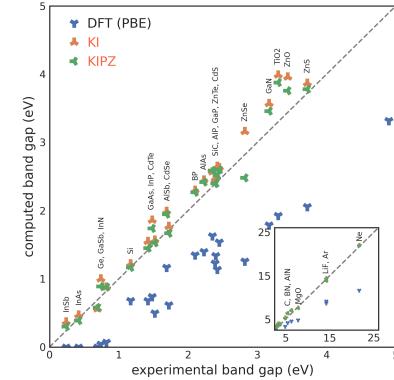
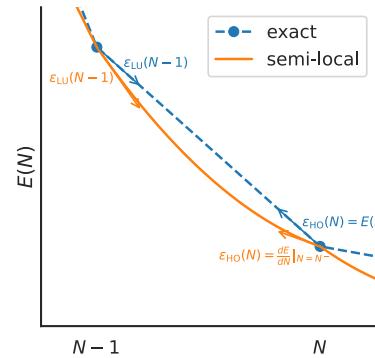
- is inspired by the intrinsic errors of approximate DFT
- relies on spin-resolved linear response
- includes a term to correct for static correlation error
- is double-counting-free



¹A. C. Burgess *et al.* *Phys. Rev. Lett.* 133, 26404 (2024), A. C. Burgess *et al.* *Phys. Rev. B* 107, L121115 (2023)

Summary

Understanding and correcting the failures of approximate DFT can yield simple but predictive functionals



Acknowledgements



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Burgess



Nicola
Colonna



Miki Bonacci



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Poliukhin



Marija
Stojkovic



Junfeng Qiao



Yannick
Schubert

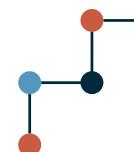


Nicola Marzari

... and many
others!



Engineering and
Physical Sciences
Research Council



**Swiss National
Science Foundation**

MARVEL


Thank you!

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

spare slides

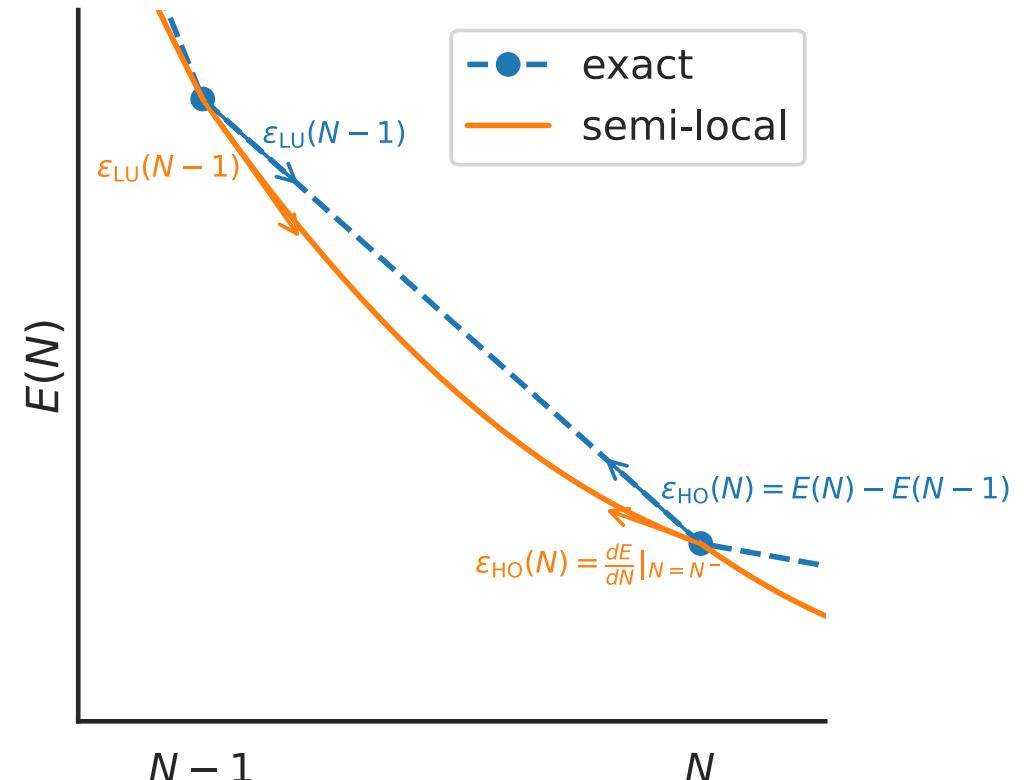
Imposing generalised piecewise linearity

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



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

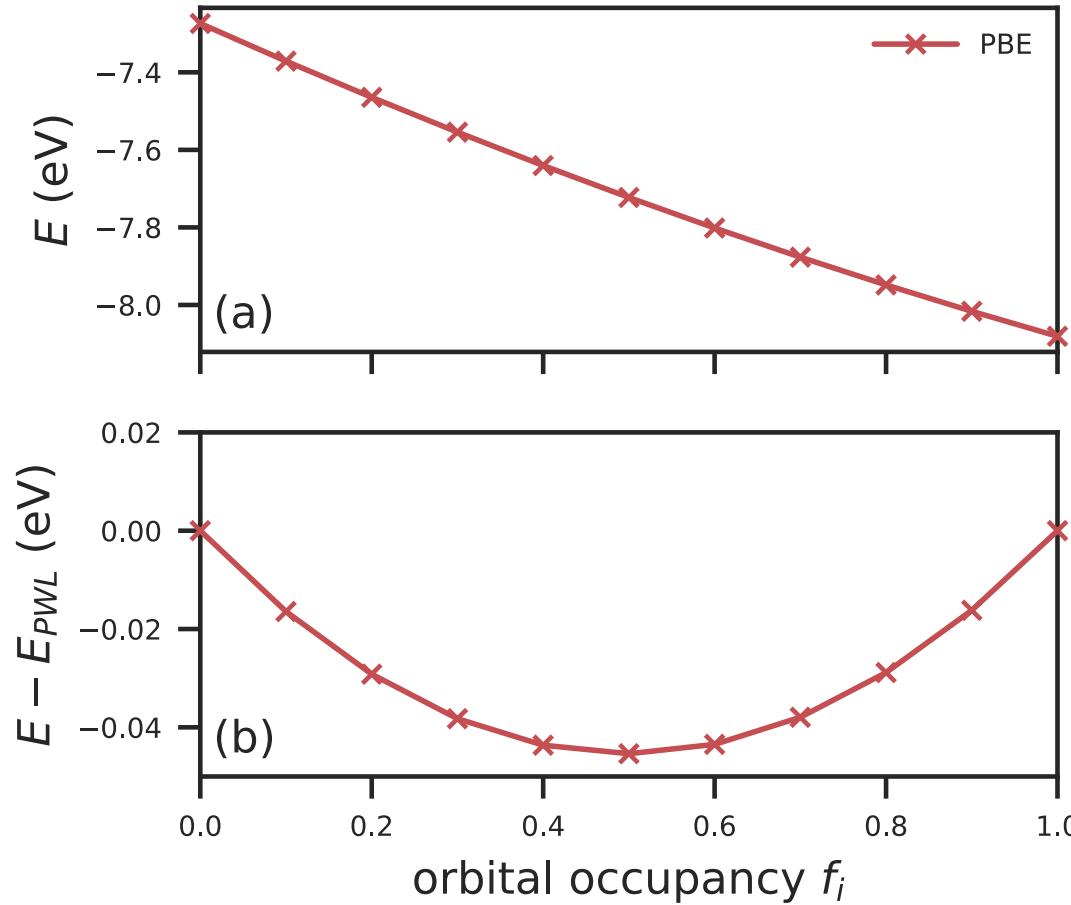
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 &= E^{\text{DFT}}[\rho] + \sum_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}
 \end{aligned}$$

Electronic screening via parameters

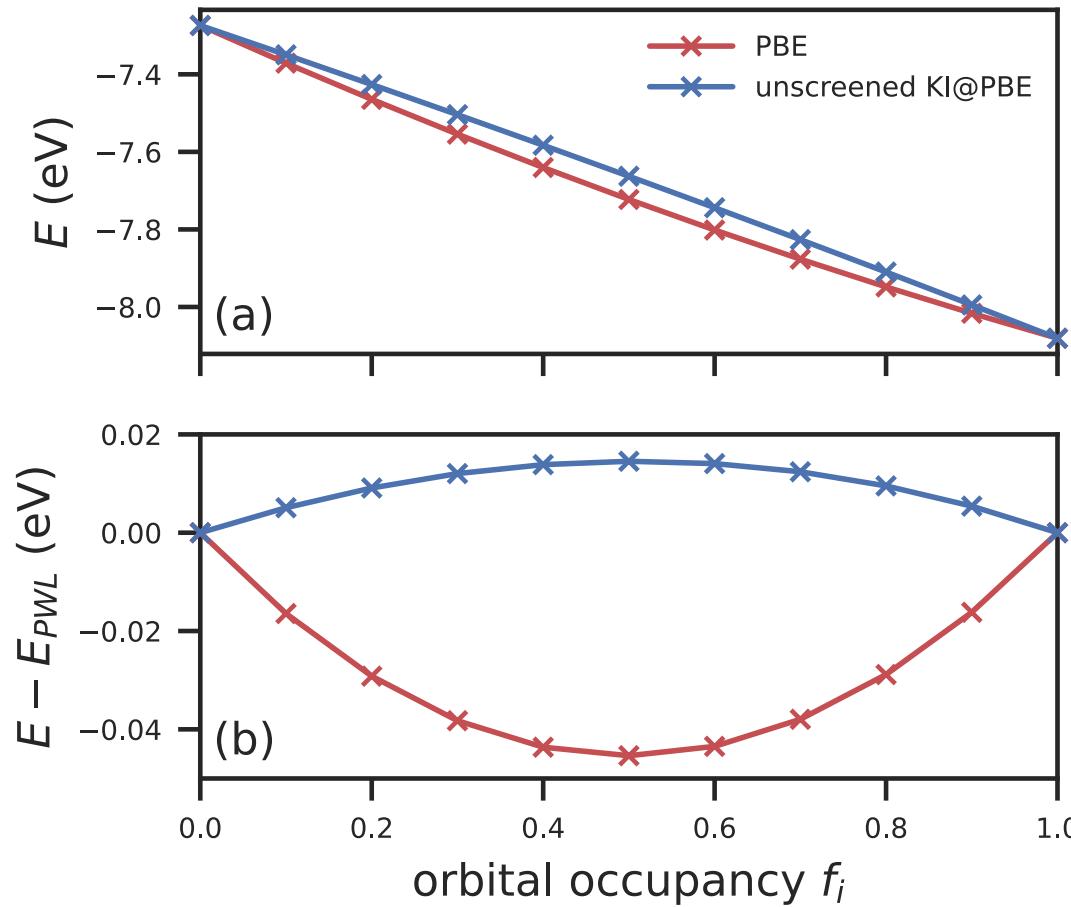
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cannot evaluate directly cannot evaluate directly cannot evaluate directly

