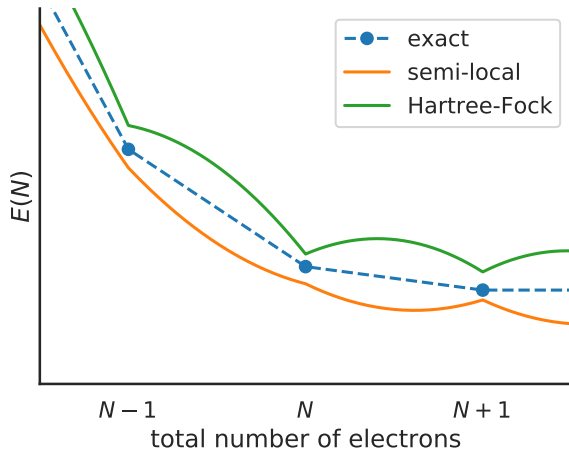


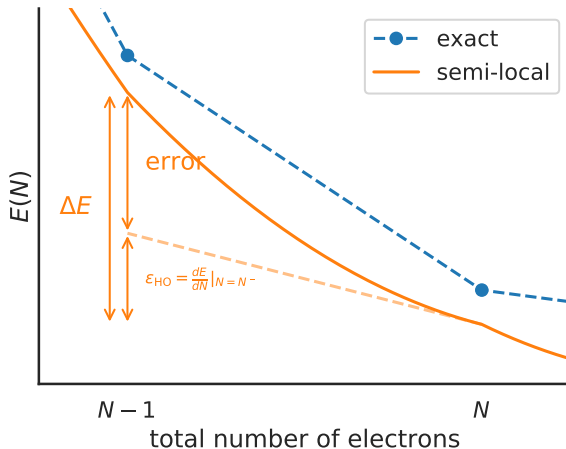
&koopmans

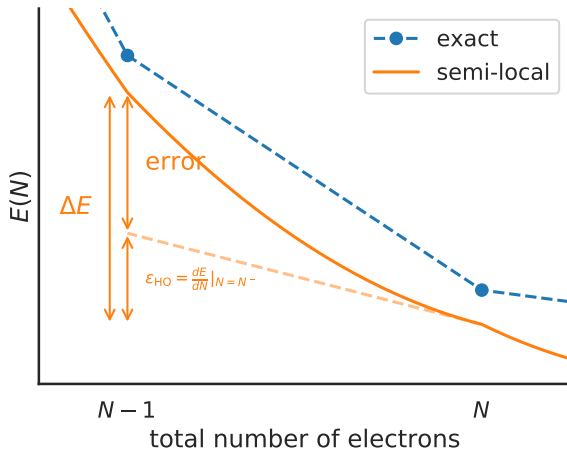
an open-source package for accurately predicting spectral properties

- what Koopmans functionals are
- the results Koopmans functionals give
- `koopmans v1.0b` has just been released!

- band gap is almost universally too small
- problems with “strongly correlated” systems (e.g. TMOs)
- problems with vdW interactions
- eigenvalues are formally meaningless
- self-interaction error
- static correlation error







Consequences for band gaps, densities, band structures, spectra...

	DFT+ U	Koopmans
designed to correct SIE, as defined by...	erroneous global curvature in total energies	dependence of ε_i on $f_i \forall i$ (canonical orbitals)
by construction...	corrects local curvature in total energies	removes dependence of ε_i on f_i and guarantees $\varepsilon_i = E_i(N \pm 1) - E(N)$ (variational orbitals)
correction applied to...	selected subspaces only (e.g. $3d$ orbitals)	the entire system
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corrective parameters are...	$\{U^I\}$, defined with respect to charge-neutral excitations (if using LR)	$\{\alpha_i\}$, defined with respect to charged excitations

How can we address self-interaction in a computationally efficient way?

