MARVEL
Swiss National Science Foundation

Koopmans functionals in practice

workflows, automation, and more...

Edward Linscott | EPFL | Advanced QUANTUM ESPRESSO Tutorial | 31 Aug 2023

Outline

- What does a Koopmans calculation actually involve?
- What tools are there for performing these calculations?
- Where can I find out more?

Core theory

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

I. Dabo et al. *Phys. Rev. B* 82.11 (2010), 115121

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Differences to semi-local functionals:

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Differences to semi-local functionals:

- different flavours

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Differences to semi-local functionals:

- different flavours
- orbital-density dependence

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Differences to semi-local functionals:

- different flavours
- orbital-density dependence
- screening

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Flavours of Koopmans functionals

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One degree of freedom: what should be the gradient of this linear term?

Flavours of Koopmans functionals

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- the base functional $\rightarrow$ “KI" (Koopmans integral). Enforces IP theorem. Does not affect energy/density!

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- “pKIPZ” = KIPZ Hamiltonian evaluated on the KI solution
- “K” = an earlier iteration based off half-filling rather than integer endpoints (no longer used)

Orbital-density-dependence

$$-\int_0^{f_i} \varepsilon_i(f)df + f_i \int_0^1 \varepsilon_i(f)df = E_{\text{Hxc}}[\rho] + E_{\text{Hxc}}[\rho - \rho_i] + f_i \left(-E_{\text{Hxc}}[\rho - \rho_i] + E_{\text{Hxc}}[\rho - \rho_i + n_i]\right)$$

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$$v_i/\alpha_i = v_{\text{scalar}} + \delta_{ij} v_{\text{diag}}(\mathbf{r}) + (1 - \delta_{ij}) v_{\text{nondiag}}(\mathbf{r})$$

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For filled orbitals with KI:

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

Orbital-density-dependence

Initialise with MLWFs, then (optionally) solve with CG minimisation:

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

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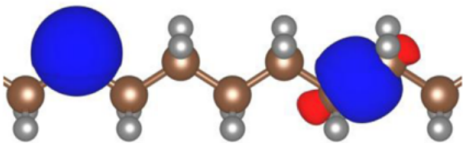
Gives rise to a set of minimising orbitals (localised/variational)



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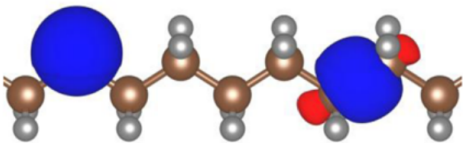
Diagonalising at the minimum gives rise to diagonalising orbitals (delocalised/canonical)



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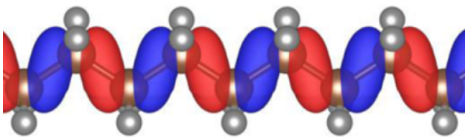

(b) canonical

Screening

- What is screening (in the context of Koopmans functionals)?

$$\underbrace{\frac{dE}{df_i}}_{\text{including relaxation}} \xleftarrow{\quad ? \quad} \underbrace{\frac{\partial E}{\partial f_i}}_{\text{excluding relaxation}}$$

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- In Hartree-Fock (the original "Koopmans' theorem"):

$$E_{ee}^{HF} = \frac{1}{2}\sum_{ij} f_i f_j \int d\mathbf{r} d\mathbf{r}' \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{\mathbf{r}-\mathbf{r}'} - \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})}{\mathbf{r}-\mathbf{r}'}$$

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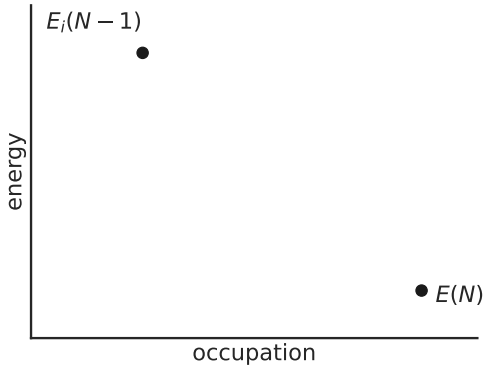
- How to choose an appropriate value for α_i? Return to the original idea of Koopmans functionals:

$$\varepsilon_i^{\text{Koopmans}} = E_i(N-1) - E(N)$$

Screening



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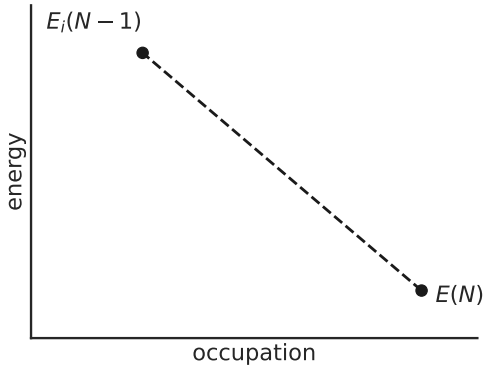

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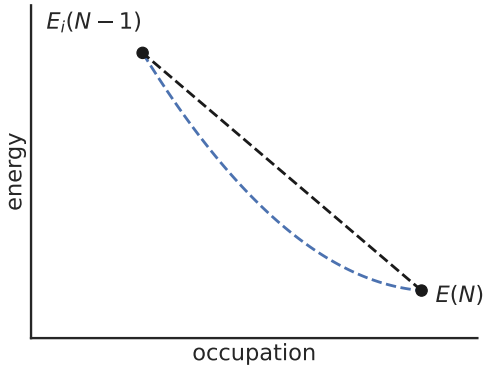

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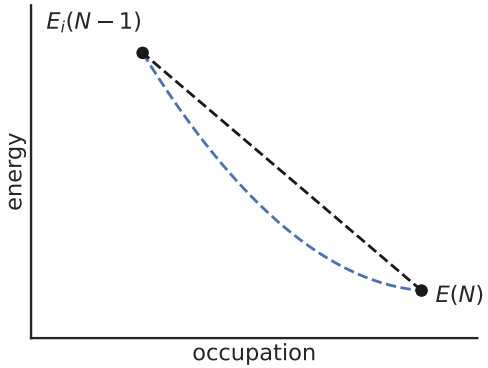

$$\lambda_{ii}(\alpha) \equiv \langle\varphi_i|\hat{h}^{\text{DFT}} + \alpha\hat{v}^{\text{Koopmans}}|\varphi_i\rangle = \left.\frac{dE^{\text{Koopmans}}}{df_i}\right|_{f_i=s}$$

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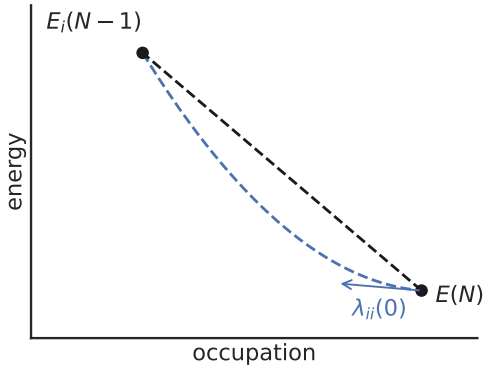

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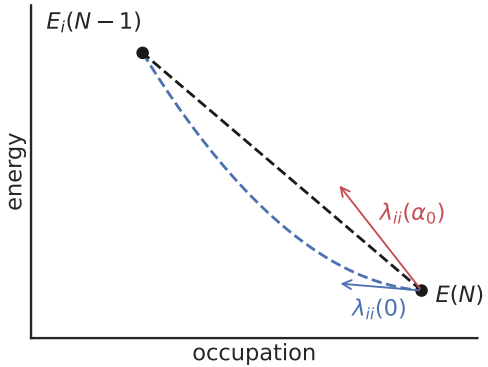