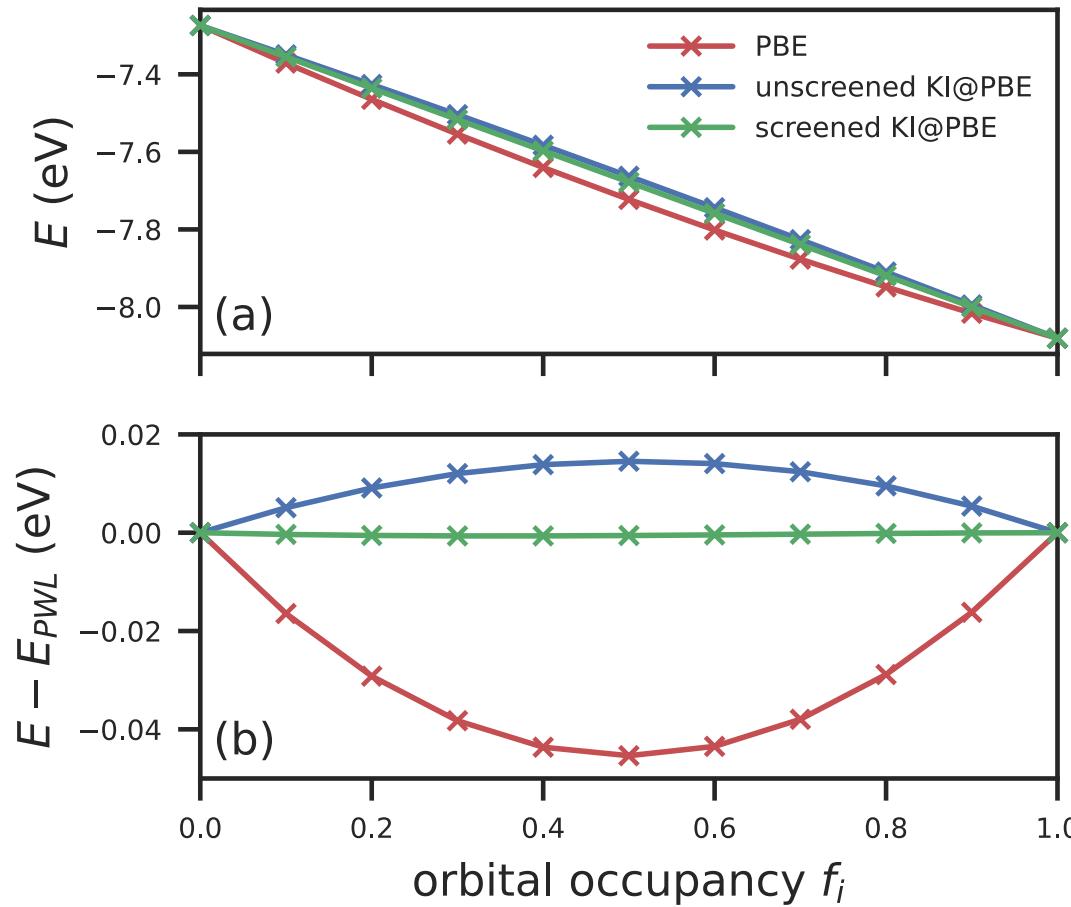
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screening parameter uses frozen orbitals uses frozen orbitals uses frozen orbitals

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)

²N. Marzari *et al.* *Rev. Mod. Phys.* 84, 1419–1475 (2012)

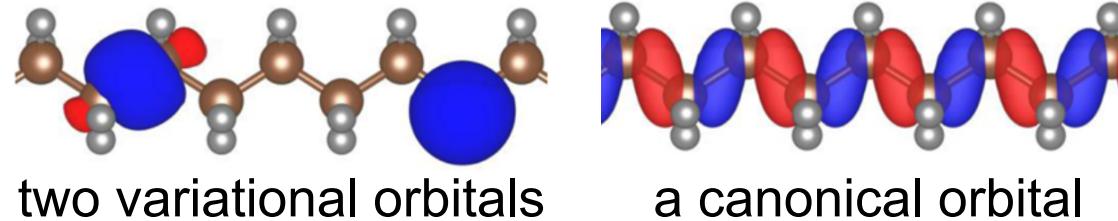
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- loss of unitary invariance¹



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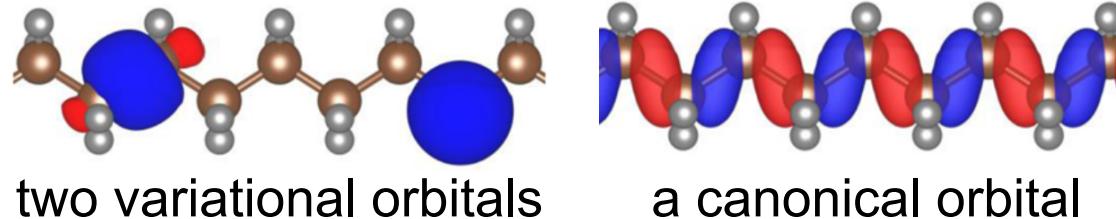
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$$v_{i \in \text{occ}}^{\text{KI}} = -E_{\text{Hxc}}[\rho - n_i] + E_{\text{Hxc}}[\rho] - \int v_{\text{Hxc}}(\mathbf{r}', [\rho]) n_i d\mathbf{r}'$$

- loss of unitary invariance¹



- we can use MLWFs²

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

²N. Marzari *et al.* *Rev. Mod. Phys.* 84, 1419–1475 (2012)

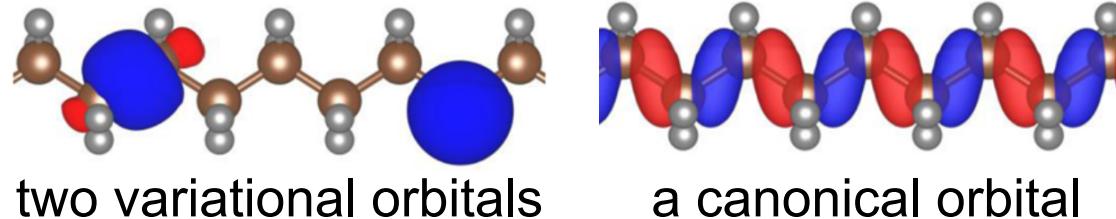
³A. Ferretti *et al.* *Phys. Rev. B* 89, 195134 (2014)

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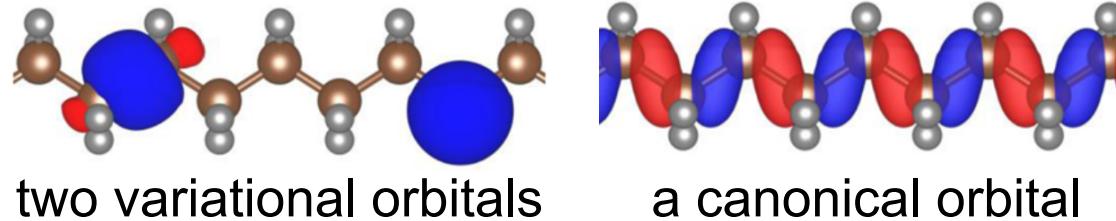
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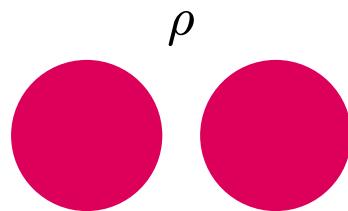
- we can use MLWFs²
- we know $\hat{H}|\varphi_i\rangle$ but not \hat{H}
- a natural generalisation of DFT towards spectral functional theory³

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

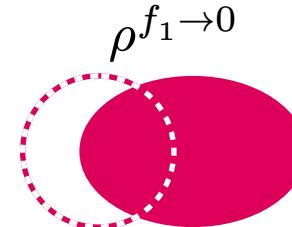
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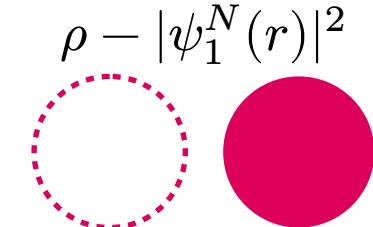
Frozen orbital approximation