→ Koopmans spectral functionals

- theory
- results
- outstanding problems
- future directions and lessons we can learn

By way of introduction: DFT+ U

Key idea: construct a functional such that the orbital energies

$$\epsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

possess two key properties:

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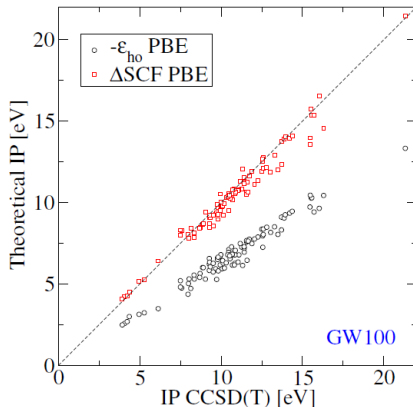
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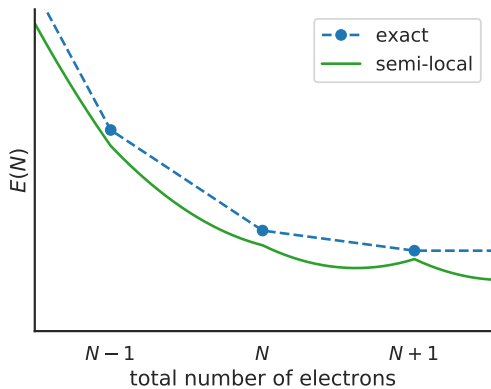
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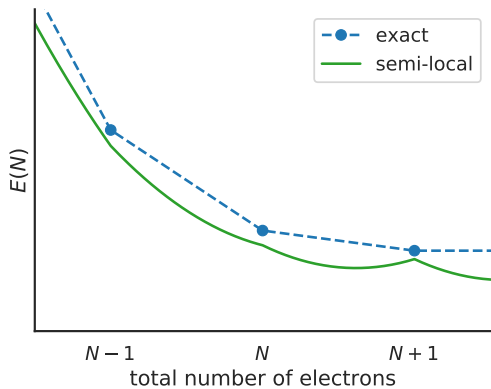
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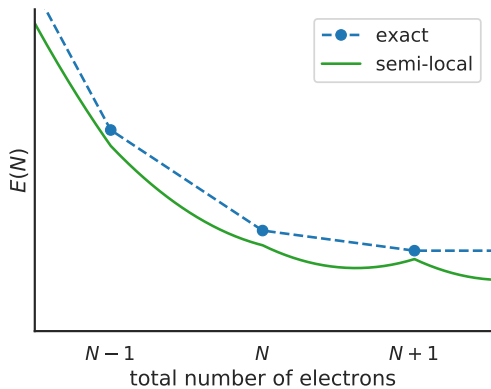
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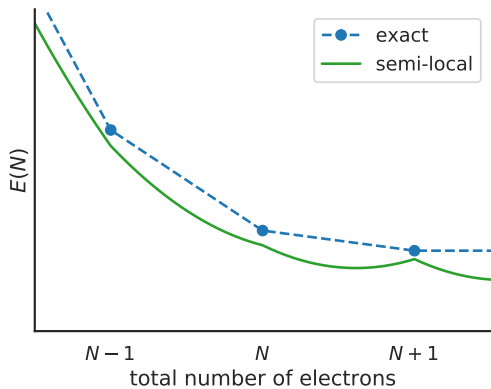
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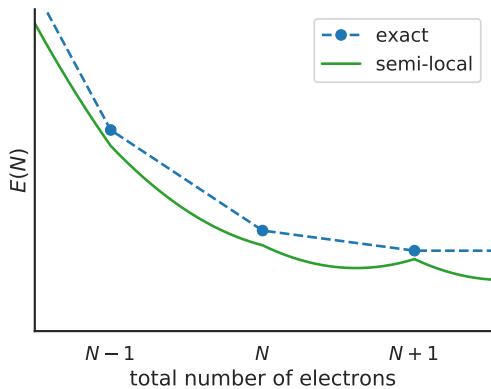


