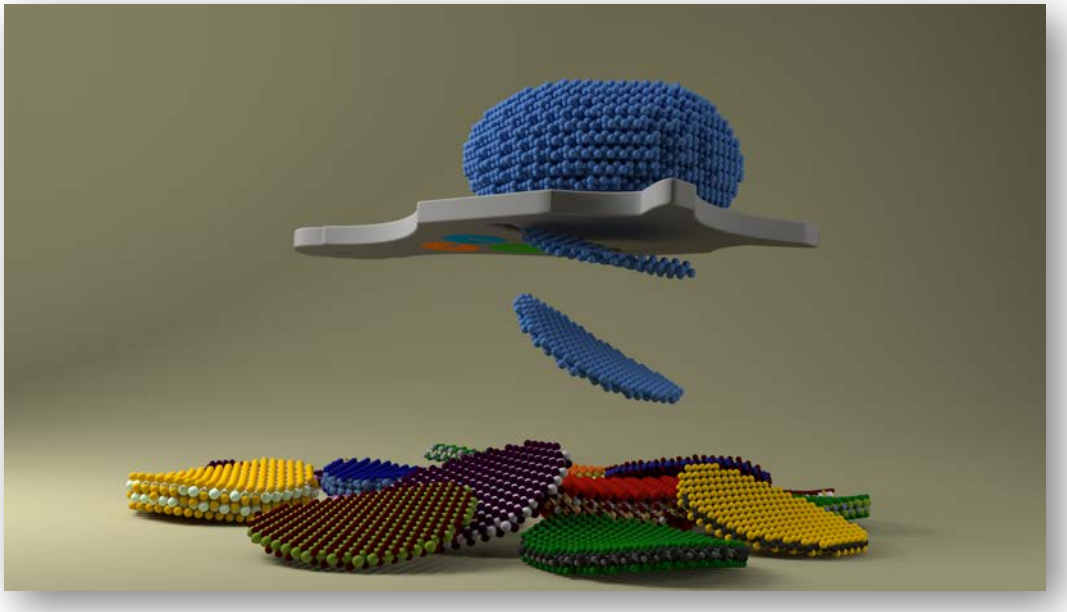
MSE-468 Lectures 9-10

DFT in action



Points to discuss from lab 1

- **Grades > ~60/100 are sufficient to pass the exam. The final grade will be considering all labs.**
- **Please read the comments in the PDF, they are there to help you improve!**

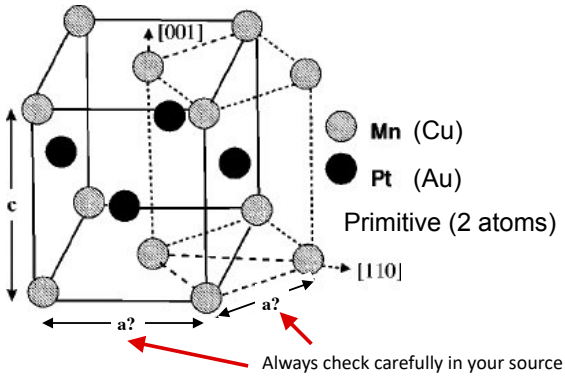
- Both functionals are fitted to reproduce certain properties —> lattice constant can be very accurate with both (small differences don't have a strong meaning)
  - *For properties that are not fitted, they might be quite off with LJ as it has only 2 parameters (e.g. bulk modulus, if it's not fitted)*
- Potential energies are in general not comparable, especially between methods
  - *Only differences such as formation energies matter*

Points to discuss from lab 1

- You define a threshold before you do your calculations (not the other way around)
  - *You want to have convergence up to XYZ and see how large your supercell etc. has to be to satisfy this condition*
- Be careful on how to define the structure. If it is the primitive or the conventional cell, the sites and lattice can change, e.g.
  - AuCu I (L10) is bcc (https://aflowlib.org/p/AB_tP2_123_a_d-001/)
  - AuCu II (L10) is FCC (https://link.springer.com/article/10.1007/BF01106562)
  - *Always check whether your results make sense, for example, if your cell increases the volume many orders of magnitude, your results are probably wrong*

Points to discuss from lab 1

CuAu $L1_0$



Conventional:
- Au: [0, 0, 0]
- Au: [0.5, 0.5, 0]
- Cu: [0.5, 0, 0.5]
- Cu: [0, 0.5, 0.5]

Primitive:
- Au: [0, 0, 0]
- Cu: [0.5, 0.5, 0.5]

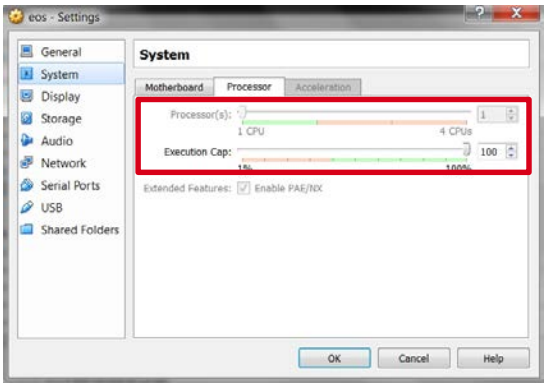
Always check carefully in your source which one is defined as **a**: the side of the *primitive cell* or of the *conventional cell*?

Remember also the discussion on "no face-centered tetragonal exists" a few lectures ago!

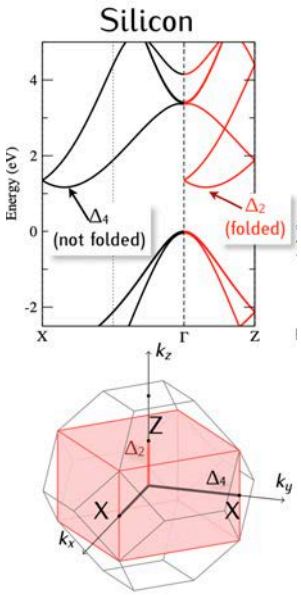
Figure adapted from http://dx.doi.org/10.1103/PhysRevB.63.144409

Points to discuss for lab 2

- Some of you find a converged k-mesh > 4x4x4.
- This, together with the clusters being down, makes calculations very slow!
- **Once you do the convergence tests on k-points, for the next steps you can just use a 4x4x4 mesh** to keep running time under control. However, **explain what you are doing, and comment on the error you expect** on the results (based on your convergence tests)
- **You can also try to run with more MPI threads**: *mpirun -np XXX:* but at most the number of cores you have in the laptop, and ensure to update your VM limits).
- In this case, you can also use *pw.x -nk YYY* (with YYY = XXX, or XXX/2, or XXX/4, …) to use YYY k-pools (requires more memory though!)



Notes on supercells and band folding



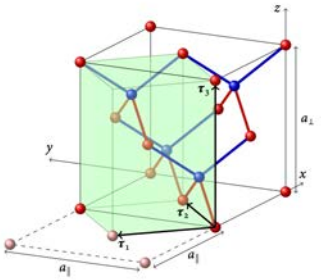


Figure 1.13 – Unit cell (green shaded parallelepiped) having one atom on each plane orthogonal to τ_3 and containing a total of four atoms. The coordinates of the basis vectors are: $\tau_1 = a_\parallel/2(-1,1,0)$, $\tau_2 = a_\parallel/2(1,1,0)$, $\tau_3 = a_\perp/2(0,0,2)$.

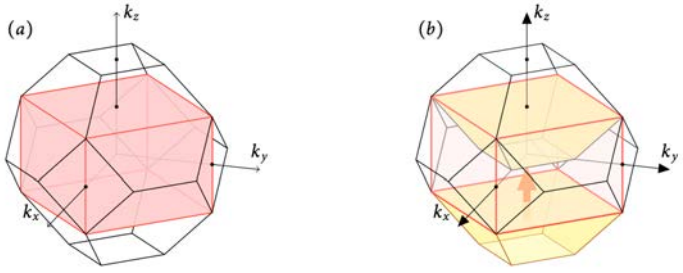
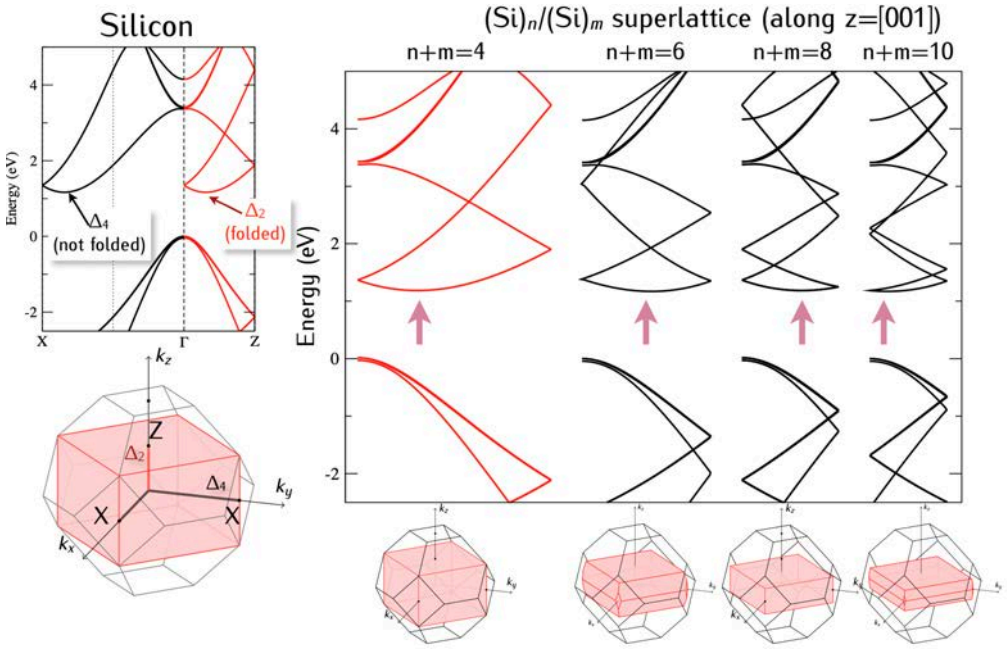
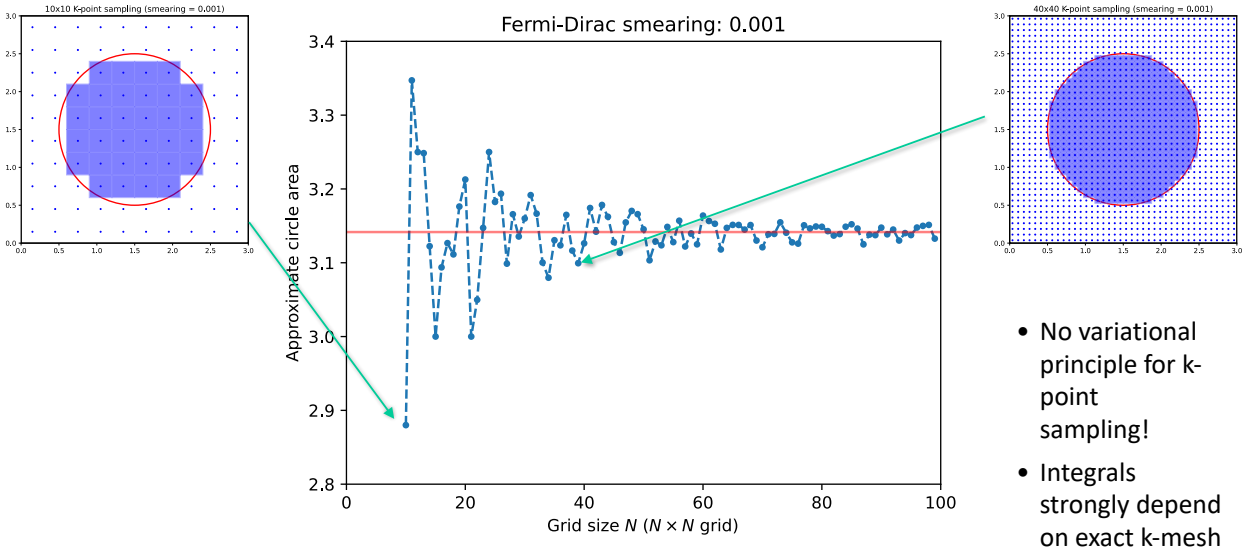


Figure 1.14 – (a) Folded Brillouin zone (red parallelepiped) corresponding to a FCC Bravais lattice with a basis vector chosen along [001] and four atoms in the unit cell. The red parallelepiped can be obtained folding the truncated octahedron as shown in panel (b).