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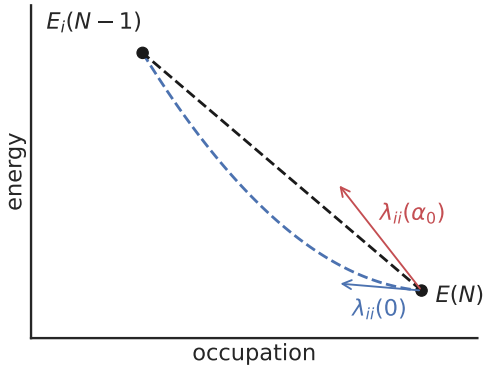
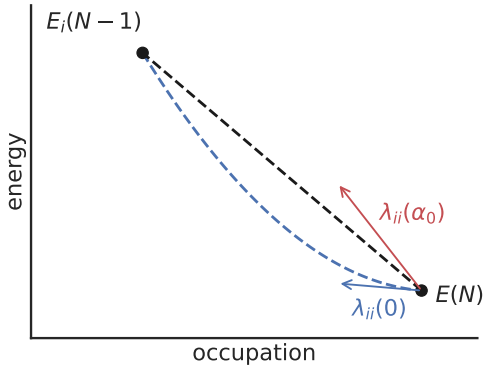


Given this, how to work out the ideal α?

Screening



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expectation value of $\hat{H}^{\text{Koopmans}}$

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Screening

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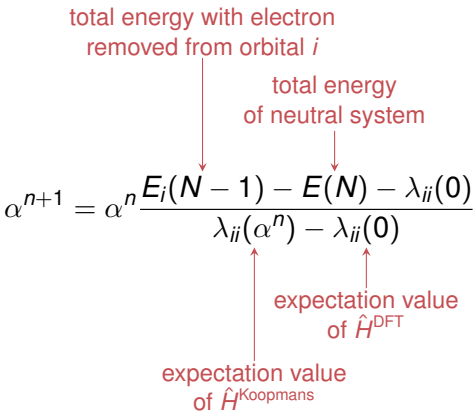
total energy with electron removed from orbital i
total energy of neutral system
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Screening via DFPT

Original formulation requires explicit charged defect calculations in a supercell

[1] N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (2019), 1905.
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Now reformulated in terms of DFPT[1]...

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... in reciprocal space[2]

$$\alpha_{\mathbf{0}i} = 1 + \frac{\sum_{\mathbf{q}} \langle v^{\mathbf{0}i}_{\text{pert},\mathbf{q}} | \Delta^{\mathbf{0}i}_{\mathbf{q}} n \rangle}{\sum_{\mathbf{q}} \langle n^{\mathbf{0}i}_{\mathbf{q}} | v^{\mathbf{0}i}_{\text{pert},\mathbf{q}} \rangle}.$$

(See Nicola Colonna's talk)

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- how are we treating the orbital-density-dependence?
  - how are we initialising our variational orbitals? (N.B. depends on the flavour!)
  - are we going to explicitly minimise the ODD?
- how are we calculating the screening parameters? (finite differences, DFPT, ML...)

The workflows

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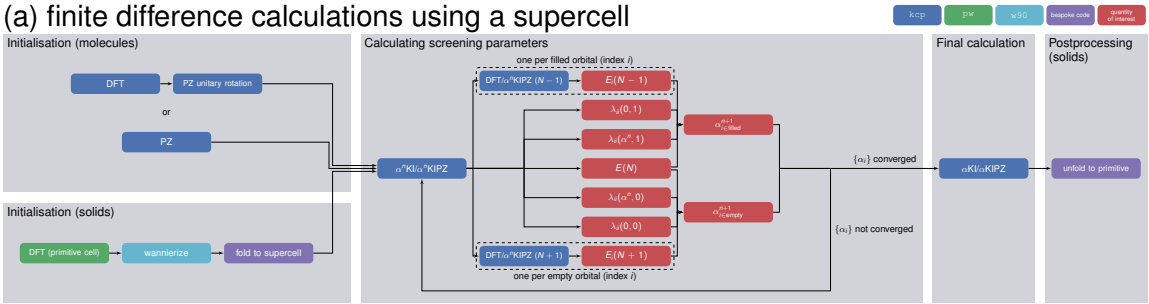
(a) finite difference calculations using a supercell