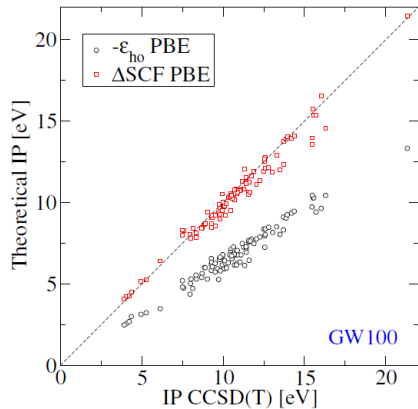






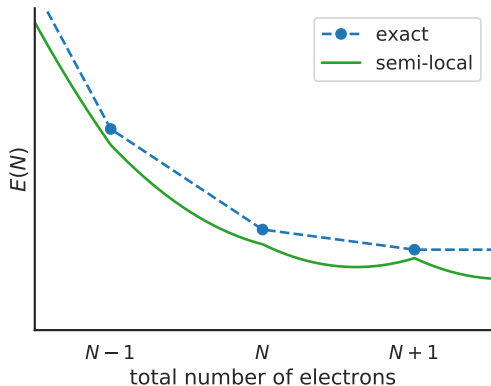






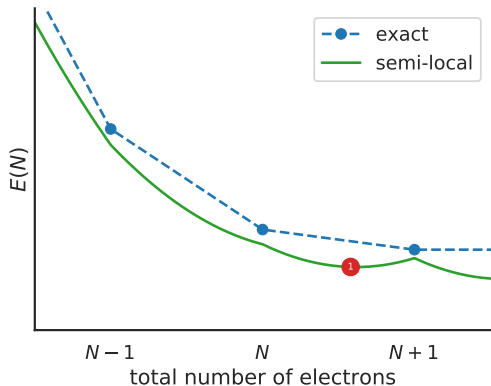
The resulting functional:

$$E_{\text{Koopmans}}[\rho, \{f_i\}, \{\alpha_i\}] = E_{\text{DFT}}[\rho] + \sum_i \alpha_i \left(- \int_0^{f_i} \varepsilon_i(f) df + f_i \int_0^1 \varepsilon_i(f) df \right)$$



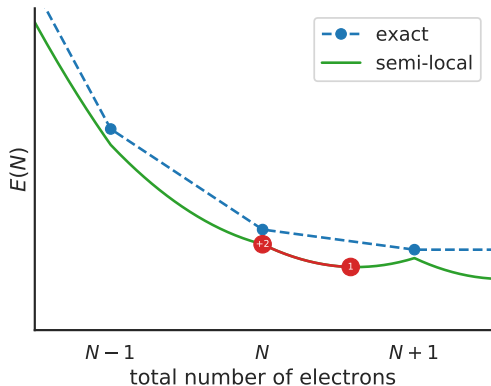
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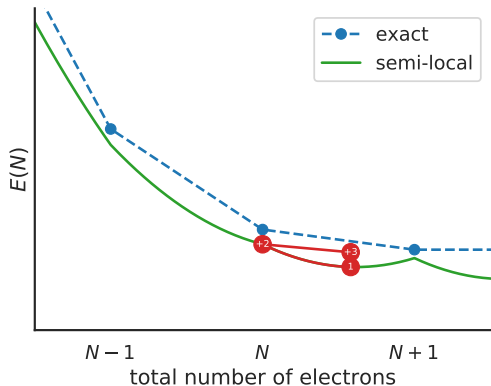
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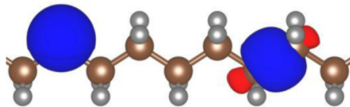
$$v_i^{\text{KI}}/\alpha_i = -E_{\text{H}}[n_i] + E_{\text{xc}}[\rho] - E_{\text{xc}}[\rho - n_i] - \int d\mathbf{r}' v_{\text{xc}}(\mathbf{r}', [\rho]) n_i(\mathbf{r}')$$

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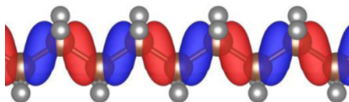
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- orbital density dependence
- variational (localised, minimising) vs canonical (delocalised, diagonalising) orbitals



(a) variational



(b) canonical

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$$\frac{dE}{df_i} \approx \alpha_i \frac{\partial E}{\partial f_i} \Rightarrow \varepsilon_i^{\text{Koopmans}} = \frac{\partial E_{\text{Koopmans}}}{\partial f_i} \approx E_i(N-1) - E(N)$$

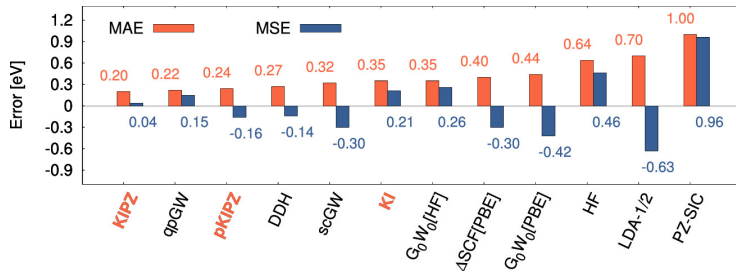
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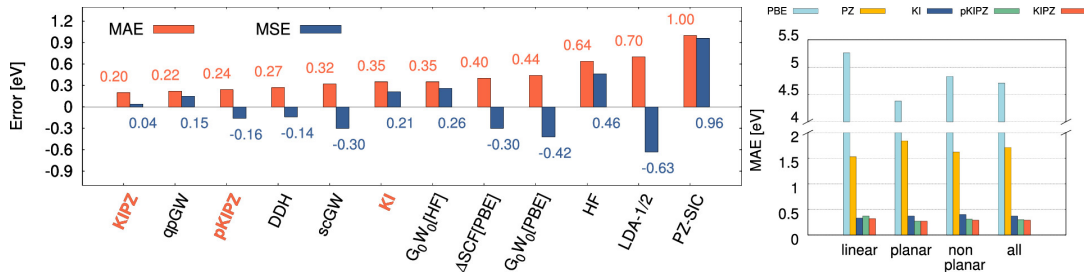
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Ionisation potentials = $E(N-1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)

