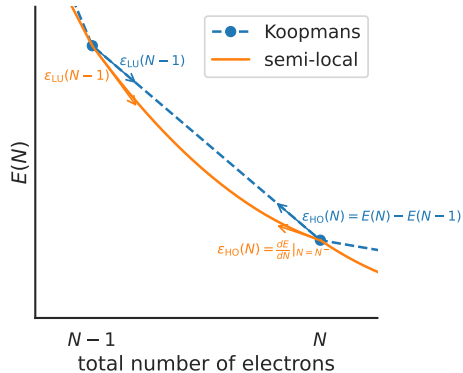# Accurate charged and neutral excitations with Koopmans functionals

Goal: spectral properties (charged excitations) with a functional theory
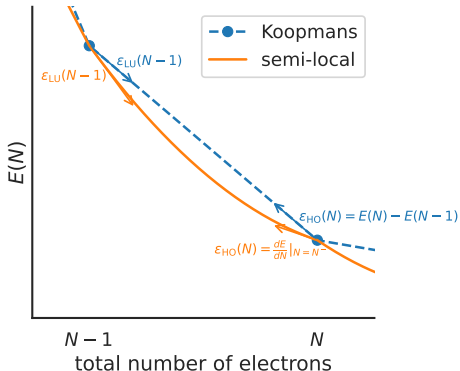
Goal: spectral properties (charged excitations) with a functional theory

Core idea: for every orbital i their energy

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

should be...

- independent of its own occupation f_i
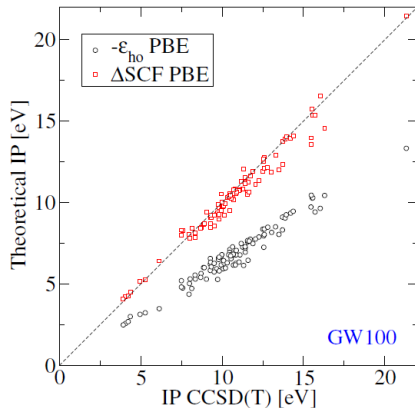- equal to the corresponding total energy difference $E_i(N-1) - E(N)$

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

should be...

- independent of its own occupation f_i
- equal to the corresponding total energy difference $E_i(N-1) - E(N)$

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

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

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Differences to semi-local functionals:

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

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Differences to semi-local functionals:

- orbital-density dependence (can use MLWF densities)

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

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

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- orbital-density dependence (can use MLWF densities)
- screening

$$\frac{dE}{df_i} \approx \alpha_i \frac{\partial E}{\partial f_i}$$

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Differences to semi-local functionals:

- orbital-density dependence (can use MLWF densities)
- screening

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

I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

Resonance with other efforts:

- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (18, 2005), 075125
- Ensemble DFT of Kronik and co-workers E. Kraisler et al. *Phys. Rev. Lett.* 110.12 (19, 2013), 126403
- Koopmans-Wannier of Wang and co-workers J. Ma et al. *Sci. Rep.* 6.1 (1 26, 2016), 24924
- Dielectric-dependent hybrid functionals of Galli and co-workers **Skone2016**
- LOSC functionals of Yang and co-workers C. Li et al. *Natl. Sci. Rev.* 5 (2018), 203
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (24, 2021), e2104556118

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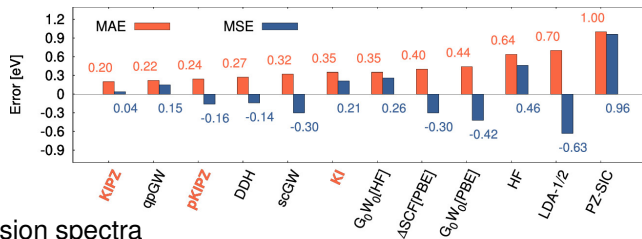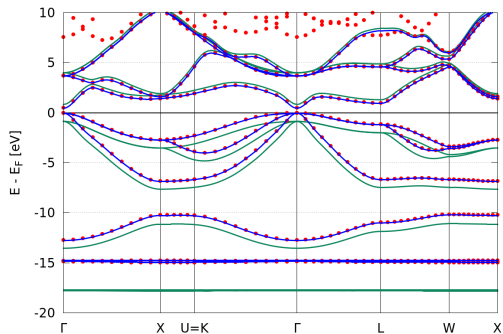