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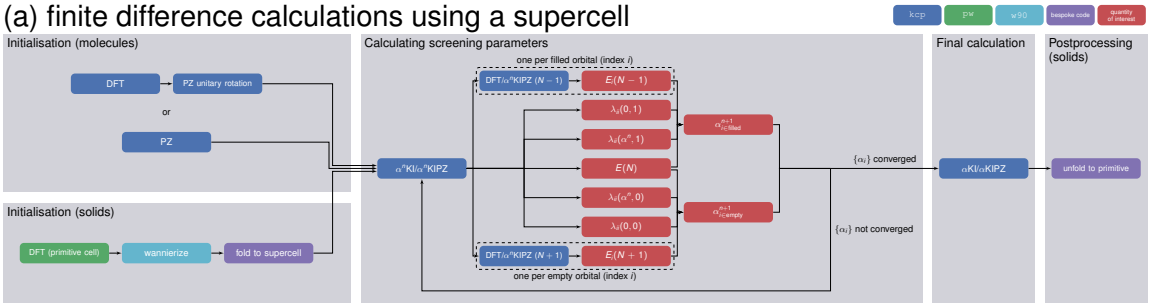
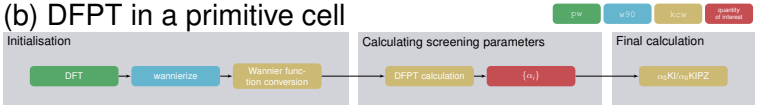


(b) DFPT in a primitive cell



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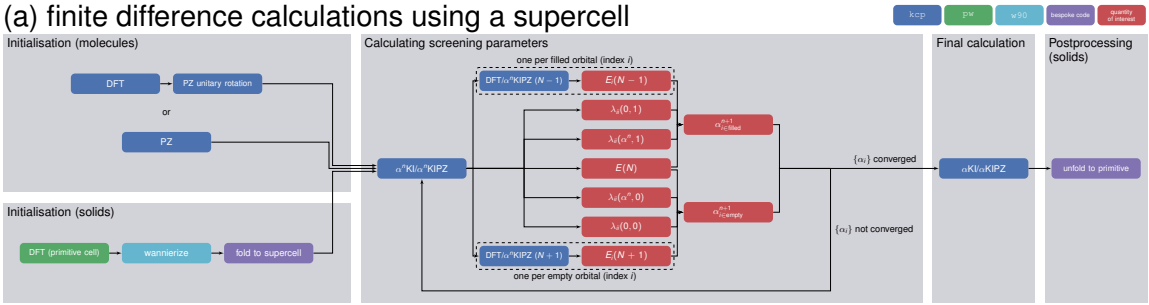

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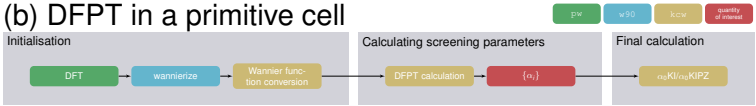

(c) via machine learning

Implementations of Koopmans functionals

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`kcp.x` (supercell implementation) is available publically

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available flavours	KI only	KI, KIPZ, pKIPZ, PZ

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scaling	$\mathcal{O}(N_{\mathbf{q}}N_{\mathbf{k}}N_{\text{orb}}^3)$	$\mathcal{O}(N_{\mathbf{k}}^3N_{\text{orb}}^3) = \mathcal{O}(N_k)\times$ primitive cell approach

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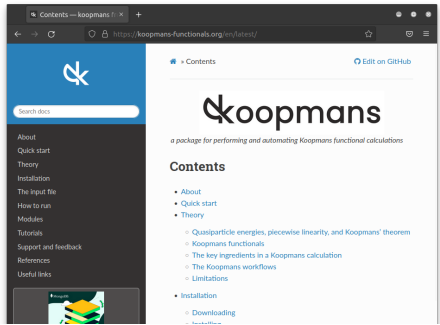
Our solution...

koopmans

- v1.0 released earlier this year[1]
- implementations of Koopmans functionals
- automated workflows
  - start-to-finish Koopmans calculations
  - Wannierisation
  - dielectric tensor
  - ...
- built on top of ASE[2]
- under the hood, calls `Quantum ESPRESSO`
- does not require expert knowledge

`koopmans-functionals.org`



[1] E. B. Linscott et al. *J. Chem. Theory Comput.* (2023)