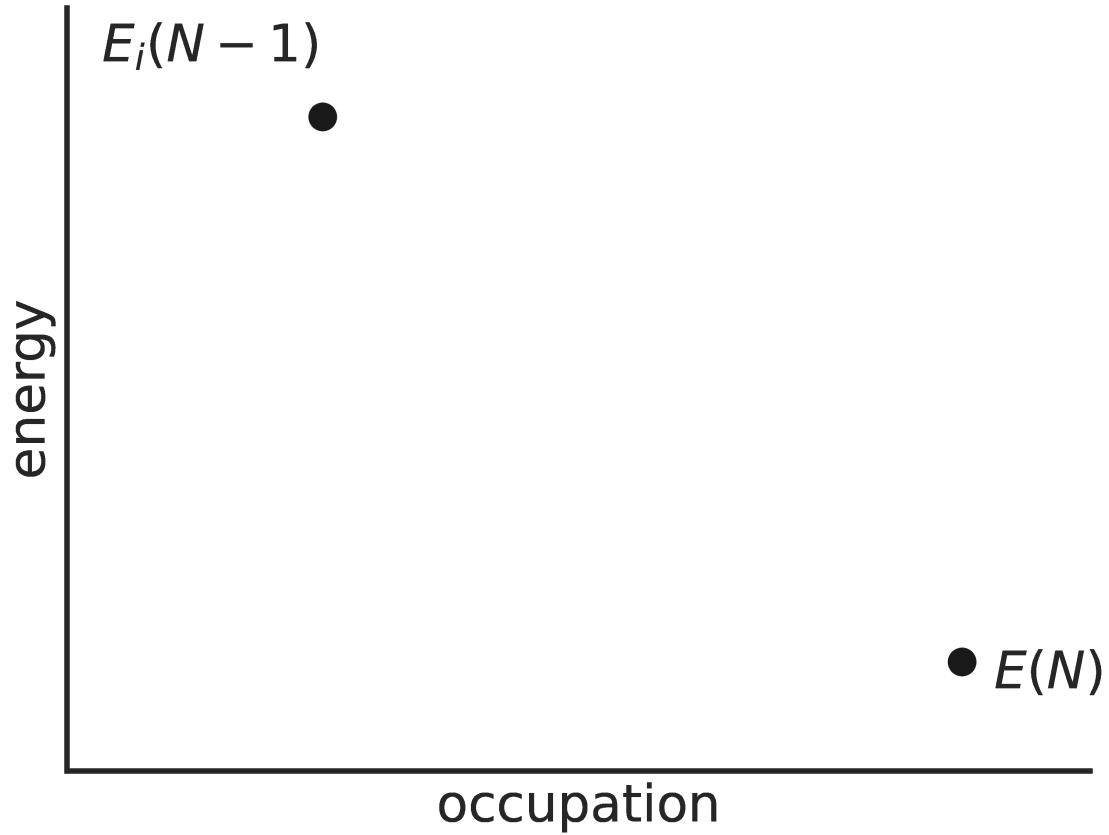
2-electron solution

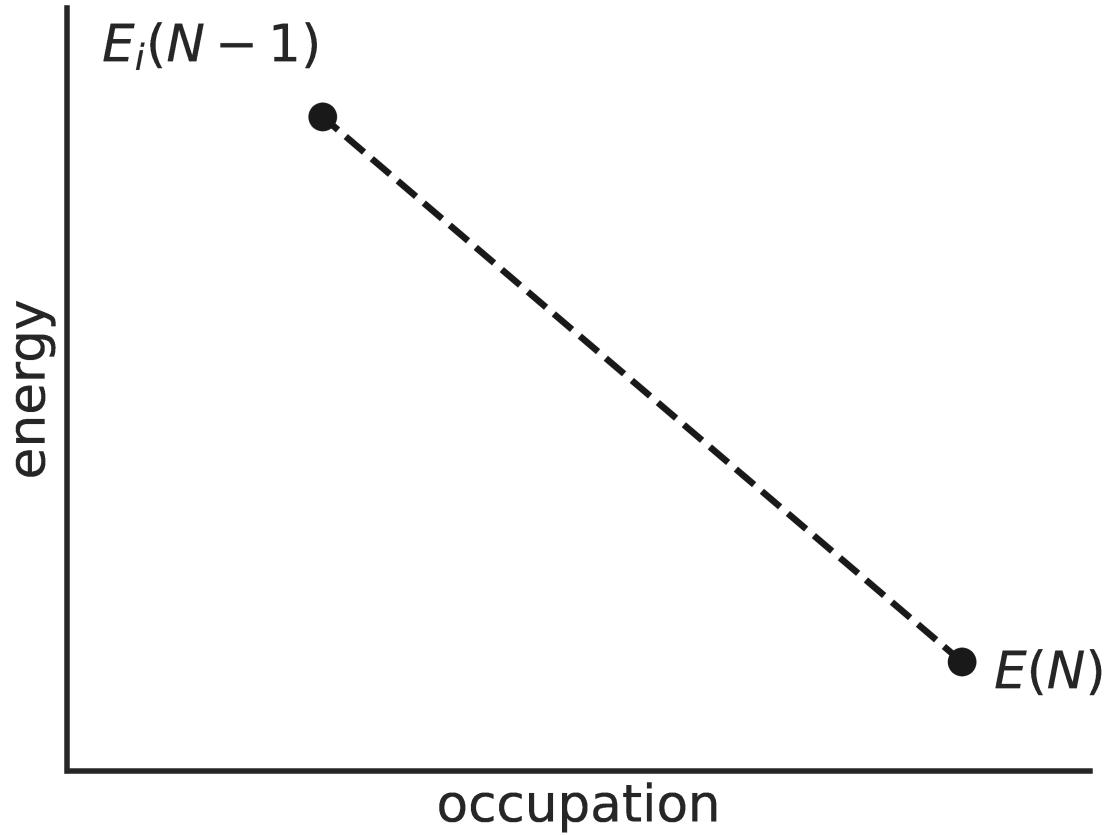


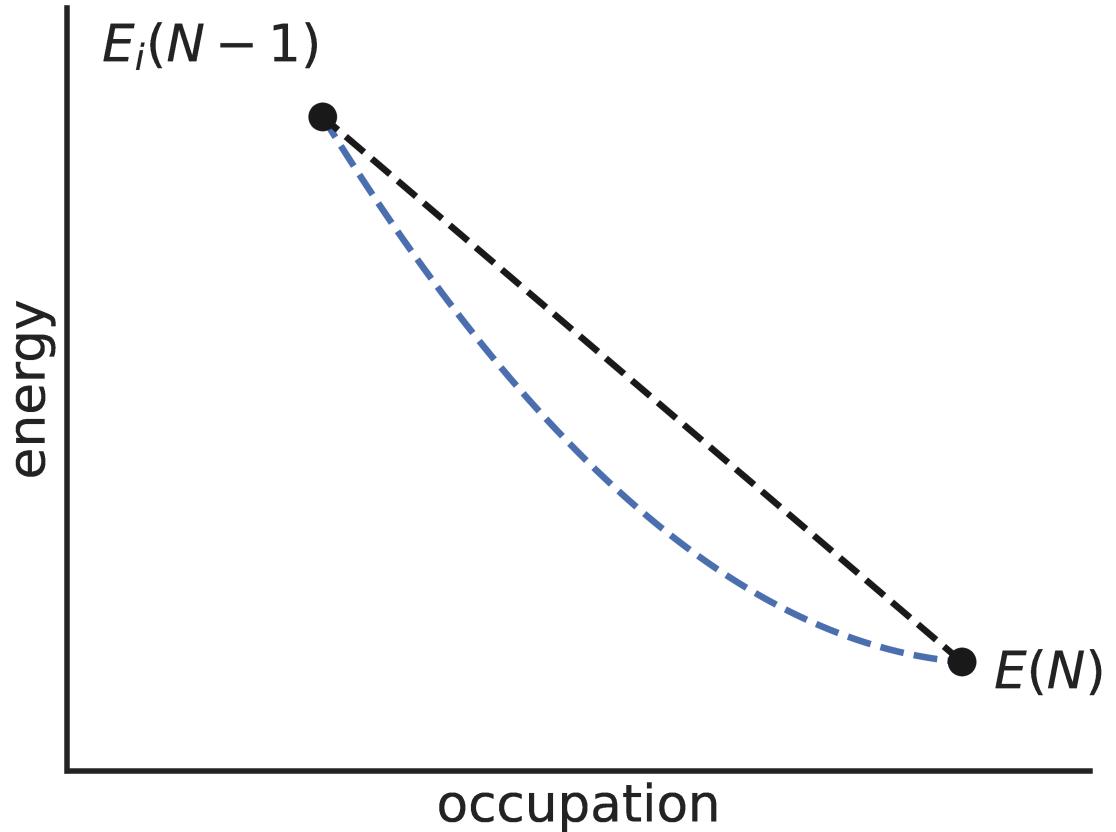
what we'd like to evaluate

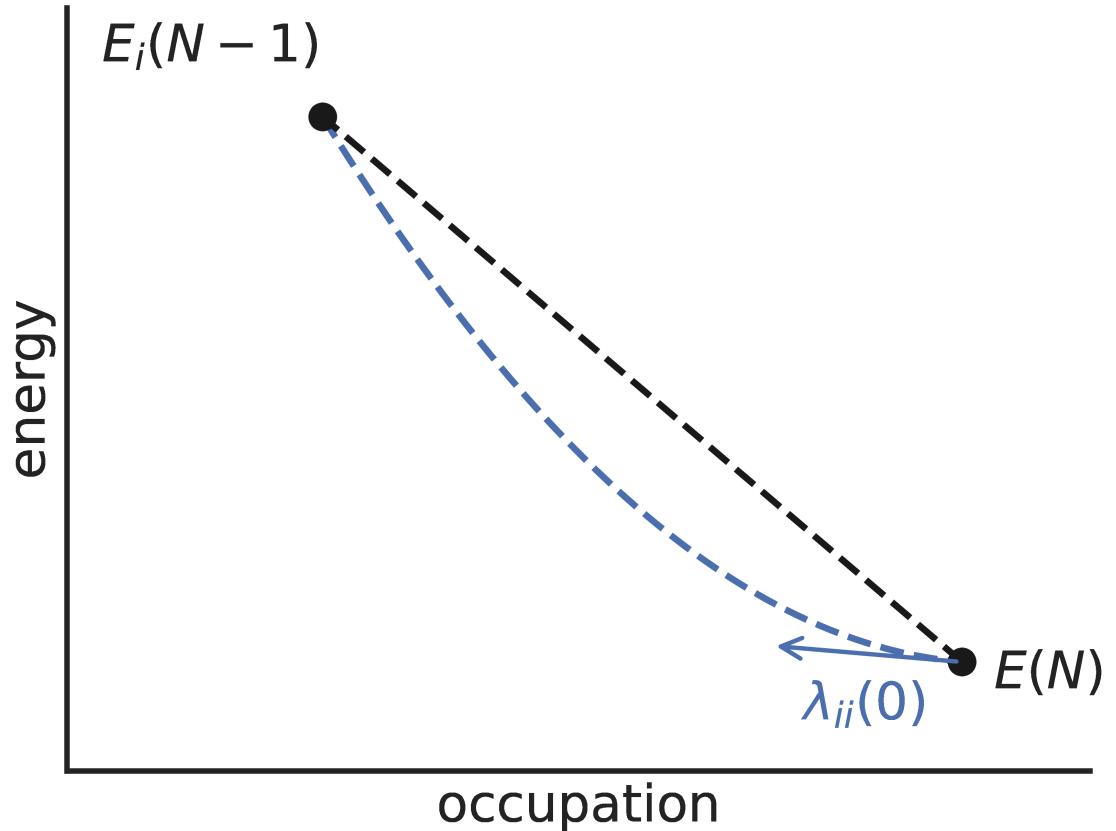


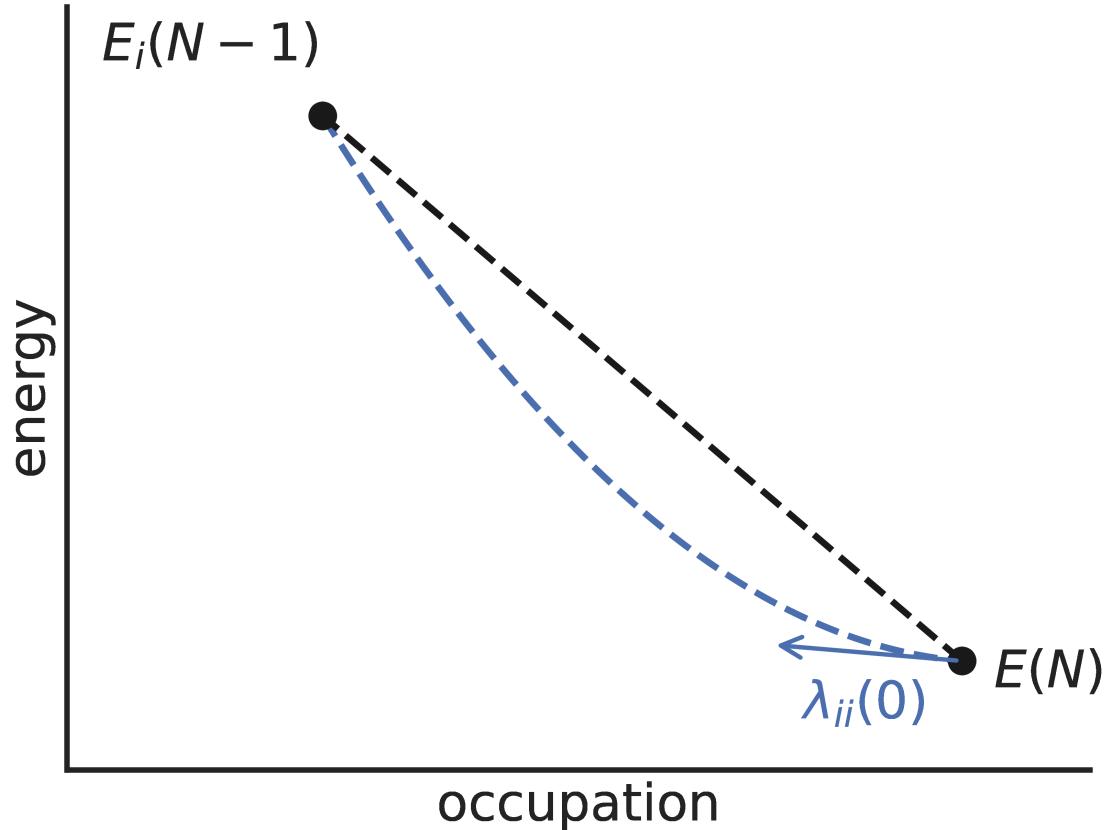
what we can quickly evaluate

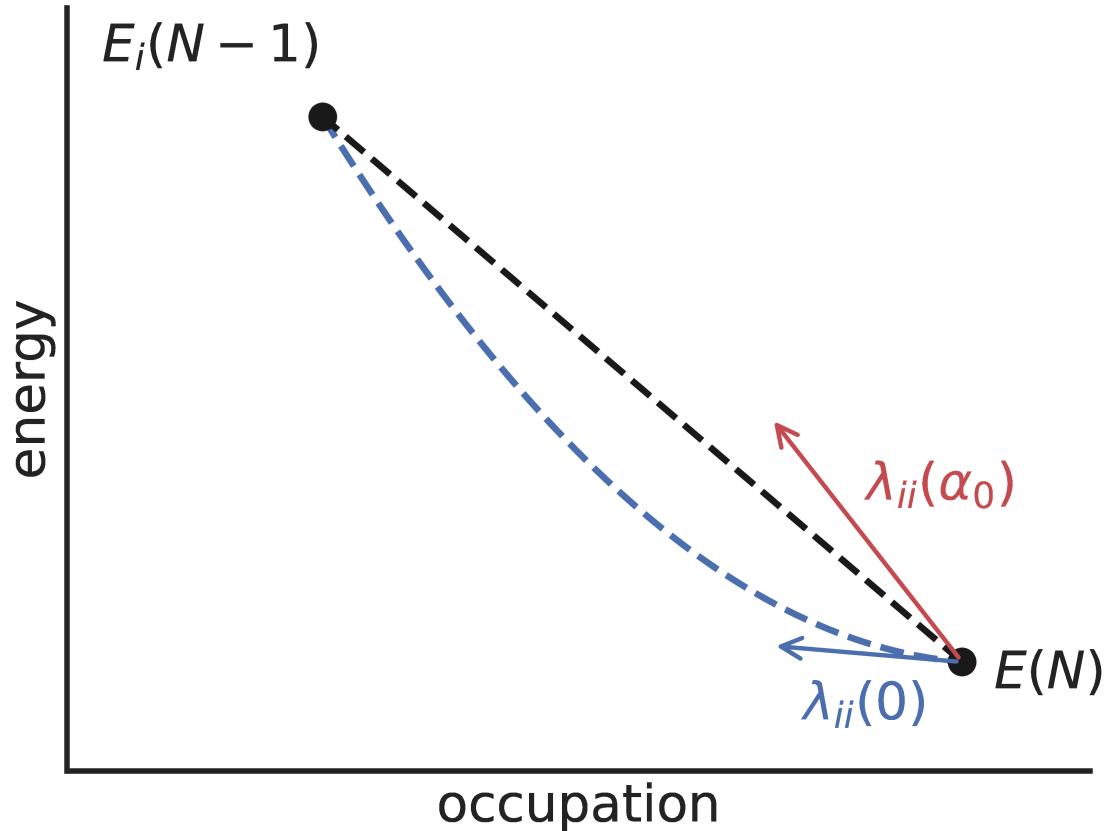


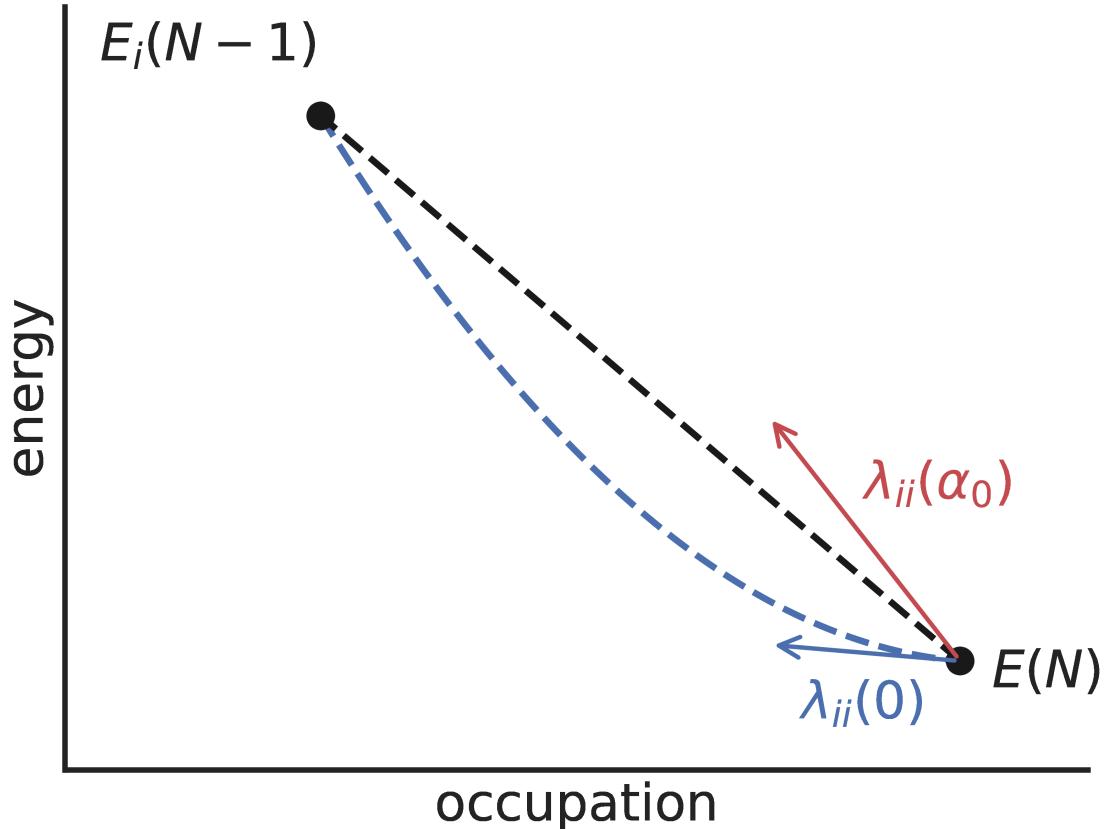








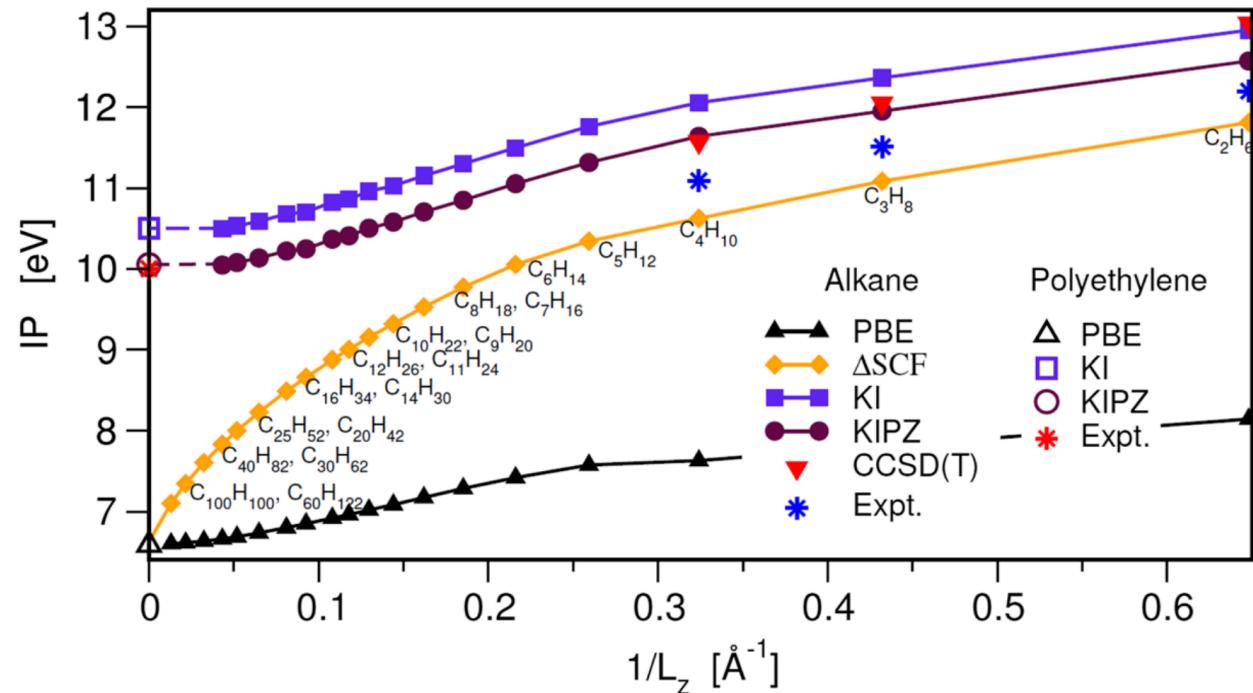