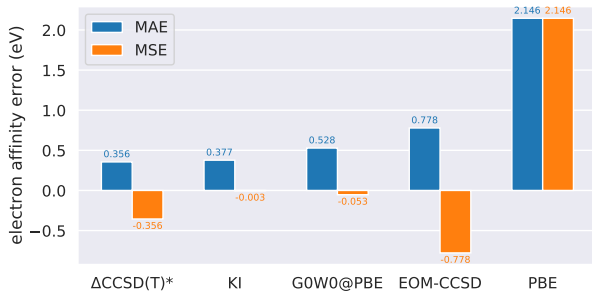


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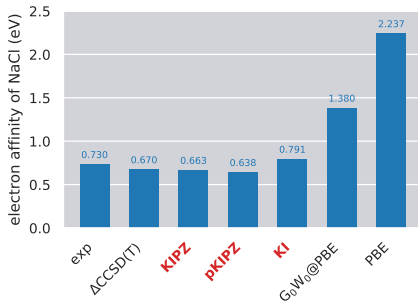


Electron affinities = $E(N) - E(N + 1) \stackrel{?}{=} -\varepsilon_{LU}$ of molecules cf. CCSD(T)/exp

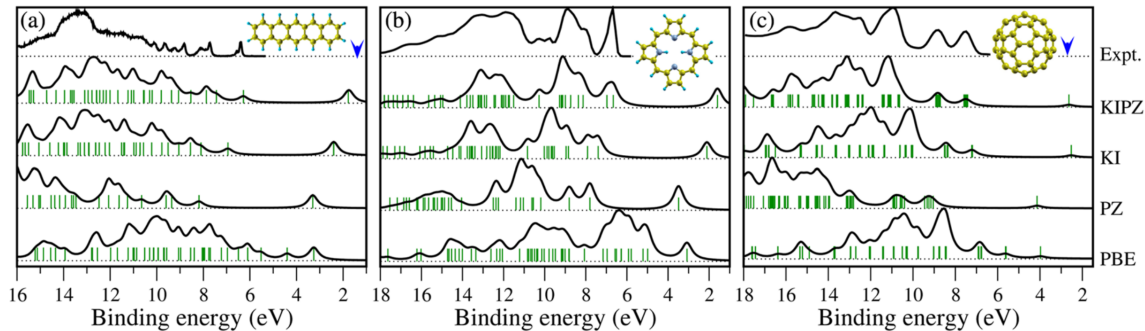
For 15 of the GW100 molecules with bound LUMOs

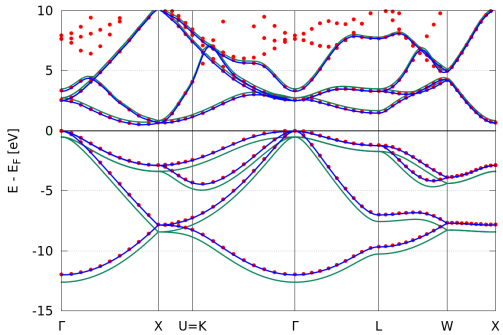


For the NaCl molecule



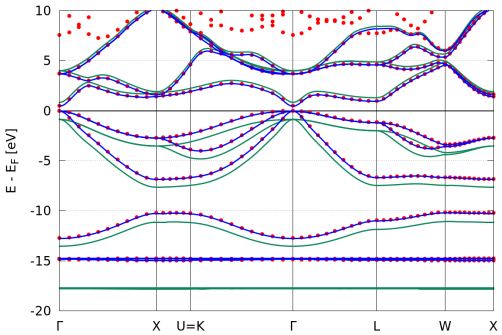
Figures from Linscott et al. (in prep)





