MARVEL

Swiss National Science Foundation

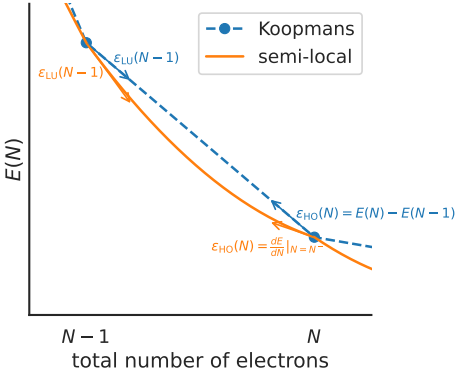
koopmans

an open-source package for accurately predicting spectral properties

Edward Linscott | Theory and Simulation of Materials, EPFL | DFT2022, Brussels, 1 Sep 2022

Koopmans functionals: theory

Goal: spectral properties with a functional theory



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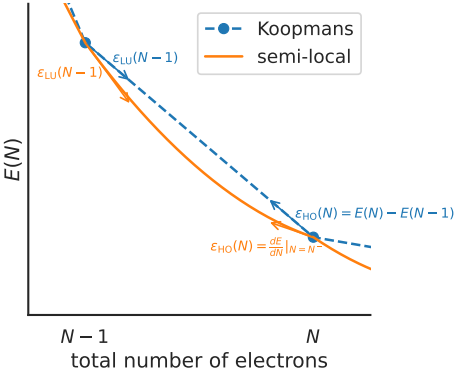
Core idea: for every orbital i their energy

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

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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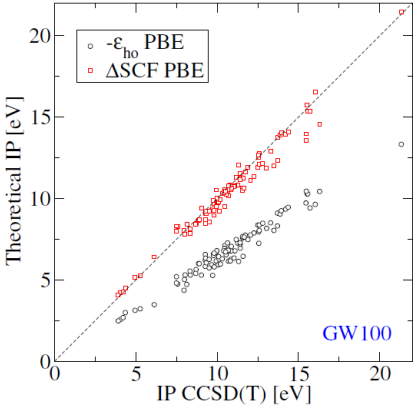

Koopmans functionals: theory

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

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:

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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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Differences to semi-local functionals:

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

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

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Differences to semi-local functionals:

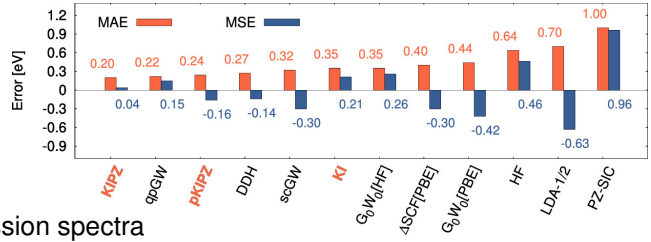
- orbital-density dependence (can use MLWF densities)
- screening

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

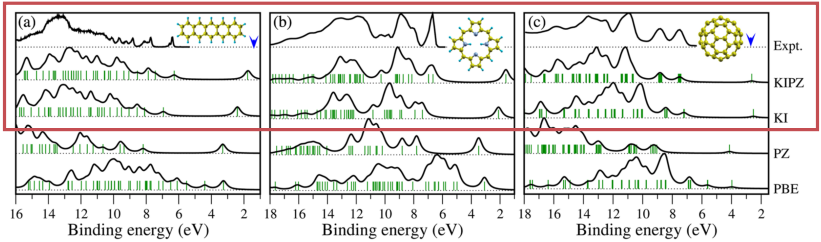
I. Dabo et al. *Phys. Rev. B* 82.11 (23, 2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (20, 2014), 075135; N. Colonna et al. *J. Chem. Theory Comput.* 15.3 (12, 2019), 1905

Koopmans functionals: results for molecules

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

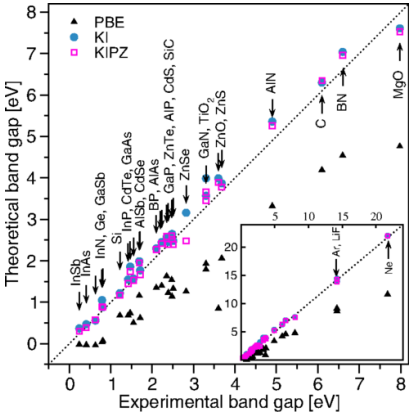


Ultraviolet photoemission spectra



N. Colonna et al. *J. Chem. Theory Comput.* 14.5 (8, 2018), 2549; N. L. Nguyen et al. *Phys. Rev. Lett.* 114.16 (24, 2015), 166405

