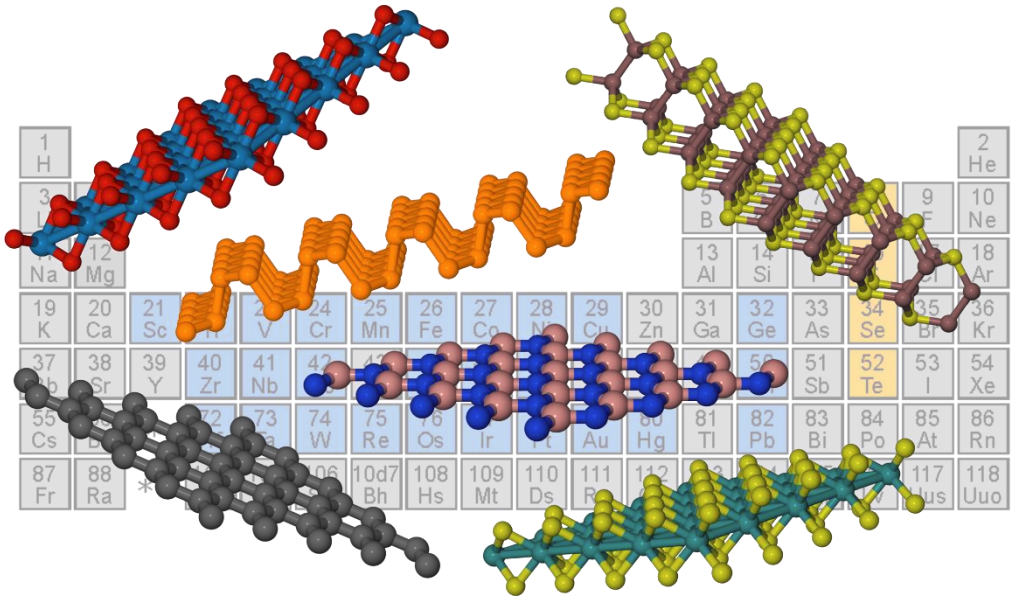

Morten N. Gjerding mogje@fysik.dtu.dk

Department of Physics, Technical University of Denmark

Hands-On DFT, Barcelona August 30, 2019

HIGH-THROUGHPUT COMPUTATIONS WITH THE ATOMIC SIMULATION ENVIRONMENT

DTU

Outline

- A high-throughput case study:
  The Computational 2D Materials Database (C2DB)
  - Model testing
  - Searching for novel materials
- The Atomic Simulation Recipes (ASR)
- Conclusions

Acknowledgements

Danmarks Grundforskningsfond
Danish National Research Foundation

Center for Nanostructured Graphene

CNG

Center for nanostructured graphene
Center of Excellence:
Nanostructured Graphene, 2012-2022.

erc
European Research Council

ERC

Designing Light-matter Interactions with Quantum Designed 2D Materials (LIMA)
ERC project 2018-2023

CAMD@DTU

- Sten Haastrup, PhD
- Anders Riis-Jensen, PhD
- Daniele Torelli, PhD
- Simone Manti, PhD
- Morten Gjerding, postdoc
- Thorsten Deilmann, postdoc Münster
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- Mohnish Pandey, postdoc Ulm

- Thomas Olsen, Assoc. Prof. DTU
- Kristian Thygesen, Prof. DTU

- Jens J. Mortensen, software developer
- Ole H. Nielsen, HPC Officer

The GPAW code

GPAW – projector augmented wave method for DFT and beyond

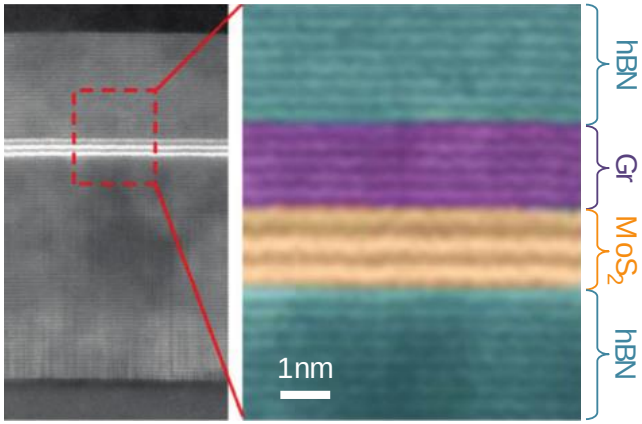
J. Enkovaara *et al.* J. Phys.:Cond. Mat. **22** (2010) ← **Review article**

