

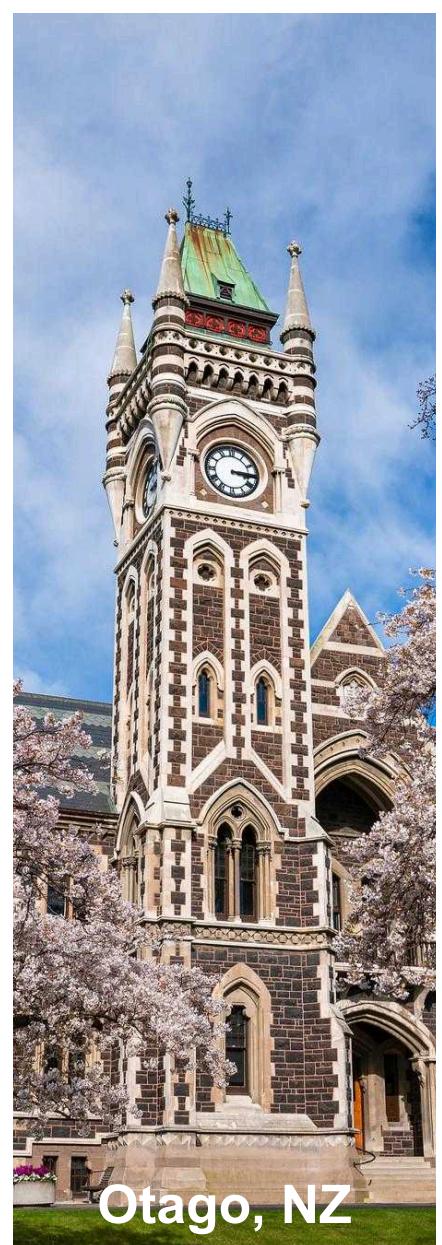
**PSI**

Center for Scientific Computing,  
Theory and Data

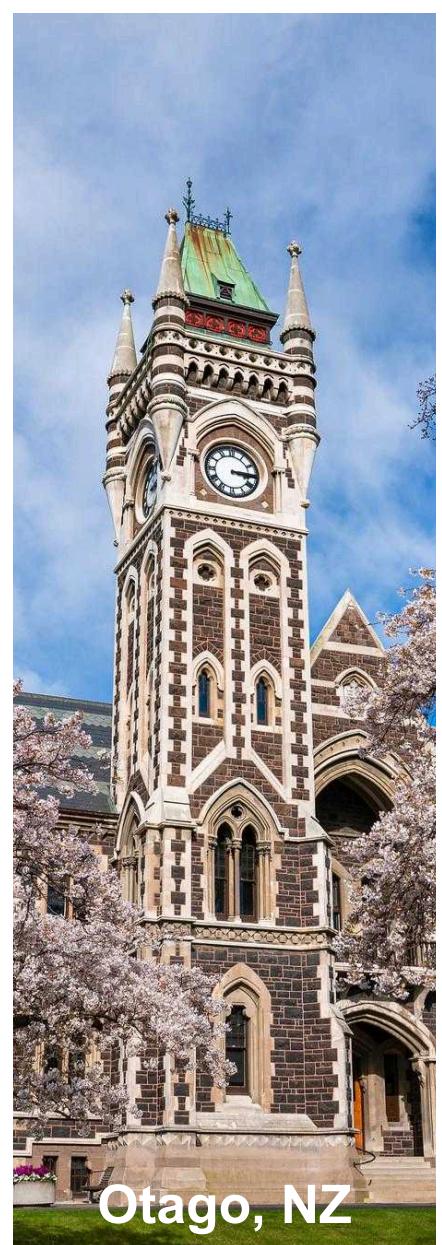
# Correcting the failures of DFT Koopmans functionals, DFT+*U*, and more

Edward Linscott

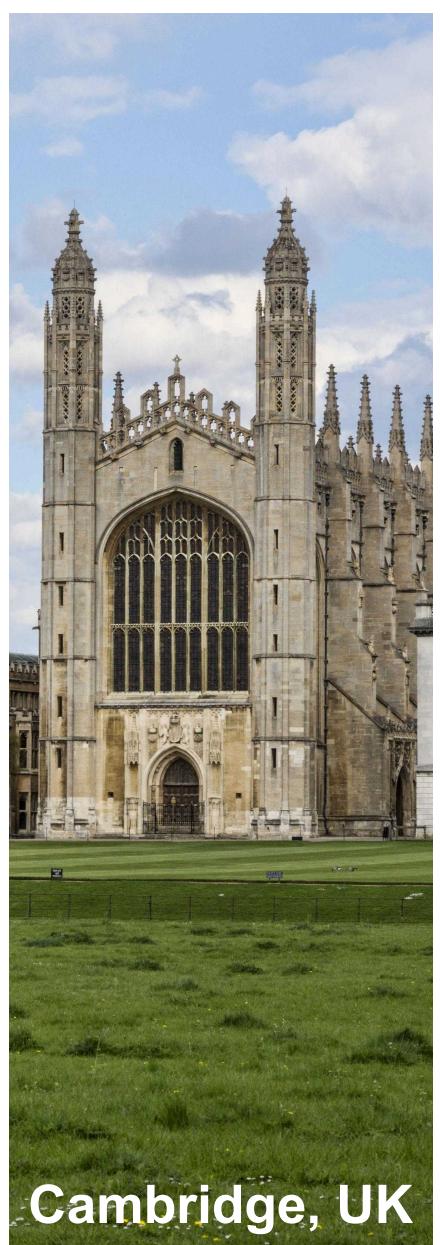
PsiQuantum, 30 October 2025



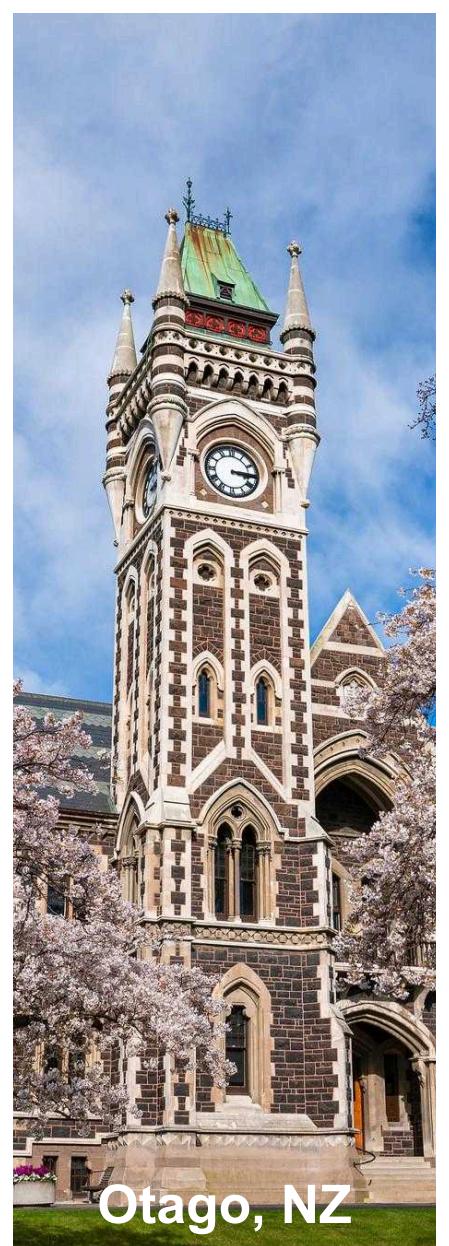
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Otago, NZ



Cambridge, UK



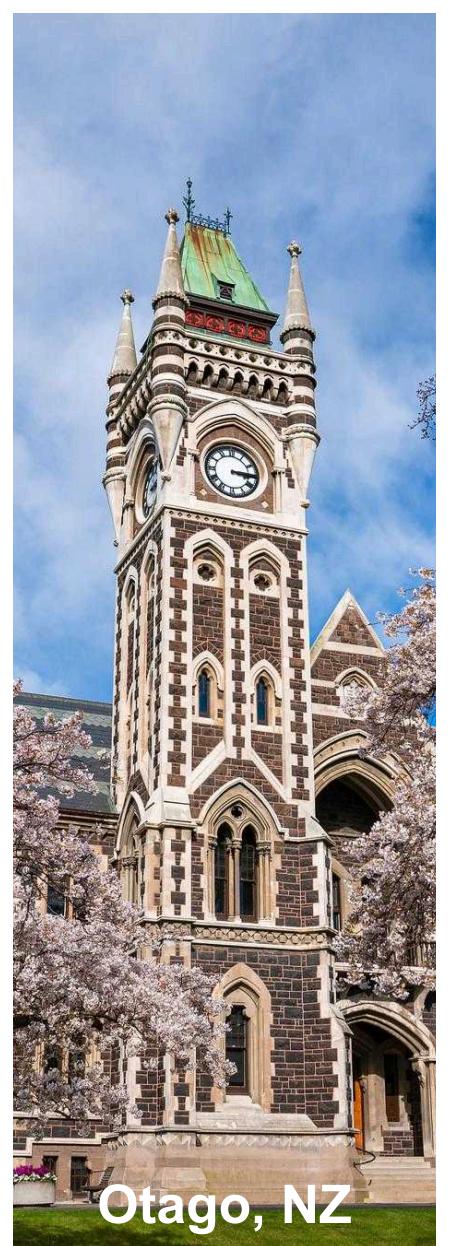
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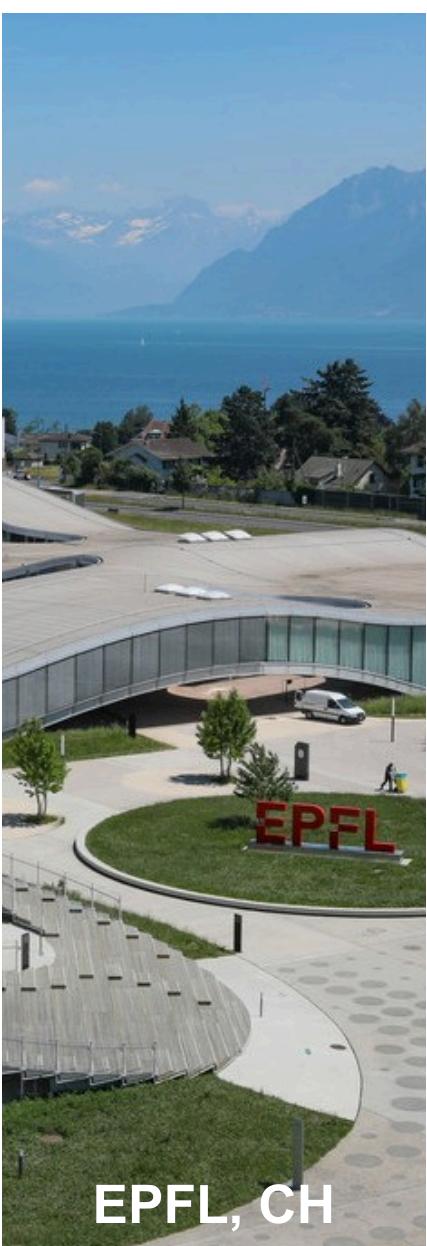
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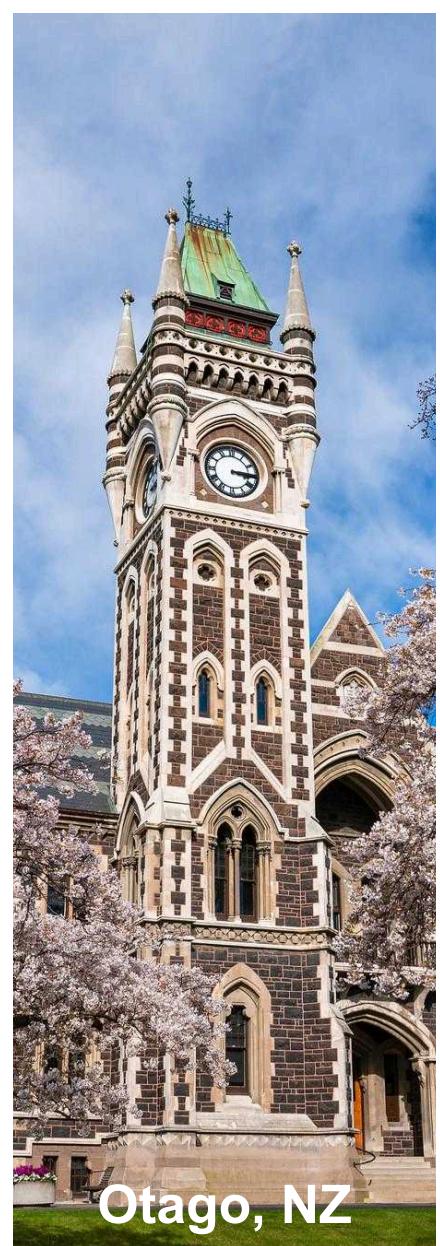
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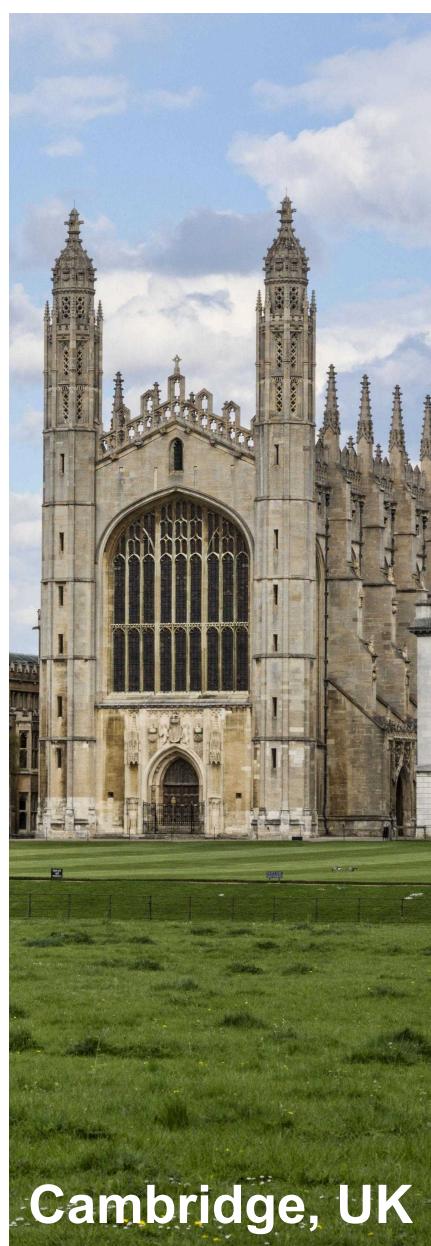
EPFL, CH



PSI, CH



Otago, NZ



Cambridge, UK



EPFL, CH



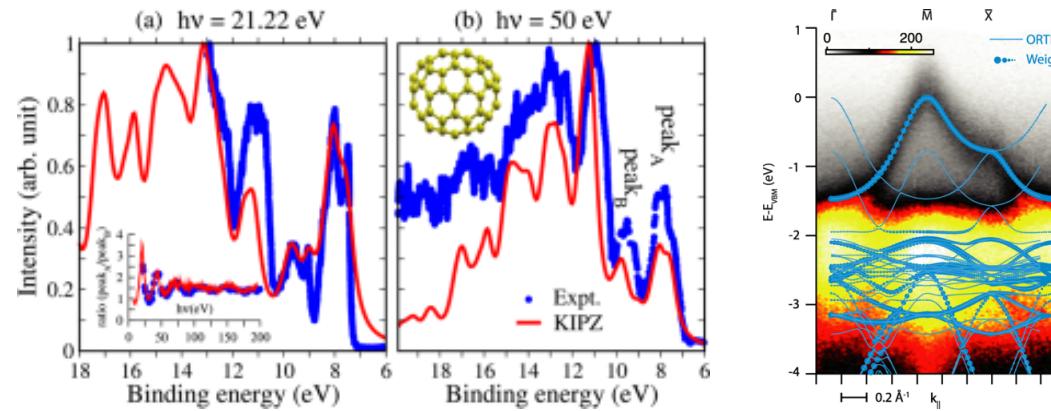
PSI, CH



... PsiQuantum  
AU?

# Predicting electronic excitations

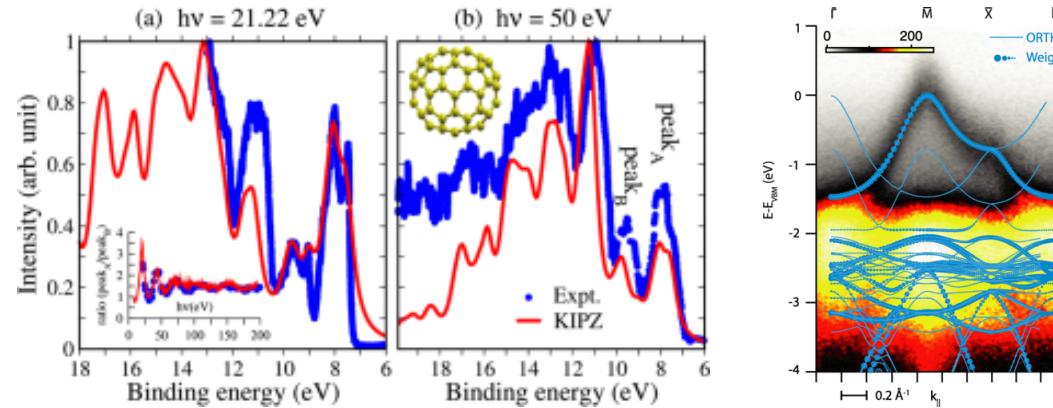
Spectral properties are fundamental to understanding molecules and materials...



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

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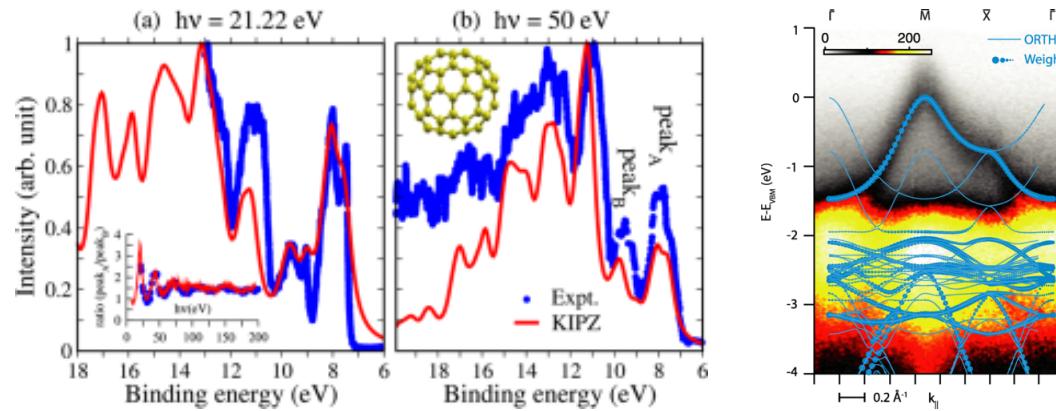


... but how can we routinely compute them?

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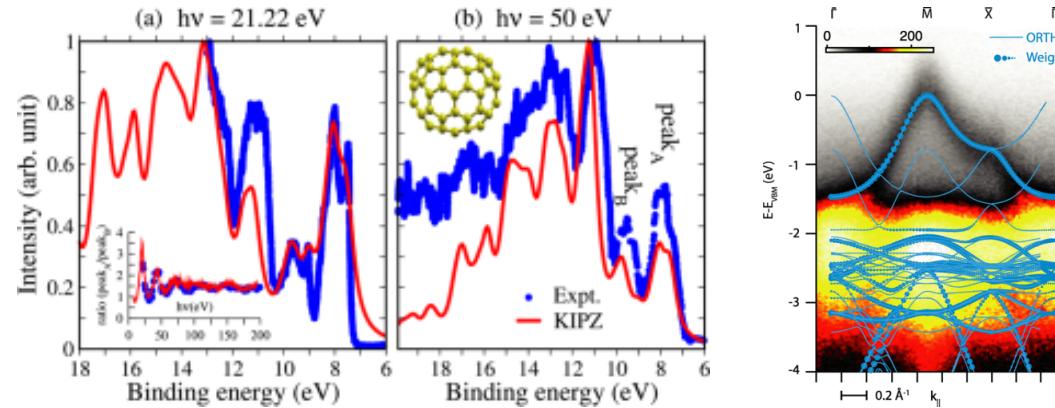
... but how can we routinely compute them?

- 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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# Predicting electronic excitations

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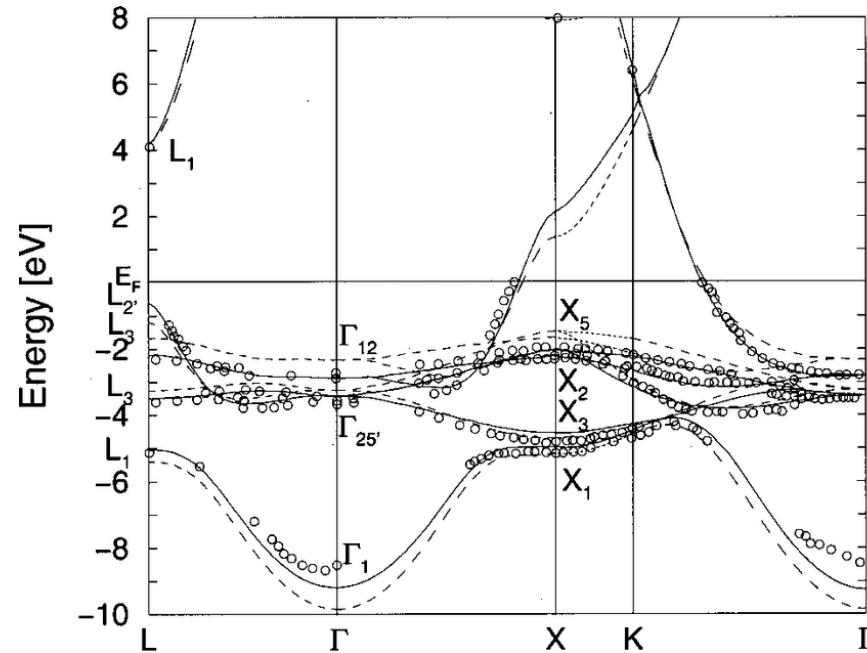
## My work: understanding and correcting these intrinsic errors

<sup>1</sup>N. 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

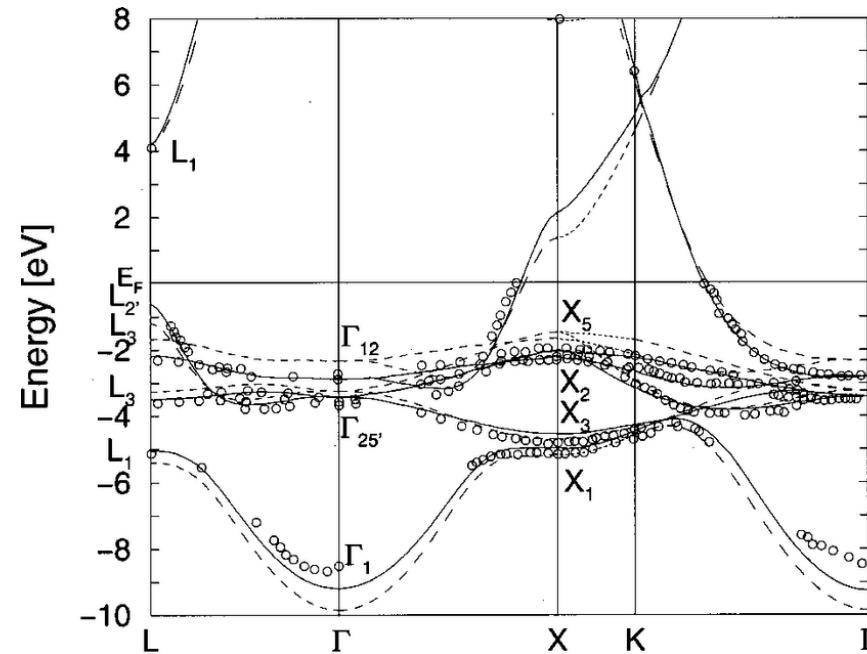
From the auxiliary, non-interacting system:



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

# Learning nothing from Icarus

From the auxiliary, non-interacting system:



... the temptation is too much!