Koopmans functionals: results for solids

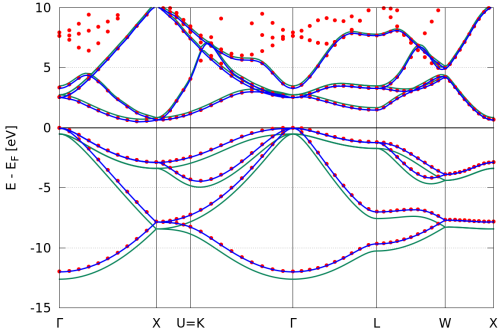


Mean absolute error (eV) across prototypical semiconductors and insulators

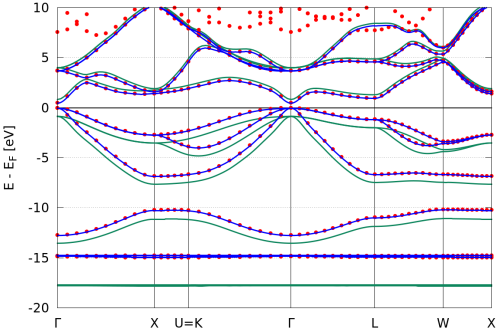
	PBE	G_0W_0	**KI**	**KIPZ**	QSGŴ
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

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

Koopmans functionals: results for solids



(a) Si, KIPZ

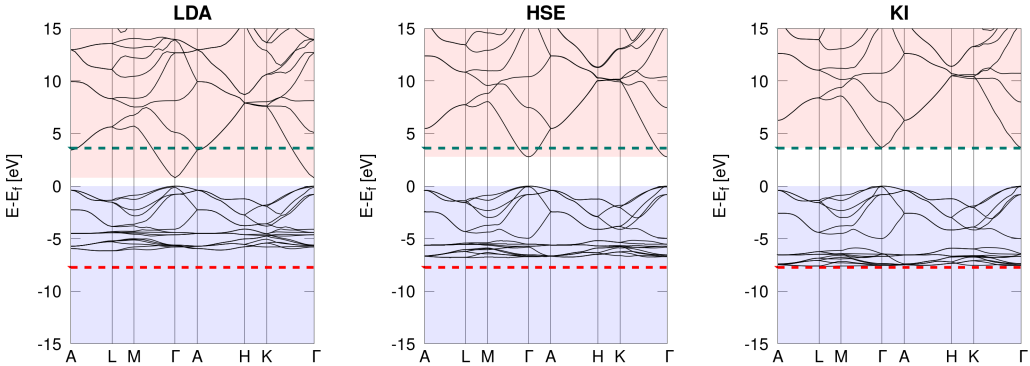


(b) GaAs, KI

		PBE	QSGŴ	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

Koopmans functionals: results for solids



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)

Koopmans functionals: the workflows

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

Koopmans functionals: the workflows

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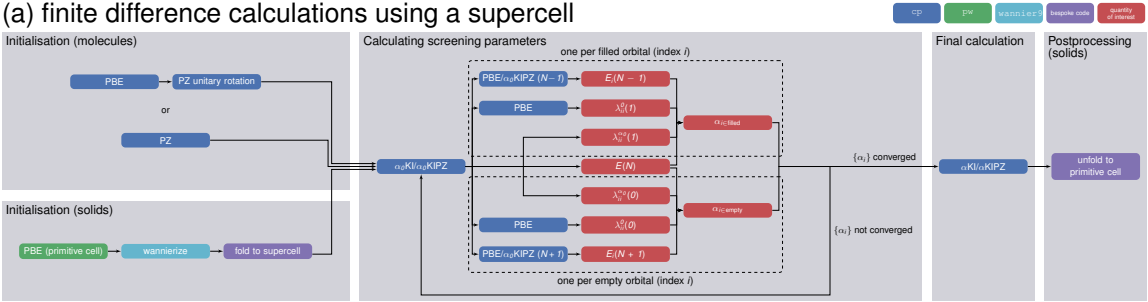
(a) finite difference calculations using a supercell