Ultraviolet photoemission spectra
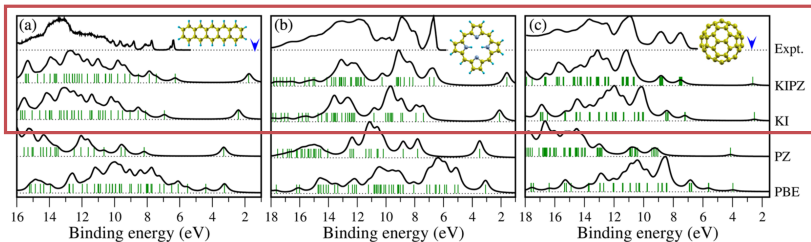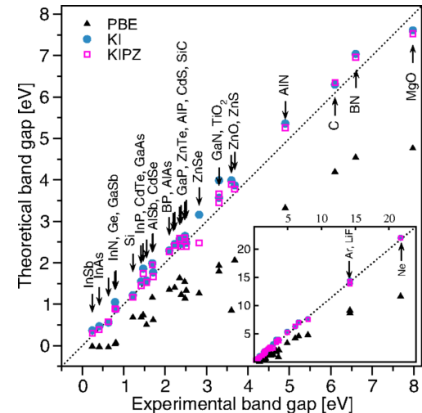
Mean absolute error (eV) across prototypical semiconductors and insulators

	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

N. L. Nguyen et al. *Phys. Rev. X* 8.2 (23, 2018), 021051
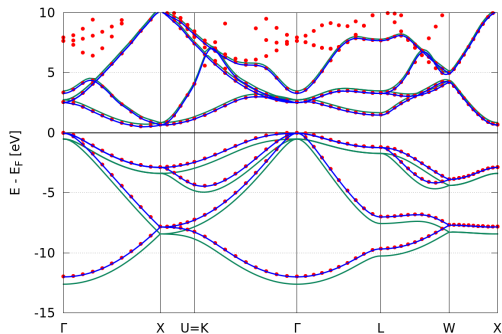
(a) Si, KIPZ

(b) GaAs, KI

		PBE	QSG$\tilde{W}$	**KI**	**pKIPZ**	**KIPZ**	exp
Si	E_{gap}	0.55	1.24	1.18	1.17	1.19	1.17
GaAs	E_{gap}	0.50	1.61	1.53	1.49	1.50	1.52
	$\langle \varepsilon_d \rangle$	14.9	17.6	16.9		17.7	18.9

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106
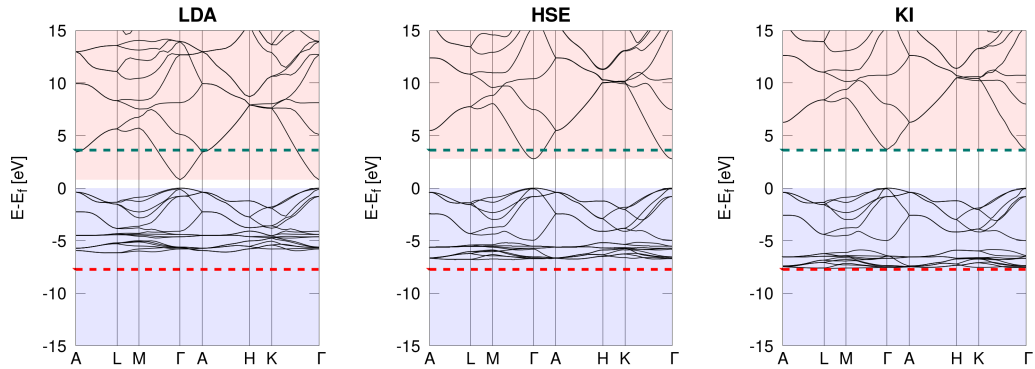
ZnO	LDA	HSE	GW_0	scG$\tilde{W}$	**KI**	exp
E_{gap} (eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle \varepsilon_d \rangle$ (eV)	−5.1	−6.1	−6.4	−6.7	−6.9	-7.5/-8.0

N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022)

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

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106; N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022);
Y. Schubert et al. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". 2022

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

(a) finite difference calculations using a supercell

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106; N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022);
Y. Schubert et al. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". 2022