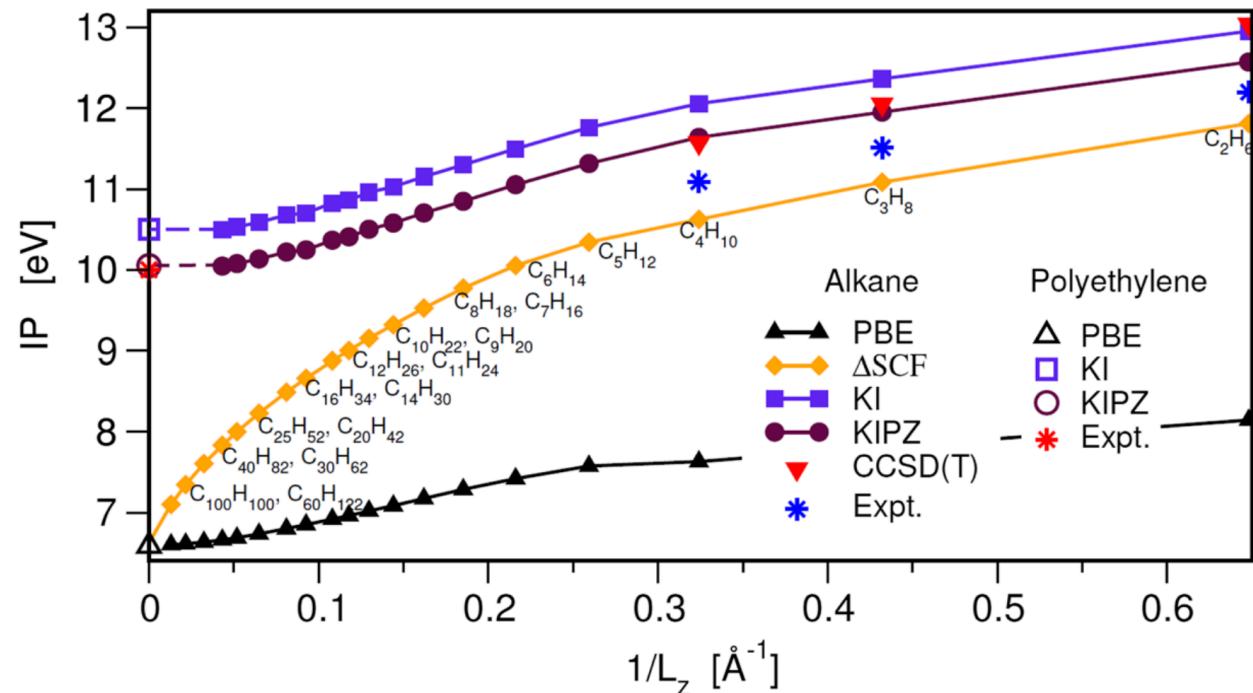
$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

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

Issues with extended systems



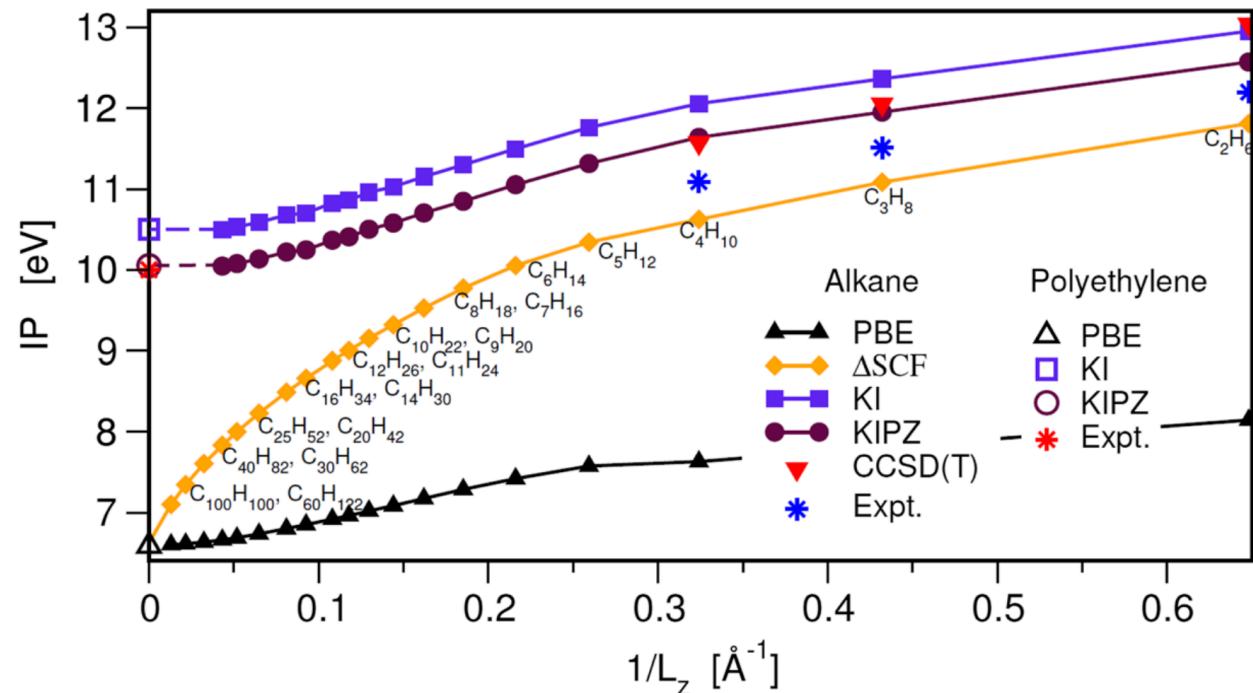
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Two options: 1. use a more advanced functional

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Issues with extended systems