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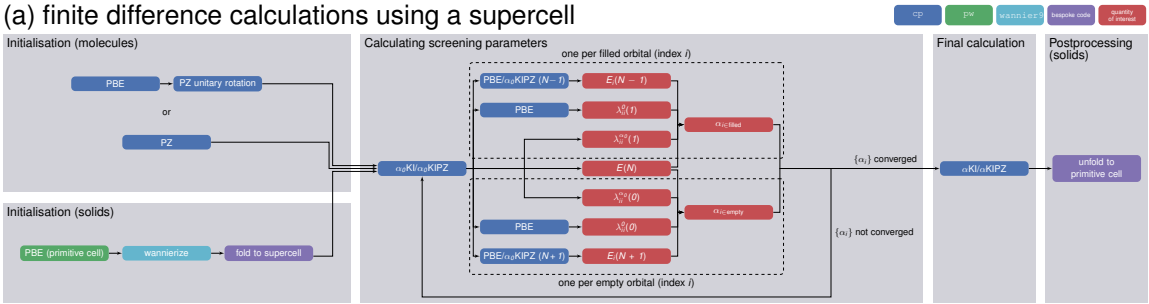
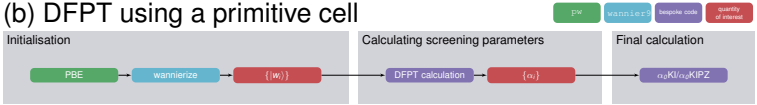


(b) DFPT using a primitive cell



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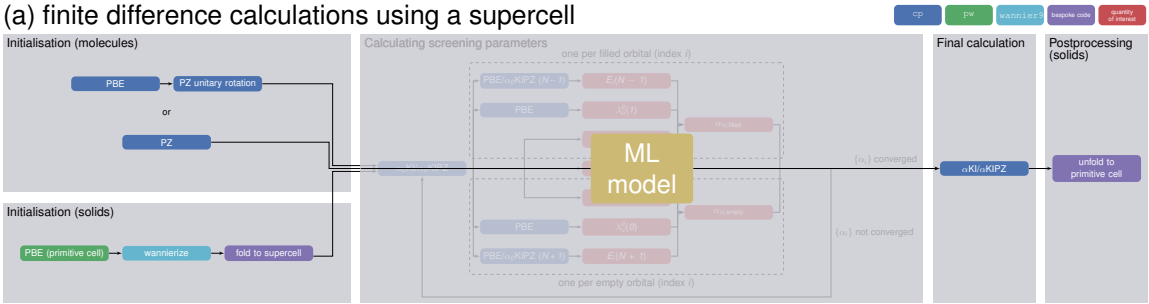

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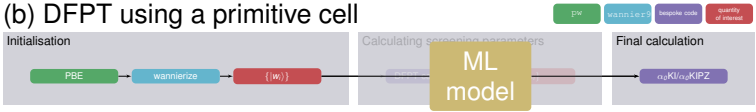


(c) via machine learning (resulting band gaps within $\sim$ 0.02 eV of explicit approach)

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

How can we make these calculations easier?

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

But complex workflows mean that...

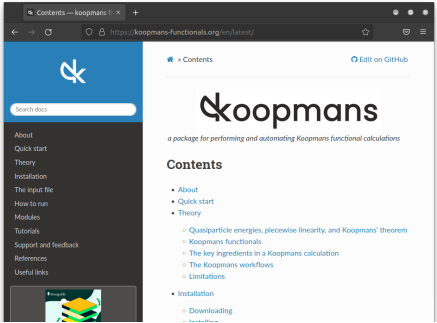
- lots of different codes that need to handshake
- lots of scope for human error
- reproducibility becomes difficult
- expert knowledge required

Our solution...

koopmans

- 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

koopmans: the input file

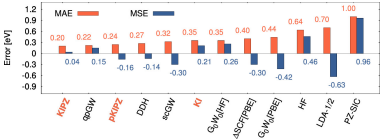

```
{
  "workflow": {
    "task": "singlepoint",
    "functional": "ki",
    "method": "dscf",
    "init_orbitals": "mlwfs",
    "alpha_guess": 0.1
  },
  "atoms": {
    "atomic_positions": {
      "units": "crystal",
      "positions": [["Si", 0.00, 0.00, 0.00],
                    ["Si", 0.25, 0.25,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

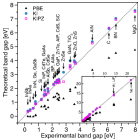
```
  "k_points": {
    "grid": [8, 8, 8],
    "path": "LGXKG"
  },
  "calculator_parameters": {
    "ecutwfc": 60.0,
    "w90": {
      "projections": [{"fsite": [0.125, 0.125, 0.125],
                       "ang_mtm": "sp3"}]
      ,
      "emp": {
        "dis_froz_max": 11.5,
        "dis_win_max":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