Notes on supercells and band folding

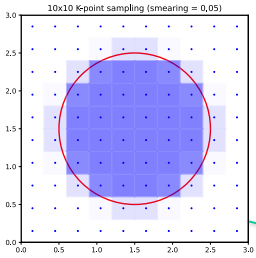


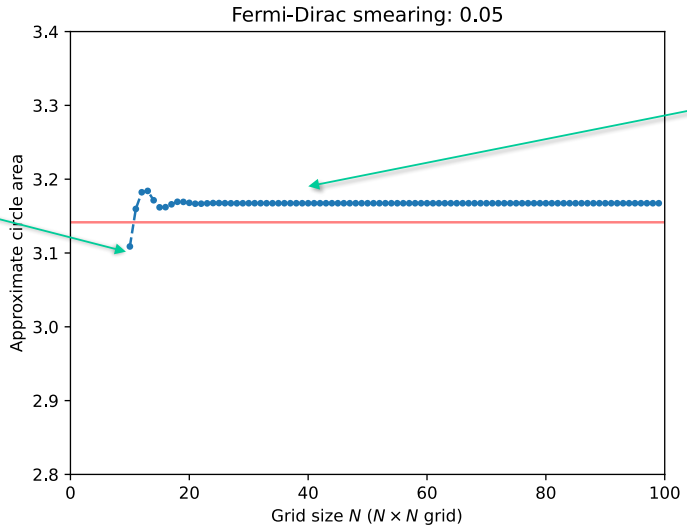
Note on k-point sampling: Analogy in 2D

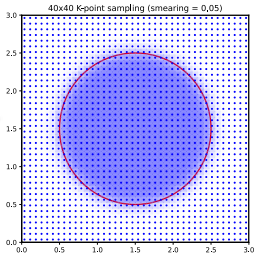


- No variational principle for k-point sampling!
- Integrals strongly depend on exact k-mesh without smearing

Note on k-point sampling: Analogy in 2D



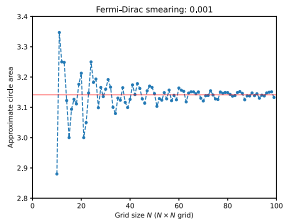


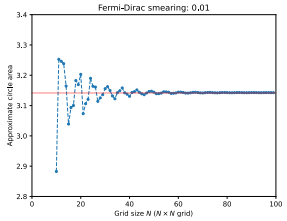


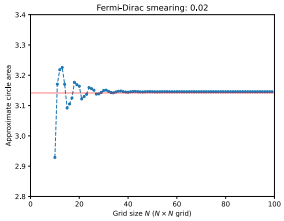
- With smearing: much smoother convergence, but… **systematic error** for large smearing (entropy contribution)

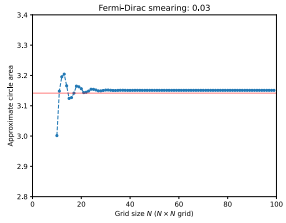
Note on k-point sampling: Analogy in 2D

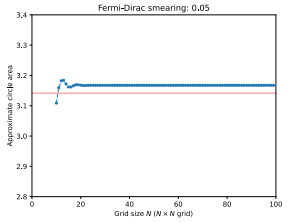
- Balance between uncontrollable errors and systematic errors

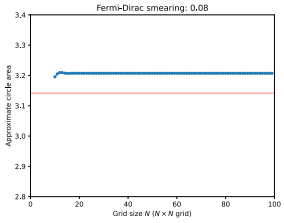






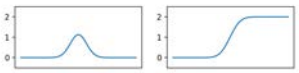




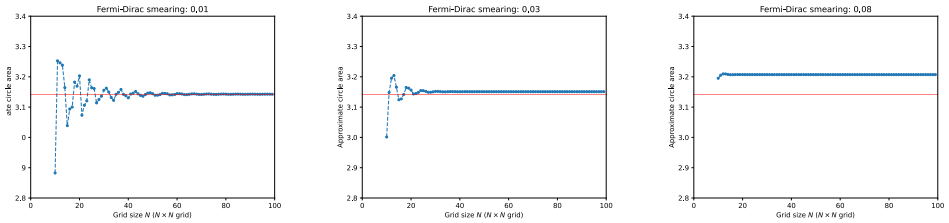


Cold smearing: larger smearing with small systematic errors

Fermi-Dirac smearing



Smearing function Integral (occupation)



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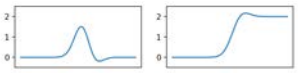

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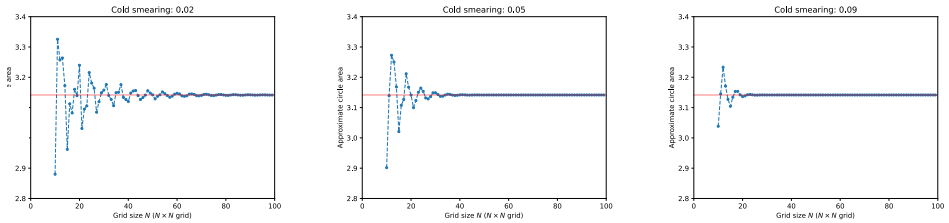
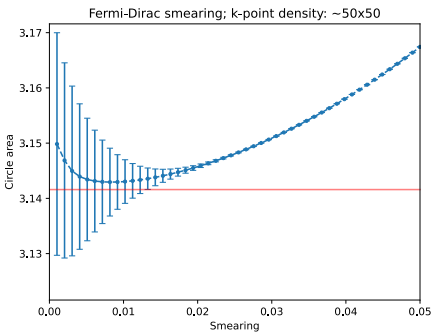


Cold smearing: larger smearing with small systematic errors

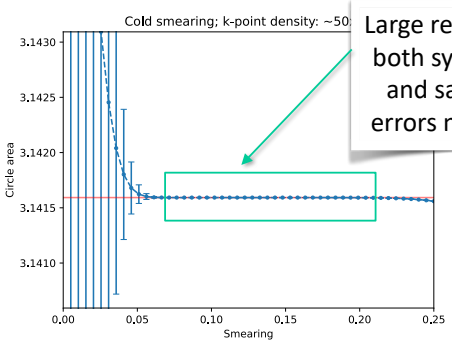
Example: 50^2 sampling points

Fermi-Dirac smearing



Note: much smaller *y* scale

Cold smearing



Large region with both systematic and sampling errors negligible

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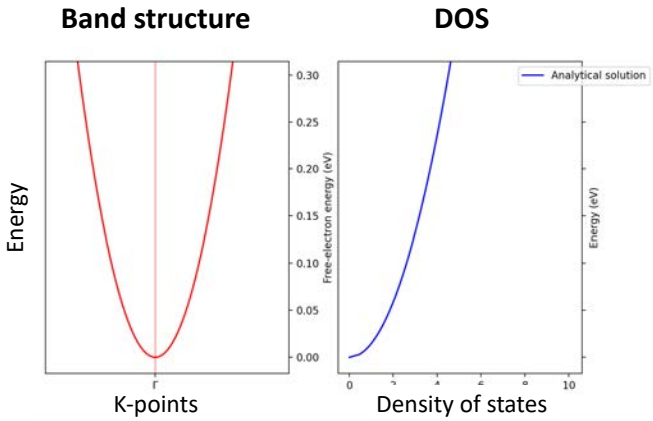
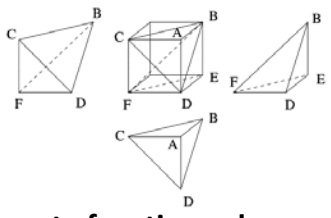
Notes on smearing and tetrahedron method for the density of states

- **Density of states (DOS)**: number of available states at a specific energy level. Units: number of states per unit volume per unit energy.
- **Integral of the DOS (over energy)**: electrons/ volume (e.g. integer number of electrons per unit cell)

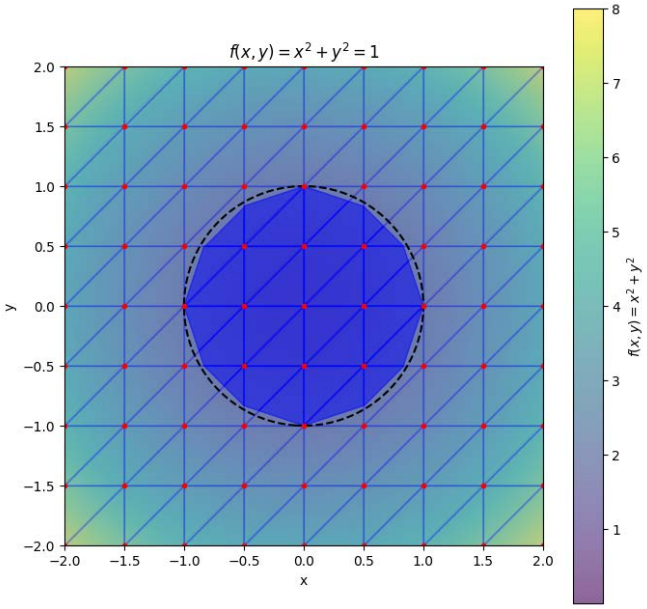


Tetrahedron method (in 2D)

- **Regular grid of k-points** used to divide space in cubes (squares) and tetrahedra (triangles)



- **Compute function values on grid** (triangle/tetrahedron **vertices**); if some vertices are inside and others outside, **linearly interpolate values on the edges/ faces**, and approximate area



Tetrahedron method

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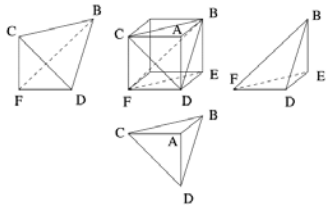

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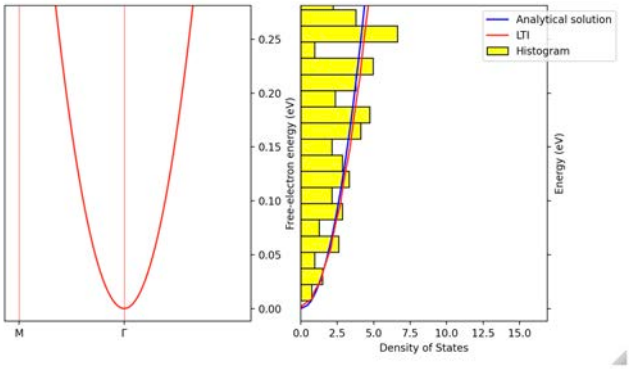
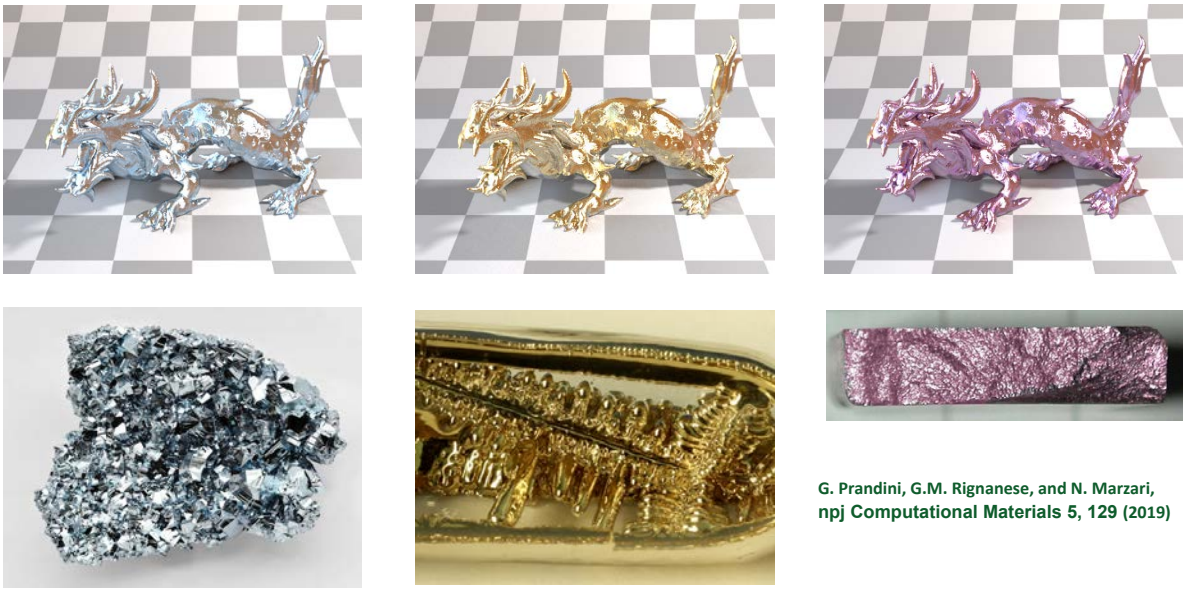


Example for a free-electron gas, comparing histogram with linear tetrahedron method

Some results from DFT

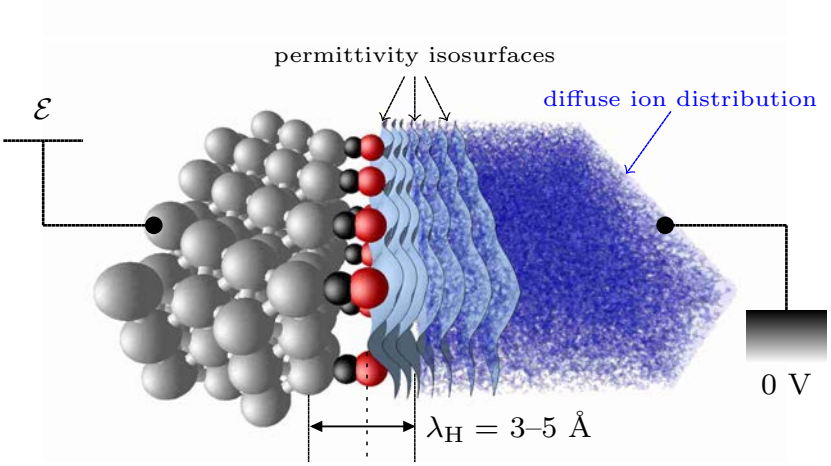
Multi-scale/physics: color and reflectivity



G. Prandini, G.M. Rignanese, and N. Marzari,
npj Computational Materials 5, 129 (2019)

Need the "true" band structure (not the Kohn-Sham, with wrong gap):
many-body perturbation theory (GW approximation)

Multi-scale/physics: electrochemistry



Dabo, Bonnet, Li and Marzari, *"Ab-initio Electrochemical Properties of Electrode Surfaces"*, in Fuel Cell Science: Theory, Fundamentals and Bio-Catalysis, A. Wiecowski and J. Norskov (2011).

O. Andreussi, I. Dabo and N. Marzari, "Revised self-consistent continuum solvation in electronic structure calculations", J. Chem. Phys. 136, 064102 (2012). www.quantum-environment.org

Magnetic spectroscopies: NMR Chemical Shifts

- **NMR**: Nuclear Magnetic Resonance
- Nuclear magnetic levels are affected by the local chemical neighbourhood
- *Resonance frequencies (or their shift) are a fingerprint of local environment*

C. Pickard et al., PRB 63, 245101 (2001)

F. Mauri et al., PRL 87, 085506 (2001)

Chemical shift: $\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r}) = -\vec{\vec{\sigma}}(\mathbf{r})\mathbf{B}.$

TABLE I. ^{11}B NMR chemical shifts δ_{BTE} and ^{13}C NMR chemical shifts δ_{TMS} in the closo-borane molecules. By ortho, meta, and antipodal we indicate the B atoms which are 1st, 2nd, and 3rd nearest neighbors of the C atom, respectively.

Molecule	Atomic site	Experiment	Theory
		B δ_{BTE}	B δ_{BTE}
$(B_{12}H_{12})^{2-}$		−14.9[a]	(−14.9)
$(B_{11}CH_{12})^{-}$	Ortho	−16.3[b]	−16.2
	Meta	−13.3[b]	−11.7
	Antipodal	−6.9[b]	−5.4
		C δ_{TMS}	Cδ_{TMS}
$(B_{11}CH_{12})^{-}$		54.6[c]	(54.6)

[a]In CD_3CN solvent, Ref. [18].
[b]In hexadeuterioacetone, Ref. [19].
[c]Ref. [20].