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# Learning nothing from Icarus

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

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

<sup>1</sup>C.-O. Almbladh *et al.* *Phys. Rev. B* 31, 3231–3244 (1985)

<sup>2</sup>M. E. Casida. *Phys. Rev. A* 51, 2005–2013 (1995)

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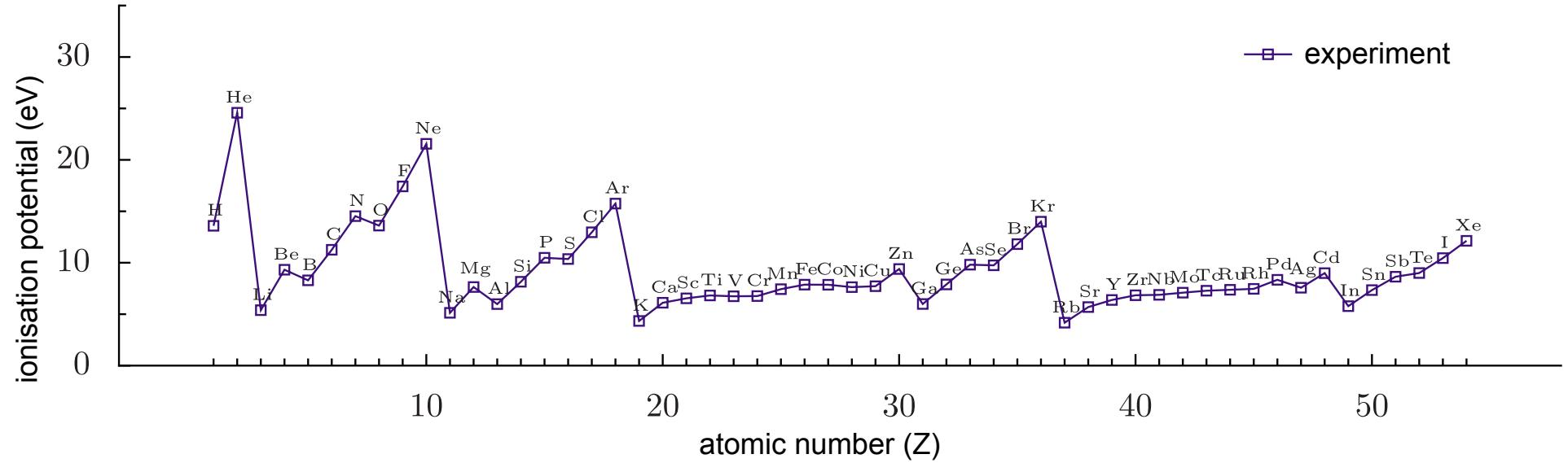
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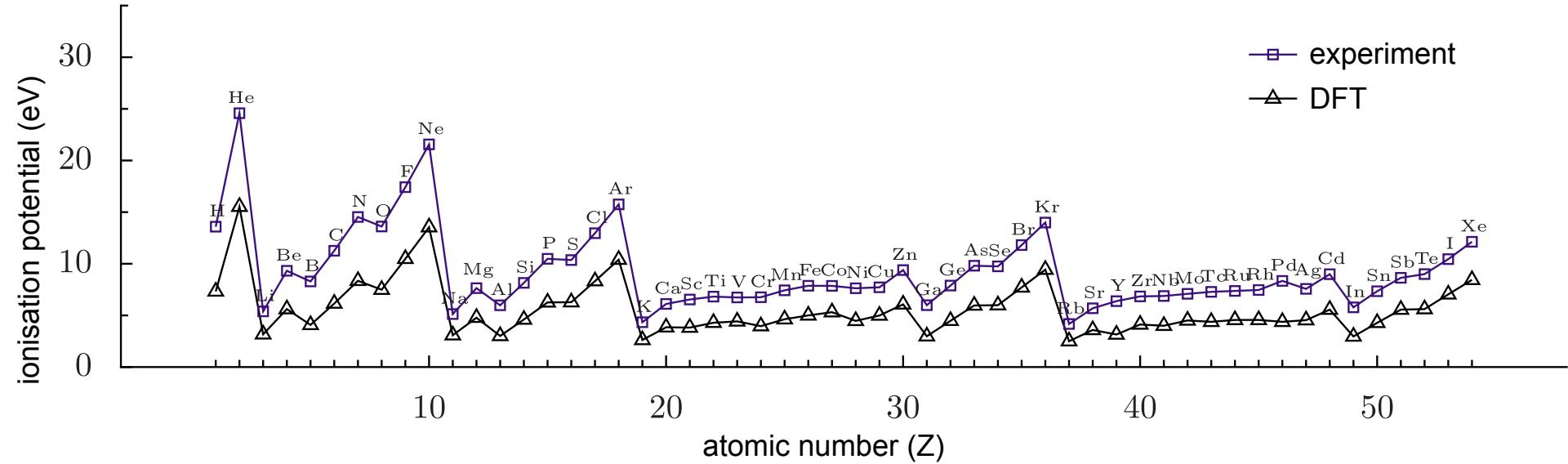
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# What's going wrong?

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

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*cf.* Janak's theorem:

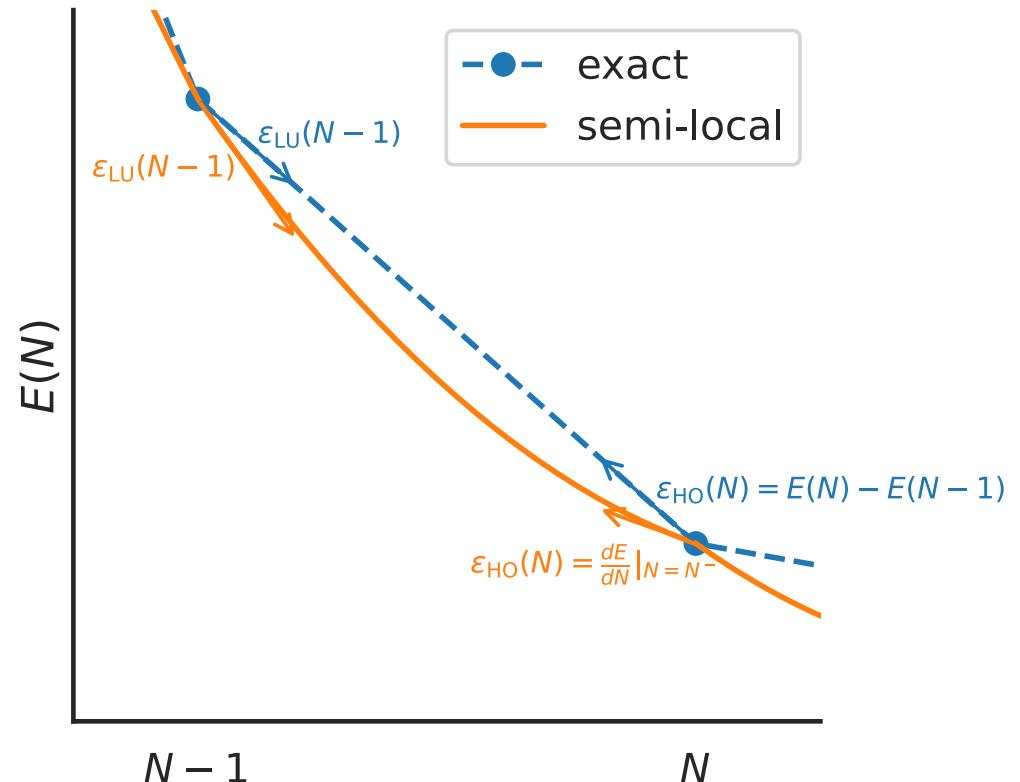
$$\varepsilon_i^{\text{DFT}} = \frac{dE^{\text{DFT}}}{df_i}$$

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

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- We showed<sup>3</sup> that the “convexity condition” follows *i.e.*

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

for all DFTs that are

- exact for all  $v$ -representable densities
- size-consistent
- translationally invariant

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for all DFTs that are

- exact for all  $v$ -representable densities
- size-consistent
- translationally invariant
- ... and that similar reasoning applies to total energy as a function of total magnetisation<sup>4</sup>

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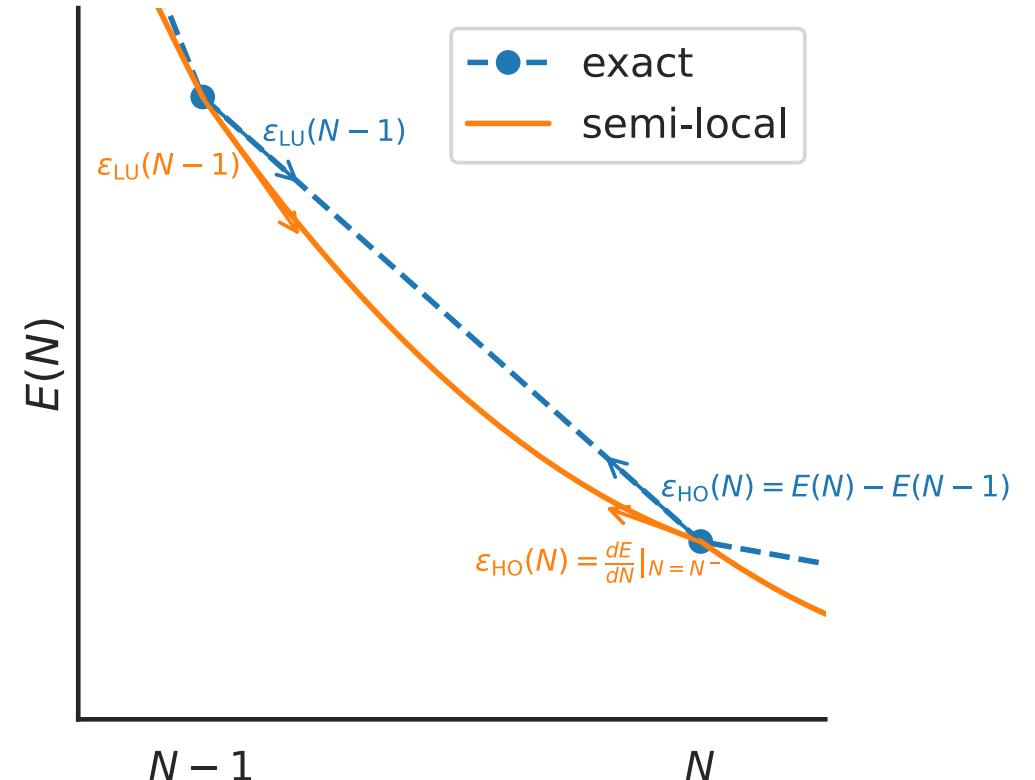
<sup>4</sup>A. C. Burgess *et al.* *Phys. Rev. Lett.* 133, 26404 (2024)

**Core idea: enforce piecewise linearity**

# Imposing generalised piecewise linearity

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

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

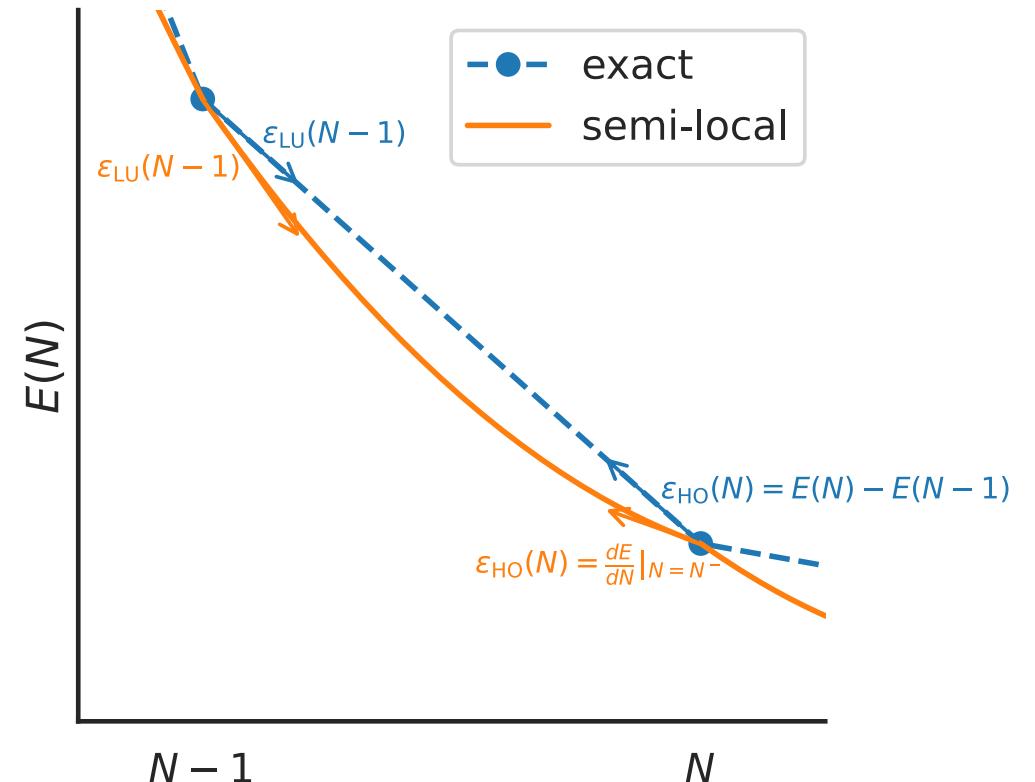


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removes dependence on  $f_i$



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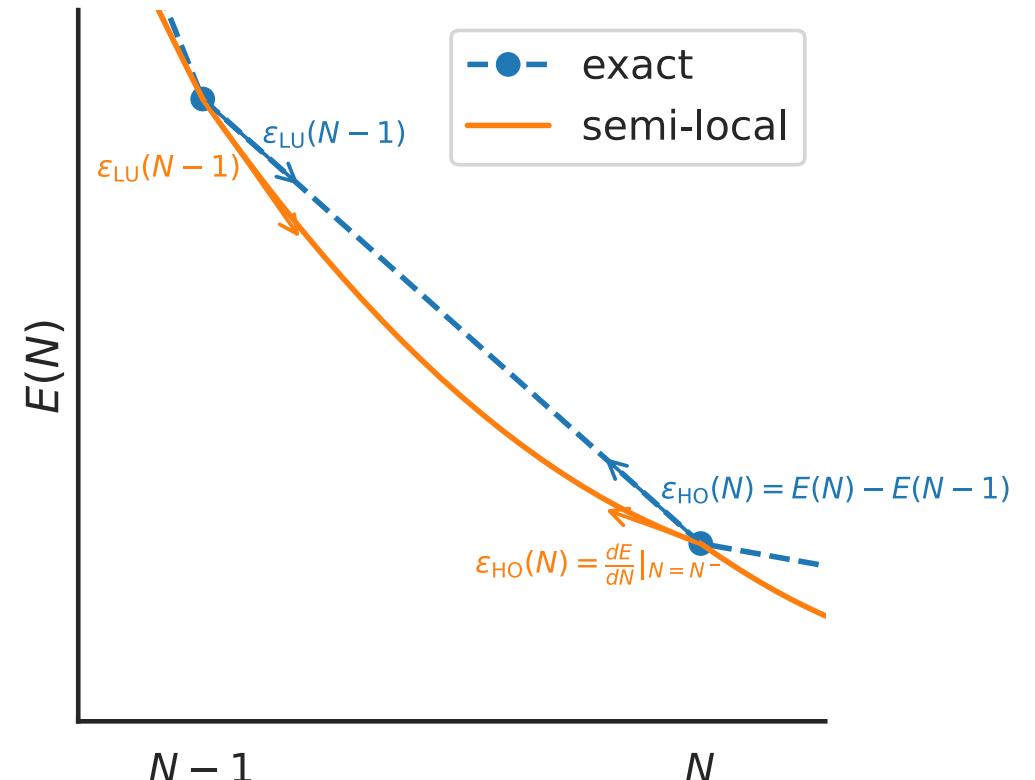
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$$+ f_i \int_0^1 \langle \varphi_i | \hat{h}^{\text{DFT}}(f) | \varphi_i \rangle df \right)$$

removes dependence on  $f_i$

restores linear dependence on  $f_i$

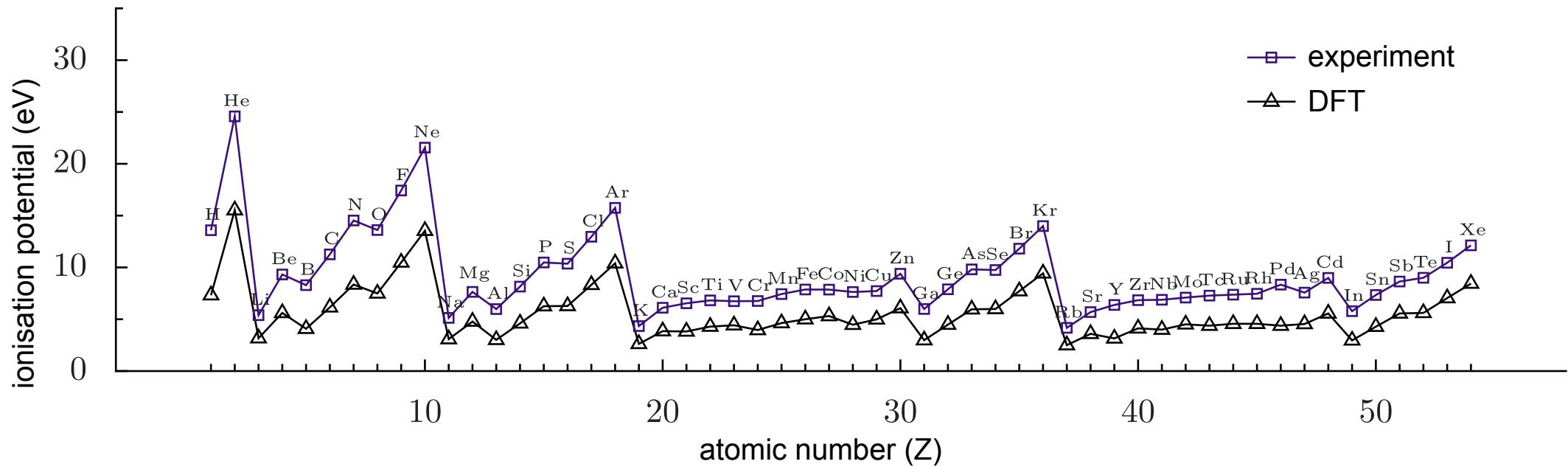


# Details for the experts

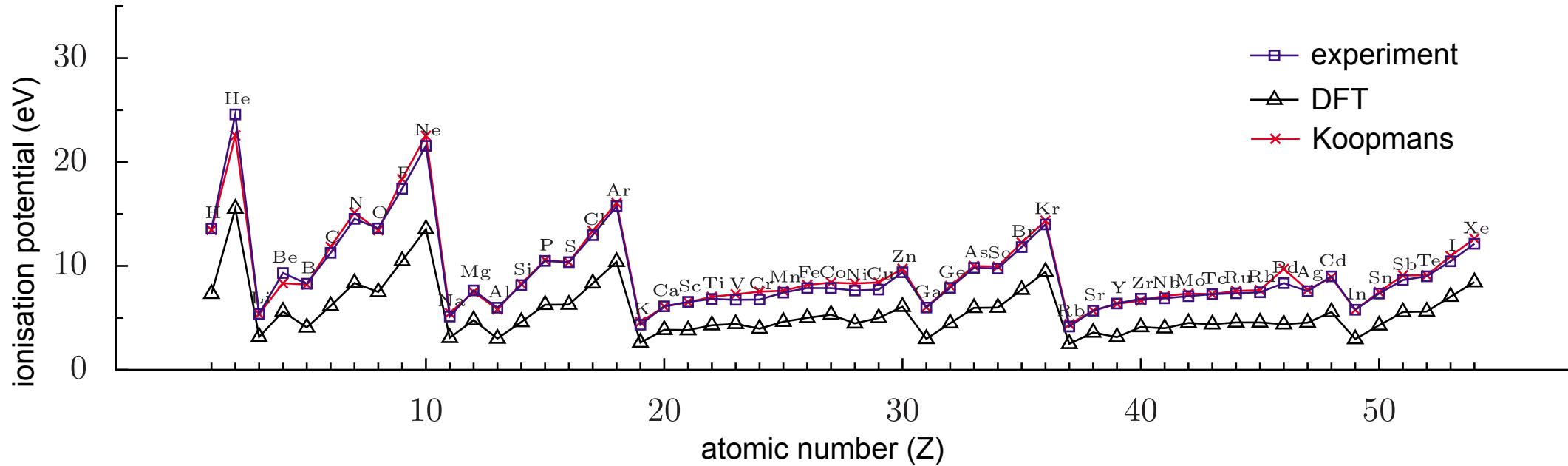
$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] = E^{\text{DFT}}[\rho] + \sum_i \alpha_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho - \rho_i]) \right. \\ \left. + f_i (E^{\text{DFT}}[\rho - \rho_i + n_i] - E^{\text{DFT}}[\rho - \rho_i]) \right\}$$