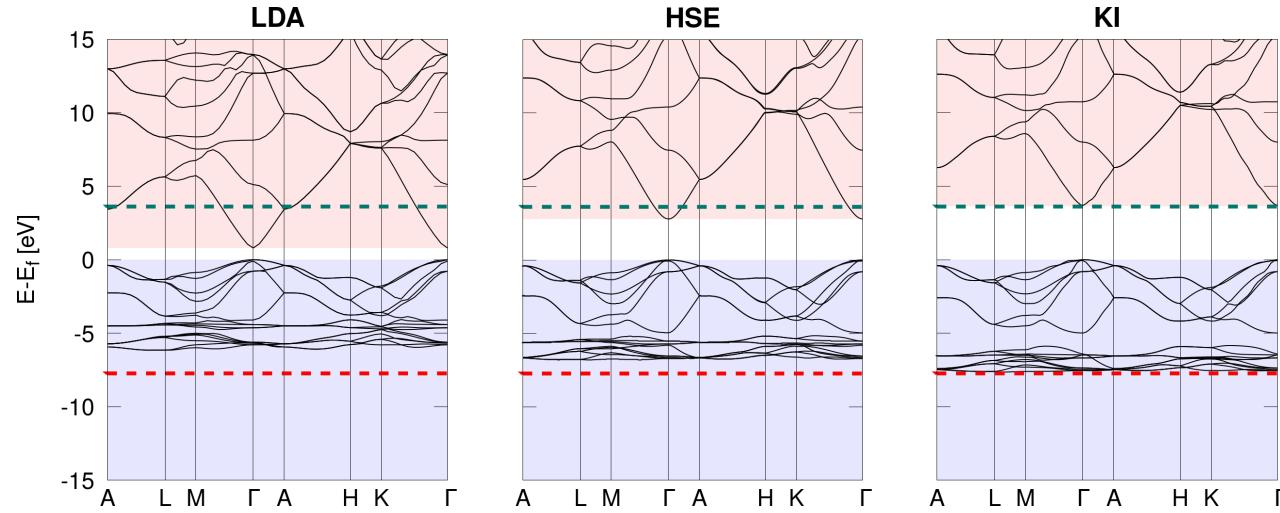


Two options: 1. use a more advanced functional, or 2. stay in the “safe” region

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

Issues with extended systems

ZnO¹

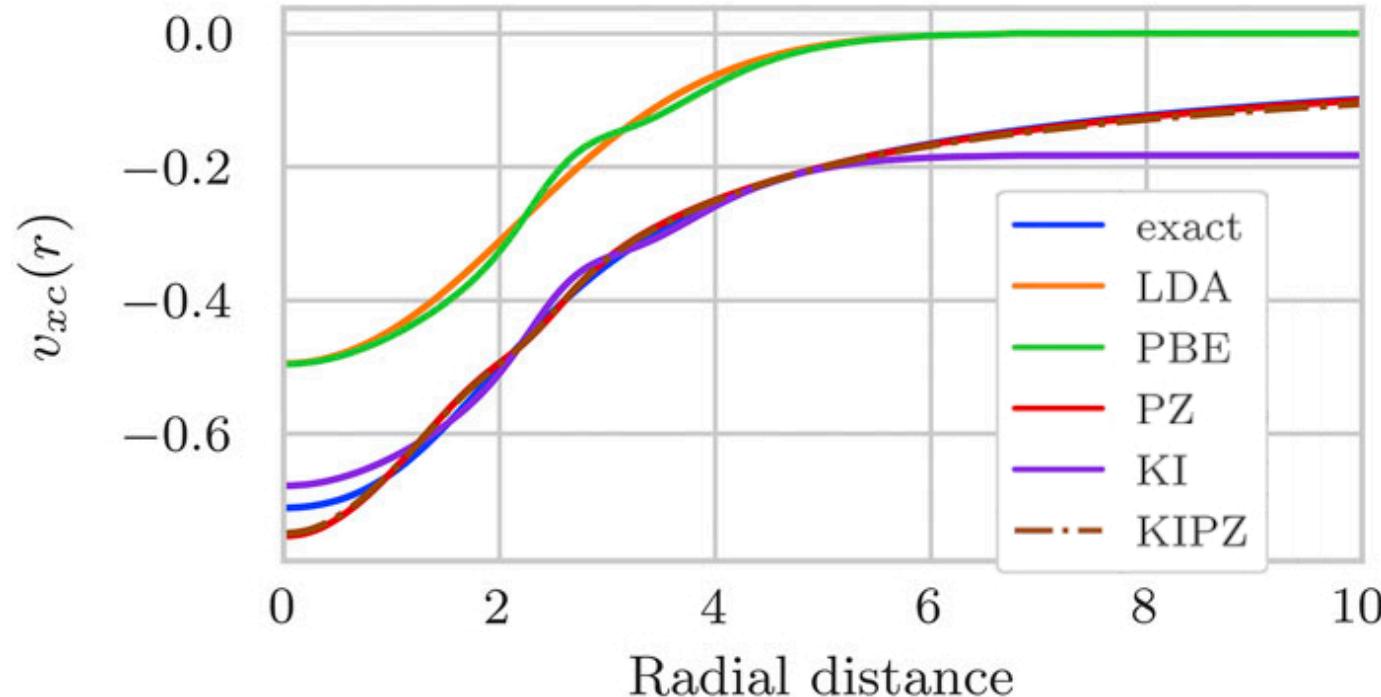


	LDA	HSE	GW_0	$scG\tilde{W}$	KI	exp
E_{gap}	0.79	2.79	3.0	3.2	3.68	3.60
$\langle \varepsilon_d \rangle$	-5.1	-6.1	-6.4	-6.7	-6.93	-7.5 to -8.81
Δ	4.15				4.99	5.3

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)

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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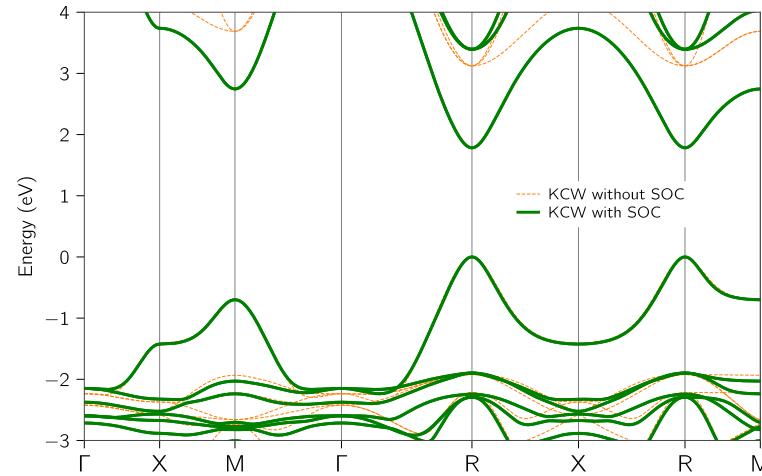
↓

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

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

Non-collinear spin

CsPbBr₃



	LDA	HSE	G_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)

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)

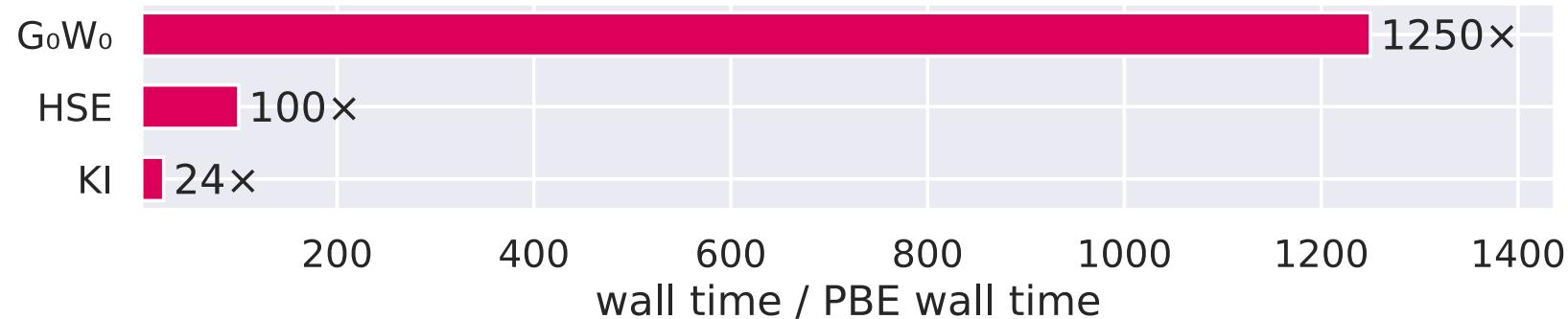
⁴J. Ma *et al.* *Sci. Rep.* 6, 24924 (2016)

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

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

Computational cost and scaling

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)

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- must be computed *ab initio* via...

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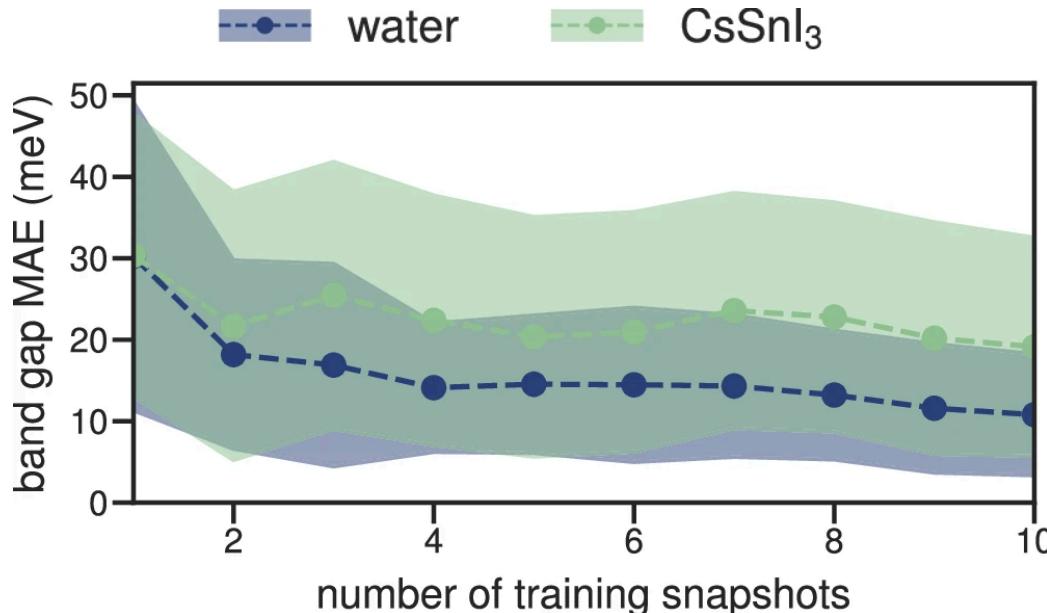
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 - DFPT²: $\mathcal{O}(N_{\mathbf{k}}^2 N^3)$

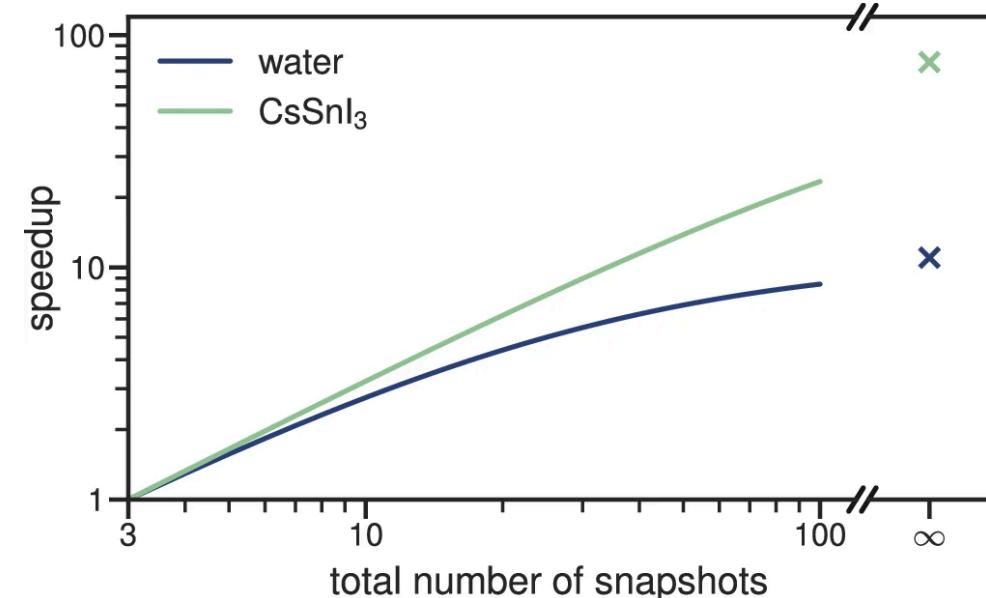
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Machine-learned electronic screening