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

(a) finite difference calculations using a supercell

(b) DFPT using a primitive cell

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106; N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022); Y. Schubert et al. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". 2022
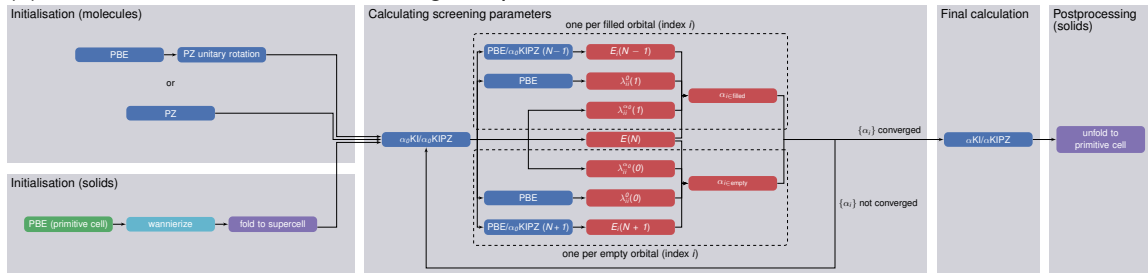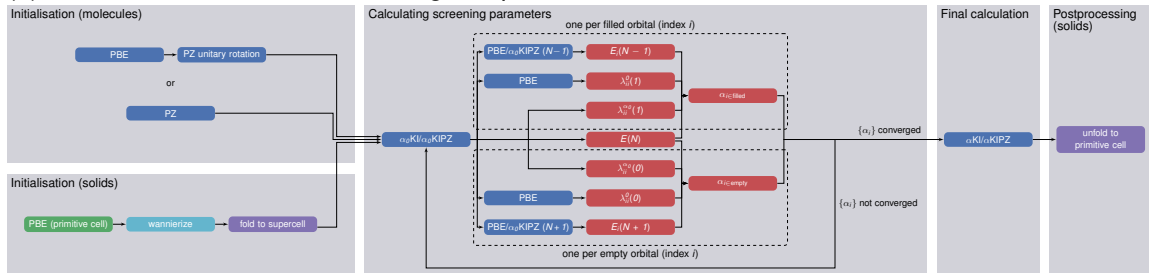
Screening coefficients $\{\alpha_i\}$ must be determined first, via. . .

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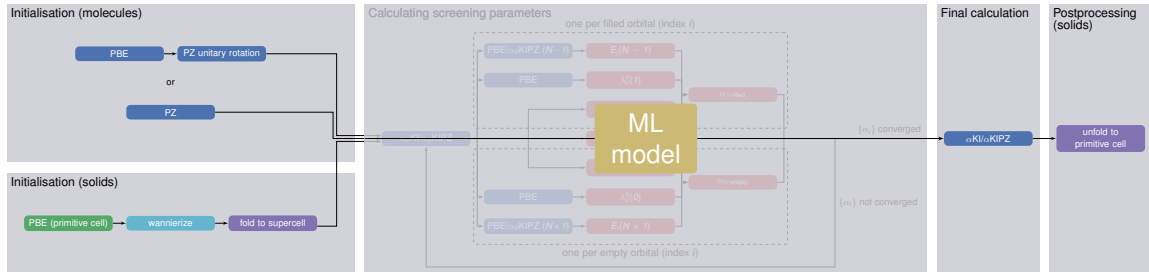
(b) DFPT using a primitive cell

(c) via machine learning (resulting band gaps within ~ 0.02 eV of explicit approach)

R. De Gennaro et al. *Phys. Rev. B* 106.3 (5, 2022), 035106; N. Colonna et al. *J. Chem. Theory Comput.* (4, 2022); Y. Schubert et al. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". 2022

`kcw.x` (DFPT implementation) is distributed in Quantum ESPRESSO v7.1 onwards

But complex workflows mean that...

- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

ckoopmans

- beta version just released[1]
- implementations of Koopmans functionals
- automated workflows
  - start-to-finish Koopmans calculations
  - Wannierisation
  - dielectric tensor
  - convergence tests
  - ...
- built on top of ASE[2]
- does not require expert knowledge

`koopmans-functionals.org`
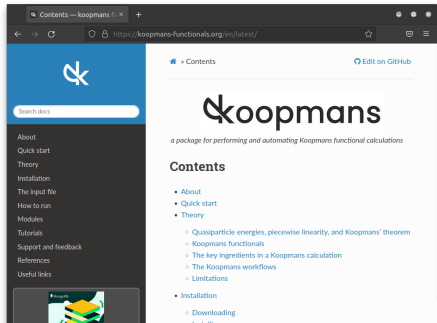
[1] Linscott et al., in prep

[2] A. H. Larsen et al. *J. Phys. Condens. Matter* 29.27 (12, 2017), 273002

```
{
  "workflow": {
    "task": "singlepoint",
    "functional": "ki",
    "method": "dscf",
    "init_orbitals": "mlwfs",
    "alpha_guess": 0.1
  },
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      "positions": [["Si", 0.00, 0.00, 0.00],
                    ["Si", 0.25, 0.25, 0.25]]
    },
    "cell_parameters": {
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      "ibrav": 2,
      "celldm(1)": 10.262
    }
  },
```

```
  "k_points": {
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    "path": "LGXKG"
  },
  "calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
      "projections": [{"fsite": [0.125, 0.125, 0.125],
                       "ang_mtm": "sp3"}]
      ,
      "emp": {
        "dis_froz_max": 11.5,
        "dis_win_max": 17.0
      }
    }
  }
}
```

```python
from ase.build import bulk
from koopmans.kpoints import Kpoints
from koopmans.projections import ProjectionBlocks
from koopmans.workflows import SinglepointWorkflow

# Use ASE to create bulk silicon
atoms = bulk('Si')

# Define the projections for the Wannierization (same for filled and empty manifold)
si_proj = [{'fsite': [0.25, 0.25, 0.25], 'ang_mtm': 'sp3'}]
si_projs = ProjectionBlocks([{'filled': True, **si_proj},
                             {'filled': False, **si_proj}],
                            atoms=atoms)

# Create the workflow
workflow = SinglepointWorkflow(atoms = atoms,
        projections = si_projs,
        ecutwfc = 40.0,
        kpoints = Kpoints(grid=[8, 8, 8], path='LGXGKG', cell=atoms.cell),
        calculator_parameters = {'pw': {'nbnd': 10},
        'w90_emp': {'dis_froz_max': 10.6, 'dis_win_max': 16.9}})

# Run the workflow
workflow.run()
```
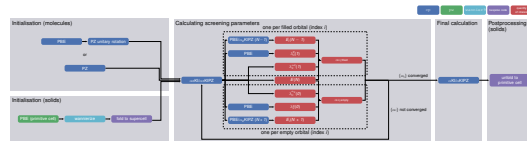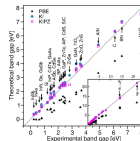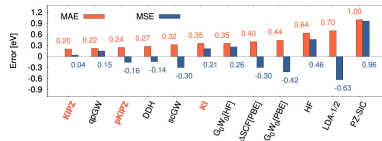
- Koopmans functionals are a class of functionals that treat spectral properties on the same footing as total energy differences (via GPWL)
- they can give orbital energies and band structures with comparable accuracy to state-of-the-art GW
- the release of `koopmans` means you don't need expert knowledge to run Koopmans functional calculations

Want to find out more? Go to `koopmans-functionals.org`

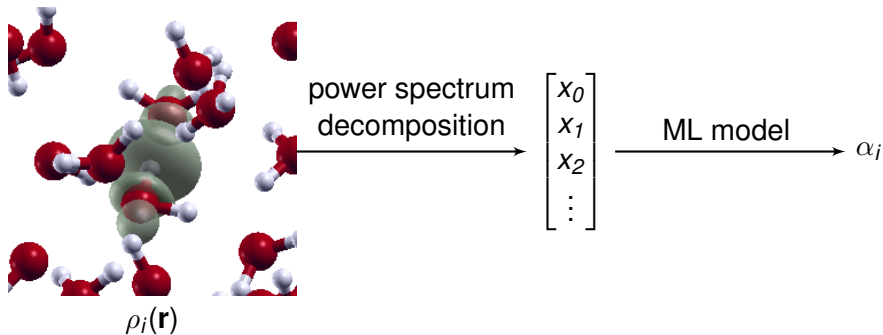SPARE SLIDES

Recap from earlier

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

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

are...