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

# Results



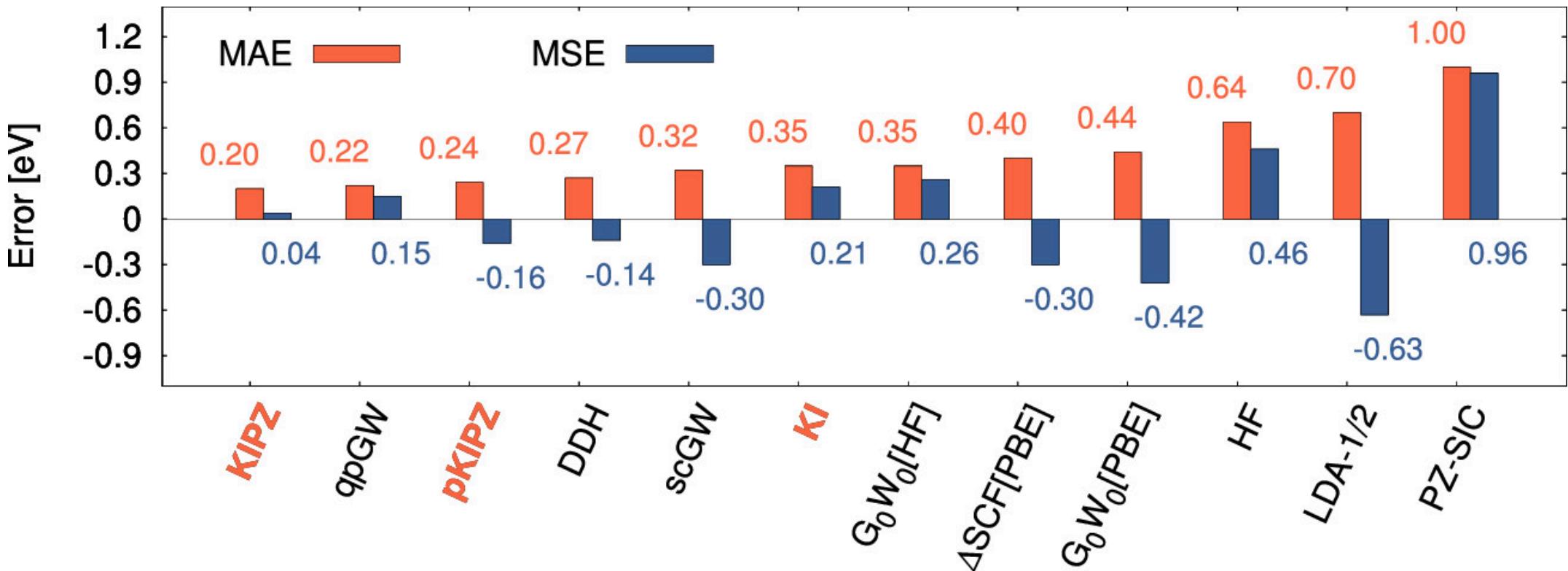
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# Molecules

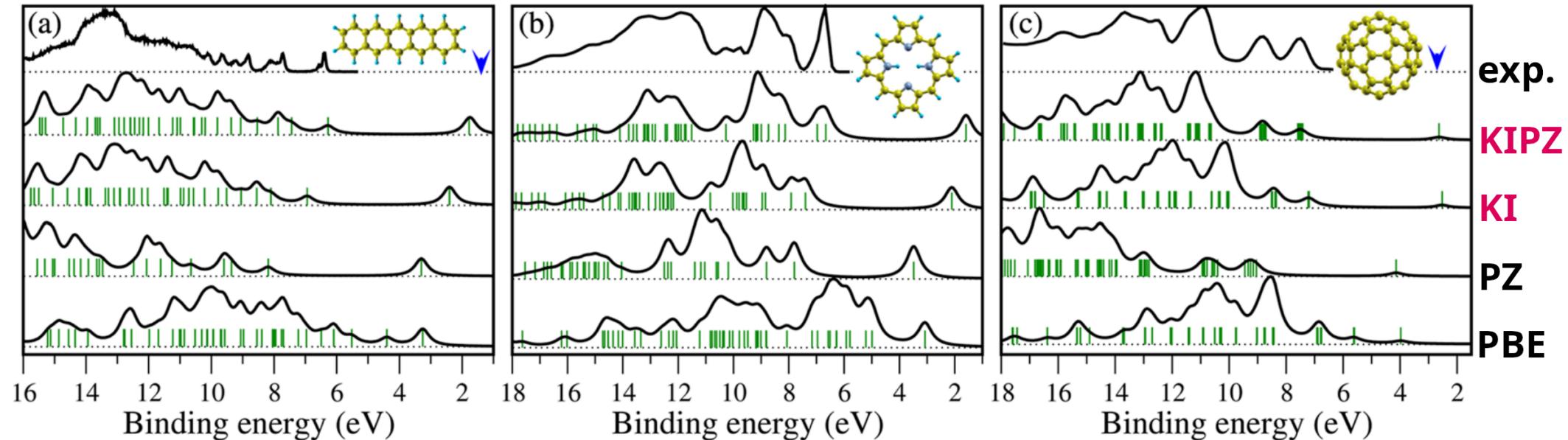
## Ionisation potentials<sup>1</sup>



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

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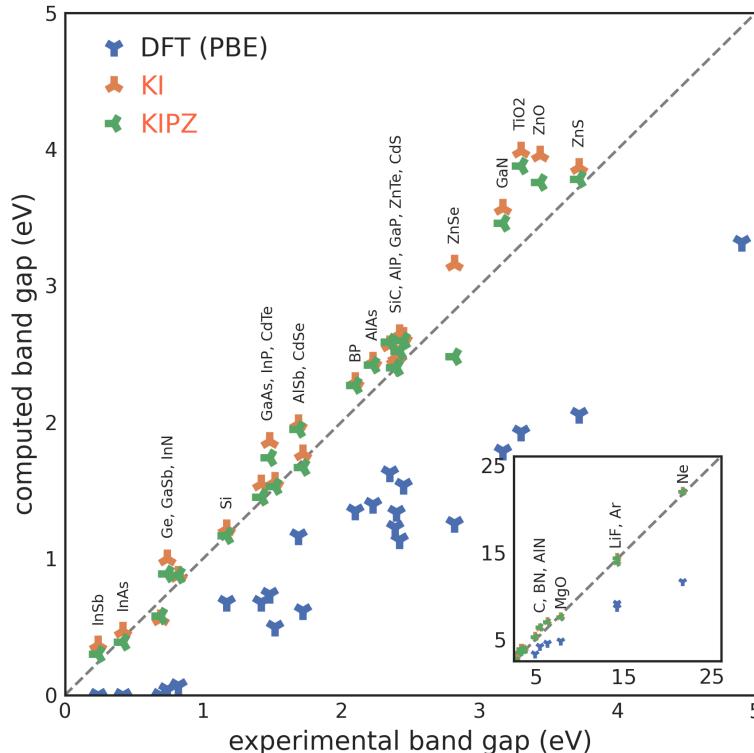
## UV photoemission spectra<sup>1</sup>



<sup>1</sup>N. L. Nguyen et al. Phys. Rev. Lett. 114, 166405 (2015)

# Materials

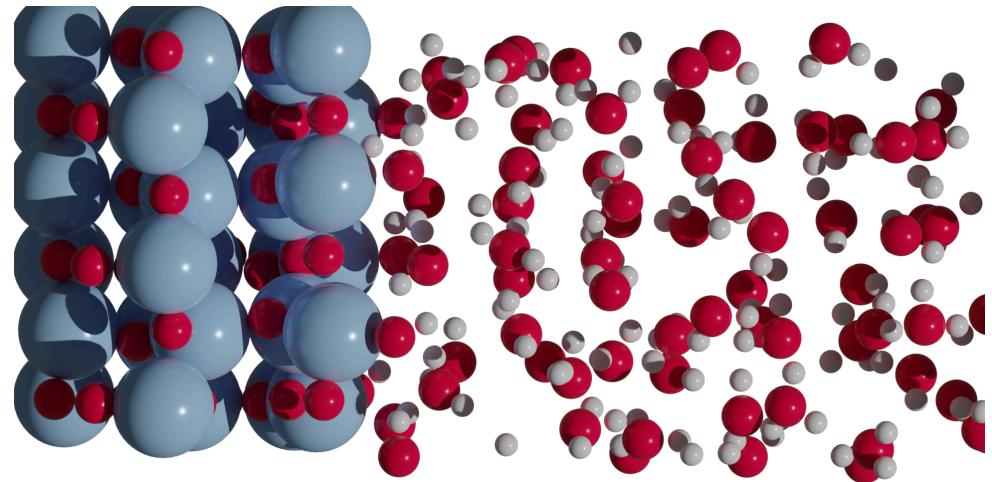
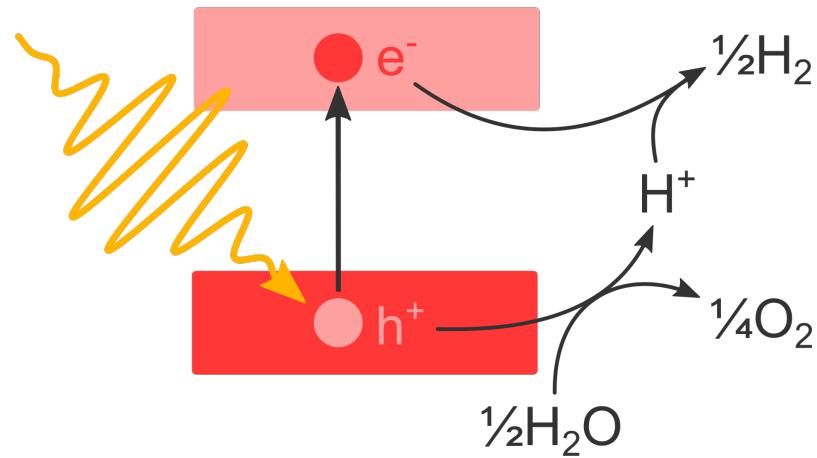
## Prototypical semiconductors and insulators<sup>1</sup>



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

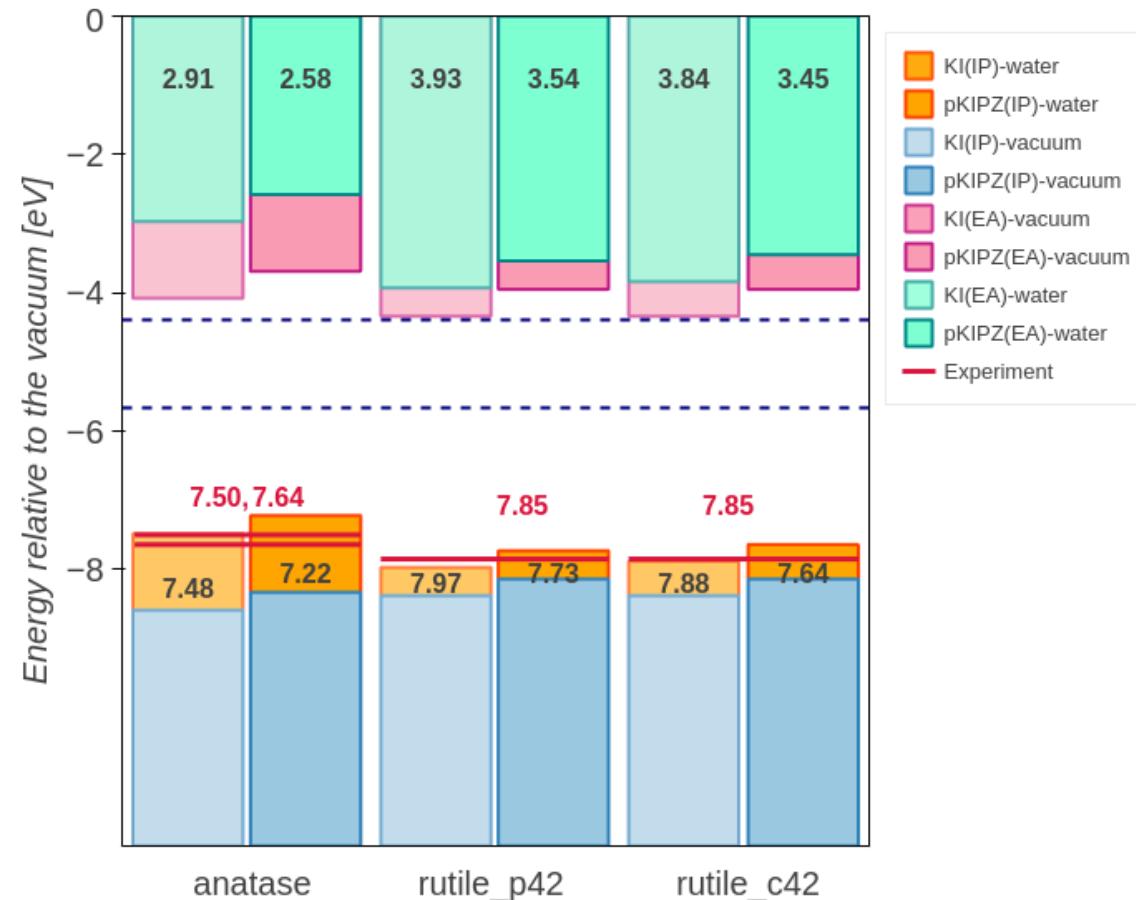
<sup>1</sup>N. L. Nguyen *et al.* Phys. Rev. X 8, 21051 (2018)

# Photocatalysis



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

# Photocatalysis



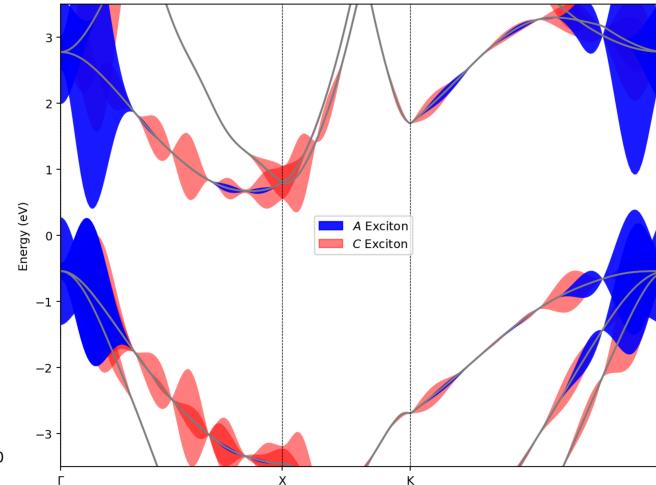
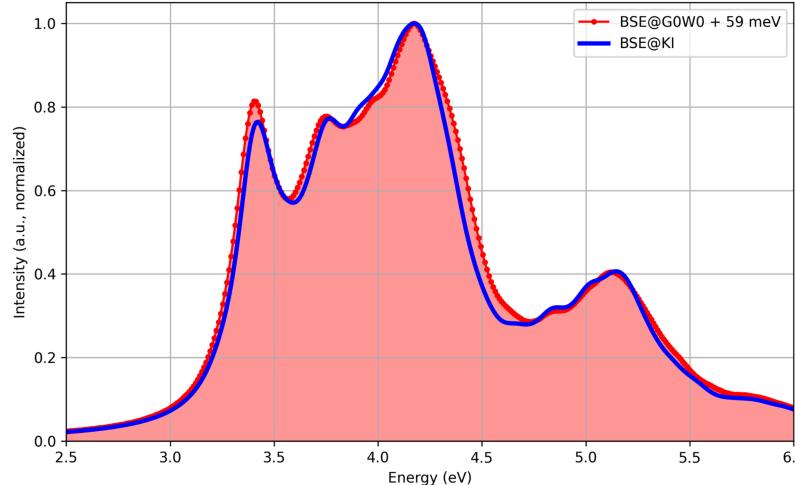
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# Optical spectra

Solve the BSE, using Koopmans eigenvalues in lieu of GW

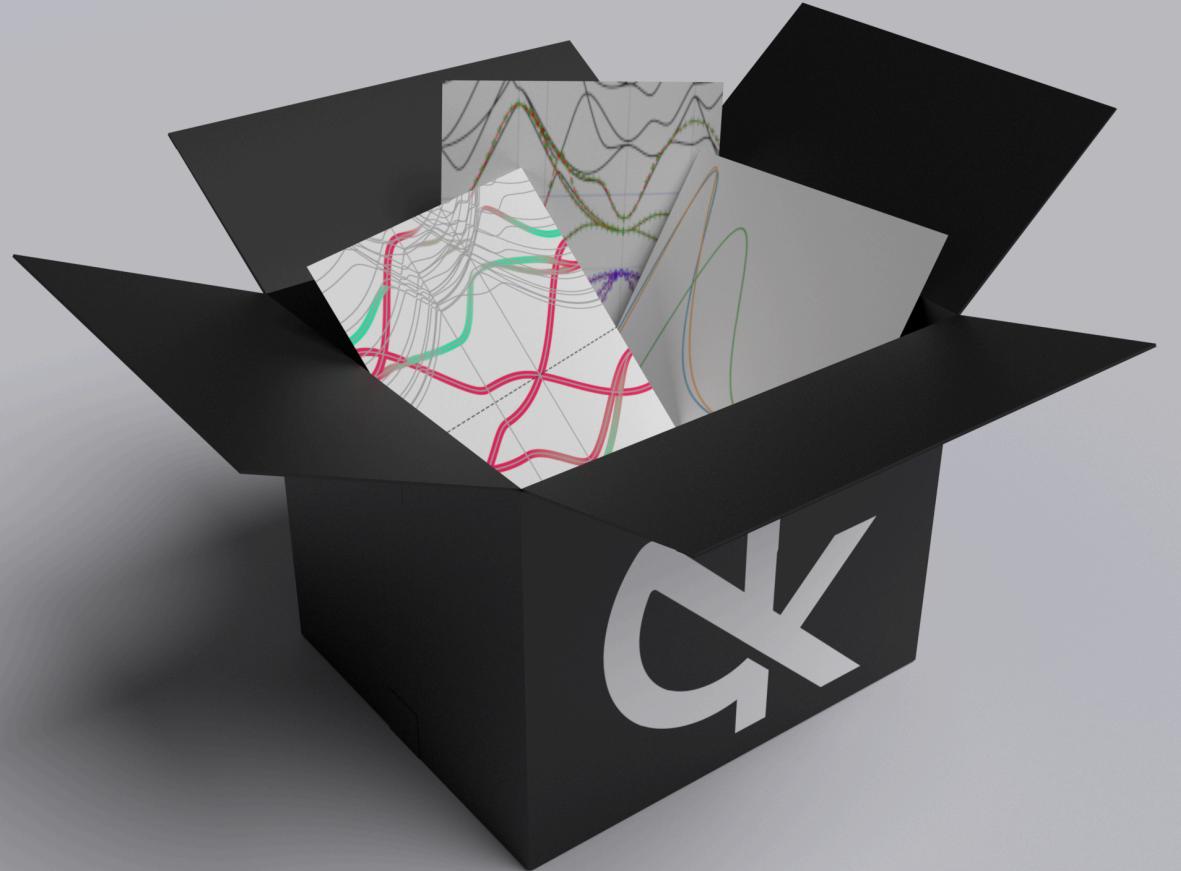
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Solve the BSE, using Koopmans eigenvalues in lieu of GW



silicon	indirect gap	direct gap	first excitonic peak	excitonic binding energy
<b>qKI+BSE</b>	1.12	3.31	3.42	0.09
<b>G<sub>0</sub>W<sub>0</sub>+BSE</b>	1.17	3.25	3.34	0.09

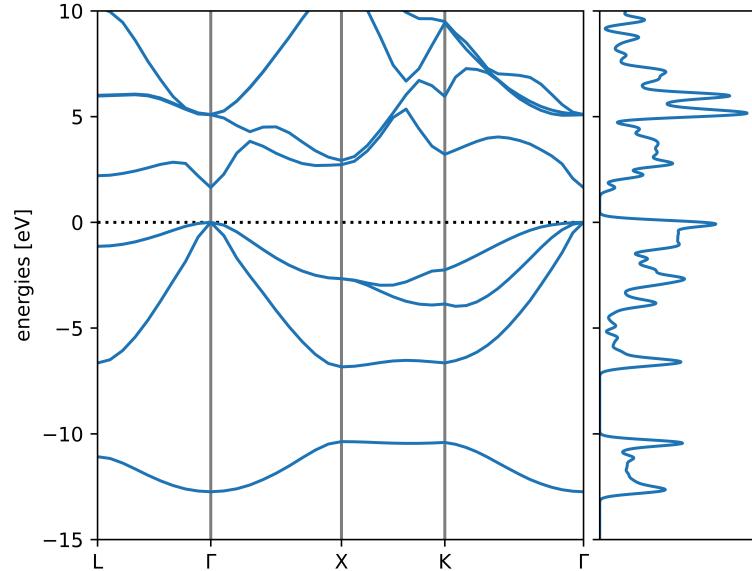
koopmans



Our goal:

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

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```



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



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

See [koopmans-functionals.org](http://koopmans-functionals.org)

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

# An alternative approach: DFT + $U$

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

<sup>1</sup>E. 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

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

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site and spin indices  
 local occupation matrix

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

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site and spin indices local occupation matrix

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

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

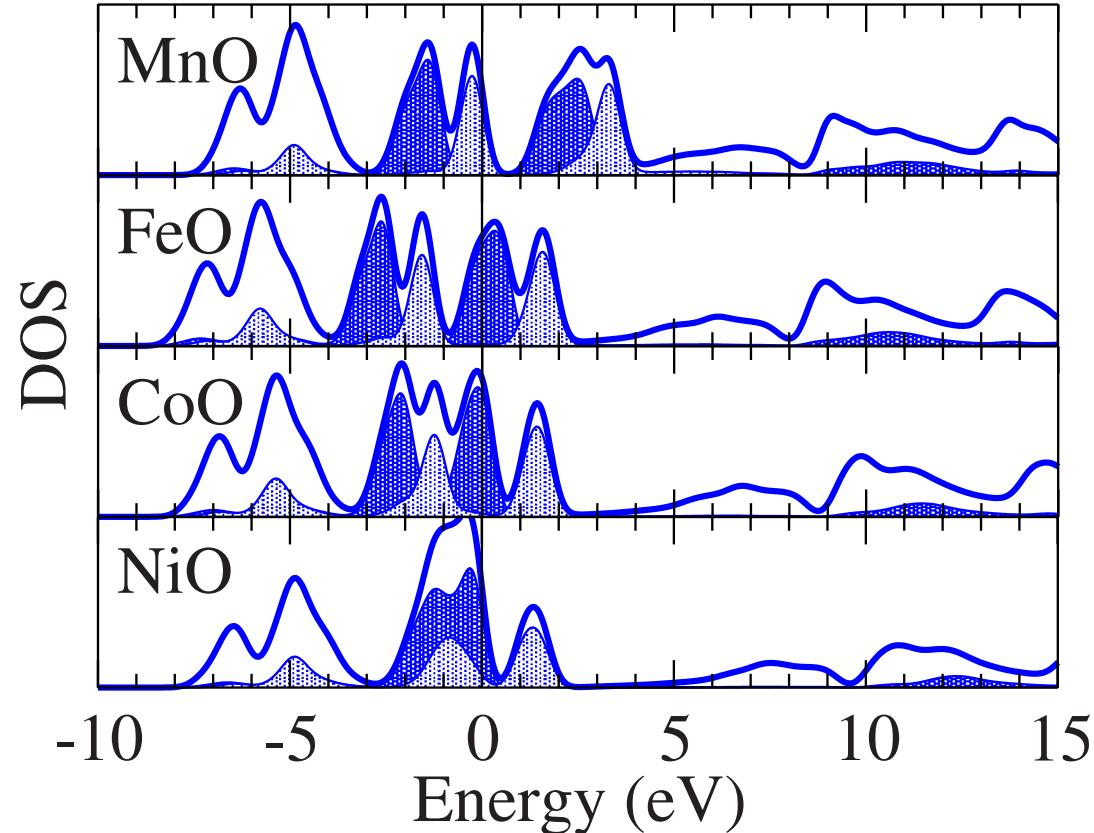
$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\mathbf{n}^{I\sigma} (1 - \mathbf{n}^{I\sigma})]$$

Hubbard parameter  
 site and spin indices  
 local occupation matrix

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

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

# The historical derivation of DFT+ $U$



<sup>1</sup>C. Rödl *et al.* Phys. Rev. B 79, 235114 (2009)

# The historical derivation of DFT+U

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.<sup>1</sup> 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

<sup>1</sup>R. G. Parr *et al.* (Oxford University Press, Oxford, 1989).