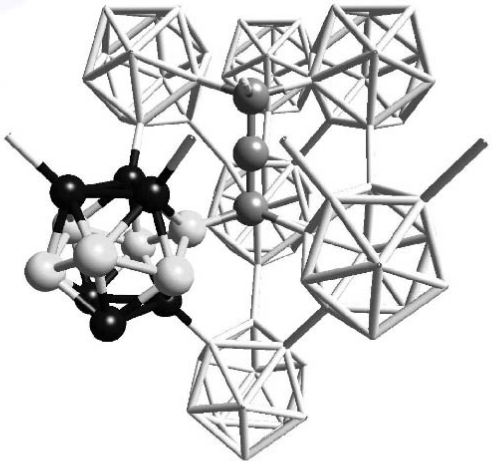
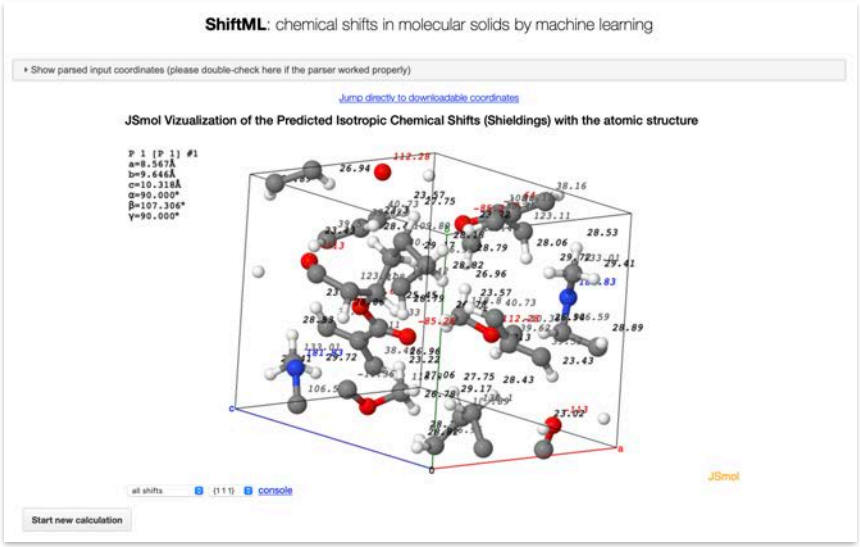


FIG. 1. Atomic structure of B_4C. The black atoms are on the so-called polar sites, bonded to neighboring icosahedra. The white atoms form a puckered hexagon and are in equatorial sites. The grey atoms form the chain, to which the equatorial atoms are bonded.

Chemical shifts using Machine Learning



https://www.materialscloud.org/work/tools/shiftml

M. Ceriotti's group:

- [1] F. M. Paruzzo et al., Nature Communications, 9, 4501 (2018)
- [2] F. Musil et al., JCTC, 15 906 (2019)

Article

Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride

Nature 578, 66 (2020)

https://doi.org/10.1038/s41586-020-1955-z
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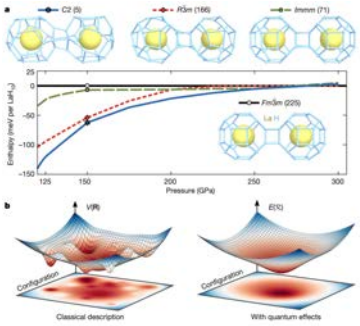
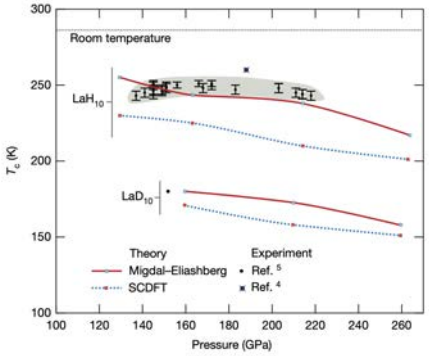
Published online: 5 February 2020

Ion Errea[1,2,3], Francesco Belli[1,2], Lorenzo Monacelli[4], Antonio Sanna[5], Takashi Koretsune[6], Terumasa Tadano[7], Raffaello Bianco[2], Matteo Calandra[8], Ryotaro Arita[9,10], Francesco Mauri[4,11] & José A. Flores-Livas[4*]

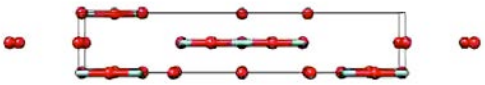
The discovery of superconductivity at 200 kelvin in the hydrogen sulfide system at





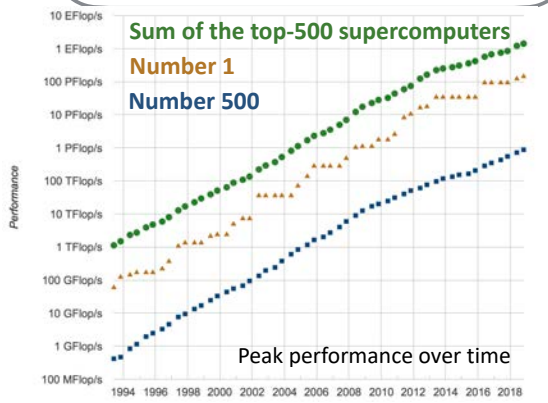
Quantum atomic fluctuations crucial to stabilize crystal structure (classical approach not enough!)

High-throughput simulations



Aim: Run simulations on tens of thousands of materials to **discover novel functional materials**

The high-throughput era



Accuracy and predictive power of quantum engines

150,000x increase in the past 20 years

1 month (2005)

↓

10 seconds (2025)

Result: materials design and discovery via ***high-throughput computations***

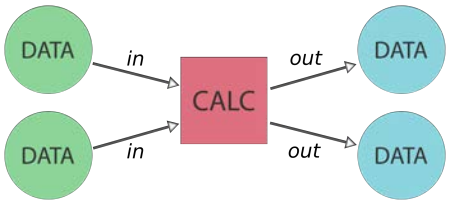
Challenges in high-throughput HPC

- **Workflow automation**
  - Need tools to define complex workflows with advanced error handling
  - An automated, robust and scalable engine to run the workflows
- **Data management**
  - Data should be stored reliably and efficiently
  - Stored data should be interoperable and queryable
- **Reproducibility**
  - All produced data should be reproducible by storing the full provenance

Data provenance

Simple recipe

- Store data transformations or '**calculations**'
- Store its **inputs** and their metadata
- Store its **outputs** and their metadata
- Most **crucially** store the **inter-connections**



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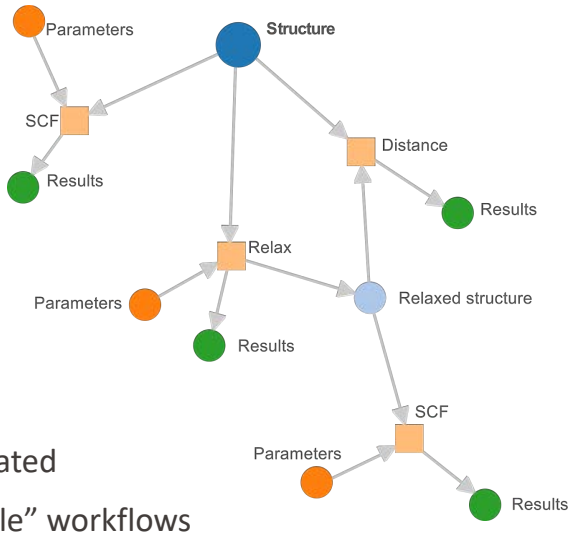

Provenance graphs

- When data gets reused, a directed graph is created
- That quickly grow in complexity even for "simple" workflows

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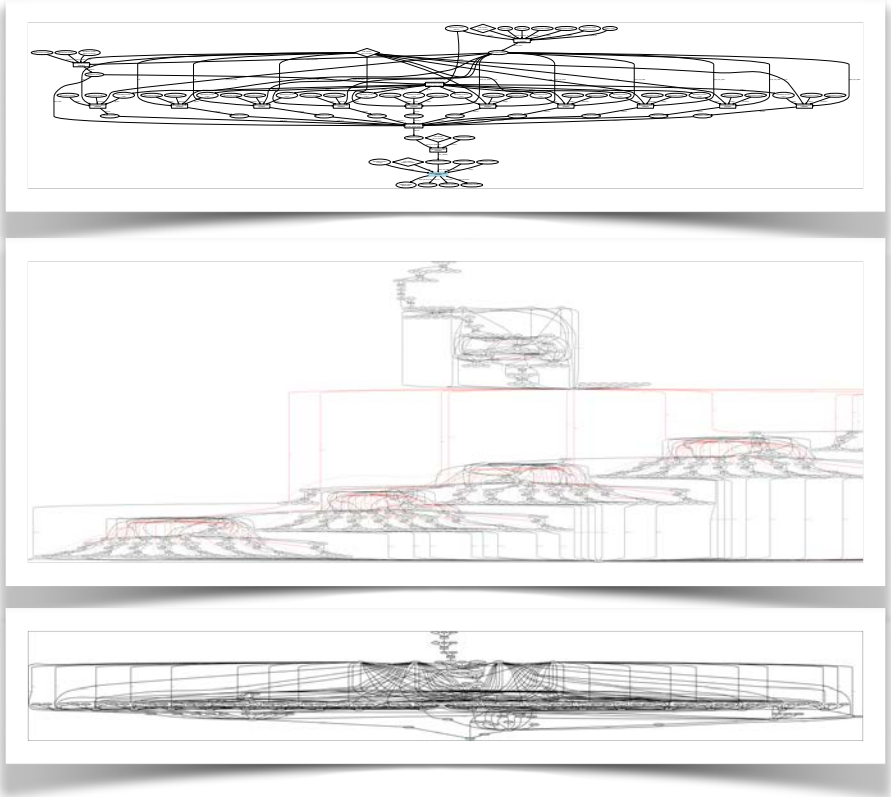
"Simple" graphs of workflows for a single material



Phonon dispersion

(atom oscillations around equilibrium positions: thermal transport, electronic mobility, …)

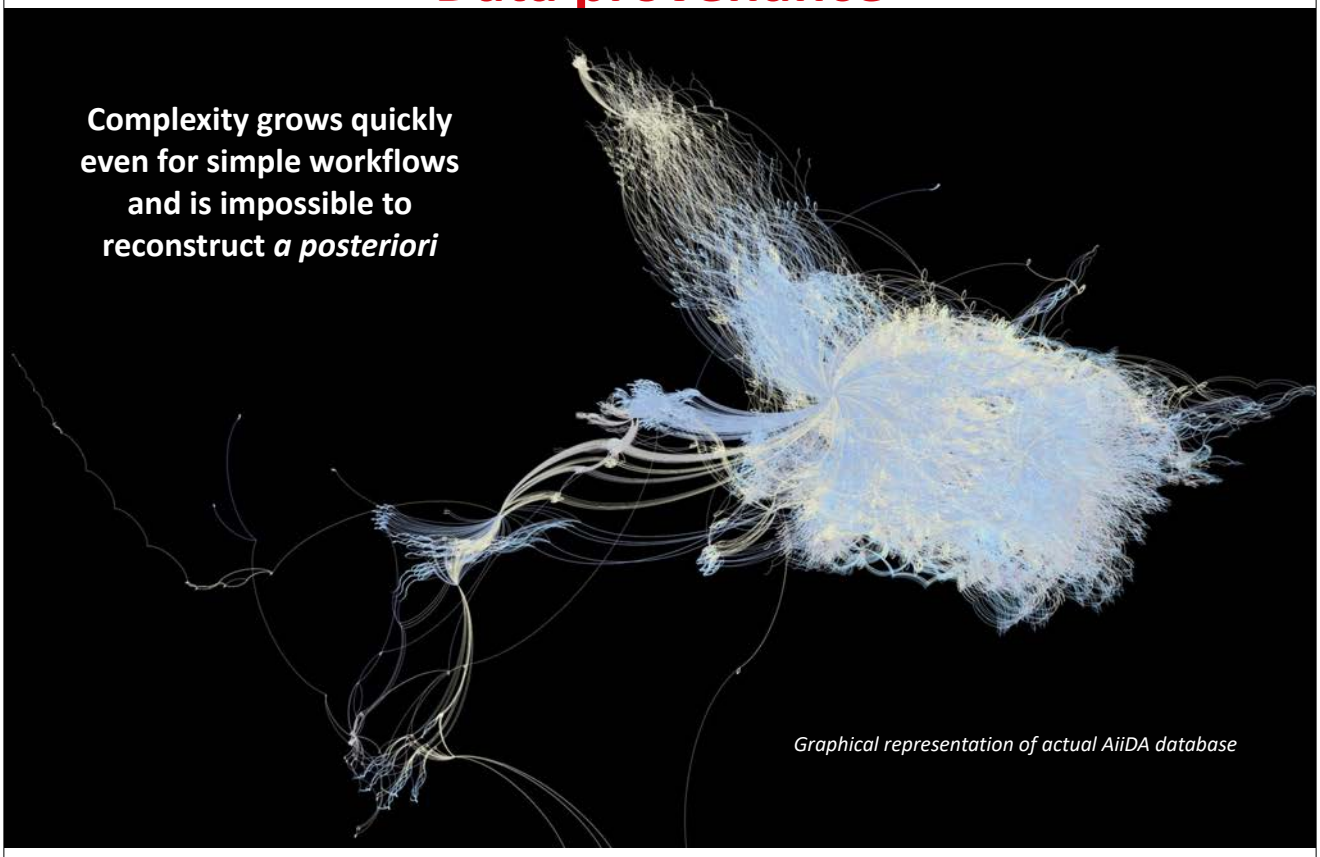
Molecular dynamics of Lithium in a solid electrolyte

(Discover novel, safe and efficient electrolytes for Li-batteries)

Elastic constants

(response of materials to stresses and deformations)

Data provenance



AiiDA

- **COMPUTATIONAL SCIENCE INFRASTRUCTURE**
- **FOR HIGH THROUGHPUT WORKFLOWS**
- **WITH FULL DATA PROVENANCE**

Language: implemented and API in python

License: MIT open source **http://www.aiida.net/**

Source: https://github.com/aiidateam/aiida-core

MIT LICENSED
open source initiative

Scalable workflow engine

Automated full data provenance

Built-in support for HPC

Flexible plugin system

G. Pizzi et al., Comp. Mat. Sci. 111, 218-230 (2016)
S.P. Huber et al., Scientific Data 7, 300 (2020)

AiiDA support: plugins and workflows

Calculation | **Data** | **Parsers** | **Transport and scheduler** | **Workflows** | **Importers & exporters**

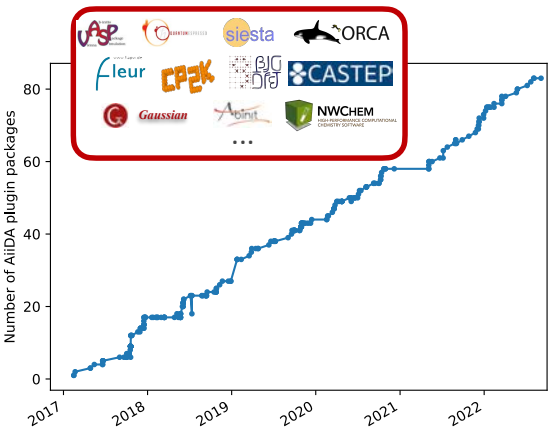
AiiDA PLUGIN REGISTRY

Registered plugin packages: 87

Calculations	123 plugins in 53 packages
Parsers	104 plugins in 54 packages
Data	96 plugins in 29 packages
Workflows	128 plugins in 37 packages
Console scripts	26 plugins in 16 packages
Other	98 plugins in 26 packages

https://aiidateam.github.io/aiida-registry/

- Almost **100 codes currently supported,** >90 workflows
- Many are **community-contributed**



The need for turn-key solutions

- Like in a car: drive without need to know how the engine works
  - Engines are "robust"
  - Just turn the key and drive
  - I need a driving license, but I don't need to learn again if I change the brand of my car

Accessible and interoperable workflows: AiiDA common workflow interfaces (ACWF)

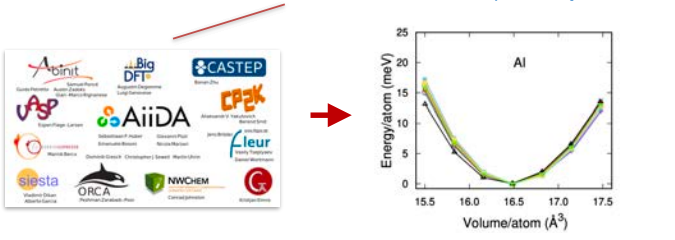
- As a non-expert, be able to ask

"Please run an **equation of state** with code **[Quantum ESPRESSO|SIESTA|VASP|...]** on the XXX supercomputer, using YY nodes, and **automatically choose numerical parameters** to get converged results."