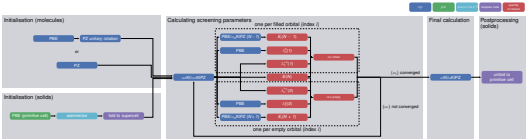
koopmans is scriptable


```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([{'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='LGXKG', 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()
```

Take home messages







- 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`
Free online school Nov 9-11 2022 *Advanced Quantum ESPRESSO tutorial: Hubbard and Koopmans functionals from linear response*. Register at `https://sites.google.com/view/hubbard-koopmans/home`
Follow @ed_linscott for updates | Slides available at `elinscott.github.io`

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Swiss National Science Foundation

SPARE SLIDES

Koopmans functionals: off-diagonal occupancies

Edward Linscott
EPFL

Recap from earlier

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

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

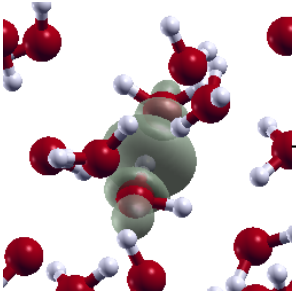
are...

- 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

Learning the screening parameters

Edward Linscott
EPFL



$\rho_i(\mathbf{r})$

power spectrum decomposition $\longrightarrow$ $\begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \vdots \end{bmatrix}$ $\xrightarrow{\text{ML model}}$ α_i

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

Details of the power spectrum

Edward Linscott
EPFL

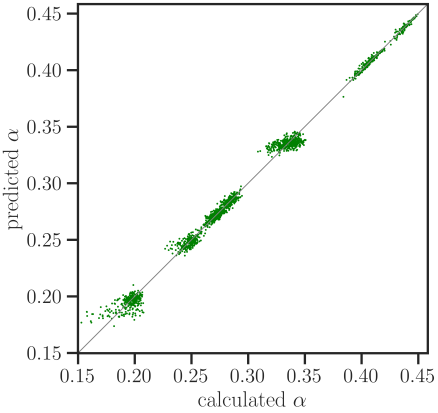
$$c^i_{nlm,k=\text{orbital}} = \int d\mathbf{r} g_{nl}(r) Y_{lm}(\theta, \varphi) \rho^i(\mathbf{r} - \mathbf{R}^i)$$

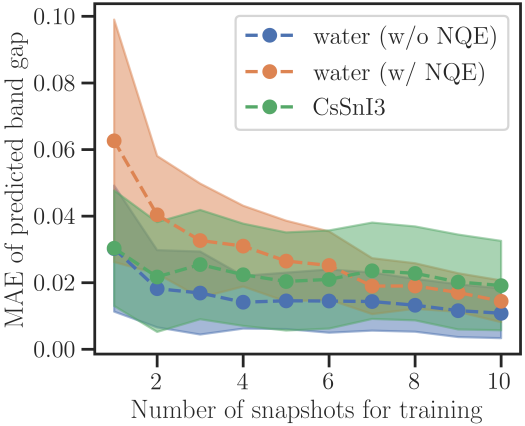
g_{nl} = orthonormalised radial Gaussian basis functions
Y_{lm} = spherical harmonics

$$p^i_{n_1 n_2 l, k_1 k_2} = \pi \sqrt{\frac{8}{2l+1}} \sum_m c^{i*}_{n_1 lm, k_1} c^i_{n_2 lm, k_2}$$

Learning the screening parameters

Edward Linscott
EPFL

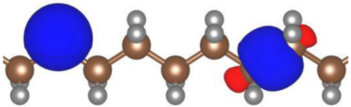




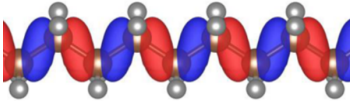
loss of accuracy of the band gap of $\sim$ 0.02 eV
(cf. when calculating screening parameters *ab initio*)

Consequences of ODD

- 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

References

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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Nguyen, N. L. et al. *Phys. Rev. Lett.* 114.16 (24, 2015).
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De Gennaro, R. et al. *Phys. Rev. B* 106.3 (5, 2022).
Colonna, N. et al. *J. Chem. Theory Comput.* (4, 2022).
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