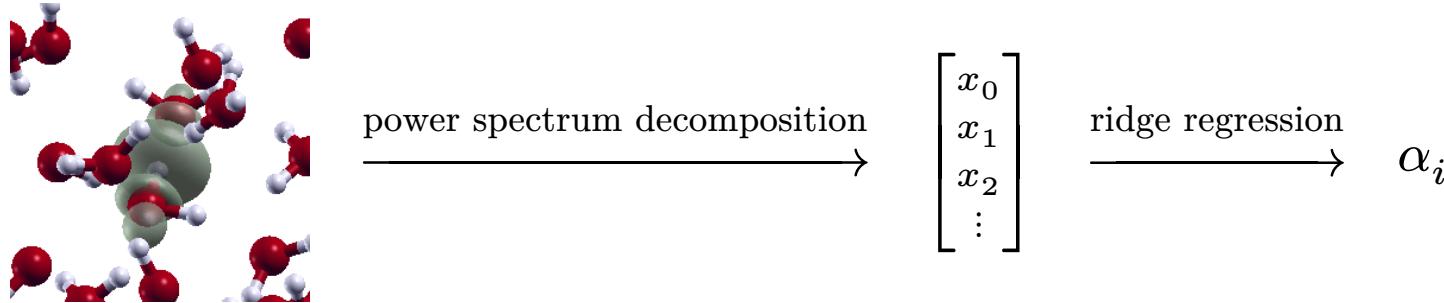
accurate to within $\mathcal{O}(10 \text{ meV})$ cf. typical
band gap accuracy of $\mathcal{O}(100 \text{ meV})$



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

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

Machine-learned electronic screening

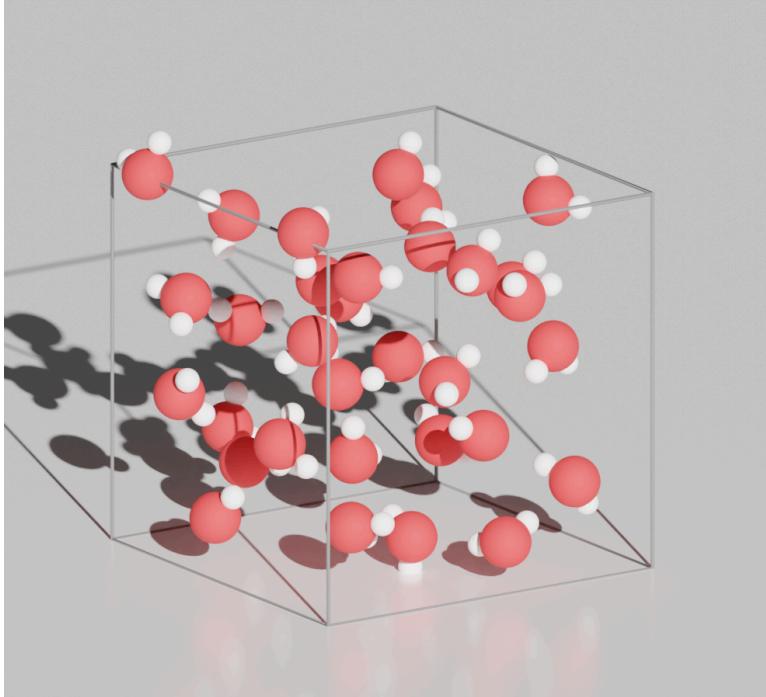


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

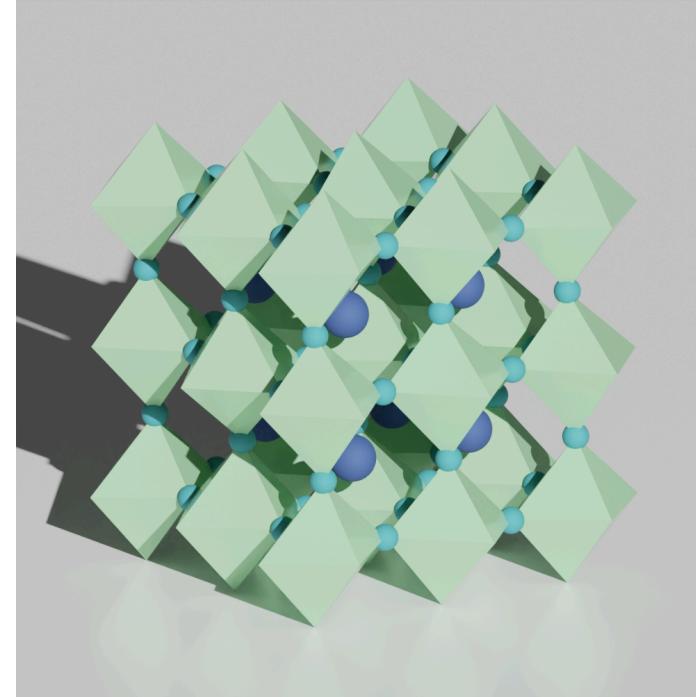
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

Machine-learned electronic screening



water

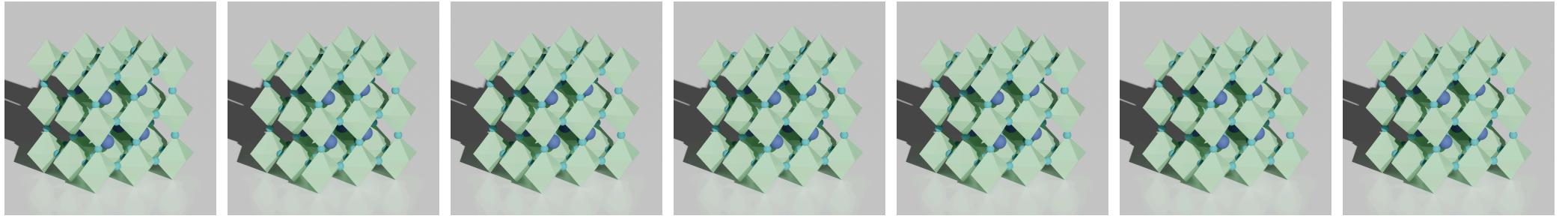


CsSnI_3

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

Machine-learned electronic screening

The use-case

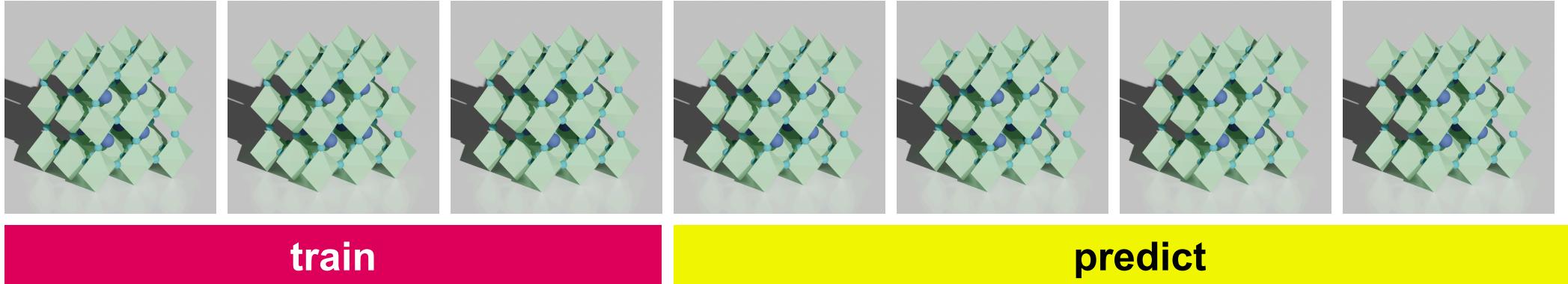


train

predict

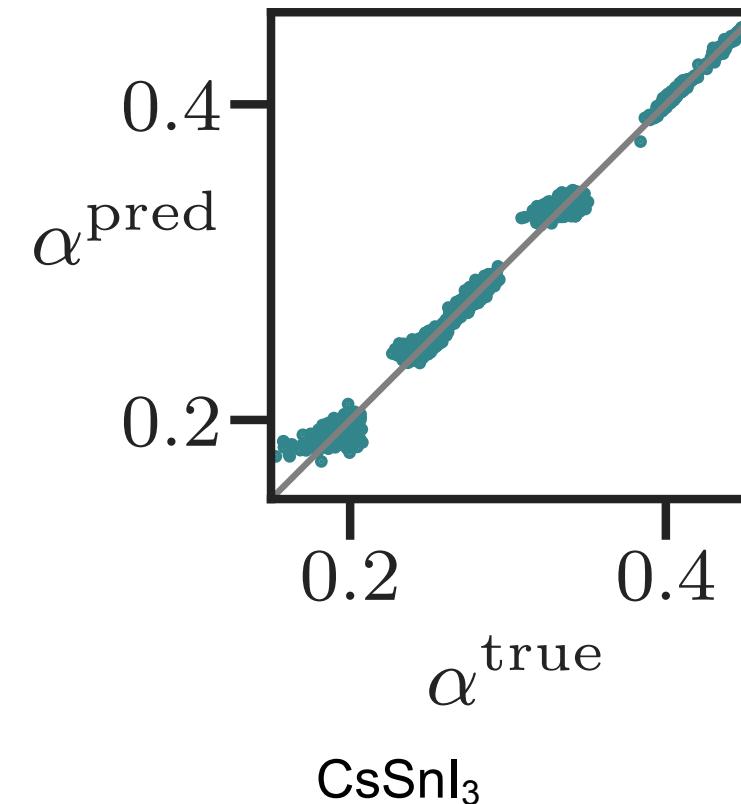
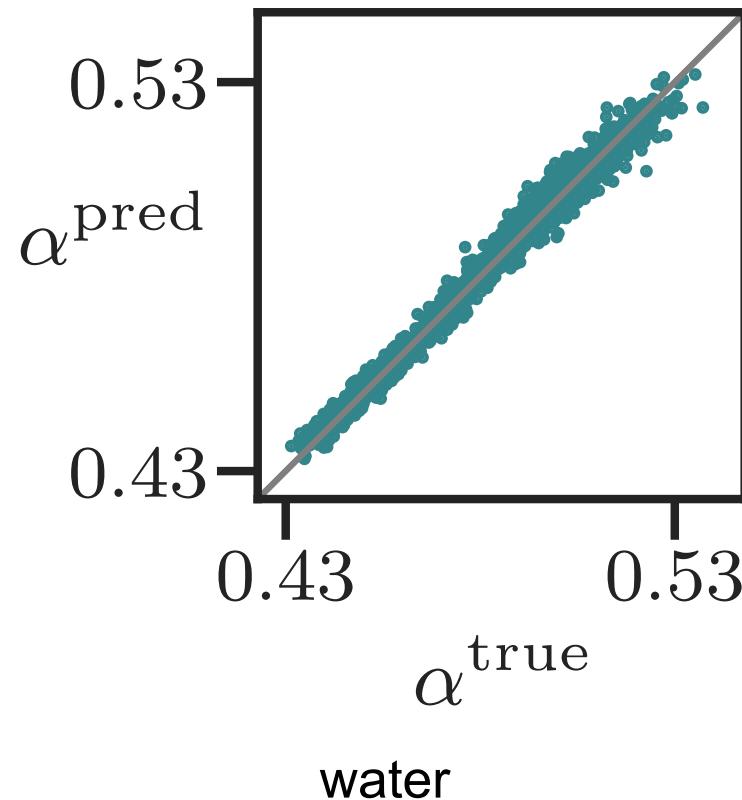
Machine-learned electronic screening