S. P. Huber et al., npj Comput. Mater. 7, 136 (2021)

- As an expert:
  - adapt the automatic parameters, if needed
  - check details of already-run simulations (by someone else): via provenance tracking

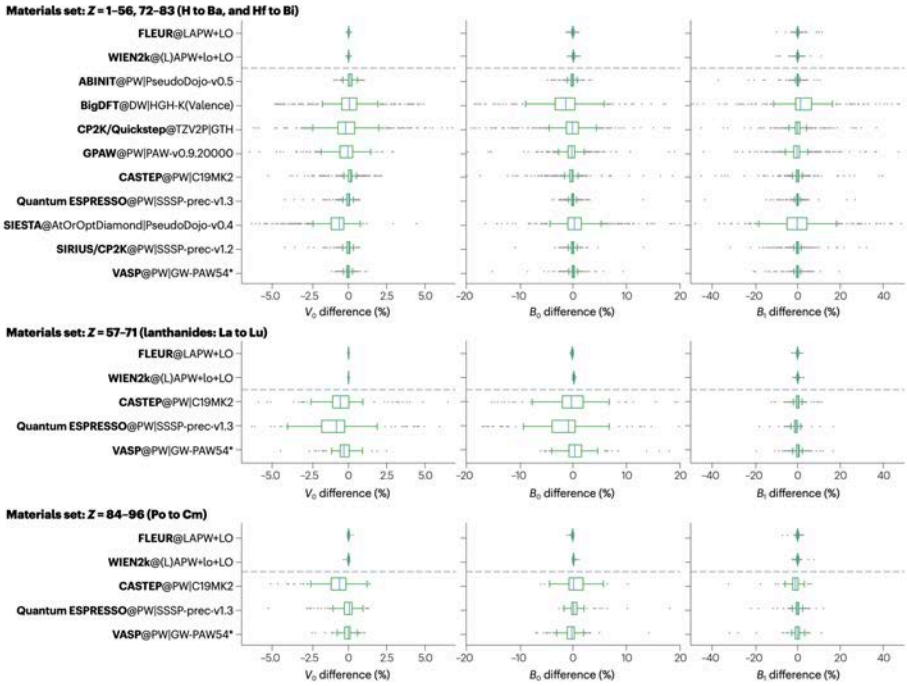
$ aiida-common-workflows launch **eos siesta** --structure=**Al** --protocol=**precise**



https://github.com/aiidateam/aiida-common-workflows/

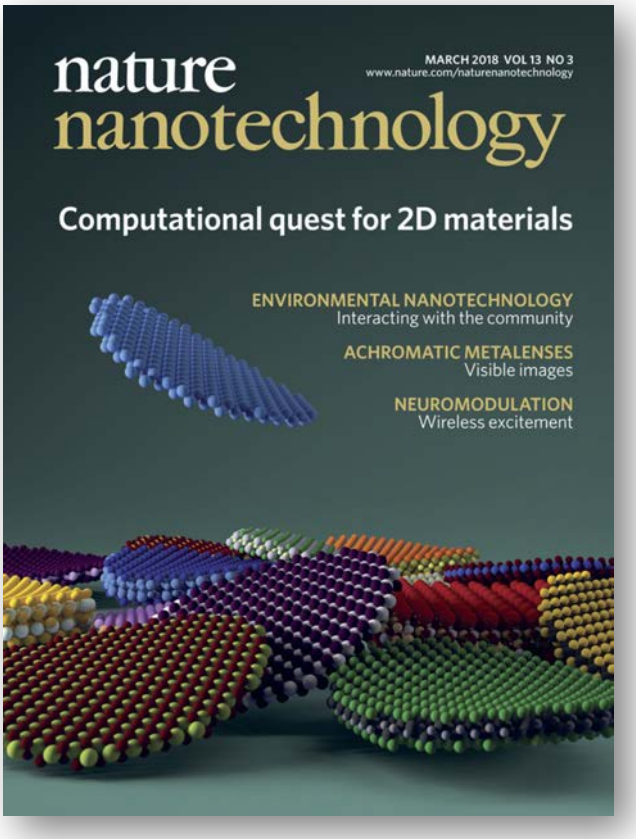
Common-workflows for verification

- Common workflows used for the verification effort discussed last time



E. Bosoni et al., Nat. Rev. Phys. 6, 45 (2024)

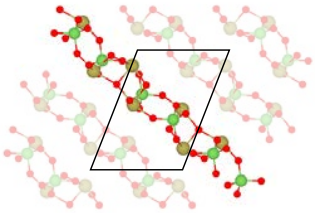
COMPUTATIONAL EXFOLIATION OF ALL KNOWN INORGANIC MATERIALS



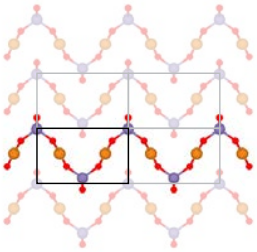
N. Mounet et al., Nature Nanotech 13, 246–252 (2018)

Robust algorithm to identify layers, but also 1D or 0D clusters

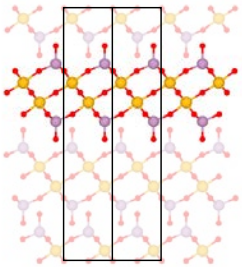
Layers not parallel to a crystallographic axis



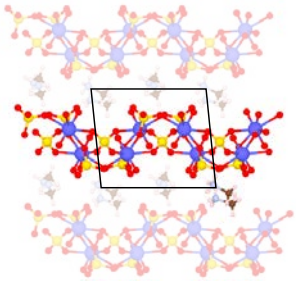
Layers spanning multiple unit cells



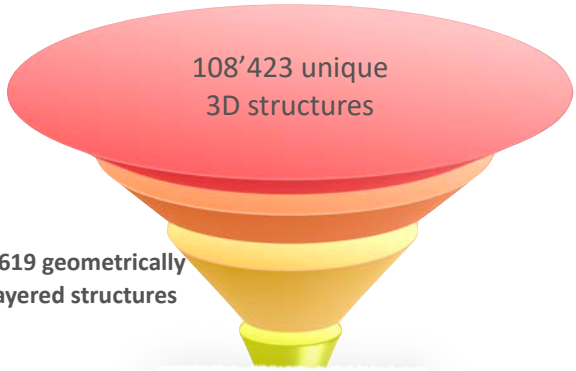
Layers with no empty space along stacking direction



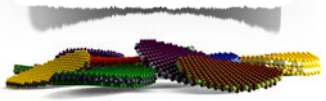
Layers with subunits (e.g. 0D intercalates)



Start: ~480'000 non-unique 3D structures from ICSD + COD



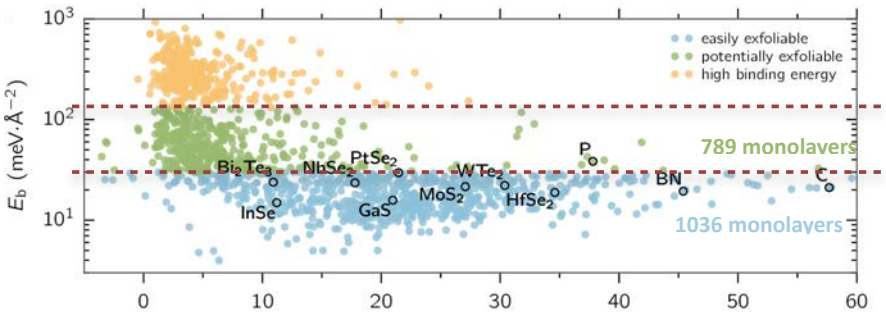
DFT filtering: 1'825 exfoliable structures



Filtering exfoliable structure with simulations: binding energy

- Large portfolio of ~1800 exfoliable layered materials from experimentally-known compounds
- 500'000+ DFT calculations

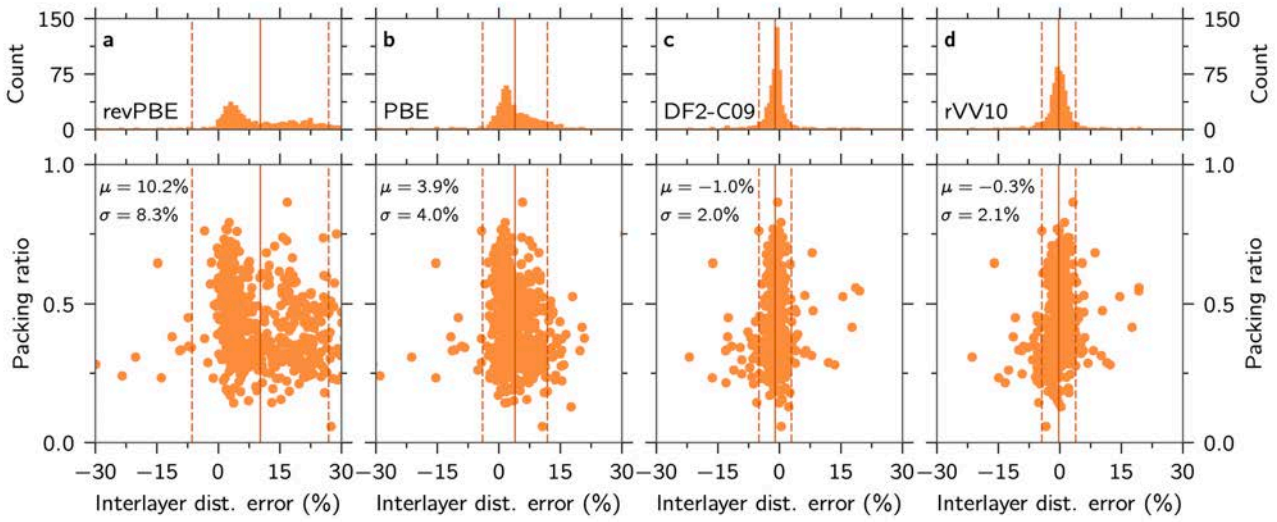
Binding energy



Difference in interlayer distance when computed with/without vdW functionals (%)

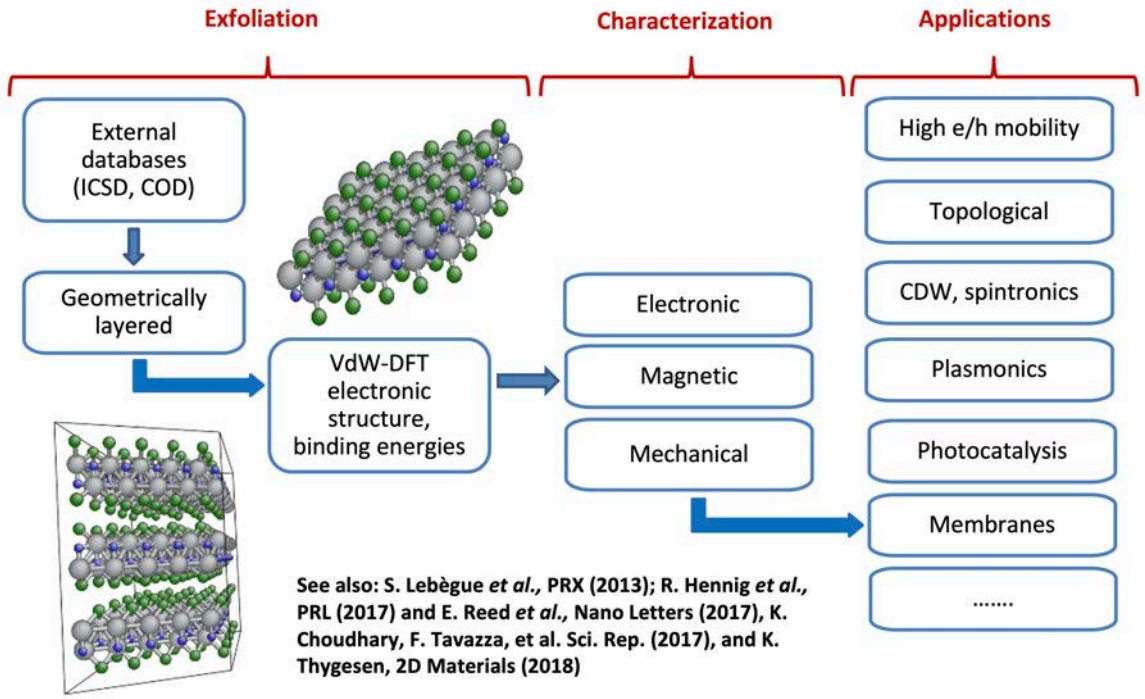
N. Mounet et al., Nature Nanotech 13, 246–252 (2018)

van-der-Waals functionals: benchmark



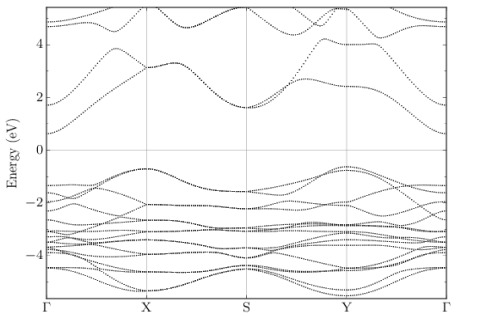
N. Mounet et al., Nature Nanotech 13, 246–252 (2018)