- independent of the corresponding occupancies f_i
- equal to the corresponding total energy difference $E_i(N-1) - E(N)$

zero band gap $\rightarrow$ occupancy matrix for variational orbitals is off-diagonal
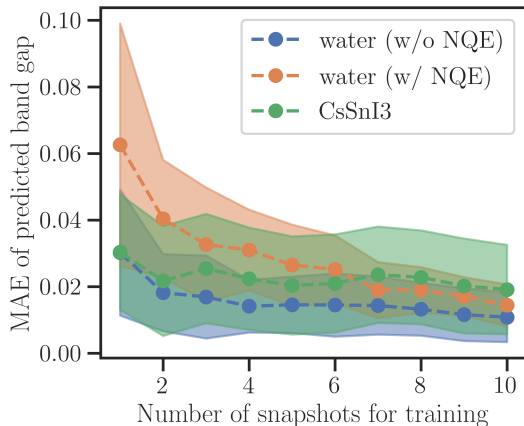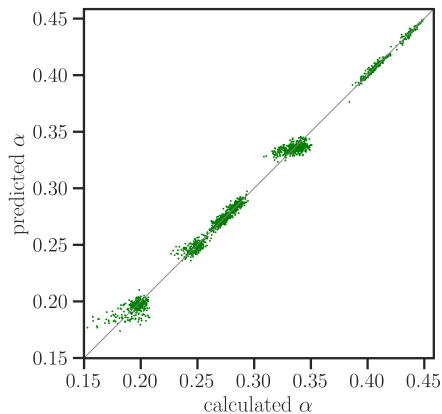
$\rho_i(\mathbf{r})$ → power spectrum decomposition → $\begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix}$ → ML model → α_i

Y. Schubert et al. "Predicting Screening Parameters For Fast Koopmans Spectral Functional Calculations". 2022

Edward Linscott

EPFL

$$c^i_{nlm,k=\text{orbital}} = \int d\mathbf{r}\, g_{nl}(r)\, Y_{lm}(\theta, \varphi)\, \rho^i(\mathbf{r} - \mathbf{R}^i)$$

g_{nl} = orthonormalised radial Gaussian basis functions
Y_{lm} = spherical harmonics

$$p^i_{n_1 n_2 l, k_1 k_2} = \pi \sqrt{\frac{8}{2l+1}} \sum_m c^{i*}_{n_1 lm, k_1} c^i_{n_2 lm, k_2}$$
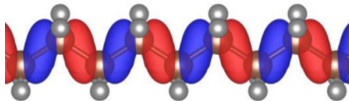
loss of accuracy of the band gap of ~ 0.02 eV
(cf. when calculating screening parameters *ab initio*)

- a natural generalisation in the direction of spectral functional theory[1]
- variational (localised, minimising) vs canonical (delocalised, diagonalising) orbitals
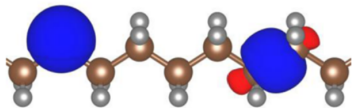
(a) variational

(b) canonical

- ODD functional means that we know $\hat{H}|\varphi_i\rangle$ for variational orbitals $\{|\varphi_i\rangle\}$ but we don't know $\hat{H}$ in general
- Difficulties when it comes to calculating transport properties/spectra
- Perhaps a DFT+U-projector approach is more convenient?

[1] A. Ferretti et al. *Phys. Rev. B* 89.19 (27, 2014), 195134.
N. L. Nguyen et al. *Phys. Rev. X* 8.2 (23, 2018), 021051

Dabo, I. et al. *Phys. Rev. B* 82.11 (23, 2010).

Borghi, G. et al. *Phys. Rev. B* 90.7 (20, 2014).

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Anisimov, V. I. et al. *Phys. Rev. B* 72.7 (18, 2005).

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Wing, D. et al. *Proc. Natl. Acad. Sci.* 118.34 (24, 2021).

Colonna, N. et al. *J. Chem. Theory Comput.* 14.5 (8, 2018).

Nguyen, N. L. et al. *Phys. Rev. Lett.* 114.16 (24, 2015).

Nguyen, N. L. et al. *Phys. Rev. X* 8.2 (23, 2018).

De Gennaro, R. et al. *Phys. Rev. B* 106.3 (5, 2022).

Colonna, N. et al. *J. Chem. Theory Comput.* (4, 2022).

Schubert, Y. et al. 2022.

Larsen, A. H. et al. *J. Phys. Condens. Matter* 29.27 (12, 2017).

Ferretti, A. et al. *Phys. Rev. B* 89.19 (27, 2014).