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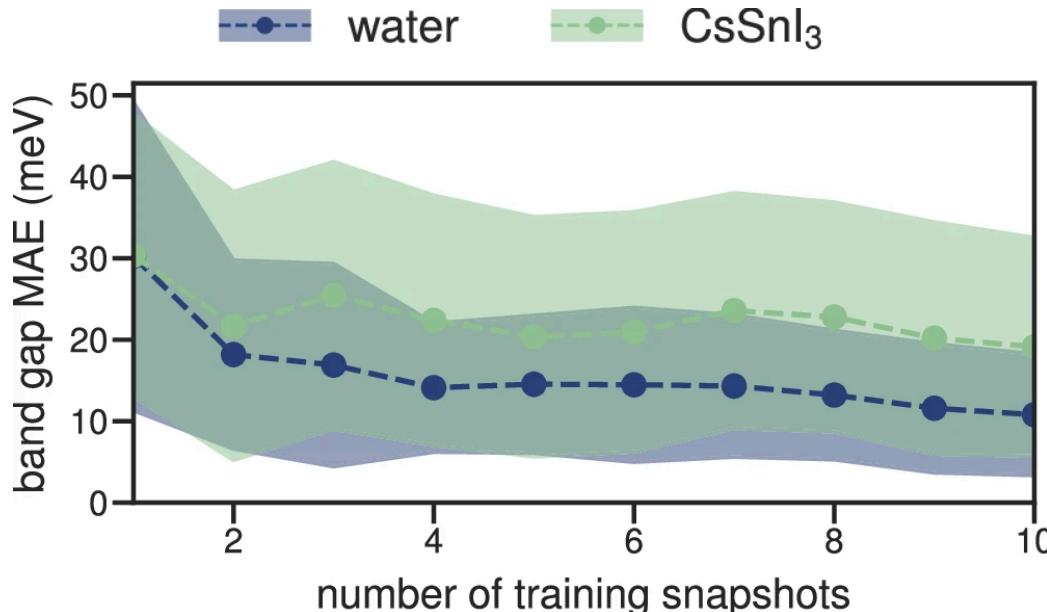
N.B. not a general model

Machine-learned electronic screening

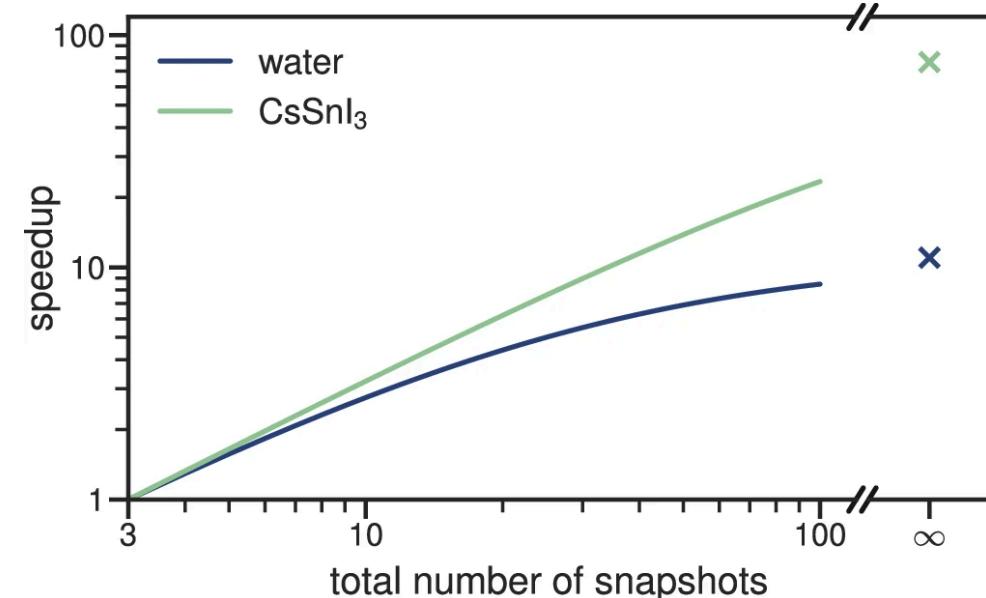


¹Y. Schubert *et al.* *npj Comput Mater* 10, 1–12 (2024)

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

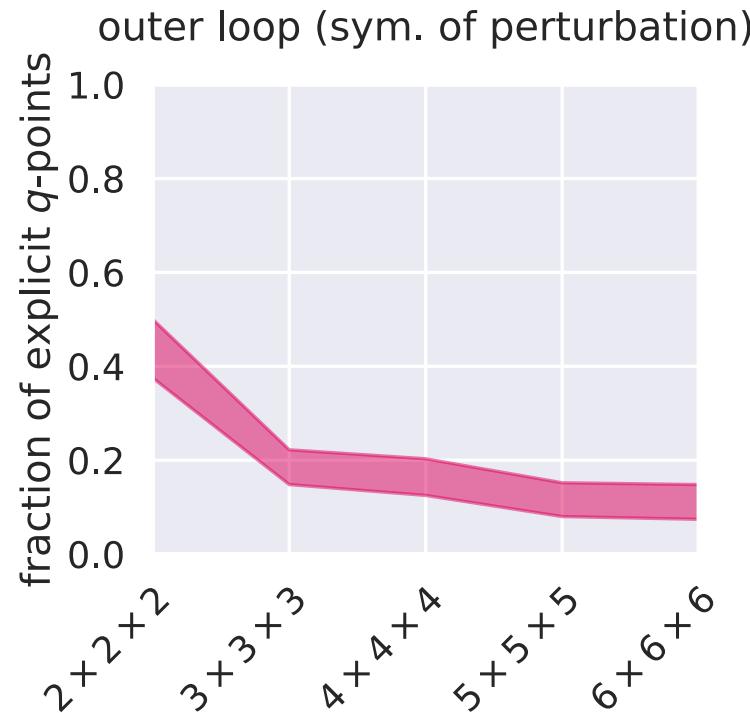
To compute screening parameters via DFPT...

```

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

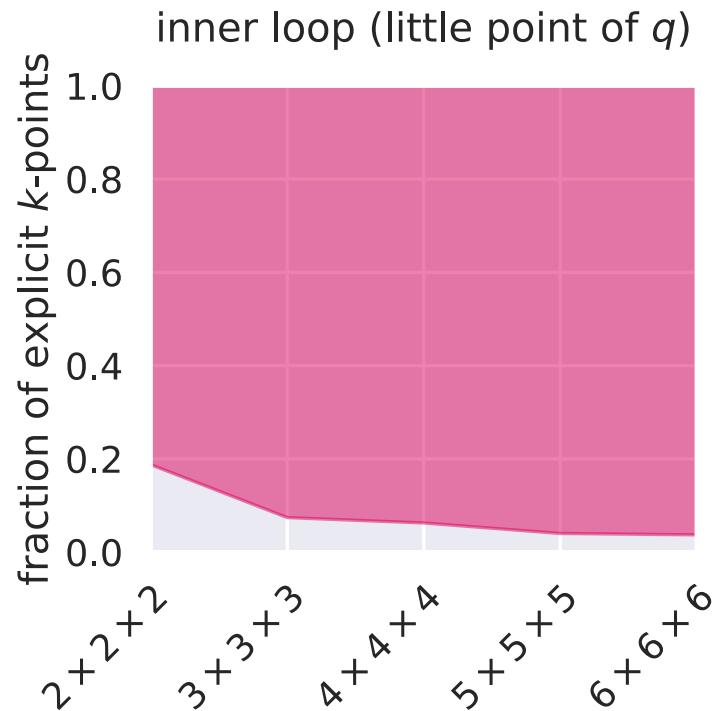
```

Taking advantage of symmetries



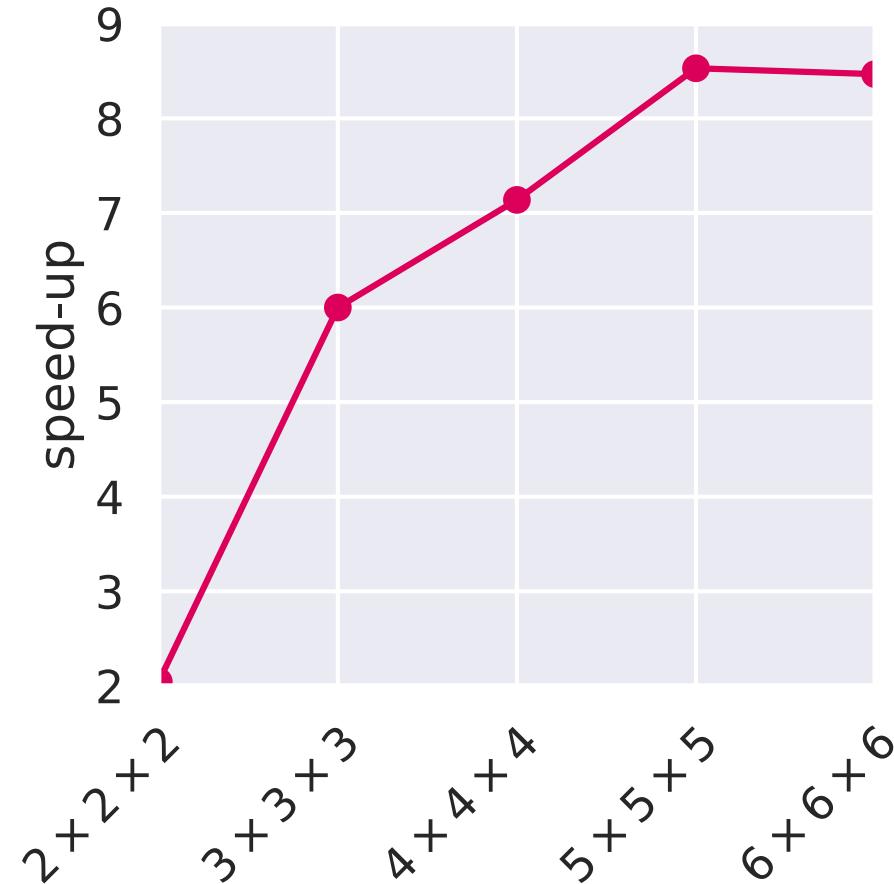
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$ (the symmetry of the perturbation; lower than that of the primitive cell)

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



Automated Wannierisation

```
{  
  "workflow": {  
    "functional": "ki",  
    "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}]]  
    }  
  },  
},
```

```

    "kpoints": {
        "grid": [6, 6, 6]
    },
    "calculator_parameters": {
        "ecutwfc": 60.0,
        "w90": {
            "projections": [
                [{"site": "As", "ang_mtm": "d"}, {"site": "Ga", "ang_mtm": "d"}, {"site": "As", "ang_mtm": "sp3"}], [{"site": "Ga", "ang_mtm": "sp3"}]
            ],
            "dis_froz_max": 14.6,
            "dis_win_max": 18.6
        },
        "ui": {
            "smooth_int_factor": 2
        }
    }
}

```

Automated Wannierisation

Koopmans functionals rely heavily on Wannier functions...