HIGH-THROUGHPUT COMPUTATIONAL EXFOLIATION

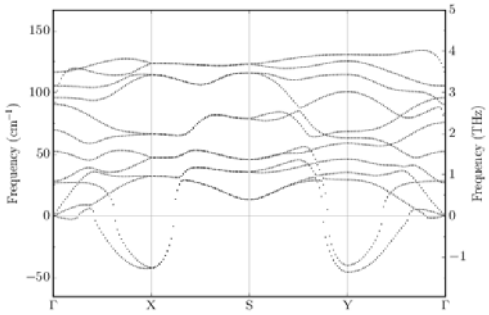


See also: S. Lebègue *et al.*, PRX (2013); R. Hennig *et al.*, PRL (2017) and E. Reed *et al.*, Nano Letters (2017), K. Choudhary, F. Tavazza, et al. Sci. Rep. (2017), and K. Thygesen, 2D Materials (2018)

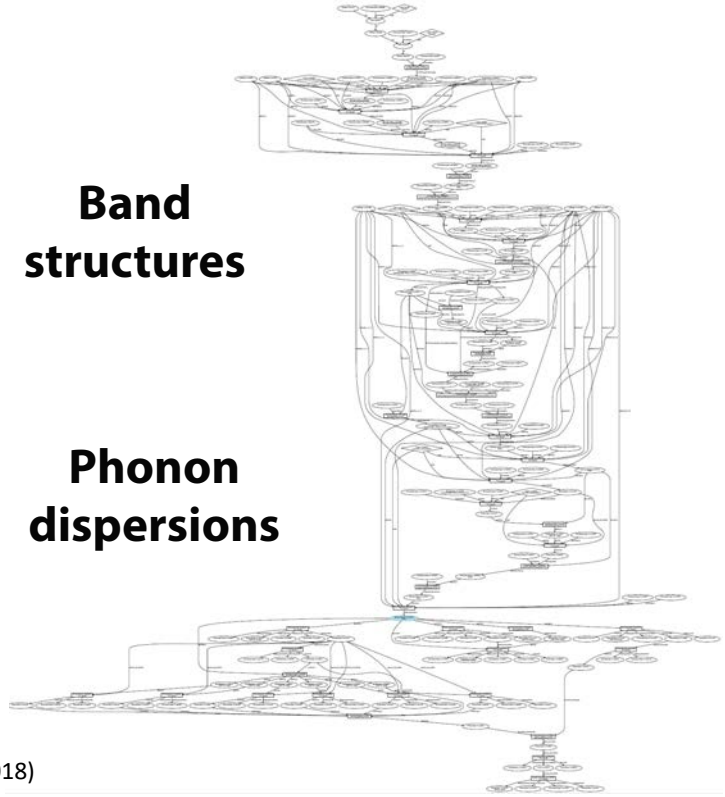
ALL AUTOMATED WITH AiiDA (http://aiida.net)



Band structures

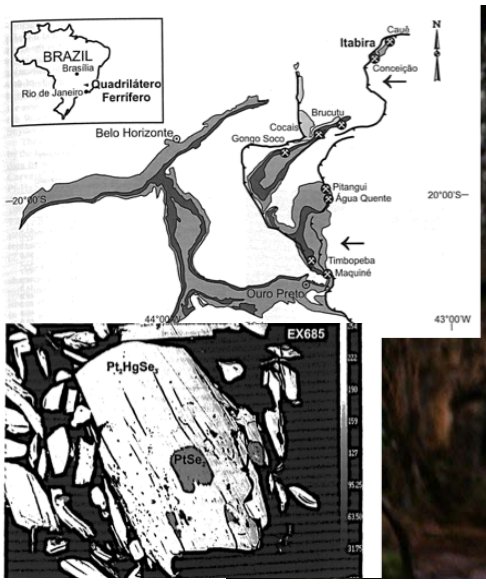


Phonon dispersions



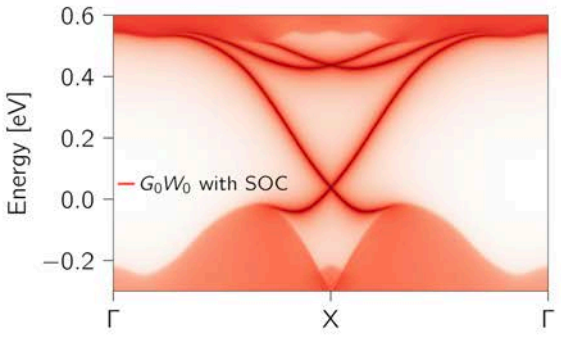
N. Mounet et al., Nature Nanotech 13, 246–252 (2018)

THE DISCOVERY OF JACUTINGAITE



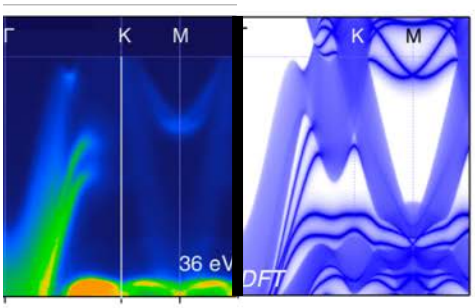
THE DISCOVERY OF JACUTINGAITE

Monolayer: room-temperature Kane-Mele quantum spin Hall insulator – G_0W_o with S.O.C.



A. Marrazzo et al., Phys. Rev. Lett. 120, 117701 (2018)

Bulk: topologically-protected 001-surface states, exp vs DFT



C. Cucchi et al., Phys. Rev. Lett. 124, 106402 (2020)
A. Marrazzo et al., Phys. Rev. Research 2, 012063(R) (2020)

$$H = \underbrace{t \sum_{\langle ij\rangle\alpha} c^\dagger_{i\alpha} c_{j\alpha}}_{1^{st}\text{NN}} + \underbrace{it_2 \sum_{\langle\langle ij\rangle\rangle\alpha\beta} v_{ij} s^z_{\alpha\beta} c^\dagger_{i\alpha} c_{j\beta}}_{\text{KM SOC}}$$

$$+ \underbrace{t_2' \sum_{\langle\langle ij\rangle\rangle\alpha} c^\dagger_{i\alpha} c_{j\alpha}}_{2^{nd}\text{NN}} + \underbrace{it_2'' \sum_{\langle\langle ij\rangle\rangle\alpha\beta} u_{ij} (\mathbf{s}\times\mathbf{d}^0_{ij})^z_{\alpha\beta} c^\dagger_{i\alpha} c_{j\beta}}_{\text{in-plane SOC}},$$

$$H_{J3KM} = H_{KM} + \lambda \tilde{H}_{2^{nd}NL}$$

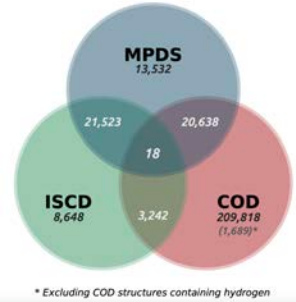
MC3D database

Michail Minotakis, Marnik Bercx, Sebastiaan Huber, Timo Reents, Nicola Marzari, GP et al.

ICSD FIZ Karlsruhe · COD · MPDS

901,210 Experimental structures

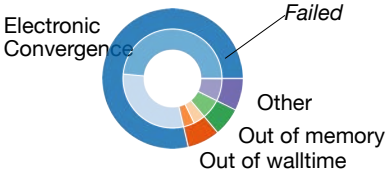
TOTAL: *277,419* *(69,290)**



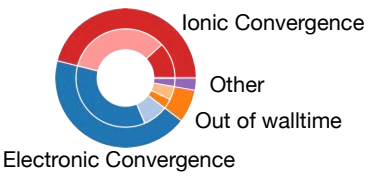
** Excluding COD structures containing hydrogen*

- Robust workflows to reduce failure rate

Reconnaissance SCF



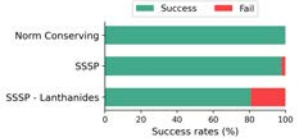
Structure Optimization



- New ensemble-DFT implementation

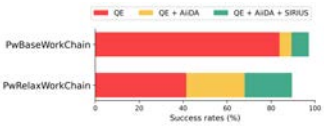
SIRIUS

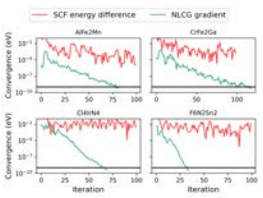
NLCG success rate



CSCS

Workchain success rates

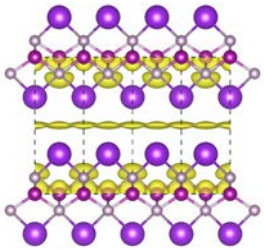


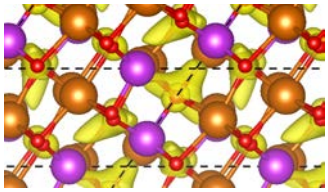


Electrides

Francisco F. Ramirez,
Marnik Bercx, Nicola Marzari, GP

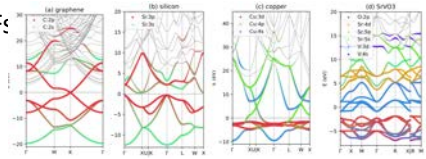
- **Electrides**:
  - materials with some of the electrons occupying interstitial spaces
  - low workfunction: excellent electron emitters; high catalytic activity
- **Goal**: Identify **novel electrides** in the MC3D
- **Result**: 352 new electrides identified, including:
  - *non-metallic candidates* (electride behaviour under doping)
  - *electrides with predominance of one spin channel* (interesting for spintronic applications)

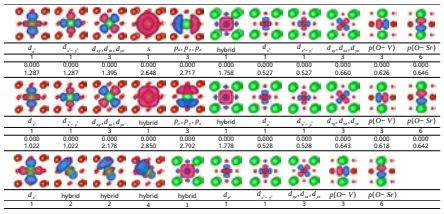




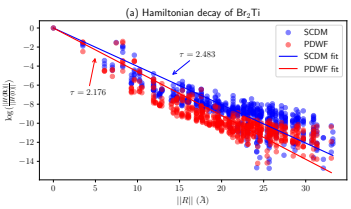
Automated Wannier functions

- **New approach based on "projectability disentanglement"**
- Automated Wannierization of 17,744 materials (1,155,049 MLWFs
- **Average band-distance error of 1.7 meV w.r.t. DFT**
- Extract information on:

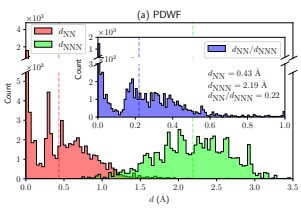




Shape



Hamiltonian hoppings decay



Position of WF centres

...

- Starting point to generate ML models to predict Hamiltonian and materials properties
- Currently extended also to spin-orbit and magnetic systems, paper to be published soon (Y. Jiang et al.): also brings Wannierization success rate to 100%!

J. Qiao *et al.*, npj comput. Mater 9, 206 (2023)
J. Qiao *et al.*, npj comput. Mater 9, 208 (2023)

Training ML models - ferroelectrics

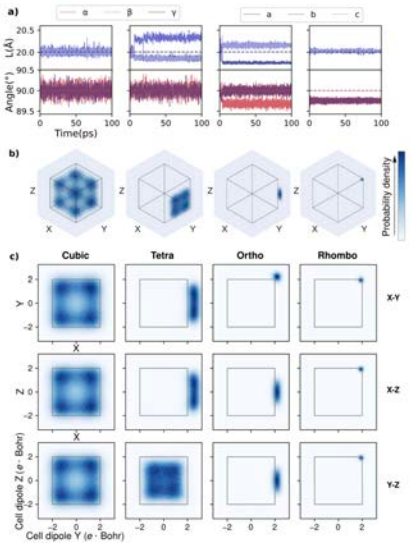
ARTICLE OPEN

Check for updates

Thermodynamics and dielectric response of $BaTiO_3$ by data-driven modeling

Lorenzo Gigli[1✉], Max Veit[1], Michele Kotiuga[2], Giovanni Pizzi[2], Nicola Marzari[2] and Michele Ceriotti[1]

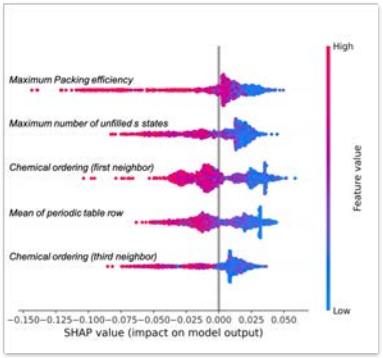
L. Gigli et al. npj Comput. Mater. 8, 209 (2022)
https://doi.org/10.1038/s41524-022-00845-0

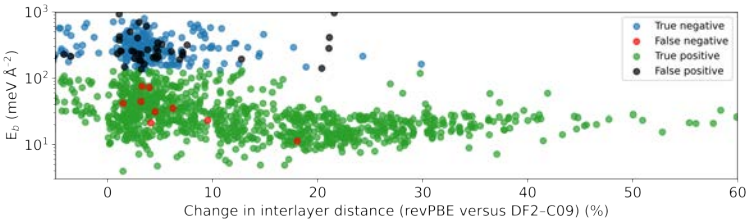


- DFT training data generated automatically with AiiDA
- Easy to check numerical settings and select those to use for ML training

Training ML models - 2D materials

- Predict if 2D systems can be exfoliated from a bulk material
- Train **excellent ML model (98% recall rate)** using DFT binding-energy results from Mounet *et al.*, Nat. Nanotech. (2018)
- Understand the 5 most important variables in the model