# The historical derivation of DFT+U

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

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**<sup>1</sup> 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  $\sigma_{\min}$  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**

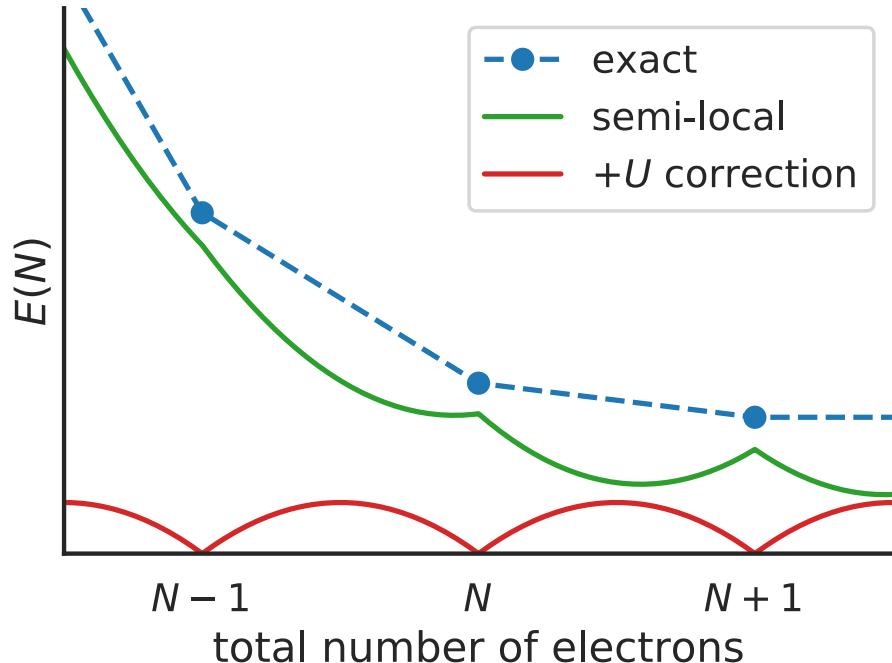
$$E_U = E_{\text{Hub}} - E_{\text{DC}} = \sum_{I\sigma} \frac{U_{\text{eff}}^I}{2} \text{Tr}(n^{I\sigma}(1 - n^{I\sigma})), \quad (9)$$

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

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

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

# The modern interpretation

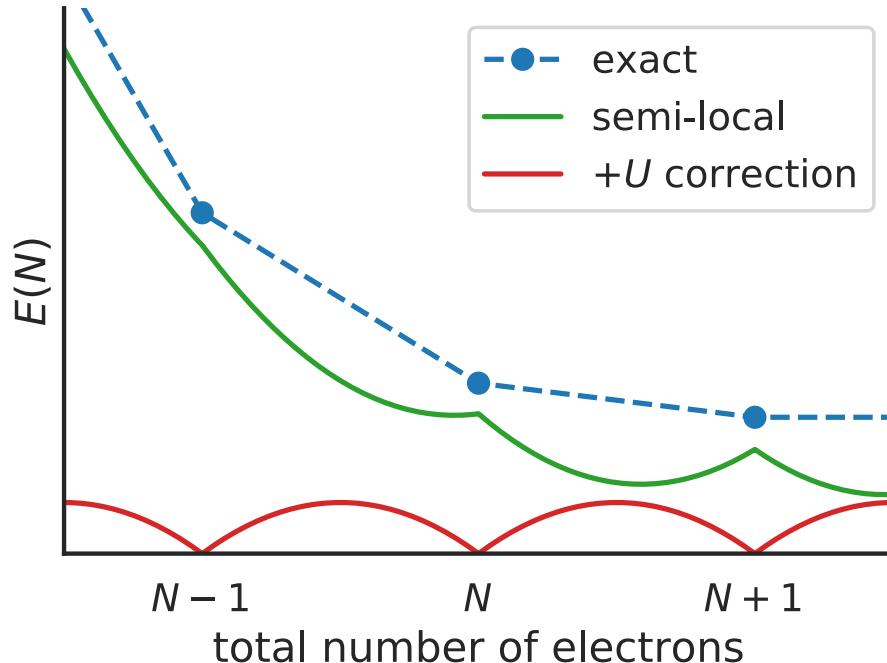


In a basis such that  $n_{ij}^{I\sigma} = \lambda_i^{I\sigma} \delta_{ij}$ ,

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

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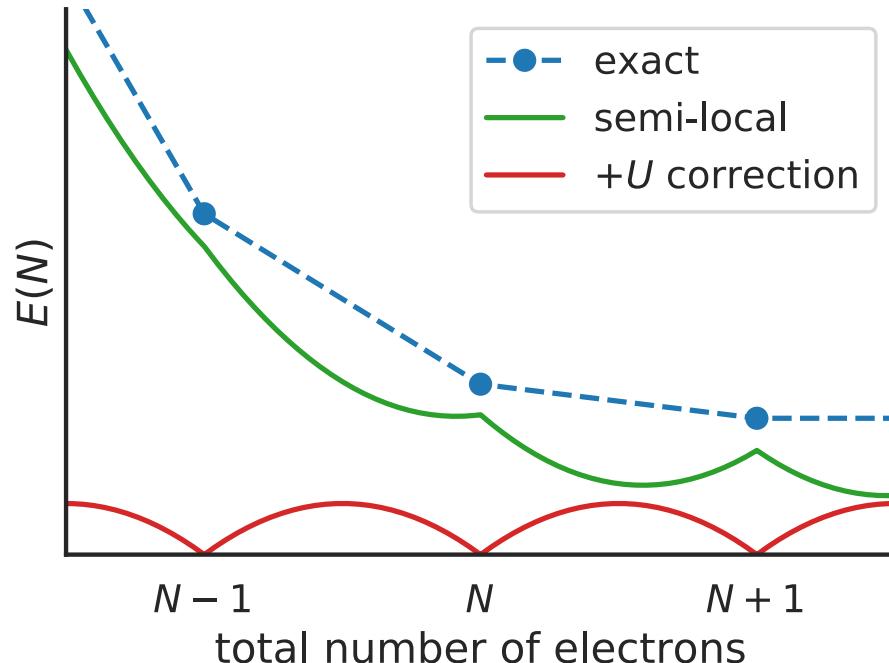
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$U$  can be measured by linear response<sup>1</sup> –  
**critical for predictive calculations**

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

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

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LR treats them together

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

Edward B. Linscott,<sup>1,\*</sup> Daniel J. Cole,<sup>2</sup> Michael C. Payne,<sup>1</sup> and David D. O'Regan<sup>3,†</sup>

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

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

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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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→

$$f_{II}^{\sigma\sigma'} \xrightarrow{?} U^{I\sigma}$$

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This is easy with spin-resolved LR:  $\frac{d^2 E_{\text{Hxc}}}{dn^2} \Big|_{\mu} = \frac{1}{4}(f^{\uparrow\uparrow} + f^{\downarrow\downarrow} + f^{\uparrow\downarrow} + f^{\downarrow\uparrow})$

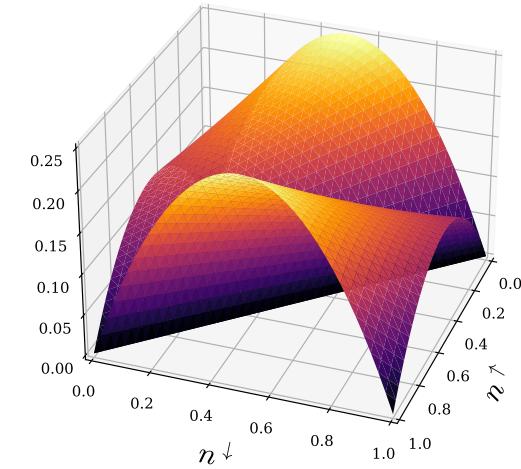
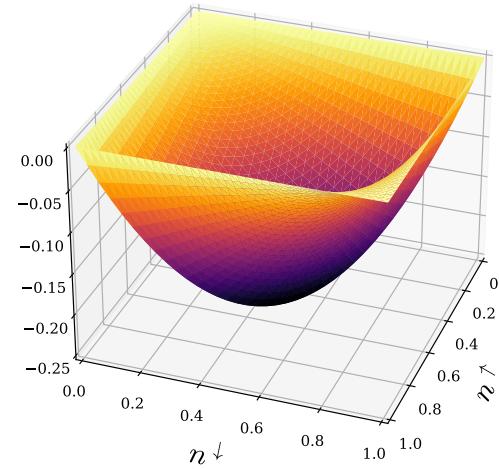
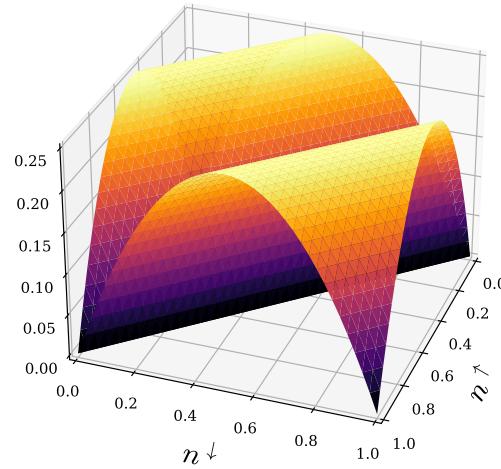
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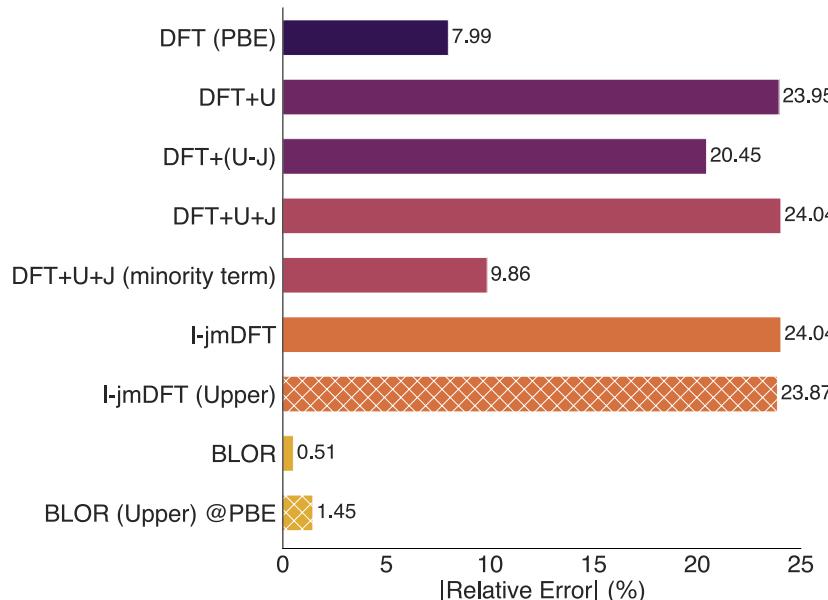
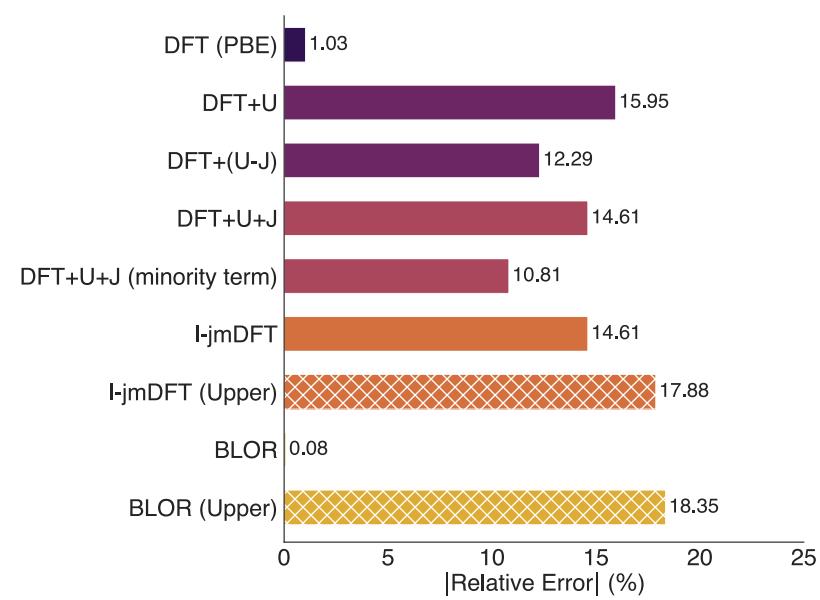
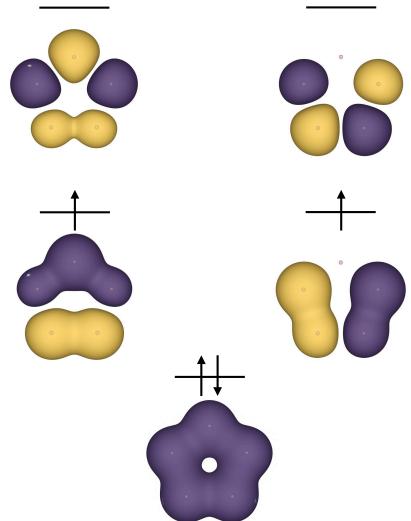
- ability to pursue more flexible, tailored corrections



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

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

stretched  $\text{H}_2$ stretched  $\text{H}_5^+$ 

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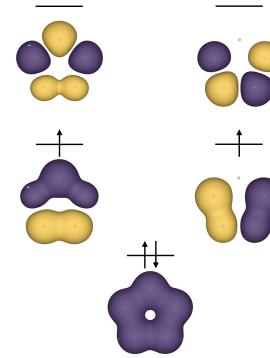
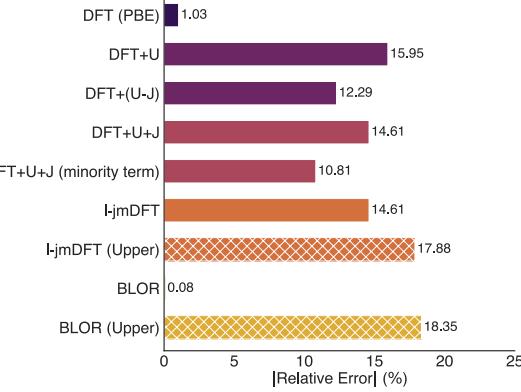
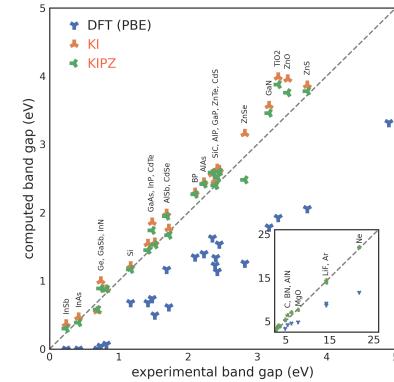
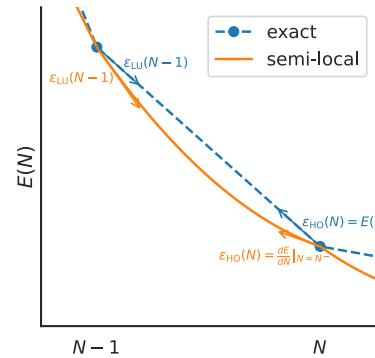
# Spin-resolved LR used in Materials Project!



<sup>1</sup>G. C. Moore et al. Phys. Rev. Mater. 8, 14409 (2024)

# Summary

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



# Acknowledgements



David  
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Stojkovic



Junfeng Qiao



Yannick  
Schubert

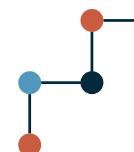


Nicola Marzari

... and many  
others!



Engineering and  
Physical Sciences  
Research Council



**Swiss National  
Science Foundation**

MARVEL



# Thank you!

*these slides are available at  [elinscott-talks/psi\\_quantum\\_presentation](https://github.com/elinscott-talks/psi_quantum_presentation)*

spare slides

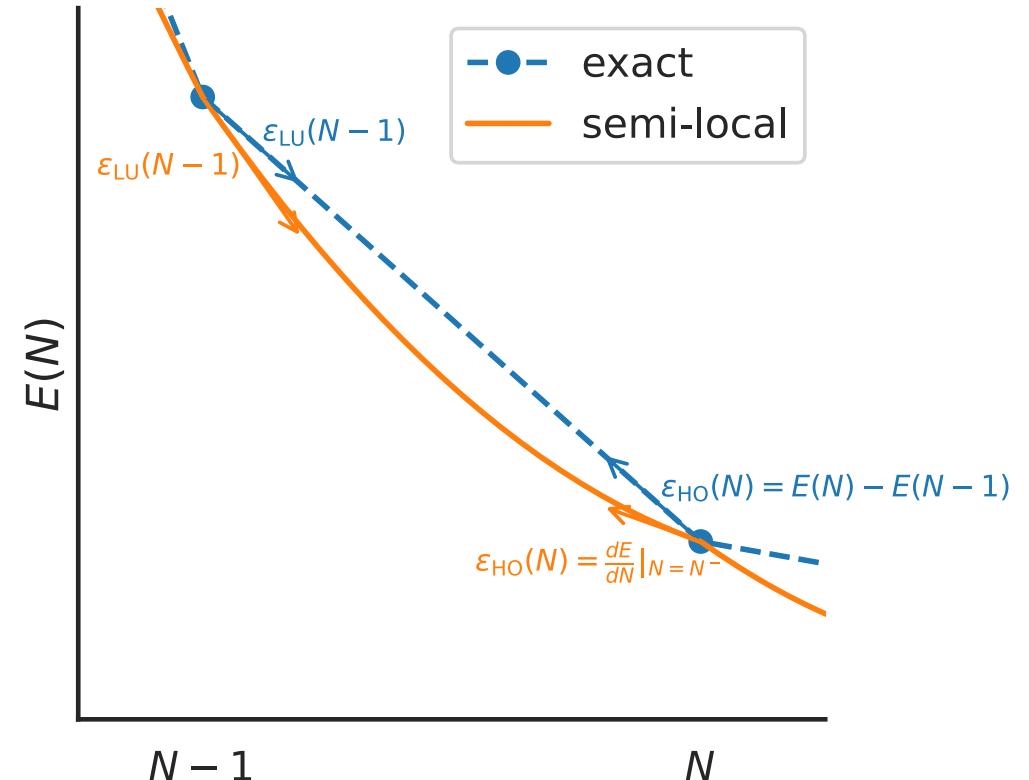
# Imposing generalised piecewise linearity

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  $\Delta E$  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