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

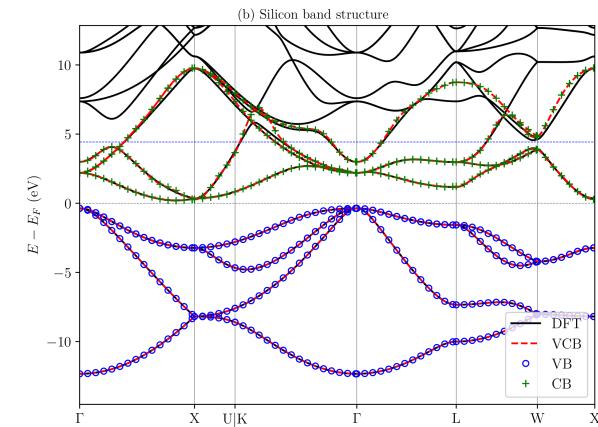
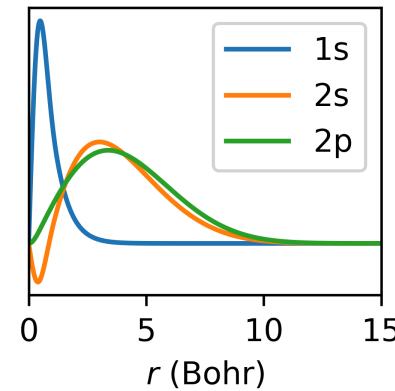
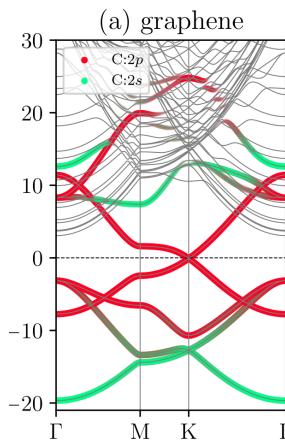
¹J. Qiao *et al.* *npj Comput Mater* 9, 208 (2023)

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

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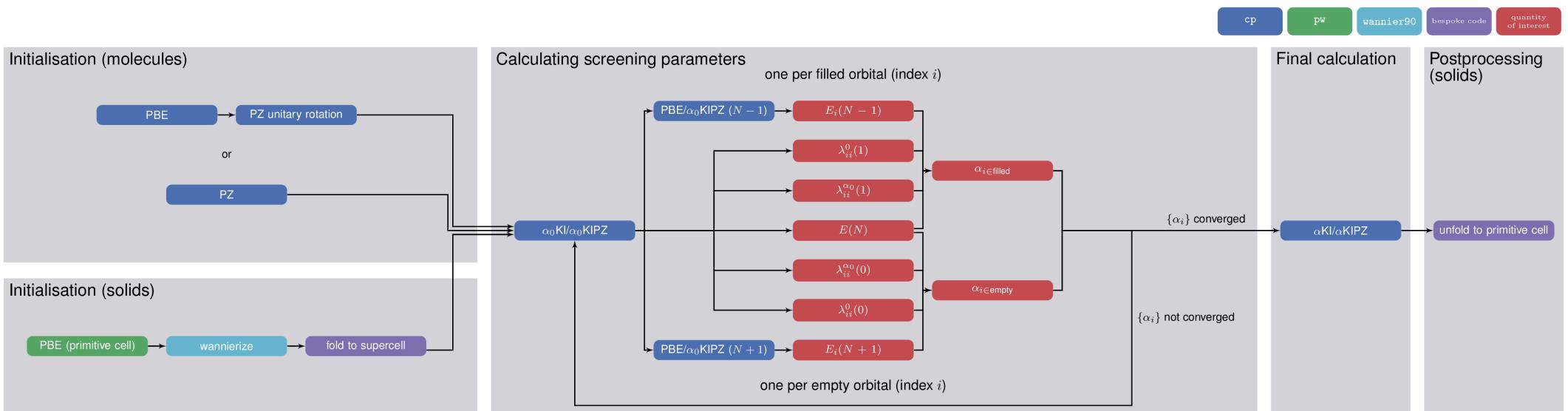
projectability-based
disentanglement¹

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
```

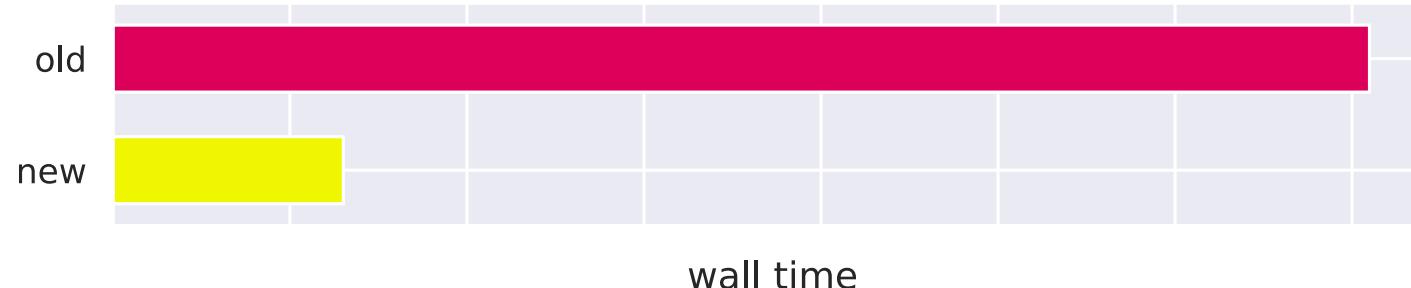
remote compute, parallel step execution, provenance-tracking, (requires configuration,
WIP...)

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

koopmans 🤝 AiiDA

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



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

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

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

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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

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

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

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

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

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

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

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

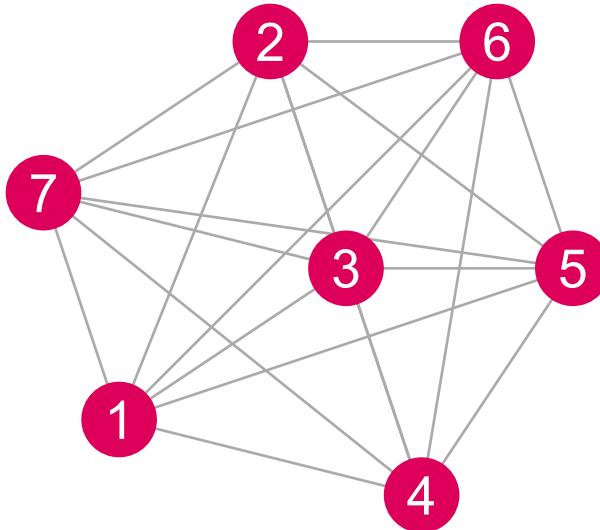
¹M. S. Hybertsen *et al.* *Phys. Rev. B* 35, 5585–5601 (1987), R. Del Sole *et al.* *Phys. Rev. B* 49, 8024–8028 (1994)

Open questions

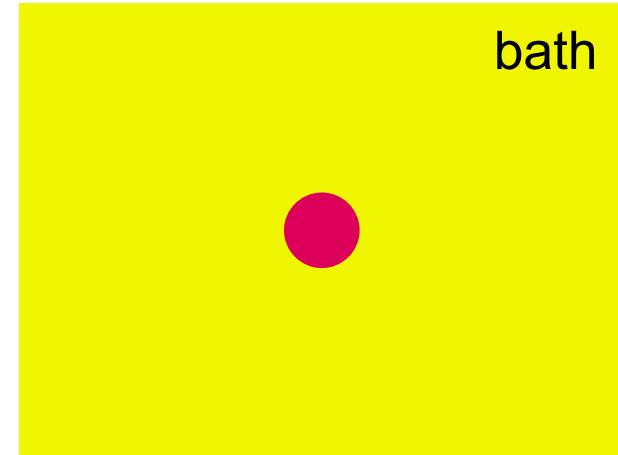
- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they 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.* *Phys. Rev. B* 89, 195134 (2014)

What is screening U ?



all sites included in response matrix
bare U



only one site included in response matrix
fully-screened U

What is screening U ?

fully-screened	$\begin{pmatrix} \chi_{11}^{\uparrow\uparrow} & & & \\ & \chi_{11}^{\downarrow\downarrow} & & \\ & & \chi_{22}^{\uparrow\uparrow} & \\ & & & \chi_{22}^{\downarrow\downarrow} \\ & & & \ddots \end{pmatrix}$	$U^{I\sigma} = \frac{1}{(\chi_0)_{II}^{\sigma\sigma}} - \frac{1}{\chi_{II}^{\sigma\sigma}}$
not screened by opposite spin	$\begin{pmatrix} \chi_{11}^{\uparrow\uparrow} & \chi_{11}^{\uparrow\downarrow} & & & \\ & \chi_{11}^{\downarrow\uparrow} & \chi_{11}^{\downarrow\downarrow} & & \\ & & \chi_{22}^{\uparrow\uparrow} & \chi_{22}^{\uparrow\downarrow} & \\ & & & \chi_{22}^{\downarrow\uparrow} & \chi_{22}^{\downarrow\downarrow} \\ & & & & \ddots \end{pmatrix}$	$f_I^{\sigma\sigma'} = [(\chi_0)_{II}^{\sigma\sigma}]^{-1} - [\chi_{II}^{\sigma\sigma}]^{-1}$ $f_I^{\sigma\sigma'} \xrightarrow{???} U^I \text{ or } U^{I\sigma}$
also not screened by other Hubbard sites	$\begin{pmatrix} \chi_{11}^{\uparrow\uparrow} & \chi_{11}^{\uparrow\downarrow} & \chi_{12}^{\uparrow\uparrow} & \chi_{12}^{\uparrow\downarrow} & \dots \\ \chi_{11}^{\downarrow\uparrow} & \chi_{11}^{\downarrow\downarrow} & \chi_{12}^{\downarrow\uparrow} & \chi_{12}^{\downarrow\downarrow} & \dots \\ \chi_{21}^{\uparrow\uparrow} & \chi_{21}^{\uparrow\downarrow} & \chi_{22}^{\uparrow\uparrow} & \chi_{22}^{\uparrow\downarrow} & \dots \\ \chi_{21}^{\downarrow\uparrow} & \chi_{21}^{\downarrow\downarrow} & \chi_{22}^{\downarrow\uparrow} & \chi_{22}^{\downarrow\downarrow} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$	$f_{IJ}^{\sigma\sigma'} = \dots$ $\text{(left as an exercise to the reader)}$

1. Conceptual consistency

spin-resolved linear response \leftrightarrow spin-resolved DFT+ U functional

¹A. C. Burgess *et al.* *Phys. Rev. B* 107, L121115 (2023)

spin-resolved linear response \leftrightarrow spin-resolved DFT+ U functional

... we didn't explore DFT+ U^σ ; instead see BLOR¹)

¹A. C. Burgess *et al.* *Phys. Rev. B* 107, L121115 (2023)

2. Unconstrained constrained linear response

Unconstrained constrained linear response

Suppose we want to compute $\frac{d^2 E_{\text{Hxc}}}{d(n^I)^2} \Big|_{\mu^I}$

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“Impose” the constraint by setting $dn^\uparrow = dn^\downarrow$ to get...

$$\frac{d^2 E_{\text{Hxc}}}{dn^2} \Big|_{\mu} = \frac{1}{4} (f^{\uparrow\uparrow} + f^{\downarrow\downarrow} + f^{\uparrow\downarrow} + f^{\downarrow\uparrow})$$

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$$\frac{d^2 E_{\text{Hxc}}}{dn^2} \Big|_{\mu} = \frac{1}{4} (f^{\uparrow\uparrow} + f^{\downarrow\downarrow} + f^{\uparrow\downarrow} + f^{\downarrow\uparrow})$$

This simple average is one choice (of many) for $M : f_I^{\sigma\sigma'} \rightarrow U^I$

3. We can recover conventional linear response

Conventional linear response

For conventional LR, $dv^{I\uparrow} = dv^{I\downarrow} = dv$

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Likewise,

$$(\varepsilon^{-1})_{\text{conv}} = \dots = \frac{1}{2} \sum_{\sigma\sigma'} (f\chi)^{\sigma\sigma'}$$

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Likewise,

$$(\varepsilon^{-1})_{\text{conv}} = \dots = \frac{1}{2} \sum_{\sigma\sigma'} (f\chi)^{\sigma\sigma'}$$

And thus

$$U = (\varepsilon^{-1} - 1) \chi^{-1} = \frac{1}{2} \frac{\sum_{\sigma\sigma'} (f\chi)^{\sigma\sigma'}}{\sum_{\sigma\sigma'} \chi^{\sigma\sigma'}}$$

4. J is free

As defined by

$$J = -\frac{1}{2} \frac{dv_{\text{Hxc}}^{\uparrow} - dv_{\text{Hxc}}^{\downarrow}}{d(n^{\uparrow} - n^{\downarrow})} = -\frac{1}{4} \frac{(f^{\uparrow\uparrow} - f^{\downarrow\uparrow})dn^{\uparrow} - (f^{\downarrow\downarrow} - f^{\uparrow\downarrow})dn^{\downarrow}}{d(n^{\uparrow} - n^{\downarrow})}$$

Different ways to define J :

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Different ways to define J :

1. while keeping $n = n^{\uparrow} + n^{\downarrow}$ fixed:

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Different ways to define J :

1. while keeping $n = n^{\uparrow} + n^{\downarrow}$ fixed:

$$J = -\frac{1}{4}(f^{\uparrow\uparrow} - f^{\downarrow\uparrow} - f^{\uparrow\downarrow} + f^{\downarrow\downarrow})$$

2. for a perturbation where $dv^{\uparrow} = -dv^{\downarrow}$

5. Easy to implement

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