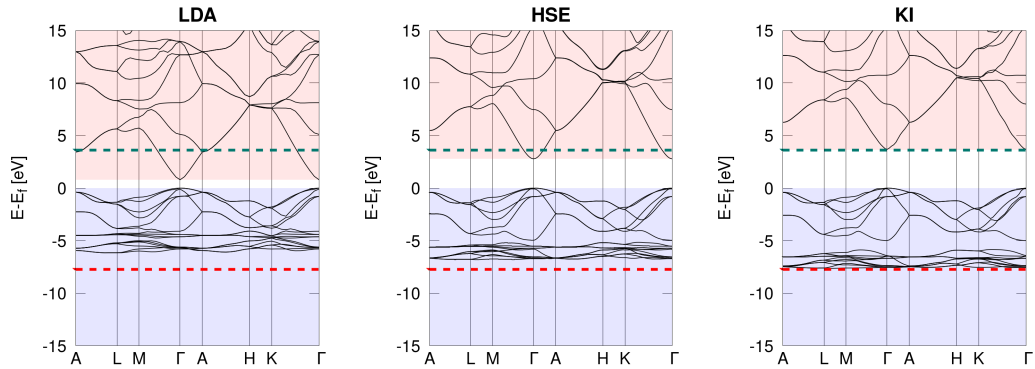
(a) Si, KIPZ

	PBE	qsGW	KIPZ	exp.
E_{gap} (eV)	0.55	1.30	1.27	1.22



(b) GaAs, KI

	PBE	qsGW	KI	exp.
E_{gap} (eV)	0.50	1.51	1.68	1.57
$\langle \varepsilon_d \rangle$ (eV)	-14.9		-17.0	-18.9



ZnO	LDA	HSE	GW_0	$\text{scGW}\tilde{W}$	KI	exp.
E_{gap} (eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle \varepsilon_d \rangle$ (eV)	-5.1	-6.1	-6.4	-6.7	-6.9	-7.5/-8.0

- determining $\{\alpha_i\}$
- how to treat metals?
- limitations of the orbital-density-dependent framework

Screening coefficients $\{\alpha_i\}$ must be determined first, either

¹ N. Colonna et al. *JCTC* 14.5 (2018), 2549.

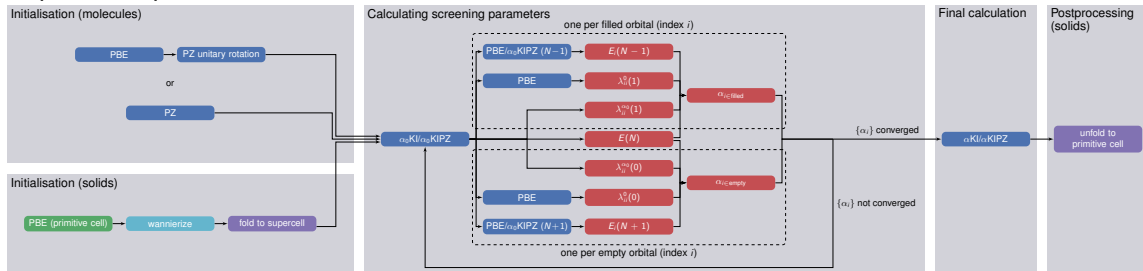
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Koopmans spectral functionals: the workflow(s)