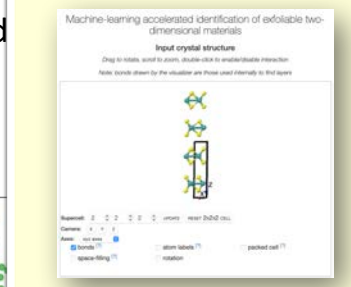


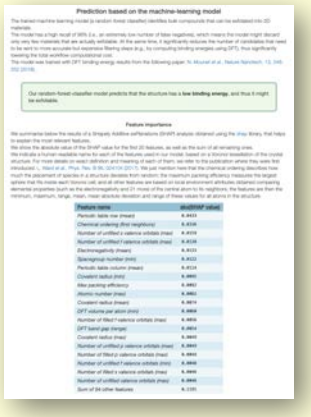
Vahdat, Agrawal, GP, Mach. Learn.: Sci. Technol. 3 (2022) 045014

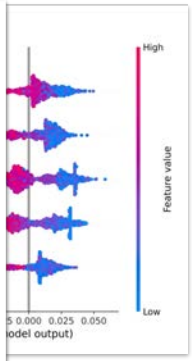
Training ML models - 2D materials

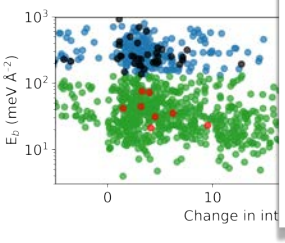
- Predict if 2D systems can be exfoliated from a bulk materi
- Train **excell** DFT binding Nat. Nanote
- Understand the model

- Also: **free online tool** to perform the prediction "live"!
  https://ml-layer-finder.materialscloud.io/
-







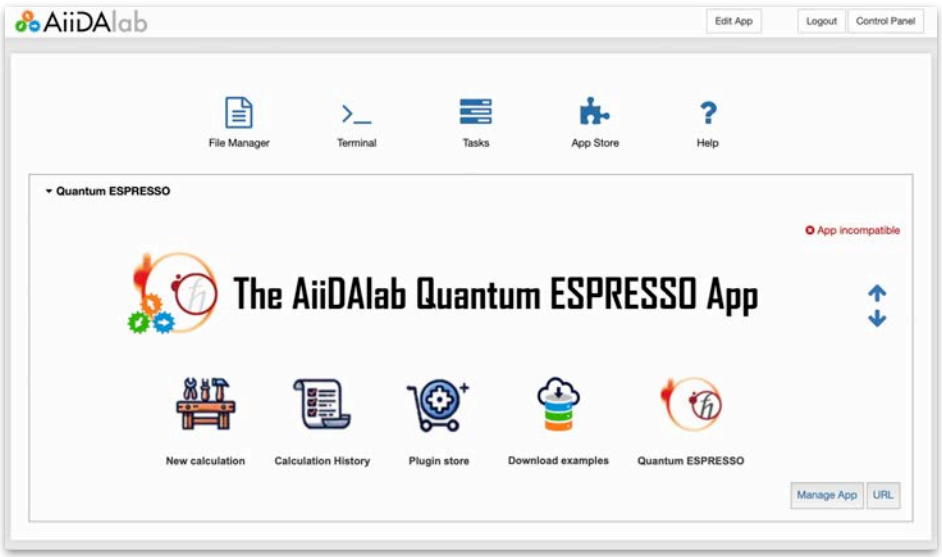


ach. Learn.:
45014

Making simulations accessible with AiiDAlab (and the AiiDAlab Quantum ESPRESSO app)

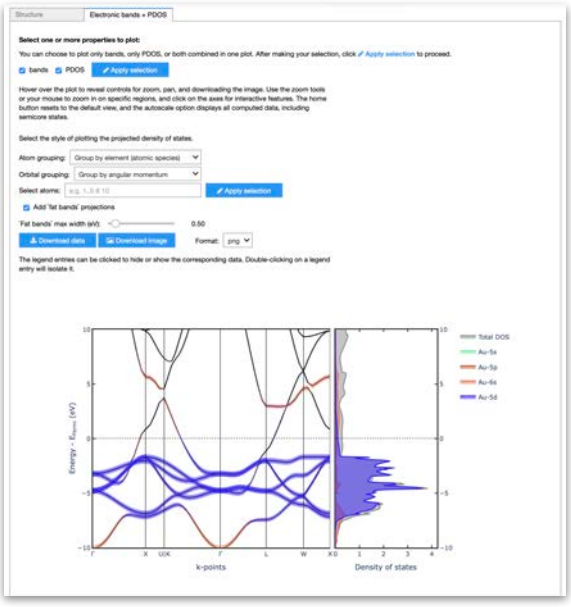
- **Goal: make simulations easy to use via robust protocols and workflows** (not only for single Quantum ESPRESSO pw.x executions, but also for more complex workflows)
  - Protocols for automatic input generation: k-points, smearing, cutoffs, pseudos, …
  - Robust workflows to fix common issues (wall time limit, non convergence, …)
  - Robust workflows for property calculation
  - GUI to facilitate use from a browser (via AiiDAlab: www.aiidalab.net)

Making simulations accessible with AiiDAlab (and the AiiDAlab Quantum ESPRESSO app)



Try on demo.aiidalab.io (no storage! Everything deleted after 12 hours)
or install locally (https://aiidalab.readthedocs.io/en/latest/usage/access/local.html)

Making simulations accessible with AiiDAlab (and the AiiDAlab Quantum ESPRESSO app)



Try on demo.aiidalab.io (no storage! Everything deleted after 12 hours)
or install locally (https://aiidalab.readthedocs.io/en/latest/usage/access/local.html)

MSE-468 Atomistic and Quantum Simulations of Materials - G. Pizzi, Spring 2025, EPFL

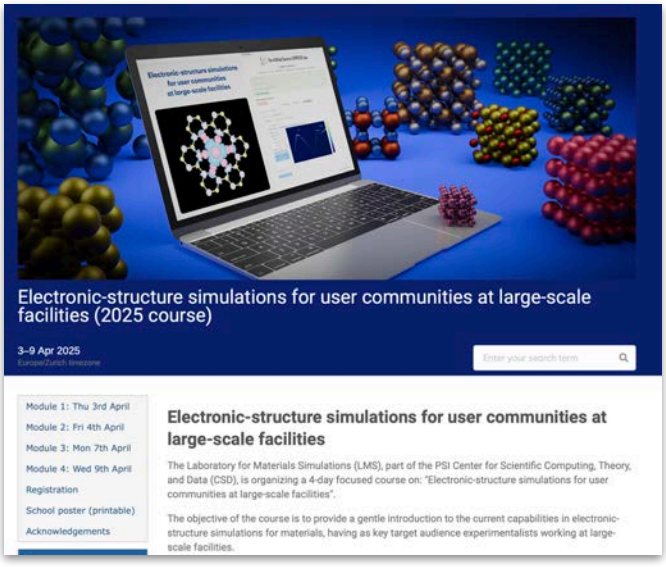
Making simulations accessible with AiiDAlab (and the AiiDAlab Quantum ESPRESSO app)

- Supported workflows (via plugins):
  - Relaxation (with magnetism, spin-orbit, …)
  - Band structure (with fat bands), DOS and PDOS
  - Bader charge analysis
  - Phonons, inelastic neutron scattering, Raman and IR
  - Muon stopping sites
  - Core-level spectroscopy (XPS, XAS)
  - Automatic determination of U and V for DFT+U+V
  - Automatic Wannier functions, Fermi surfaces, …
  - …

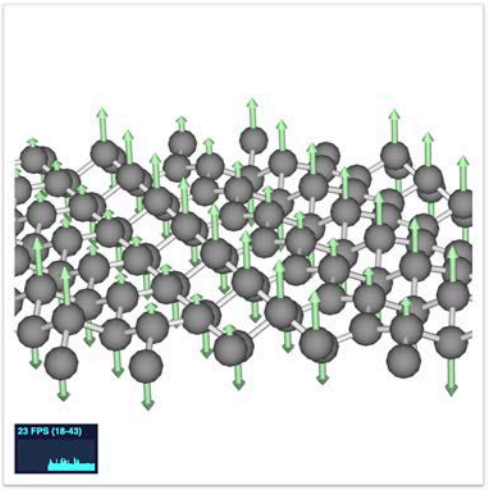
Discussed in a school at PSI this week

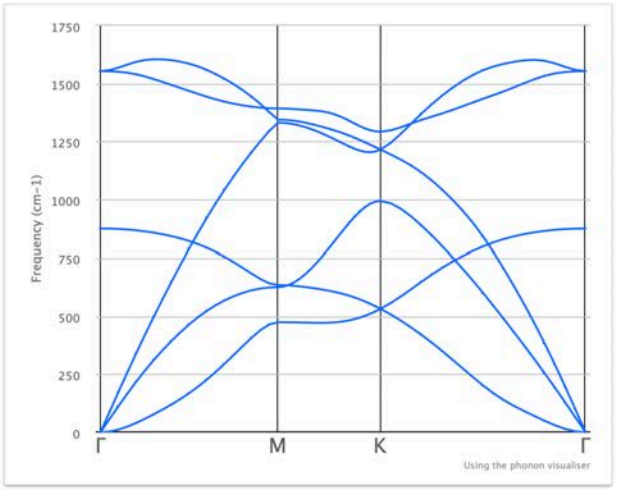
- Demo of several AiiDAlab Quantum ESPRESSO app plugins, with video recordings and slides available: check especially module 3 and 4

https://indico.psi.ch/event/17436/



Atom oscillations: phonons





Think beyond the energy

FORCES AND STRESSES IN MOLECULES

$$\frac{dE}{d\lambda} = \int n_\lambda(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

R. P. Feynman

Submitted in Partial Fulfillment of the Requirements for the
Degree of Bachelor of Science in Physics, course VIII,
of the
Massachusettes Institute of Technology

1939

Acceptance:

Instructor in charge of thesis

May 22, 1939
(Date)

Helmann-Feynman theorem

$$\frac{dE_\lambda}{d\lambda} = \frac{d}{d\lambda}\langle\Psi|\hat{H}_\lambda|\Psi\rangle = \langle\Psi|d\hat{H}_\lambda/d\lambda|\Psi\rangle$$

$$\frac{d}{d\lambda}\langle\Psi|\hat{H}_\lambda|\Psi\rangle = \langle d\Psi/d\lambda|\hat{H}_\lambda|\Psi\rangle + \langle\Psi|d\hat{H}_\lambda/d\lambda|\Psi\rangle + \langle\Psi|\hat{H}_\lambda|d\Psi/d\lambda\rangle =$$
$$\underbrace{E(\langle d\Psi/d\lambda|\Psi\rangle + \langle\Psi|d\Psi/d\lambda\rangle)}_{\frac{d}{d\lambda}\langle\Psi|\Psi\rangle} + \langle\Psi|d\hat{H}_\lambda/d\lambda|\Psi\rangle = \langle\Psi|d\hat{H}_\lambda/d\lambda|\Psi\rangle$$

$$\langle\Psi|\Psi\rangle = 1 \Rightarrow \frac{d}{d\lambda}\langle\Psi|\Psi\rangle = 0$$

Linear-response theory

Perturbation (external potential):

$$V_0 \Rightarrow V_0 + \lambda\Delta V$$

Response (charge density):

$$n_0 \Rightarrow n_\lambda = n_0 + \lambda n_1 + \dots$$

Hellmann-Feynman Theorem:

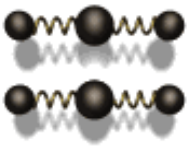
$$\frac{dE}{d\lambda} = \int n_\lambda(\mathbf{r})\frac{\partial V(\mathbf{r})}{\partial\lambda}d\mathbf{r}$$

Total energy:

$$E_\lambda = E_0 + \underbrace{\lambda\int n_0(\mathbf{r})\Delta V(\mathbf{r})d\mathbf{r}}_{1^{st}\text{ order}} + \underbrace{\frac{\lambda^2}{2}\int n_1(\mathbf{r})\Delta V(\mathbf{r})d\mathbf{r} + \dots}_{2^{nd}\text{ order}}$$

S. Baroni *et al.*, Phys. Rev. Lett. ('87), Rev. Mod. Phys. ('01)

Phonons



REVIEWS OF MODERN PHYSICS, VOLUME 73, APRIL 2001

Phonons and related crystal properties from density-functional perturbation theory

Stefano Baroni, Stefano de Gironcoli, and Andrea Dal Corso
SISSA–Scuola Internazionale Superiore di Studi Avanzati and INFM–Istituto Nazionale di Fisica della Materia, I-34014 Trieste, Italy
Paolo Giannozzi*
Chemistry Department and Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544

$$\mathbf{F}_I \equiv -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0, \qquad \det\left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} - \omega^2 \right| = 0$$

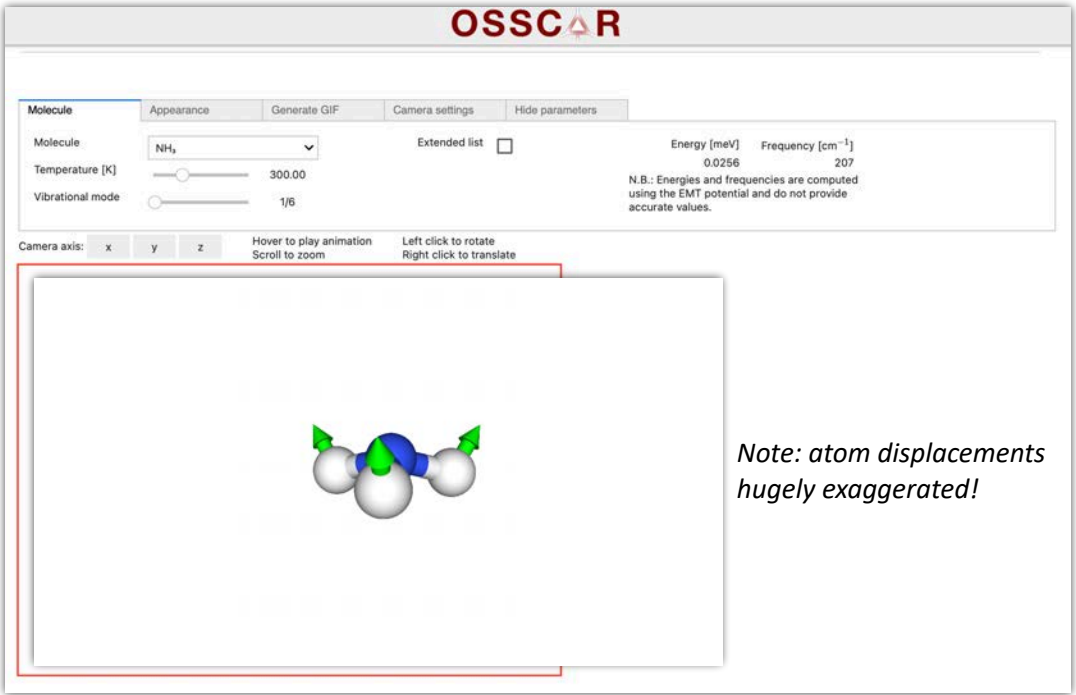
Response to different wavelengths in DFPT are decoupled:
work in reciprocal space (**q**) [with Fourier transforms]

$$C_{st}^{\alpha\beta}(l,m) \equiv \frac{\partial^2 E}{\partial u_s^\alpha(l)\partial u_t^\beta(m)} = C_{st}^{\alpha\beta}(\mathbf{R}_l - \mathbf{R}_m), \longrightarrow \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) \equiv \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^{*\alpha}(\mathbf{q})\partial u_t^\beta(\mathbf{q})}$$

$$\det\left| \frac{1}{\sqrt{M_s M_t}} \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) - \omega^2(\mathbf{q}) \right| = 0.$$