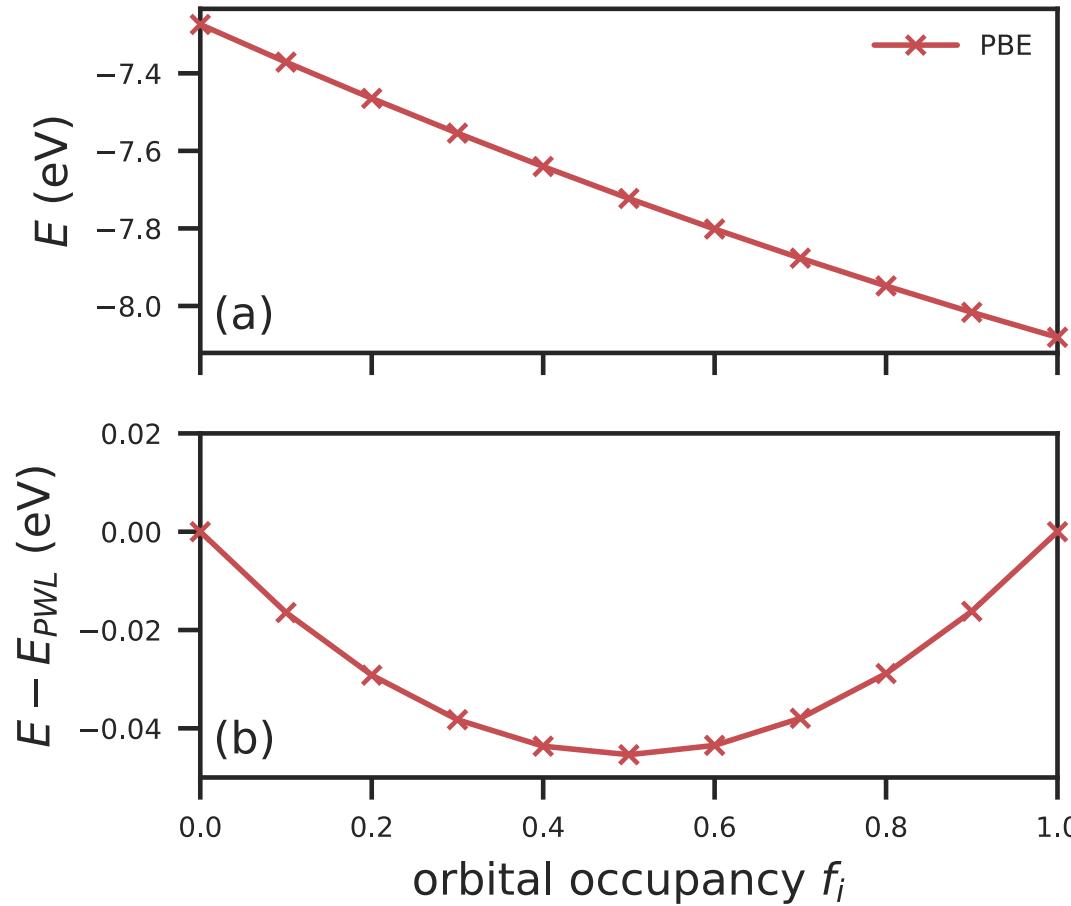
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 &= E^{\text{DFT}}[\rho] + \sum_i \left\{ - (E^{\text{DFT}}[\rho] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) + f_i (E^{\text{DFT}}[\rho^{f_i \rightarrow 1}] - E^{\text{DFT}}[\rho^{f_i \rightarrow 0}]) \right\}
 \end{aligned}$$

# Electronic screening via parameters

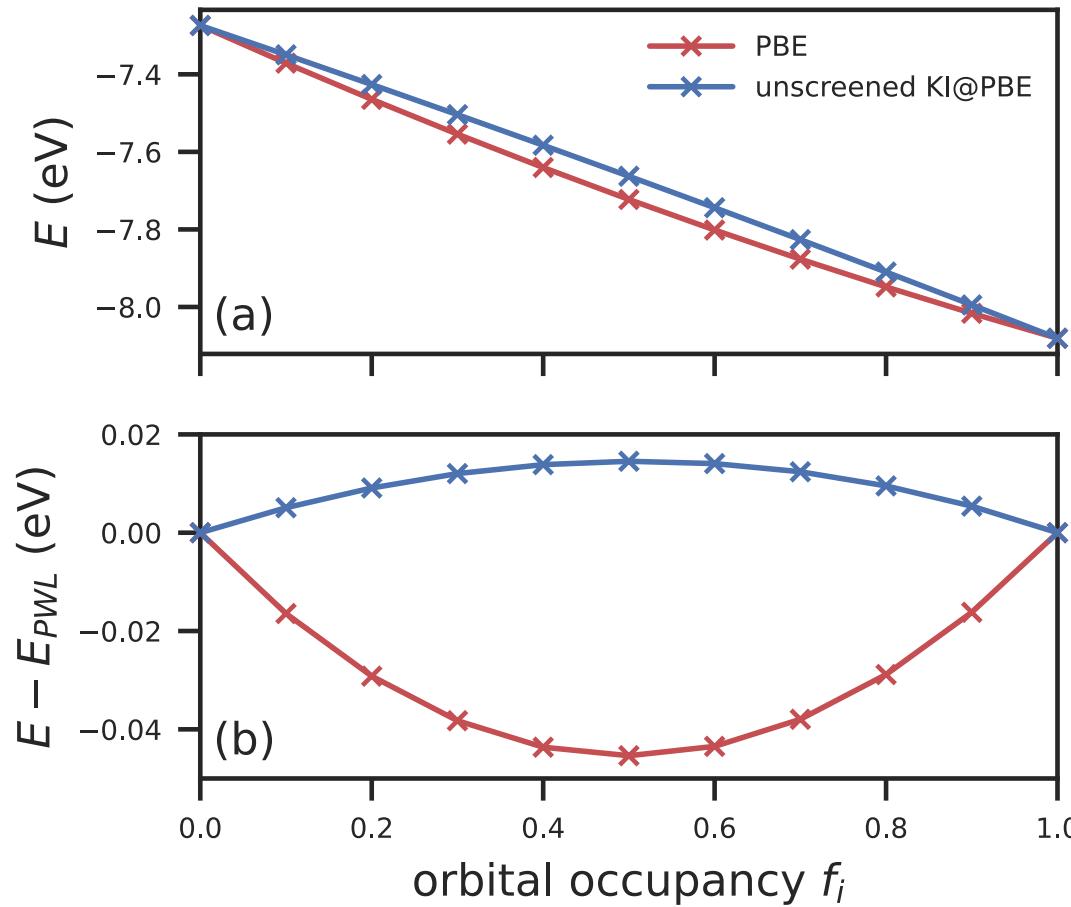
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 \end{aligned}$$

cannot evaluate directly      cannot evaluate directly      cannot evaluate directly

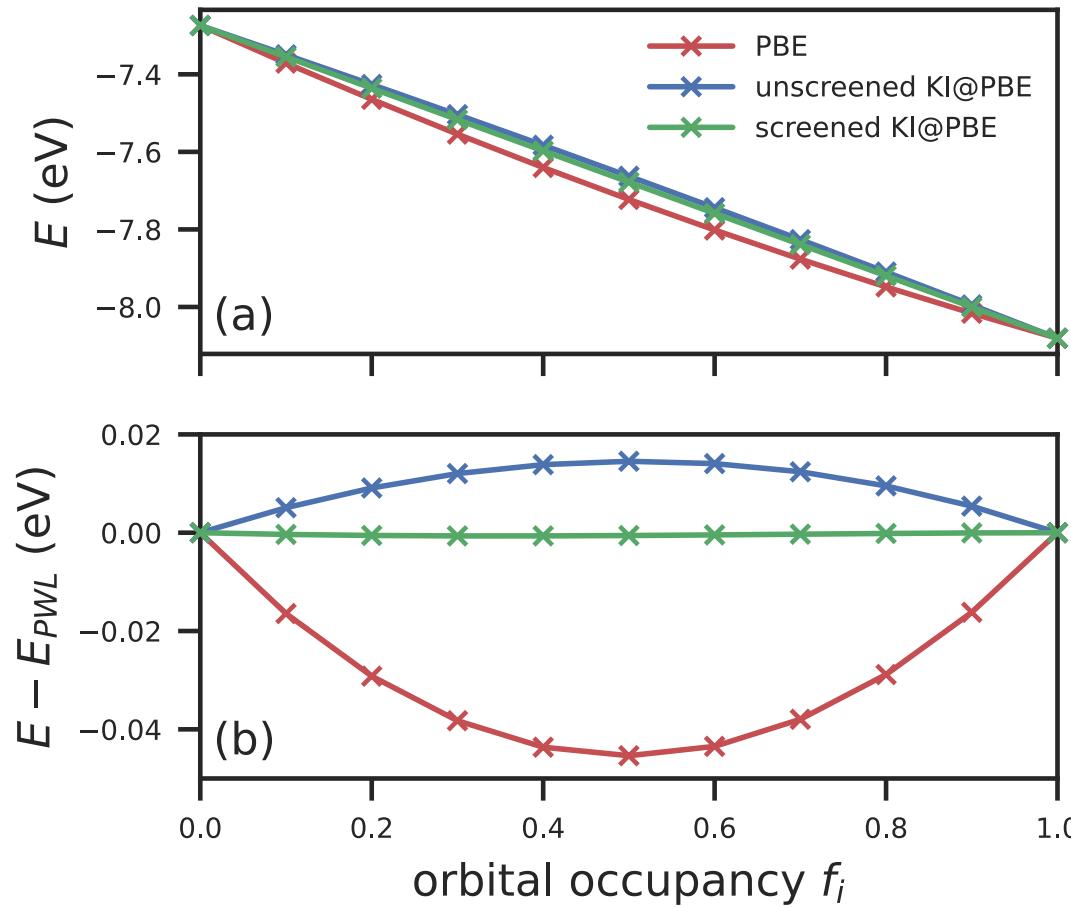
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$$E_{\alpha}^{\text{KI}}[\rho, \{\rho_i\}] \approx E^{\text{DFT}}[\rho]$$

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uses frozen orbitals                    uses frozen orbitals                    uses frozen orbitals

# Electronic screening via parameters

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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!

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

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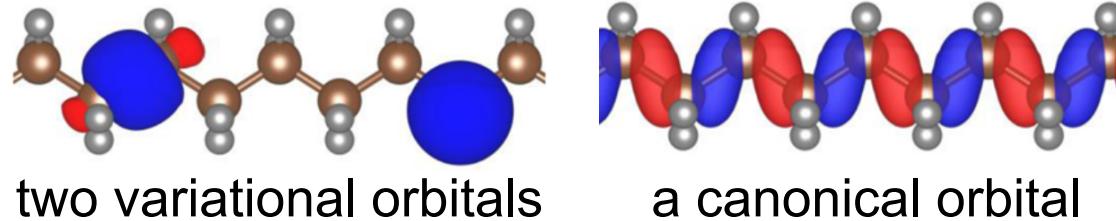
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- loss of unitary invariance<sup>1</sup>



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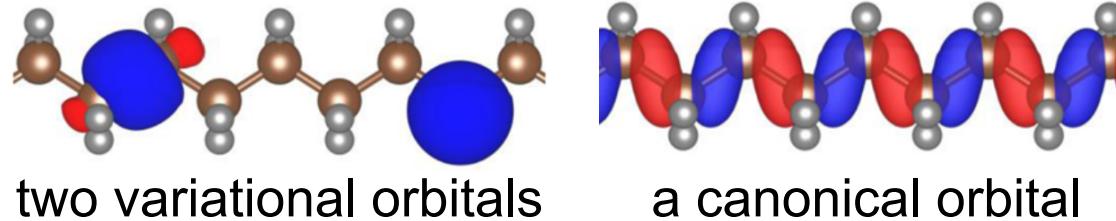
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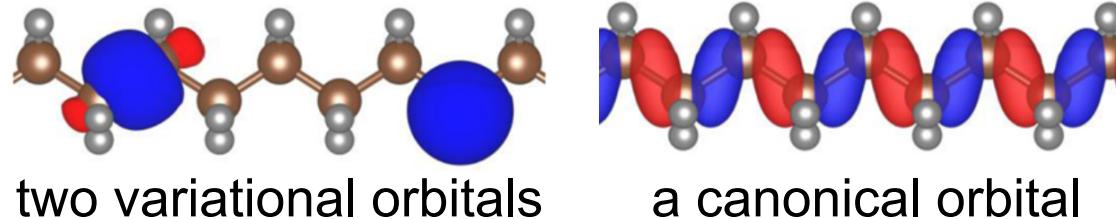
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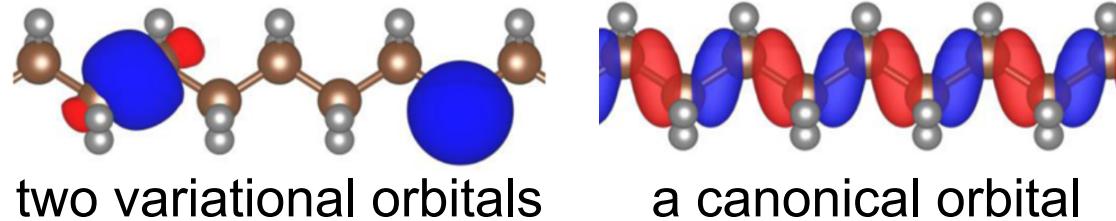
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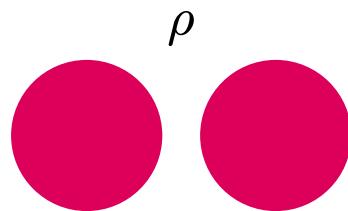
- we can use MLWFs<sup>2</sup>
- we know  $\hat{H}|\varphi_i\rangle$  but not  $\hat{H}$
- a natural generalisation of DFT towards spectral functional theory<sup>3</sup>

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

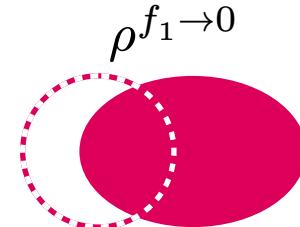
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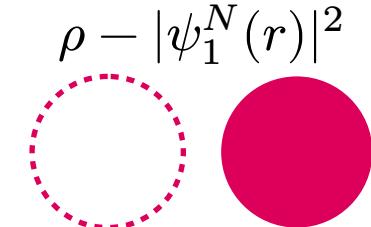
# Frozen orbital approximation