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Supercell implementation

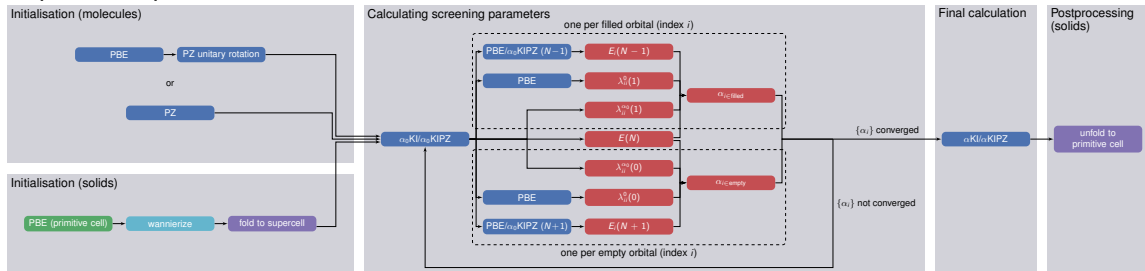


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Supercell implementation

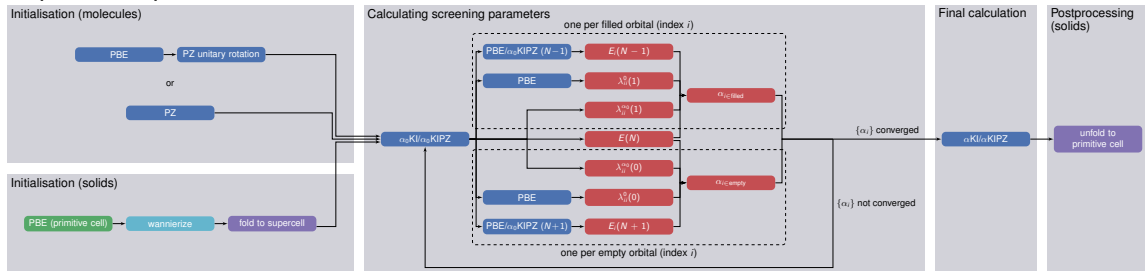


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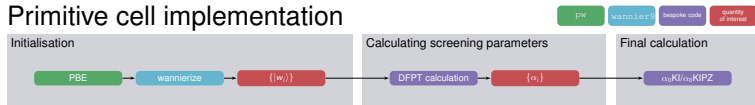
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Supercell implementation



Primitive cell implementation

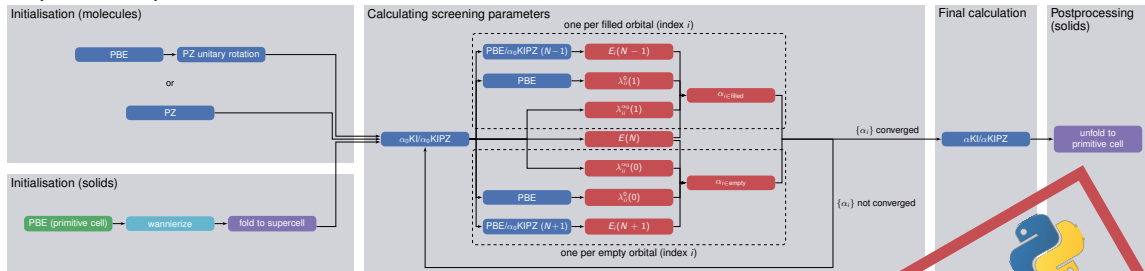


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- Difficulties when it comes to calculating transport properties/spectra
- Perhaps a DFT+ U -projector approach is more convenient?

² A. Ferretti et al. *Phys. Rev. B* 89.19 (2014), 195134.

Recap from earlier

Key idea: construct a functional such that the *variational* orbital energies

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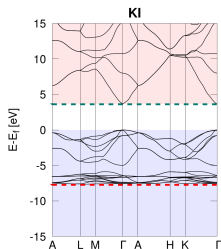
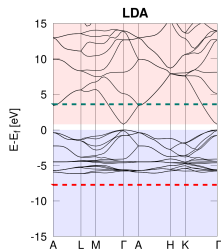
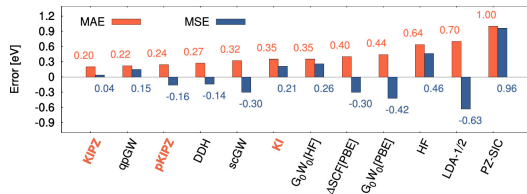
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zero band gap \rightarrow occupancy matrix for variational orbitals is off-diagonal



- orbital-density-dependent corrective terms to semi-local DFT
- comparable computational cost to DFPT
- KS eigenvalues are meaningful
- accuracy comparable to GW

caveats:

- orbital density dependence has limitations
- complicated workflow (not for much longer!)
- only for insulators

For Koopmans...

- framing Koopmans with frozen-orbital/projector-like picture
- prediction of α_i
- scope for addressing static correlation error
- off-diagonal terms

For corrections to SIE more generally...

- we can gain ground by thinking about KS energies and not just total energies
- indeed, KI corrects KS energies while leaving total energies untouched!



Nicola Marzari



Nicola Colonna



Riccardo De Gennaro



Yannick Schubert



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Look out for our papers & code release later this year (follow [@ed_linscott](https://twitter.com/ed_linscott) for updates/get in touch for alpha access!)

Shameless postdoc/fellowship plug?

For further reading on Koopmans functionals, see I. Dabo et al. *Phys. Rev. B* 82.11 (2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (2014), 075135; N. Colonna et al. *JCTC* 15.3 (2019), 1905; N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051; N. Colonna et al. *JCTC* 14.5 (2018), 2549