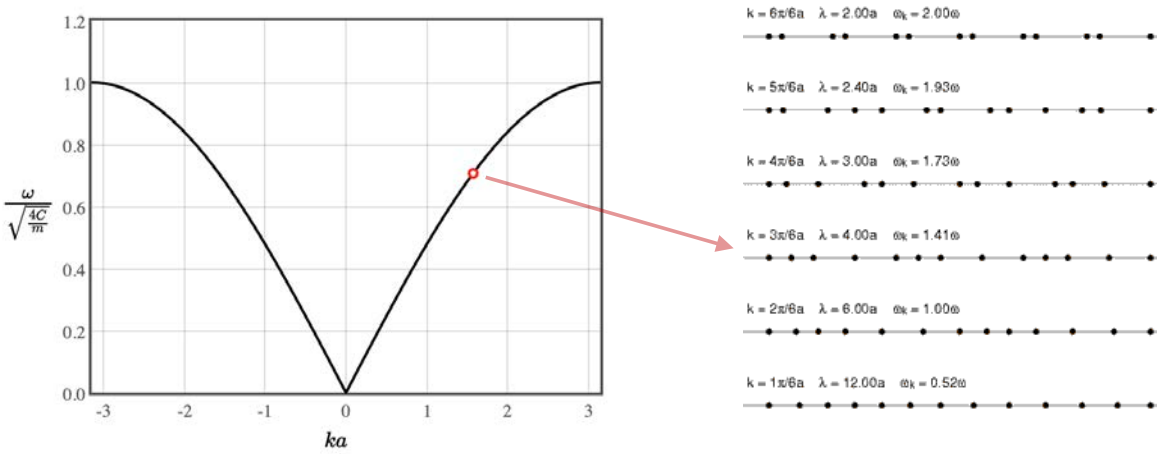
OSSCAR: molecules

https://osscar-quantum-mechanics.materialscloud.io/voila/render/lattice-vibration/Molecule_Vibration.ipynb



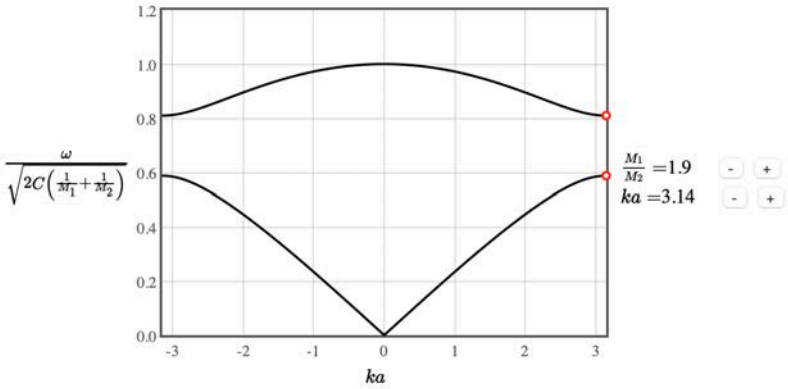
Note: atom displacements hugely exaggerated!

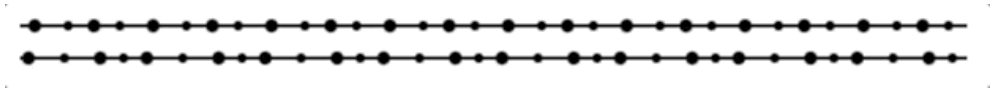
Bands, and wavevectors



http://lampx.tugraz.at/~hadley/ss1/phonons/1d/1dphonons.php
https://en.wikipedia.org/wiki/Phonon

Bands, and wavevectors



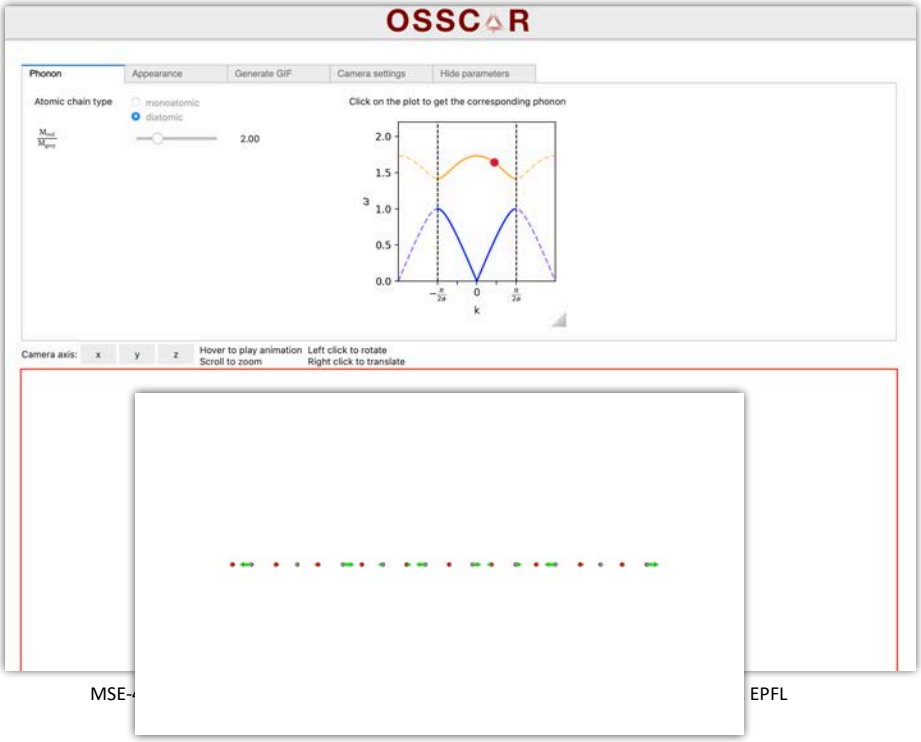


http://lampx.tugraz.at/~hadley/ss1/phonons/1d/1d2m.php

OSSCAR: 1D phonons

https://osscar-quantum-mechanics.materialscloud.io/voila/render/lattice-vibration/Phonon_1D.ipynb

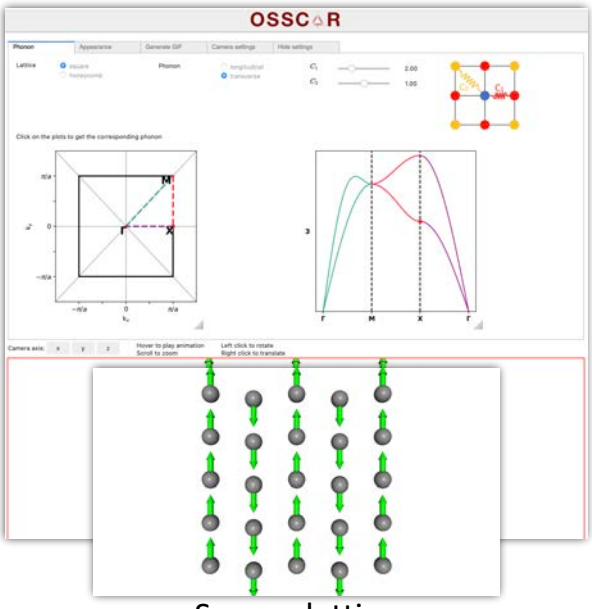
Suggested task: investigate gap opening for different masses of the 2 atoms



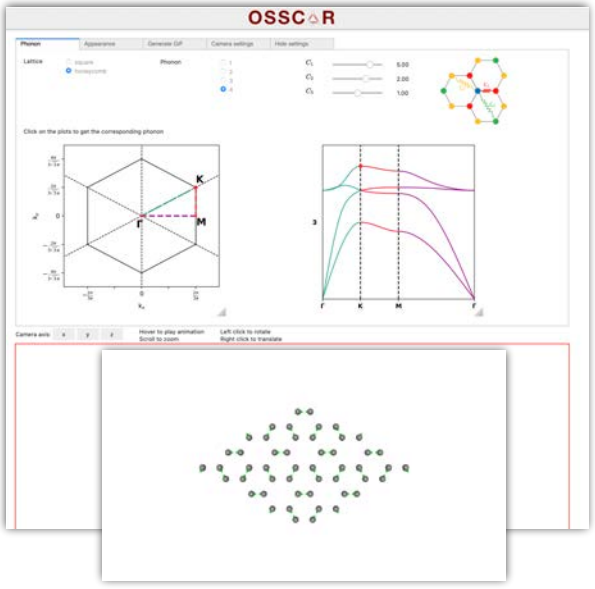
OSSCAR: 2D phonons

https://osscar-quantum-mechanics.materialscloud.io/voila/render/lattice-vibration/Phonon_2D.ipynb

Suggested task: investigate transverse vs. longitudinal waves. Inspect optical vs. acoustic waves (hexagonal case, 2 atoms in the unit cell)



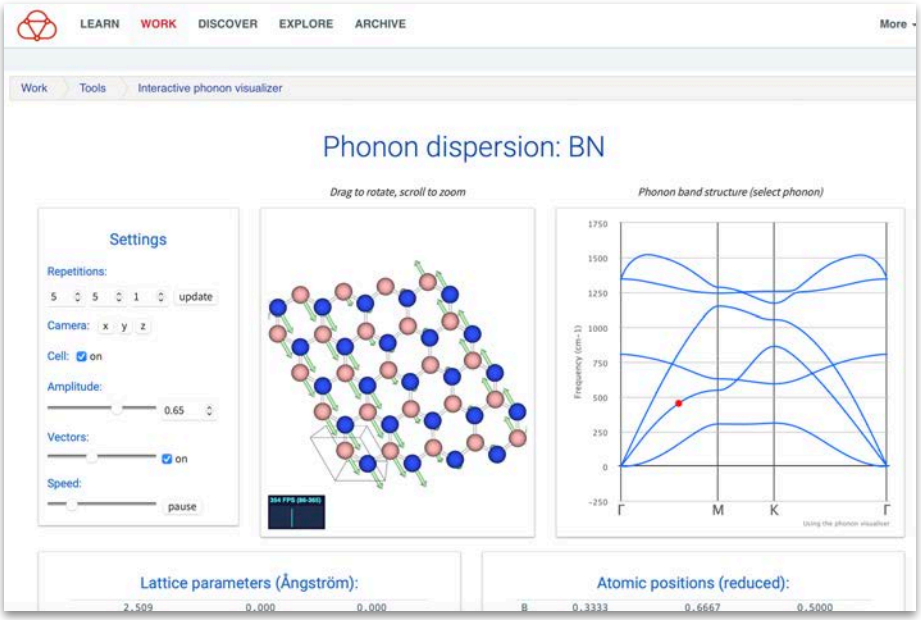
Square lattice



Hexagonal lattice

Phonon visualizer (for DFT calculations from QE)

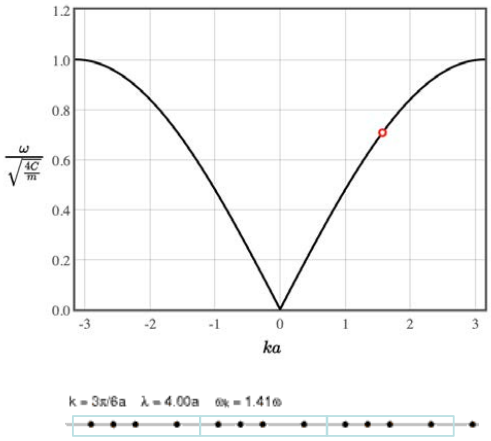
Suggested tasks: Inspect/investigate transverse vs. longitudinal modes, out-of-plane modes for 2D materials



https://interactivephonon.materialscloud.io/

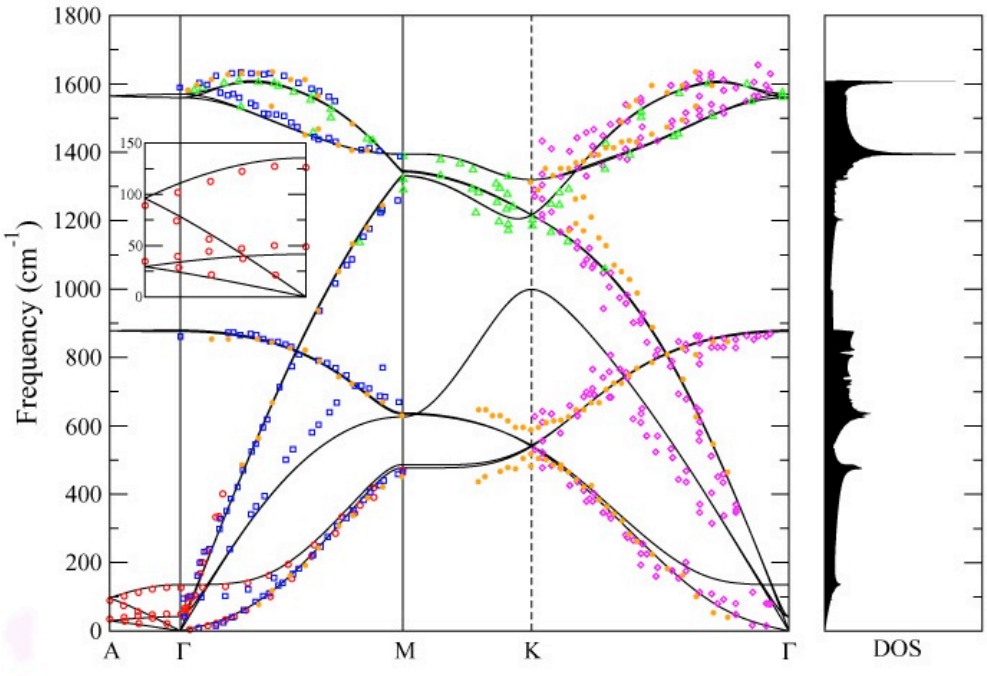
Finite-differences vs. DFPT (density-functional perturbation theory)

- Another way to compute phonons: move one atom at a time (by a little amount), compute forces.