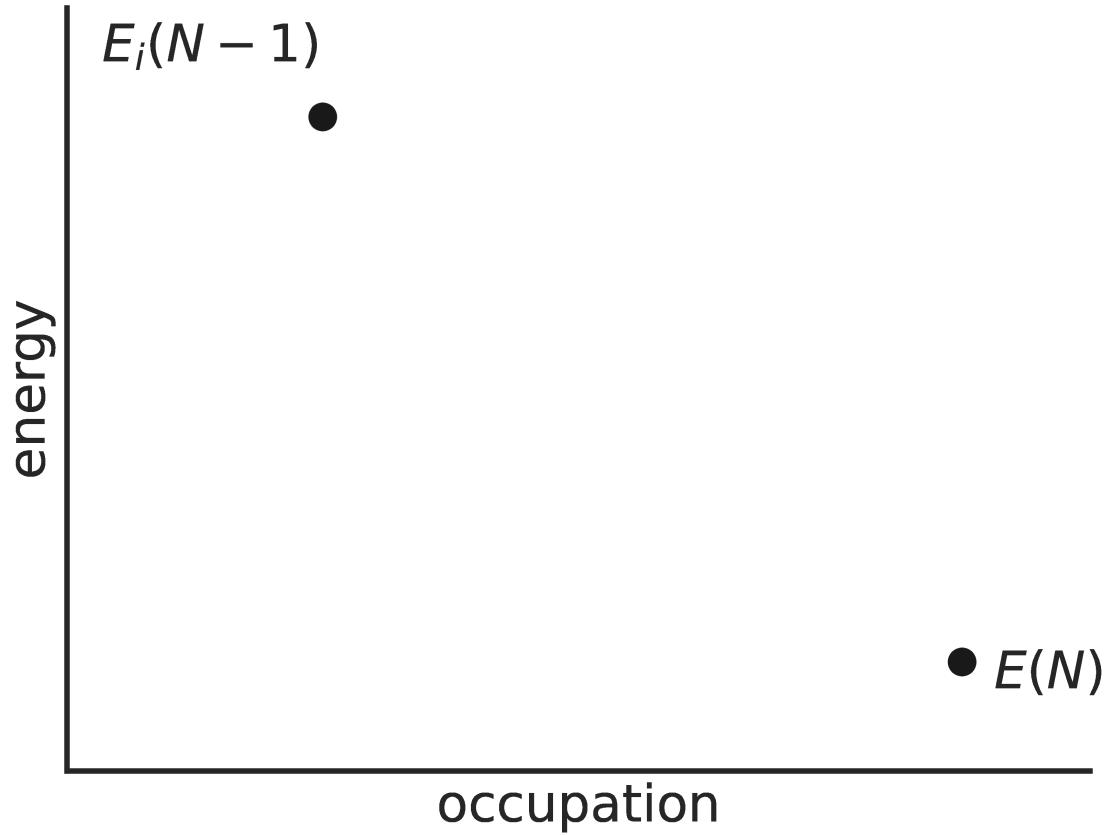
2-electron solution

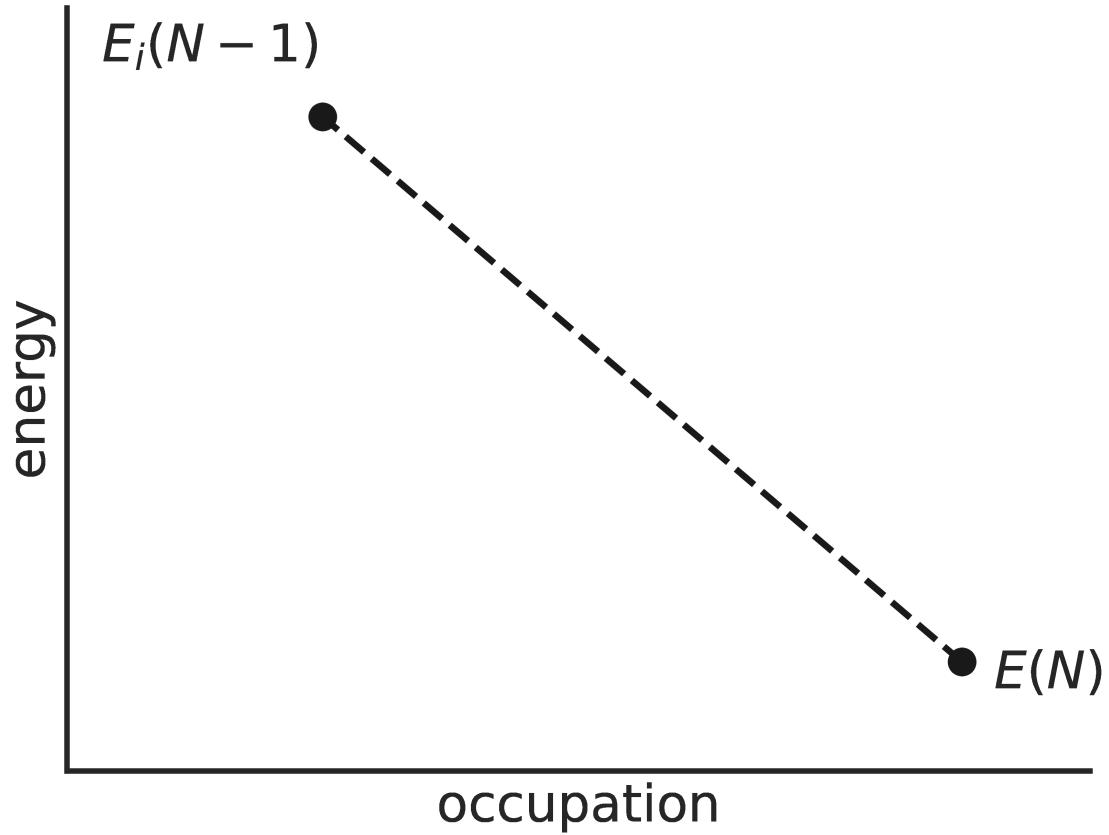


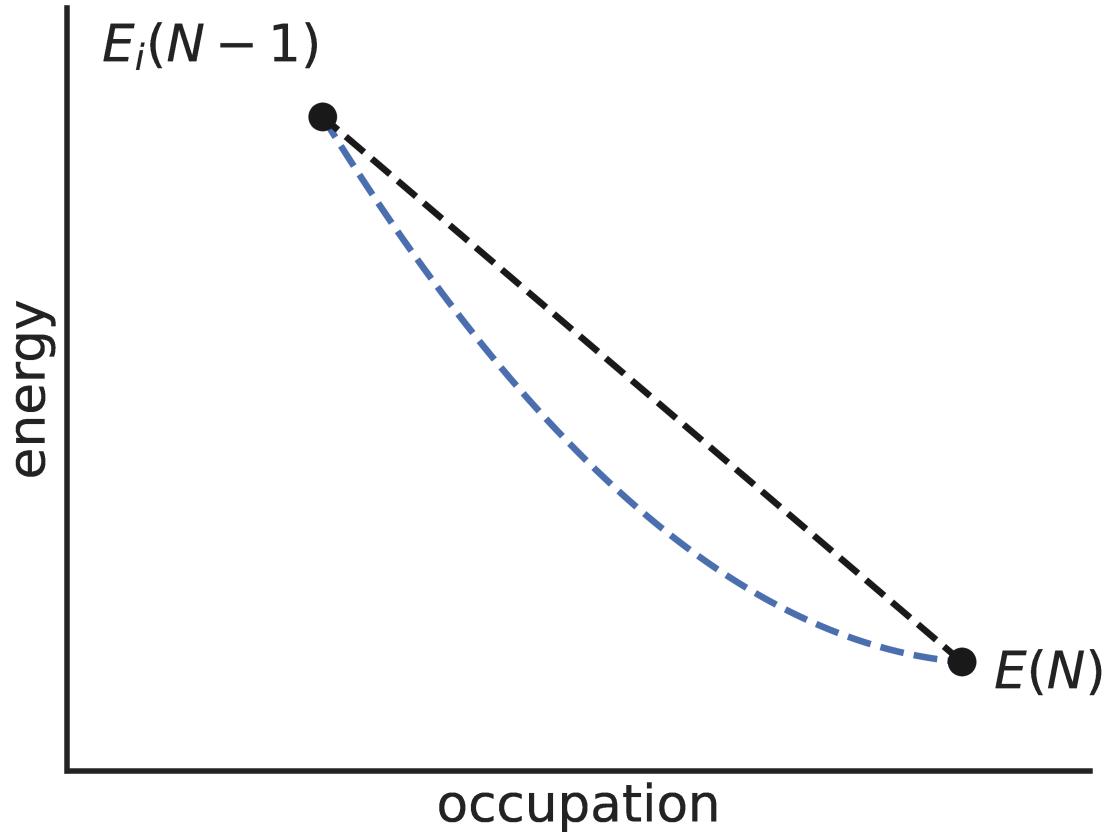
what we'd like to evaluate

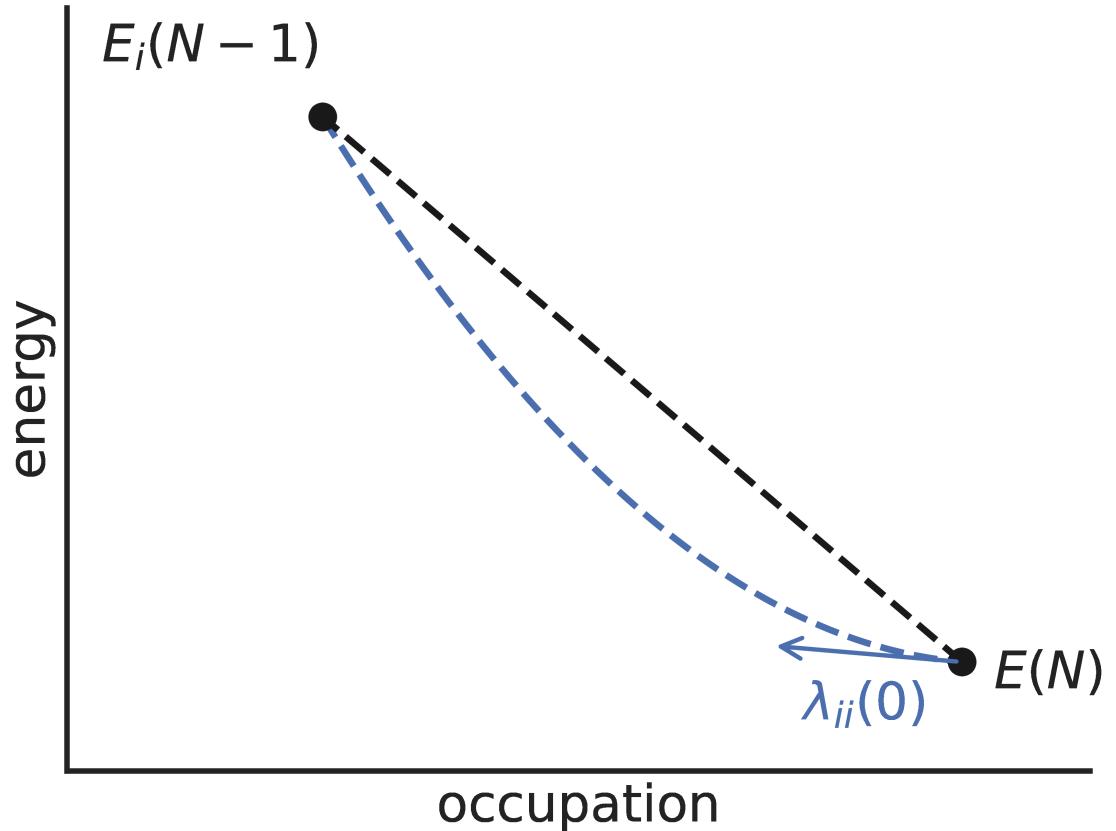


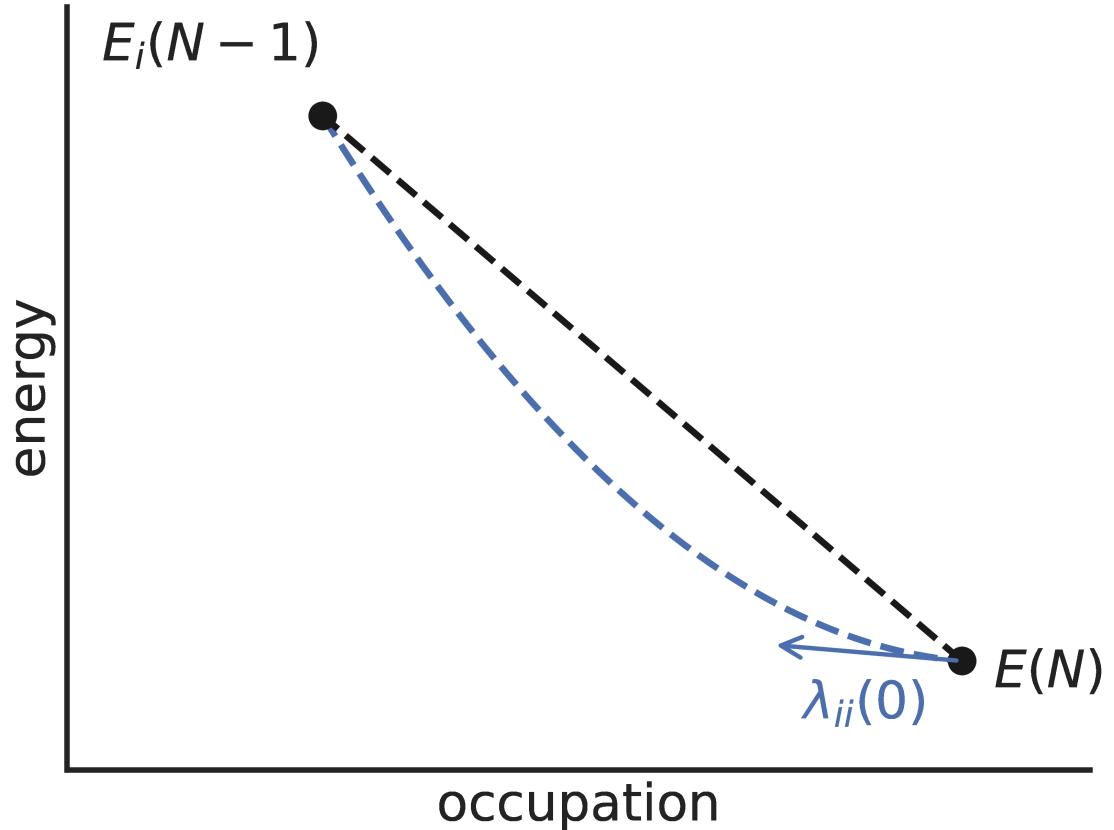
what we can quickly evaluate

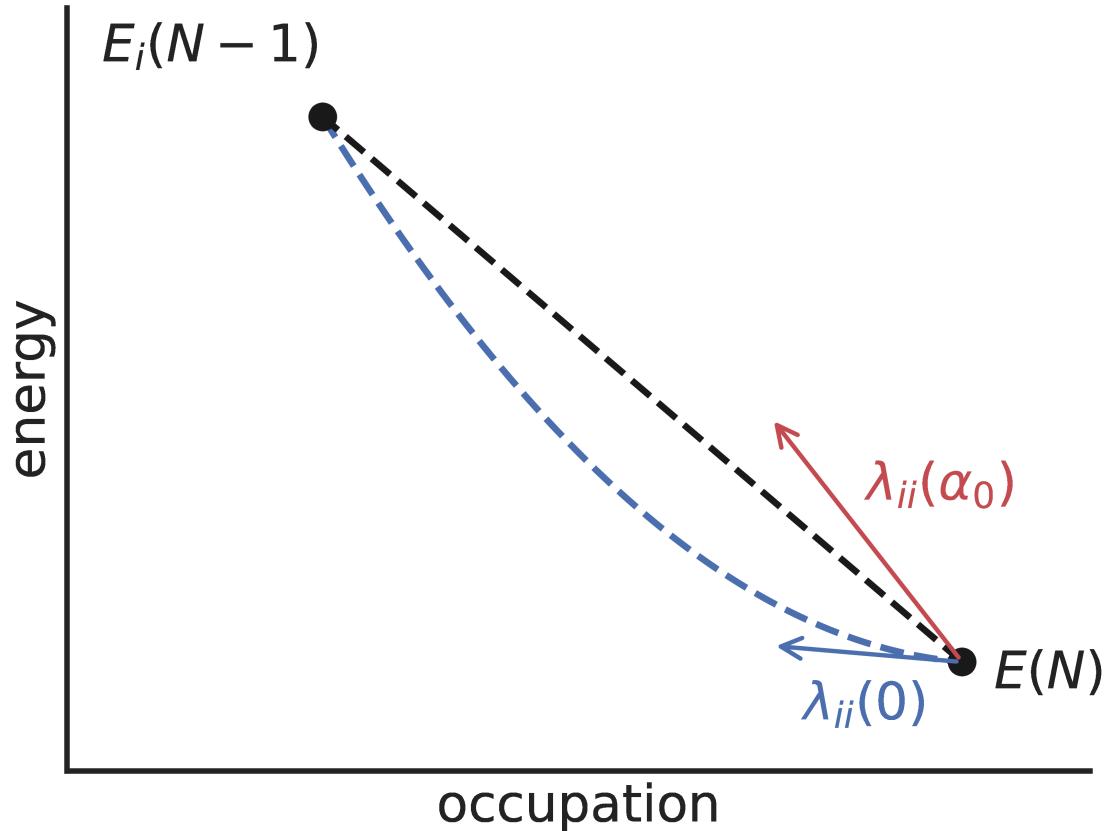


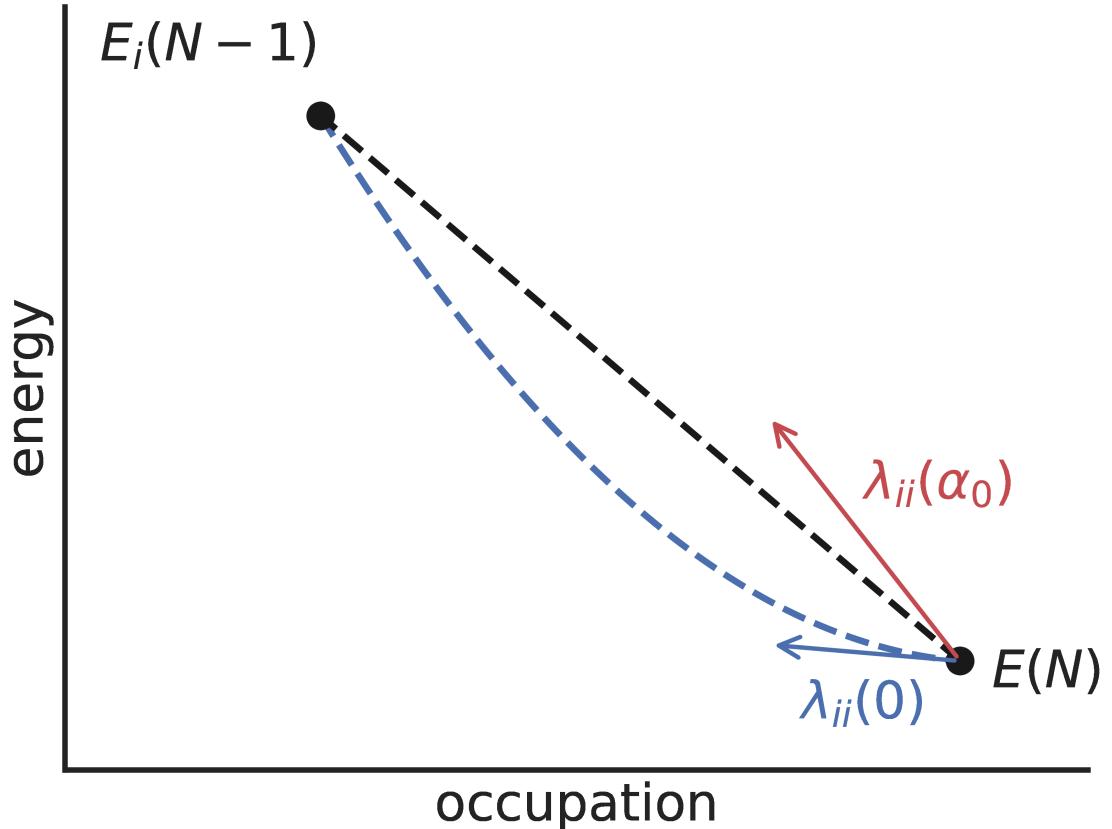








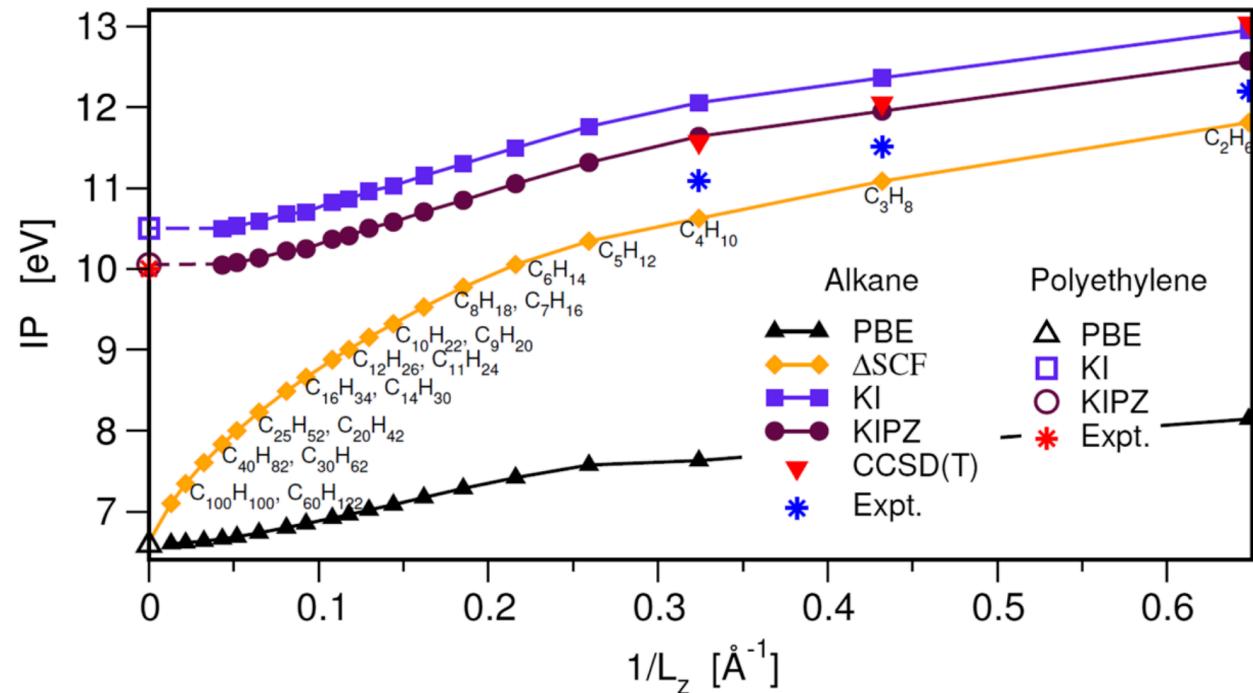




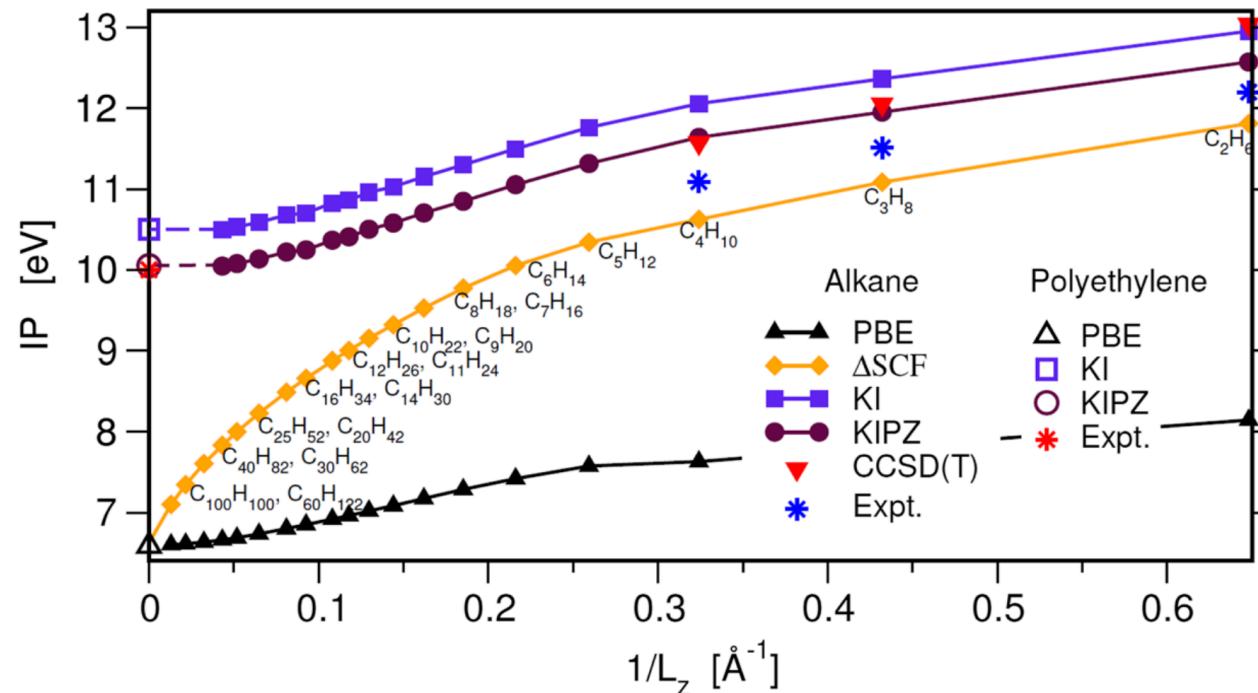
$$\alpha_i = \alpha_i^0 \frac{\Delta E_i - \lambda_{ii}(0)}{\lambda_{ii}(\alpha^0) - \lambda_{ii}(0)}$$

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

# Issues with extended systems



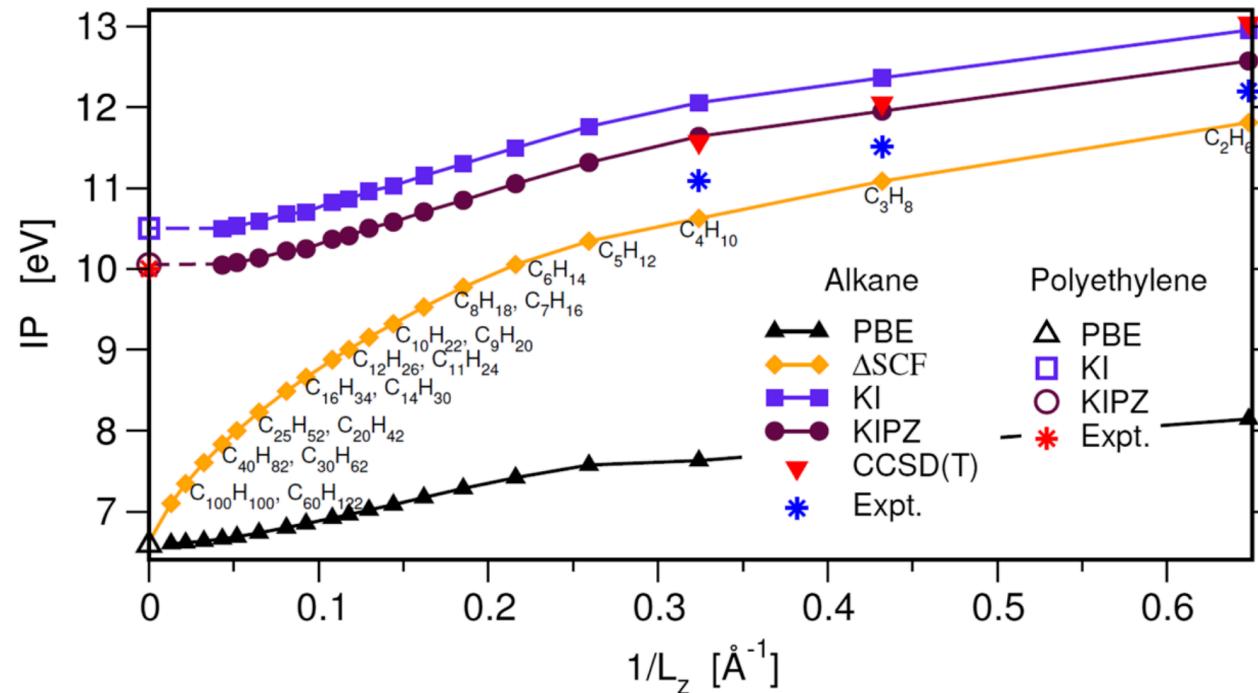
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Two options: 1. use a more advanced functional

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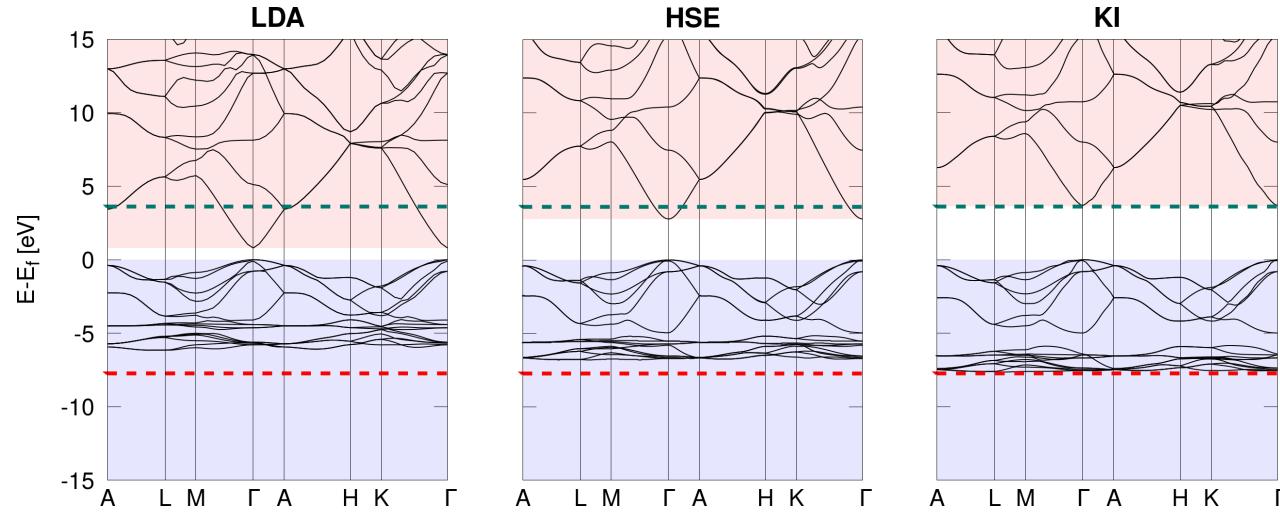