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

koopmans: the input file


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

```
  "k_points": {
    "grid": [8, 8, 8],
    "path": "LGXKG"
  },
  "calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
      "projections": [
          [{"fsite": [0.125, 0.125, 0.125],
            "ang_mtm": "sp3"}],
          [{"fsite": [0.125, 0.125, 0.125],
            "ang_mtm": "sp3"}]
      ],
      "dis_froz_max": 11.5,
      "dis_win_max": 17.0
    }
  }
}
```

koopmans is scriptable


```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.from_list([si_proj, si_proj], atoms=atoms)

# Create the workflow
workflow = SinglepointWorkflow(atoms = atoms,
        projections = si_projs,
        ecutwfc = 40.0,
        kpoints = Kpoints(grid=[8, 8, 8], path='LGXKG', cell=atoms.cell),
        calculator_parameters = {'pw': {'nbnd': 10},
        'w90': {'dis_froz_max': 10.6, 'dis_win_max': 16.9}})

# Run the workflow
workflow.run()
```

Generic structure

```
Workflow
```

Generic structure

`Workflow`

`atoms` an `ASE` `Atoms` object

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Generic structure

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Generic structure

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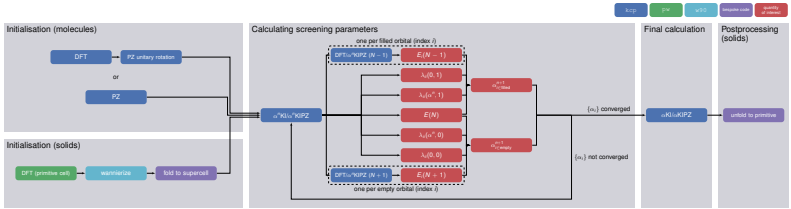
- ...

We will see examples in the hands-on!

Take home messages

Edward Linscott
EPFL | 19/21



- Koopmans functionals are more complicated than a simple semi-local DFT calculation, because of…
  - orbital-density-dependence
  - screening parameters
- Koopmans functionals are implemented in `Quantum ESPRESSO`
- the complexity of the workflows are handled by the `koopmans` package

JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

koopmans: An Open-Source Package for Accurately and Efficiently Predicting Spectral Properties with Koopmans Functionals

Edward B. Linscott,*,△ Nicola Colonna,△ Riccardo De Gennaro, Ngoc Linh Nguyen, Giovanni Borghi, Andrea Ferretti, Ismaila Dabo, and Nicola Marzari*

Cite This: https://doi.org/10.1021/acs.jctc.3c00652 Read Online

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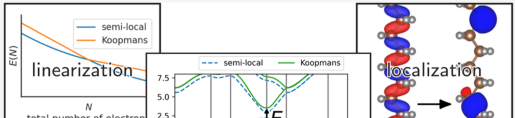
ABSTRACT: Over the past decade we have developed Koopmans functionals, a computationally efficient approach for predicting spectral properties with an orbital-density-dependent functional framework. These functionals impose a generalized piecewise linearity condition to the entire electronic manifold, ensuring that



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Nicola Marzari

Nicola Colonna

Riccardo De Gennaro

Yannick Schubert

Swiss National Science Foundation

MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

Follow @ed_linscott for updates | Slides available at github/elinscott

SPARE SLIDES

Koopmans functionals: off-diagonal occupancies

Edward Linscott
EPFL

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

Resonance with other efforts

- Wannier transition-state method of Anisimov and Kozhevnikov V. I. Anisimov et al. *Phys. Rev. B* 72.7 (2005), 075125
- Optimally tuned hybrid functionals of Kronik, Pasquarello, and others (refer back to Leeor's talk on Wednesday) L. Kronik et al. *J. Chem. Theory Comput.* 8.5 (2012), 1515; D. Wing et al. *Proc. Natl. Acad. Sci.* 118.34 (2021), e2104556118
- Ensemble DFT of Kronik and co-workers E. Kraisler et al. *Phys. Rev. Lett.* 110.12 (2013), 126403
- Koopmans-Wannier of Wang and co-workers J. Ma et al. *Sci. Rep.* 6.1 (2016), 24924
- Dielectric-dependent hybrid functionals of Galli and co-workers J. H. Skone et al. *Phys. Rev. B* 93.23 (2016), 235106
- LOSC functionals of Yang and co-workers C. Li et al. *Natl. Sci. Rev.* 5 (2018), 203