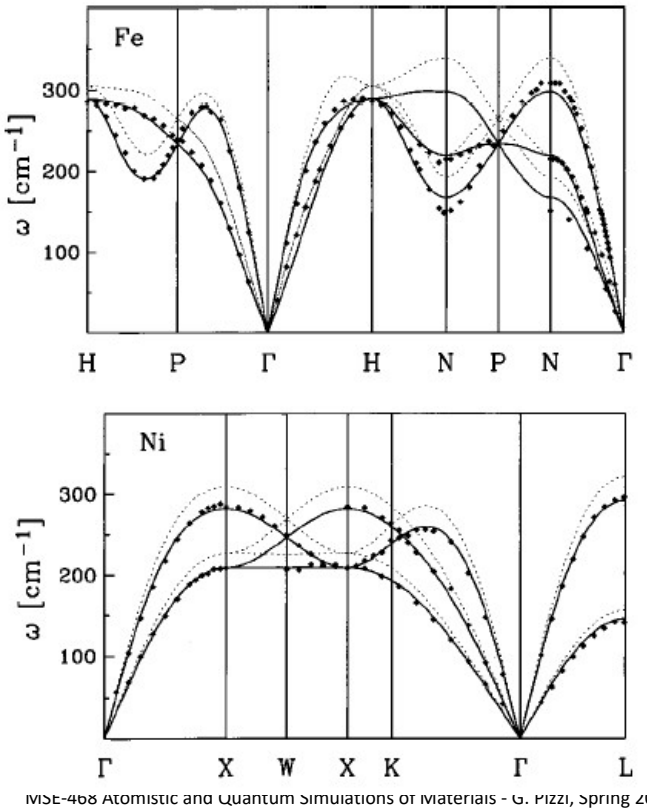
- No new theory/algorithm needed, just forces from positions
- https://phonopy.github.io/phonopy/ can compute them (interfaces to many DFT codes)
- **HOWEVER**: given a q vector, an appropriate supercell must be used (expensive!). E.g. 4x4x4 q-grid => 4x4x4 supercell
- With DFPT instead: compute phonons in primitive cell at *any* **q!** (efficient to implement with plane waves)

Graphite



N. Mounet and N. Marzari, Phys. Rev. B (2005)

Iron and Nickel – LDA and GGA

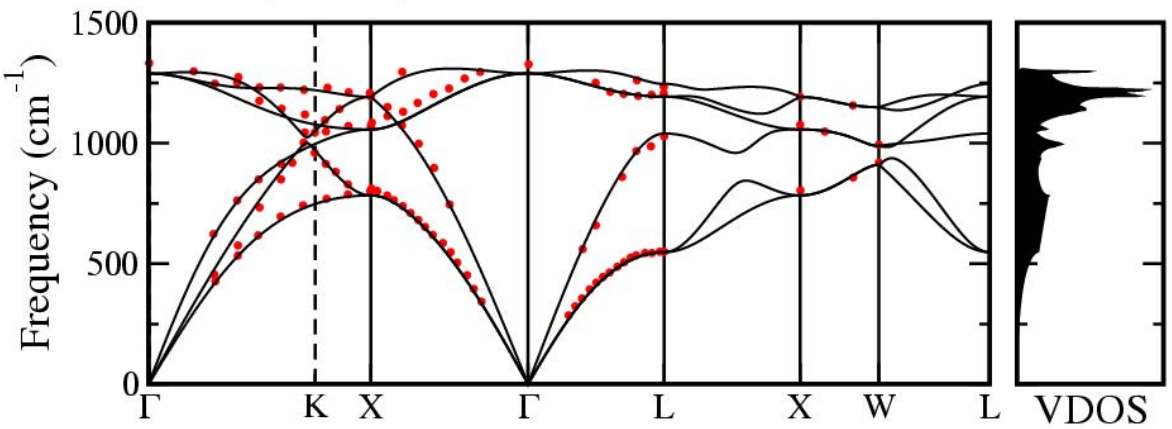


Dal Corso and
de Gironcoli (2000)

Phonons, temperature and free-energies

Phonons and temperature

- A harmonic crystal is exactly equivalent to a Bose-Einstein gas of independent, harmonic oscillators.



Phonons and conductivity

- For a harmonic crystal, the second quantization Hamiltonian commutes with the number operator ⟹ eternal life, and infinite thermal conductivity.

- Third-order anharmonicity ≡ three-body interactions ⟹ finite lifetimes/conductivity.

Anharmonicity = finite lifetimes

Third-order anharmonic interactions

The anharmonic linewidth of a zone center phonon is given by

$$\Gamma_{\mathbf{0}\nu} = \frac{\pi\hbar}{8 N_q \omega_\nu(\mathbf{0})} \sum_{\boldsymbol{q},\mu,\eta} \left| \frac{\partial^3 E}{\partial u_\nu(\mathbf{0}) \partial u_\mu(\boldsymbol{q}) \partial u_\eta(-\boldsymbol{q})} \right|^2 \frac{I^D_{\boldsymbol{q}\nu\mu\eta} + I^A_{\boldsymbol{q}\nu\mu\eta}}{\omega_\mu(\boldsymbol{q}) \omega_\eta(-\boldsymbol{q})} \quad ,$$

$$I^D_{\boldsymbol{q}\nu\mu\eta} = [n_\mu(\boldsymbol{q}) + n_\eta(-\boldsymbol{q}) + 1] \delta\left(\omega_\nu(\mathbf{0}) - \omega_\mu(\boldsymbol{q}) - \omega_\eta(-\boldsymbol{q})\right) \quad \textit{(decay)}$$

$$I^A_{\boldsymbol{q}\nu\mu\eta} = 2[n_\mu(\boldsymbol{q}) - n_\eta(-\boldsymbol{q})] \delta\left(\omega_\nu(\mathbf{0}) - \omega_\mu(\boldsymbol{q}) + \omega_\eta(-\boldsymbol{q})\right) \quad \textit{(adsorption)}$$

$$\frac{\partial^3 E}{\partial u_\nu(\mathbf{0}) \partial u_\mu(\boldsymbol{q}) \partial u_\eta(-\boldsymbol{q})}$$

calculated using DFPT and the *2n+1* theorem

Note: 2n+1 theorem

- Correction to **energy** of order 2*n* and (2*n*+1): can be evaluated from knowledge of **wavefunction** only up to order *n*
- *Examples:*
  - First correction to energy $E^{(1)}$ can be computed from uncorrected $\psi^{(0)}$ only
  - Both second $E^{(2)}$ and third $E^{(3)}$ corrections to energy can be computed from first-order correction $\psi^{(1)}$

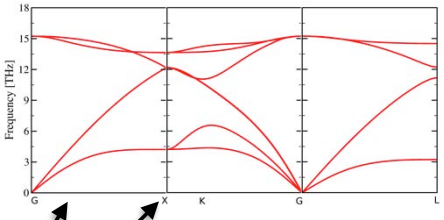
$$\Delta\psi = \sum_{n=1}^{\infty} \psi^{(n)} \lambda^n$$

$$E_{\min} = \sum_{n=0}^{\infty} E^{(n)} \lambda^n$$

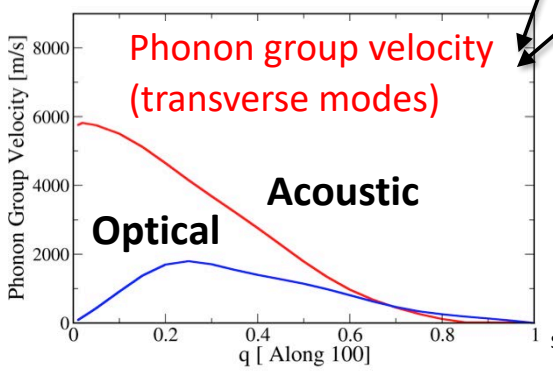
Thermal conductivity

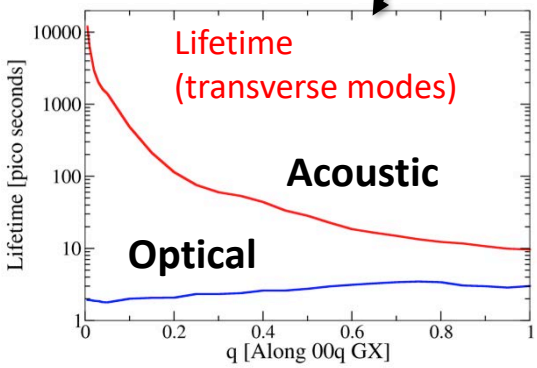
Heat current in the α direction for a temperature gradient in the β direction

λ = (***q***, *j*) [***q*** vector and branch index]

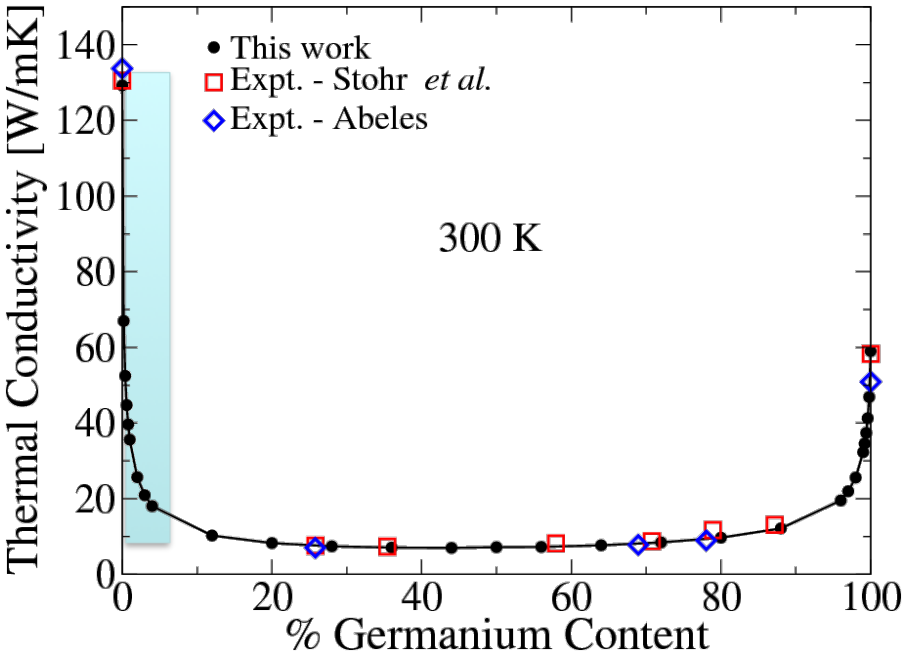


$$k_{\alpha\beta} = \frac{\hbar^2}{N\Omega k_B T^2} \sum_{\lambda} c_{\alpha\lambda} c_{\beta\lambda} \omega_\lambda^2 n_\lambda (n_\lambda + 1) \tau_\lambda$$





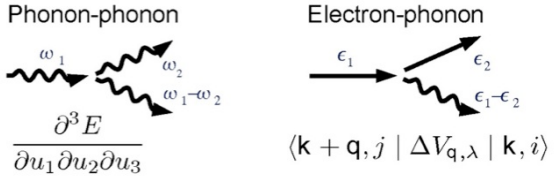
Composition dependence in SiGe alloys



J. Garg, N. Bonini, B. Kozinsky and N. Marzari, Phys. Rev. Lett. (2011)

Semiclassical transport: electrical resistivity

1. Vibrational properties from density-functional theory, electrons from many-body perturbation theory
2. Carriers' scattering rates from density-functional perturbation theory



3. Wannier interpolations for electrons
4. Transport properties from Boltzmann's equation

$$\begin{cases} \left.\frac{\partial n_\lambda}{\partial t}\right|_{scatt} = \frac{\partial \omega_\lambda}{\partial \mathbf{q}} \cdot \nabla T \left(\frac{\partial n_\lambda}{\partial T}\right) & \text{(phonons)} \\ \left.\frac{\partial f_\mu}{\partial t}\right|_{scatt} = \frac{1}{\hbar}\frac{\partial \epsilon_\mu}{\partial \mathbf{k}} \cdot \nabla T \left(\frac{\partial f_\mu}{\partial T}\right) + \frac{e}{\hbar}\mathbf{E} \cdot \frac{\partial f_\mu}{\partial \mathbf{k}} & \text{(electrons)} \end{cases}$$

Resistivity in doped graphene

FIRST-PRINCIPLES EXPTS (Efetov and Kim)

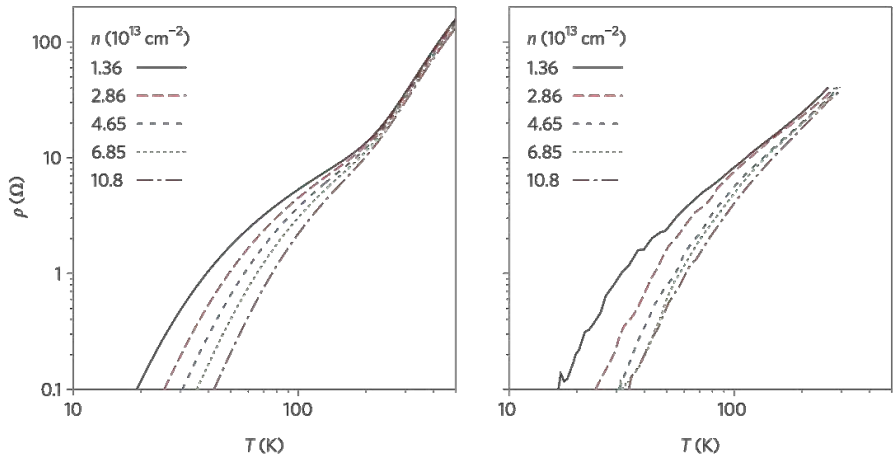


Figure 1 | Electrical resistivity of graphene as a function of temperature and doping (ρ, electrical resistivity; T, temperature; n, carrier density). Left panel: first-principles results obtained using a combination of density-functional perturbation theory, many-body perturbation theory and Wannier interpolations to solve the Boltzmann transport equation. Right panel: experimental data. Adapted from ref. 4, American Chemical Society.

C.-H. Park et al., Nano Letters (2014)
T. Y. Kim, et al., Nano Letters (2016)