Two options: 1. use a more advanced functional, or 2. stay in the “safe” region

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

# Issues with extended systems

ZnO<sup>1</sup>

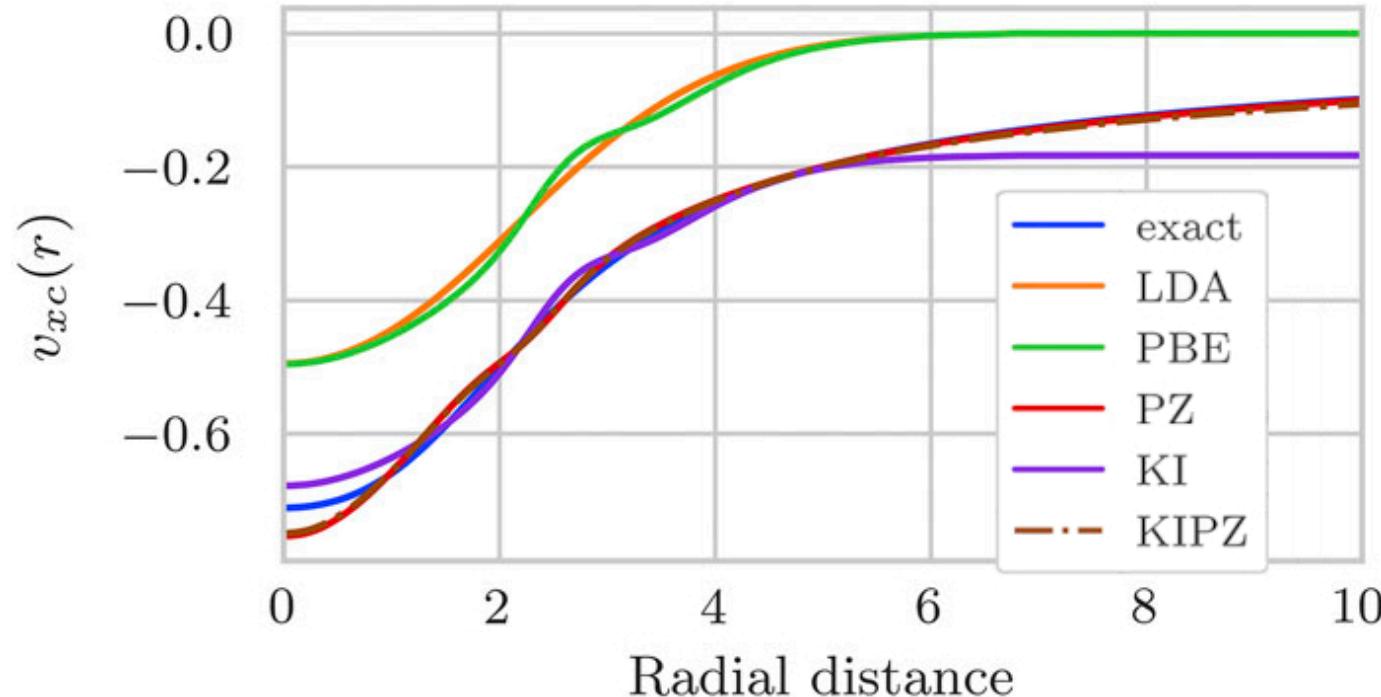


	LDA	HSE	$GW_0$	$scG\tilde{W}$	KI	exp
$E_{gap}$	0.79	2.79	3.0	3.2	<b>3.68</b>	3.60
$\langle \varepsilon_d \rangle$	-5.1	-6.1	-6.4	-6.7	<b>-6.93</b>	-7.5 to -8.81
$\Delta$	4.15				<b>4.99</b>	5.3

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

# Model systems

## Hooke's atom<sup>1</sup>



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

# Non-collinear spin

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

<sup>1</sup>A. 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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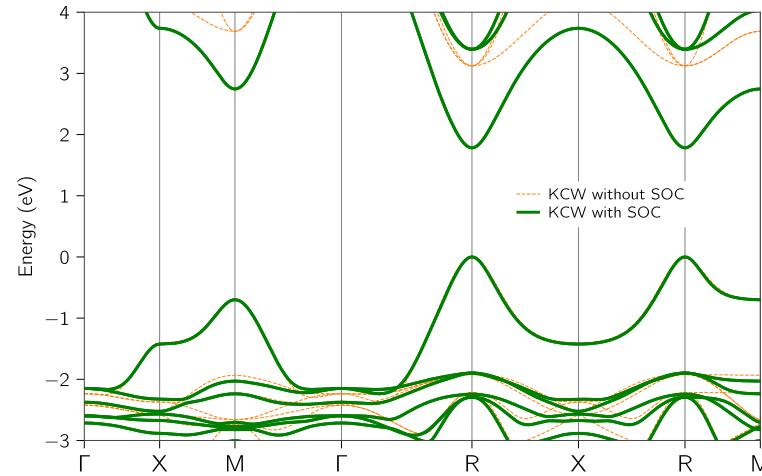
↓

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

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

# Non-collinear spin

CsPbBr<sub>3</sub>



	LDA	HSE	$G_0W_0$	$scG\tilde{W}$	KI	exp
<b>with SOC</b>	0.18	0.78	0.94	1.53	<b>1.78</b>	1.85
without SOC	1.40	2.09	2.56	3.15	3.12	

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

# Caveats

# Limitations

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

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- can break crystal point group symmetry

# Resonance with other efforts

- Wannier transition state method of Anisimov and Kozhevnikov<sup>1</sup>
- Optimally-tuned range-separated hybrid functionals of Kronik, Pasquarello, and others<sup>2</sup>
- Ensemble DFT of Kraisler and Kronik<sup>3</sup>
- Koopmans-Wannier method of Wang and co-workers<sup>4</sup>
- Dielectric-dependent hybrid functionals of Galli and co-workers<sup>5</sup>
- Scaling corrections of Yang and co-workers<sup>6</sup>

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

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

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

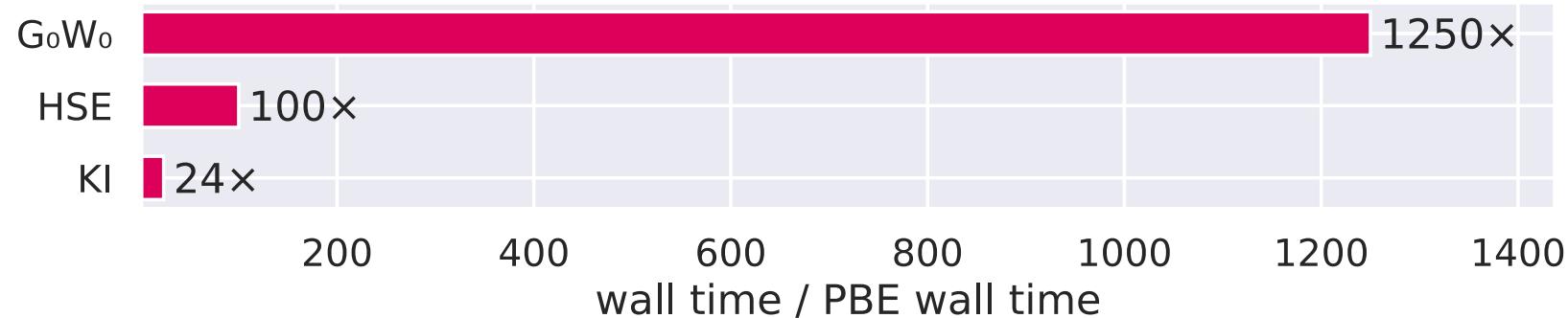
<sup>4</sup>J. Ma *et al.* *Sci. Rep.* 6, 24924 (2016)

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

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

# Computational cost and scaling

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The vast majority of the computational cost: determining screening parameters

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

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

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

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

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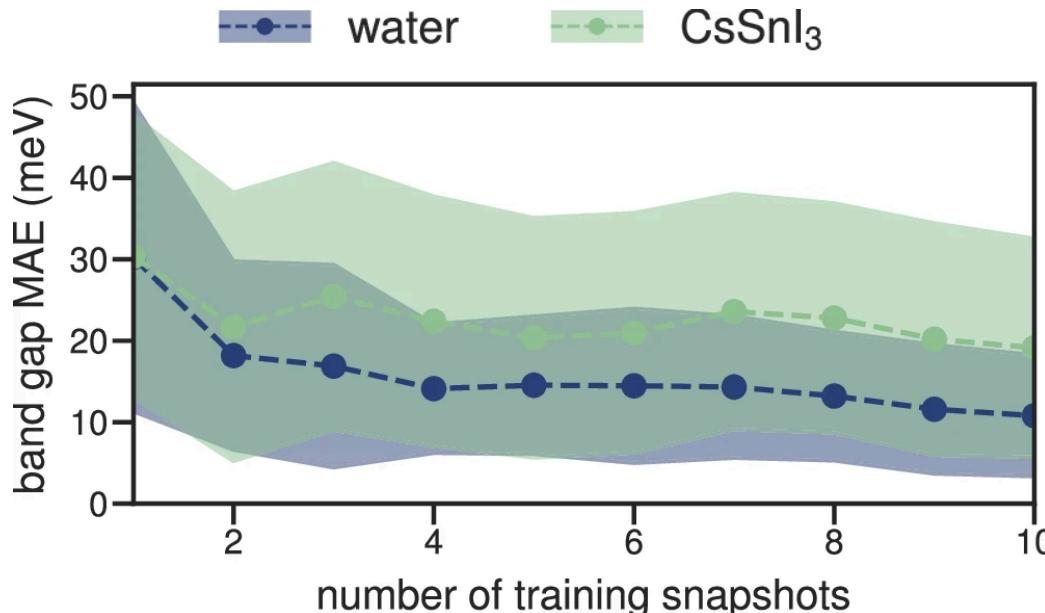
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  - DFPT<sup>2</sup>:  $\mathcal{O}(N_{\mathbf{k}}^2 N^3)$

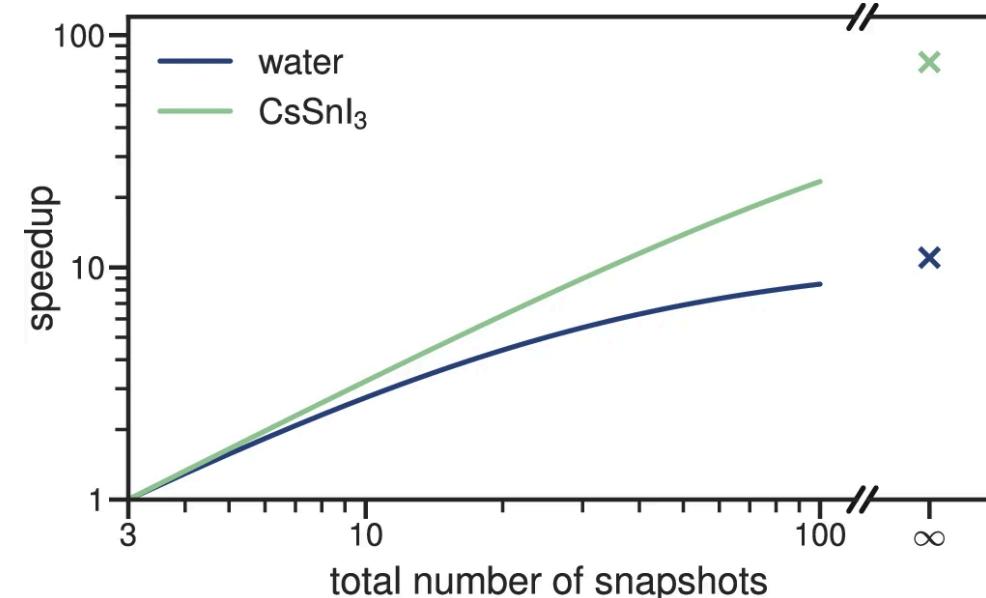
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# Machine-learned electronic screening



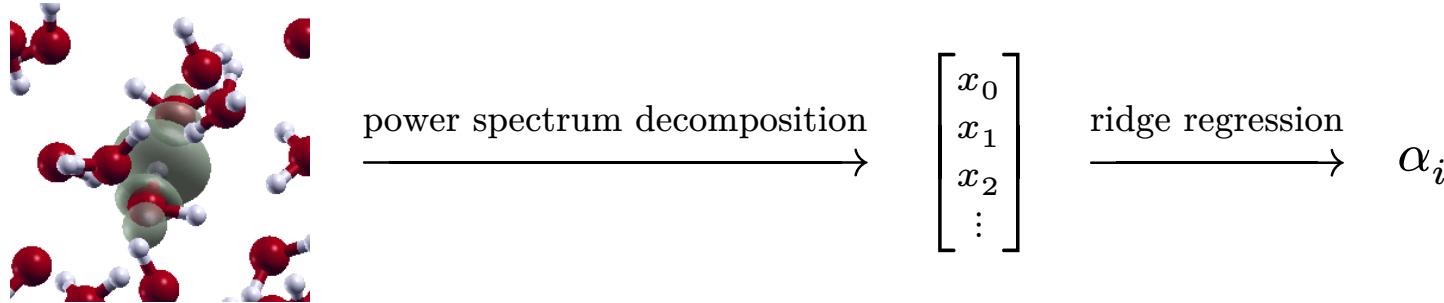
**accurate** to within  $\mathcal{O}(10 \text{ meV})$  cf. typical  
band gap accuracy of  $\mathcal{O}(100 \text{ meV})$



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

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

# Machine-learned electronic screening

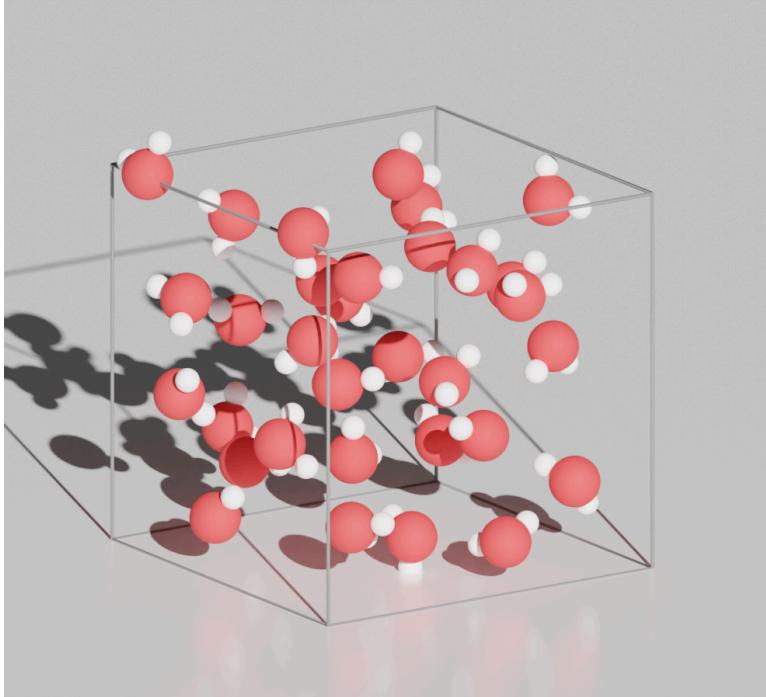


$$c_{nlm,k}^i = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) n^i(\mathbf{r} - \mathbf{R}^i)$$

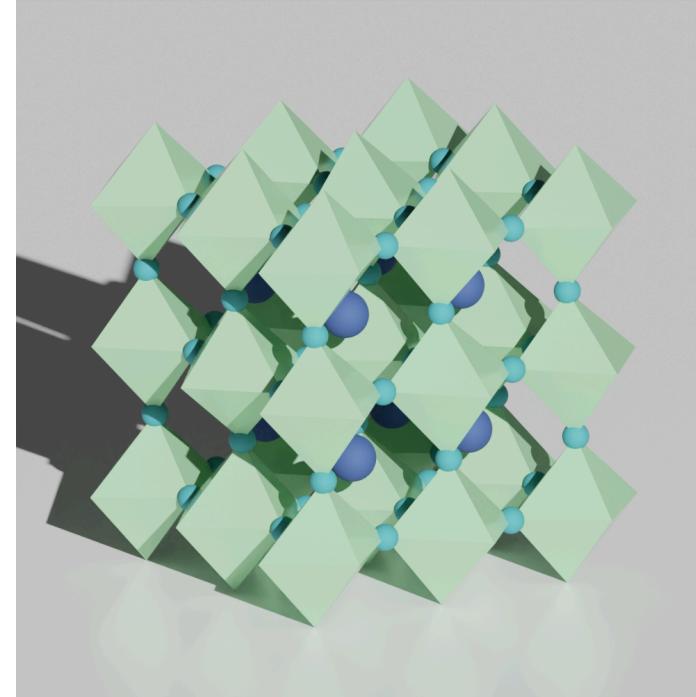
$$p_{n_1 n_2 l, k_1 k_2}^i = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{n_1 lm, k_1}^{i*} c_{n_2 lm, k_2}^i$$

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

# Machine-learned electronic screening



water

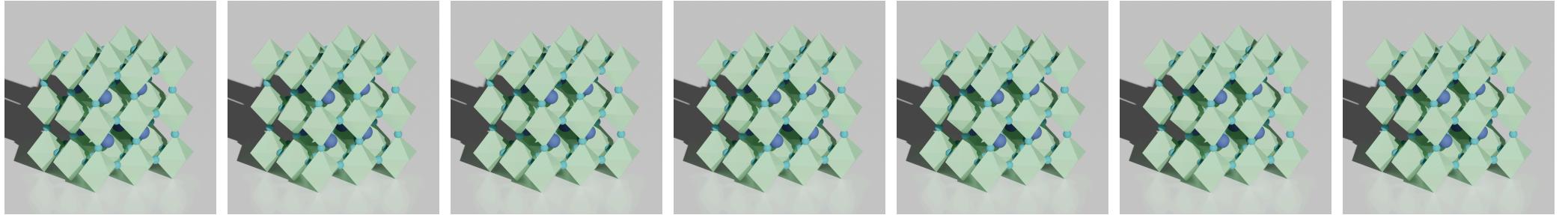


$\text{CsSnI}_3$

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

# Machine-learned electronic screening

The use-case

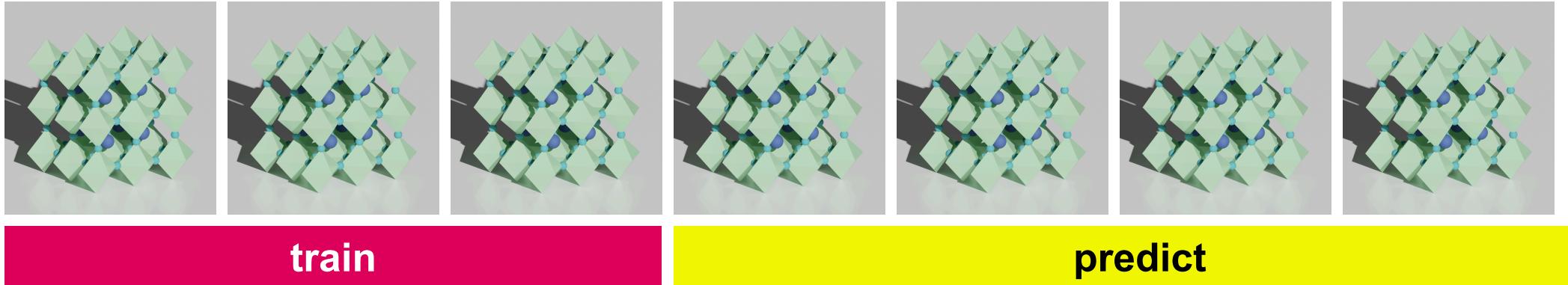


train

predict

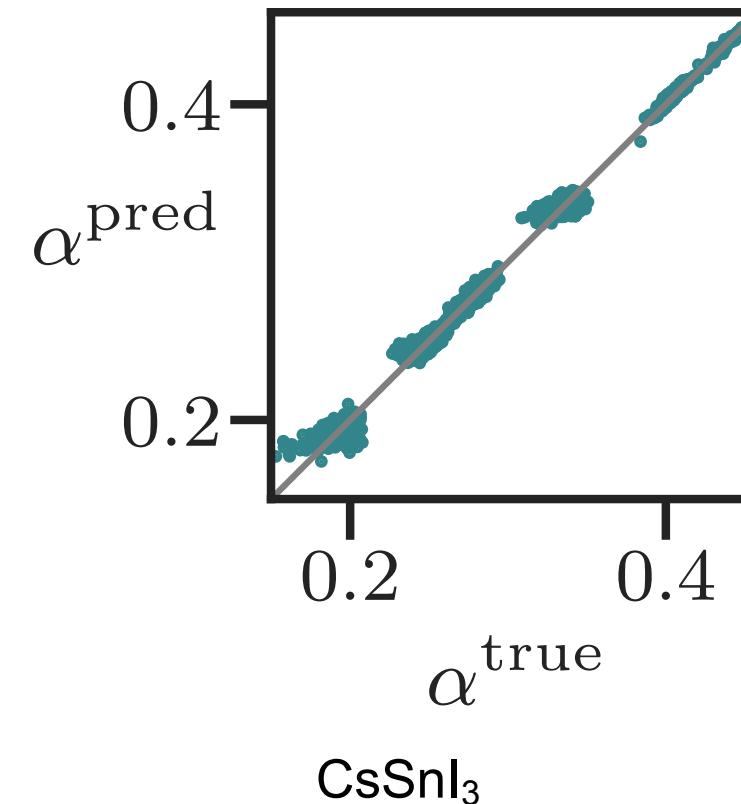
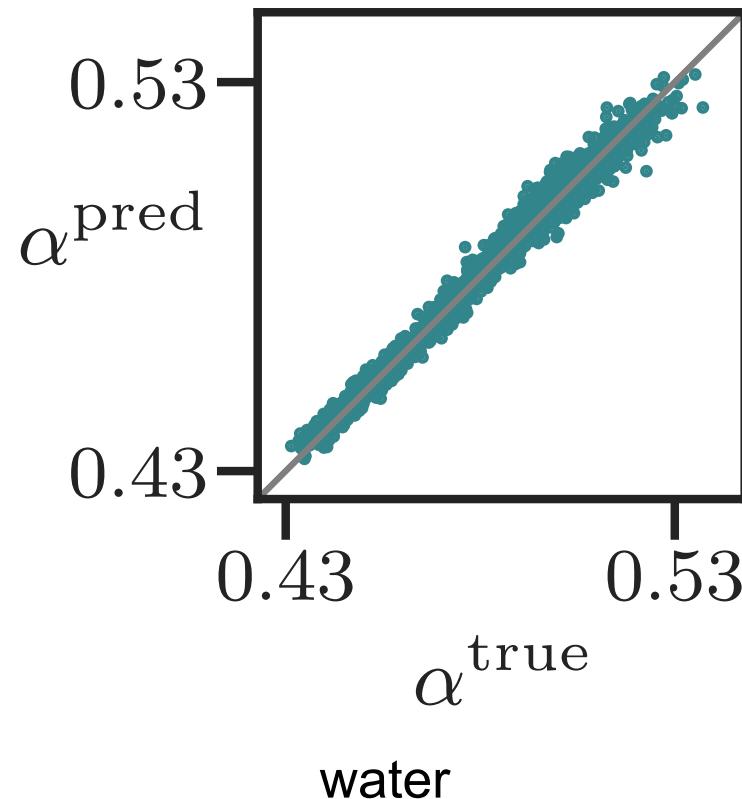
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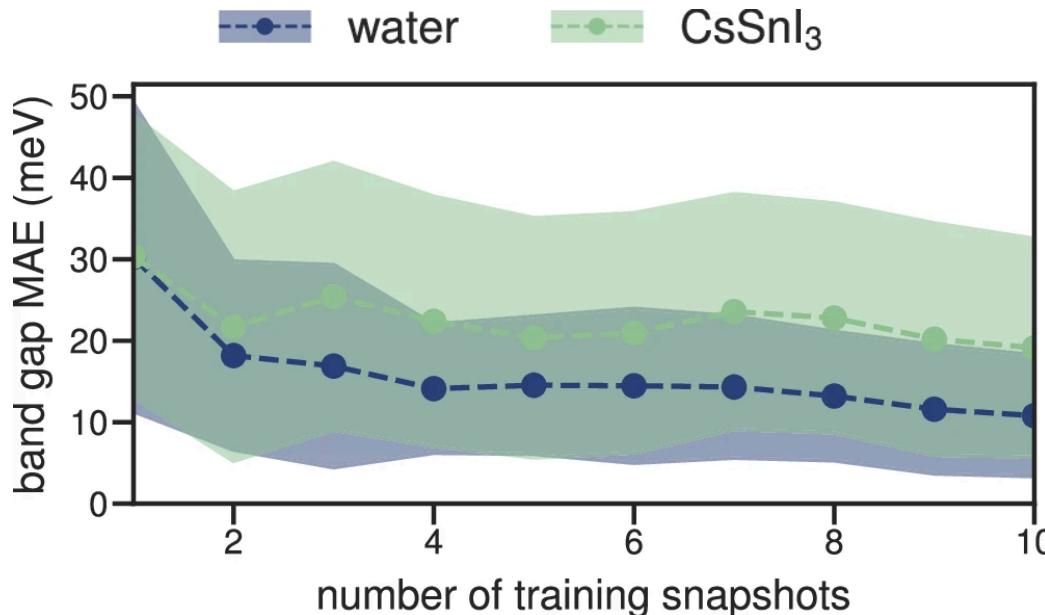
N.B. not a general model

# Machine-learned electronic screening

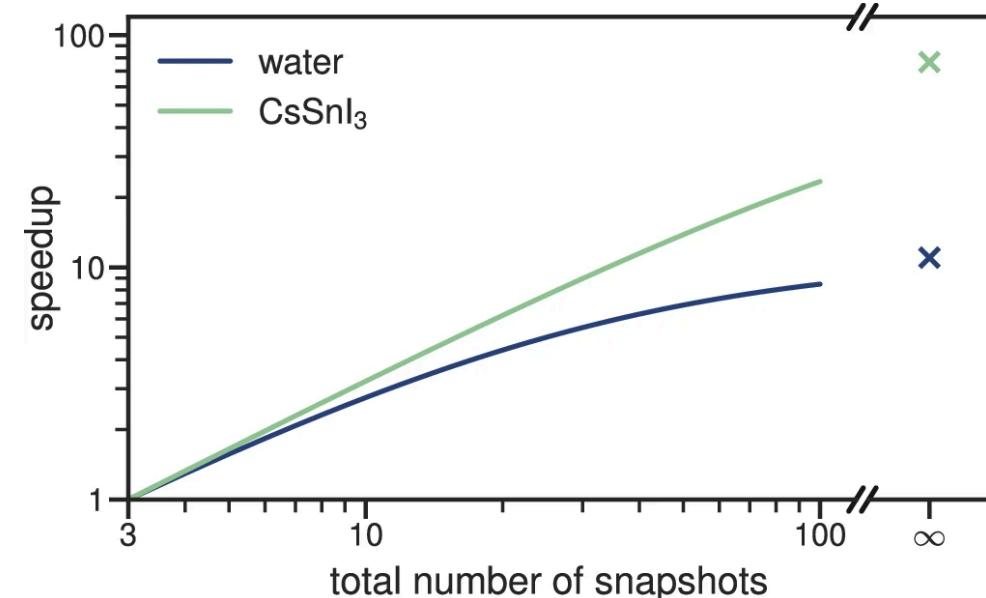


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# Machine-learned electronic screening



**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  $\mathcal{O}(100)$

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

# Taking advantage of symmetries

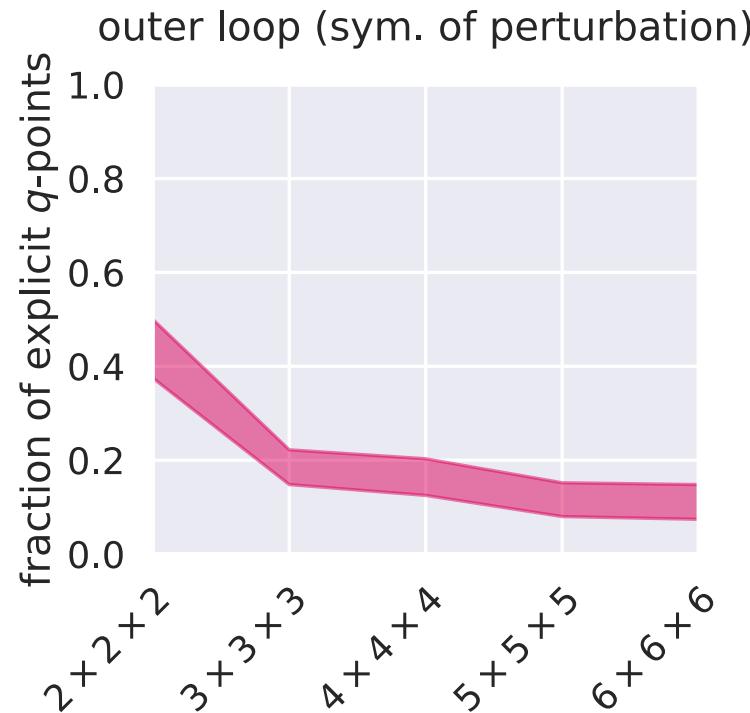
To compute screening parameters via DFPT...

```

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

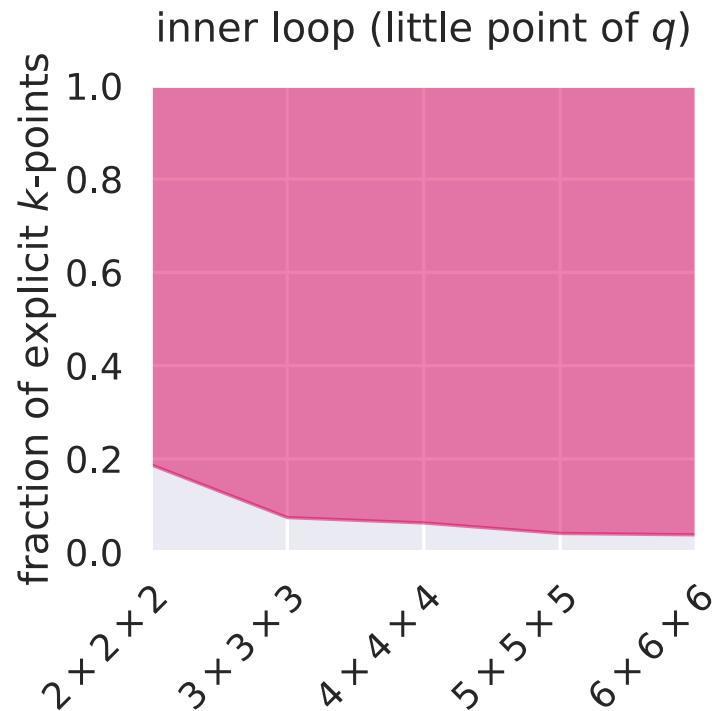
```

# Taking advantage of symmetries



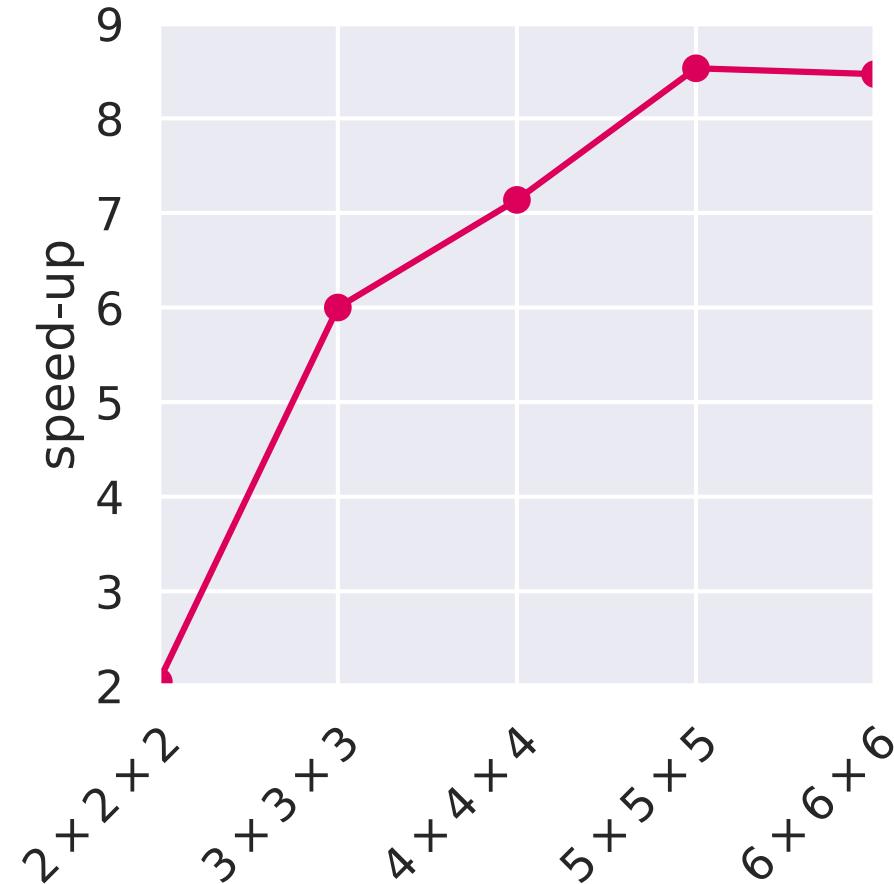
$q \in \text{BZ} \rightarrow q \in \text{IBZ}(n)$  (the symmetry of the perturbation; lower than that of the primitive cell)

# 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

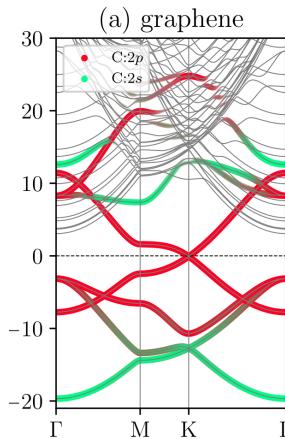
<sup>1</sup>J. Qiao *et al.* *npj Comput Mater* 9, 208 (2023)

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

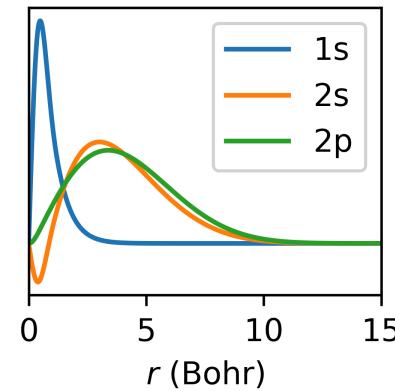
# Automated Wannierisation

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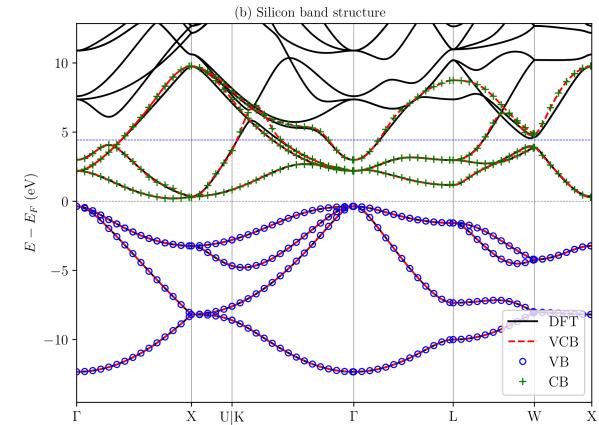
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- in place of the minimising orbitals entirely



projectability-based  
disentanglement<sup>1</sup>



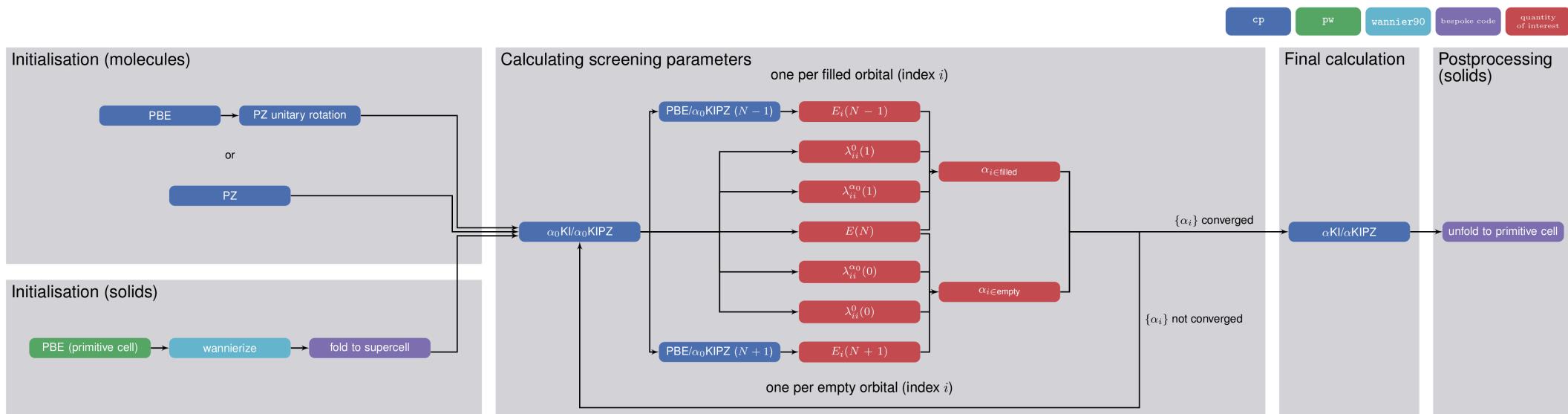
use PAOs found in  
pseudopotentials



parallel transport to separate  
manifolds<sup>2</sup>

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

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



# koopmans 🤝 AiiDA

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



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

<sup>1</sup>S. 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...)

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

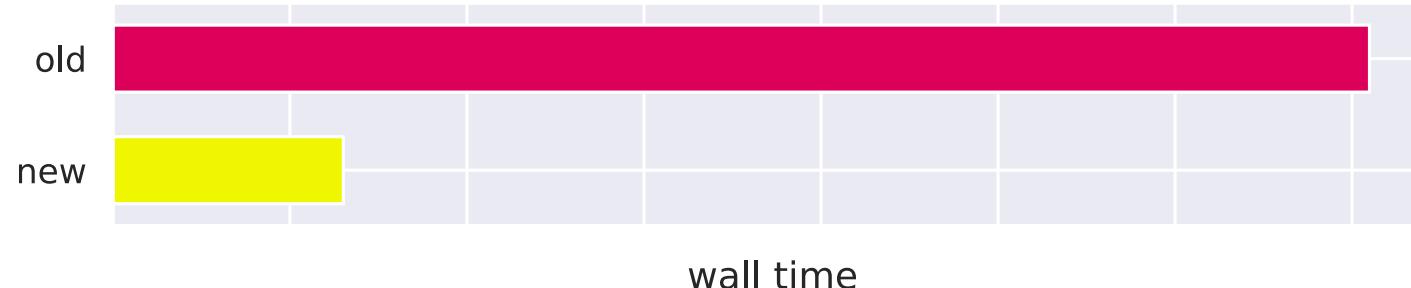
# koopmans

# AiiDA

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

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



<sup>1</sup>S. 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

<sup>1</sup>N. 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

<sup>1</sup>N. 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  $\text{GW}\Gamma_{\text{xc}}$  — local (DFT-based) vertex corrections<sup>1</sup>

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

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

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

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

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

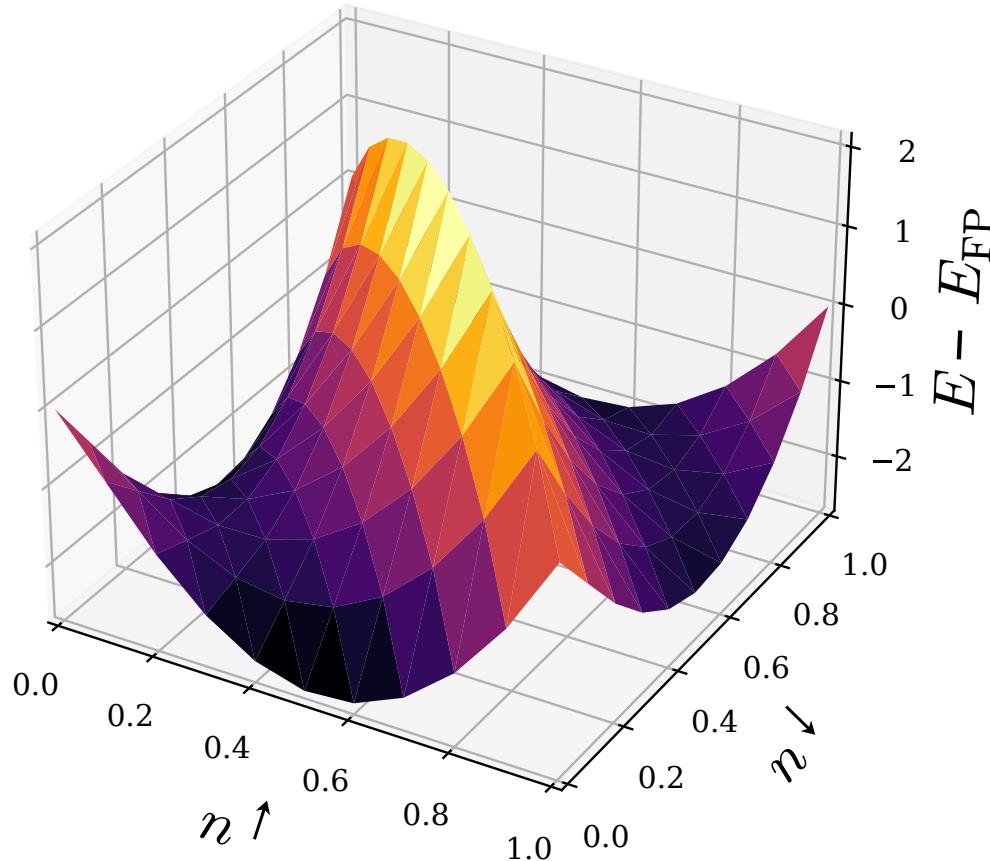
<sup>1</sup>M. S. Hybertsen *et al.* *Phys. Rev. B* 35, 5585–5601 (1987), R. Del Sole *et al.* *Phys. Rev. B* 49, 8024–8028 (1994)

# Open questions

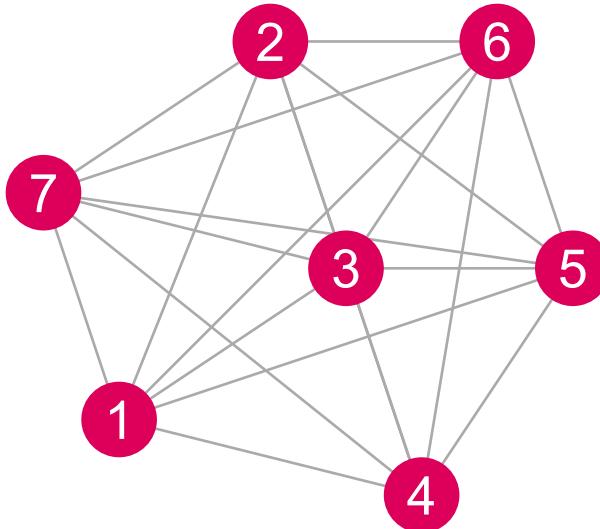
- why does correcting *local* charged excitations correct the description of delocalized excitations?
- is there a good metric for selecting variational orbitals (*i.e.* the subspace with respect to which we enforce piecewise linearity)?
- are off-diagonal corrections appropriate? What form should they take?
- how to extend to metallic systems?
- can we provide a formal basis for the Koopmans correction?
  - GKS
  - spectral functional theory<sup>1</sup>
  - ensemble DFT
  - RDMFT

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

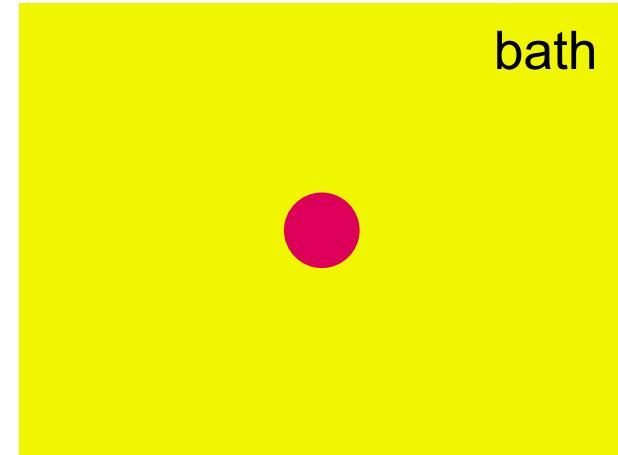
# Deviation from the flat plane condition



# 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

<sup>1</sup>A. 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+ $U^\sigma$ ; instead see BLOR<sup>1</sup>)

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

## 2. Unconstrained constrained linear response

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

**3. We can recover conventional linear response**

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

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Likewise,

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

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

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

## **5. Easy to implement**

# References

# References



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