https://wiki.fysik.dtu.dk/gpaw/ ← **Free download, GPL**

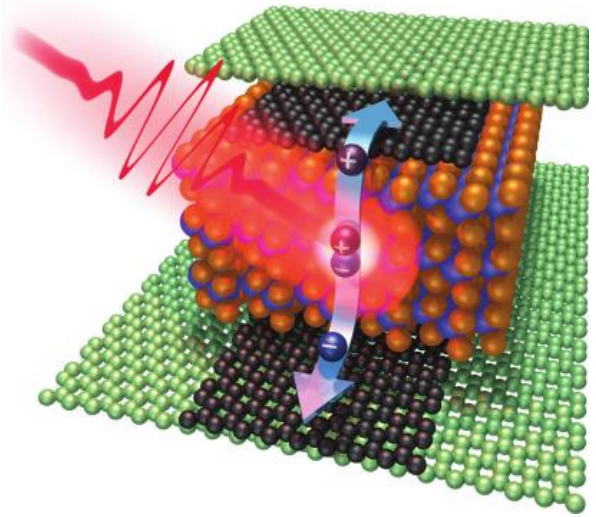
- High accuracy: Wave functions expanded on real space grids or plane waves
- High efficiency: Wave functions expanded in atomic-like orbitals (LCAO)
- Efficient parallelization (good scalability up to > 32.000 CPUs)
- Time-dependent DFT (linear response+time propagation)
- Many-body perturbation theory (GW and Bethe-Salpeter equation)
- Electron-phonon coupling
- QM/MM
- Very well integrated with the ASE

Why study 2D materials?

- **Novel properties** driven by reduced screening and quantum confinement
- Extreme thinness makes it possible to **control** electrons, spins, photons at the atomic scale
- Stacked 2D materials provide **defect free, atomically sharp** interfaces
- Ideal for **benchmarking and advancing** *ab-initio* computational methods
- Potential for **new technologies**, e.g. nanophotonics, spintronics, catalysis, batteries,…



Cui *et al.* Nature Nano 10, 534 (2015)

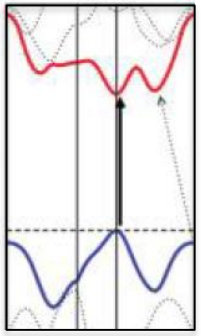


Massicotte *et al.* Nature Nano (2015)

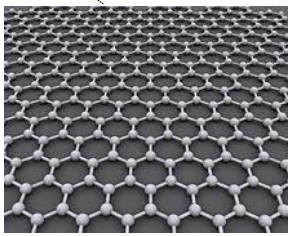
2004

Graphene Nobel Prize

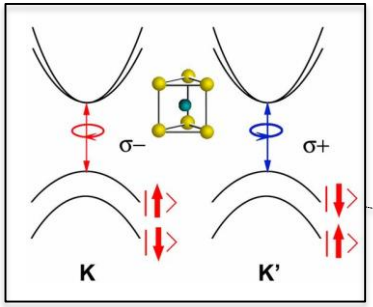
Direct-indirect transition in MoS_2



Isolation of graphene



2010



Valley polarization in MoS_2

2010

2011

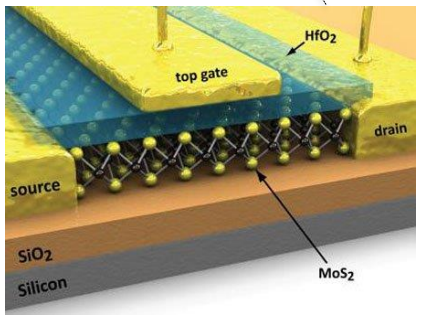
2012

Isolation of phosphorene

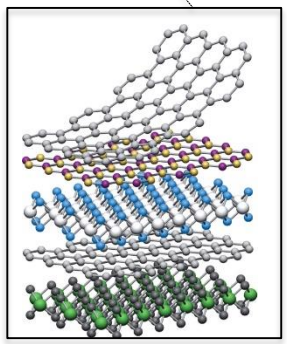
2013

2014

MoS_2 transistor

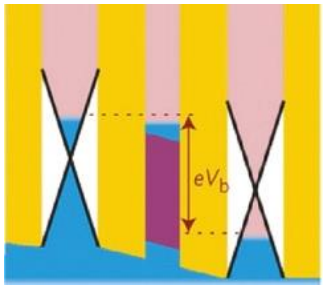


Van der Waals heterostructures



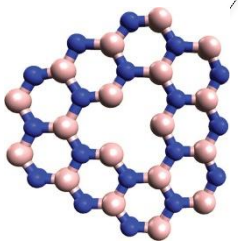
2015

Light-emitting diode



2016

2D quantum emitters

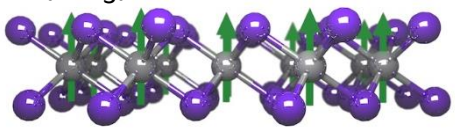


How many 2D materials?

>1000

2017

First 2D ferromagnet (CrI_3)



2018

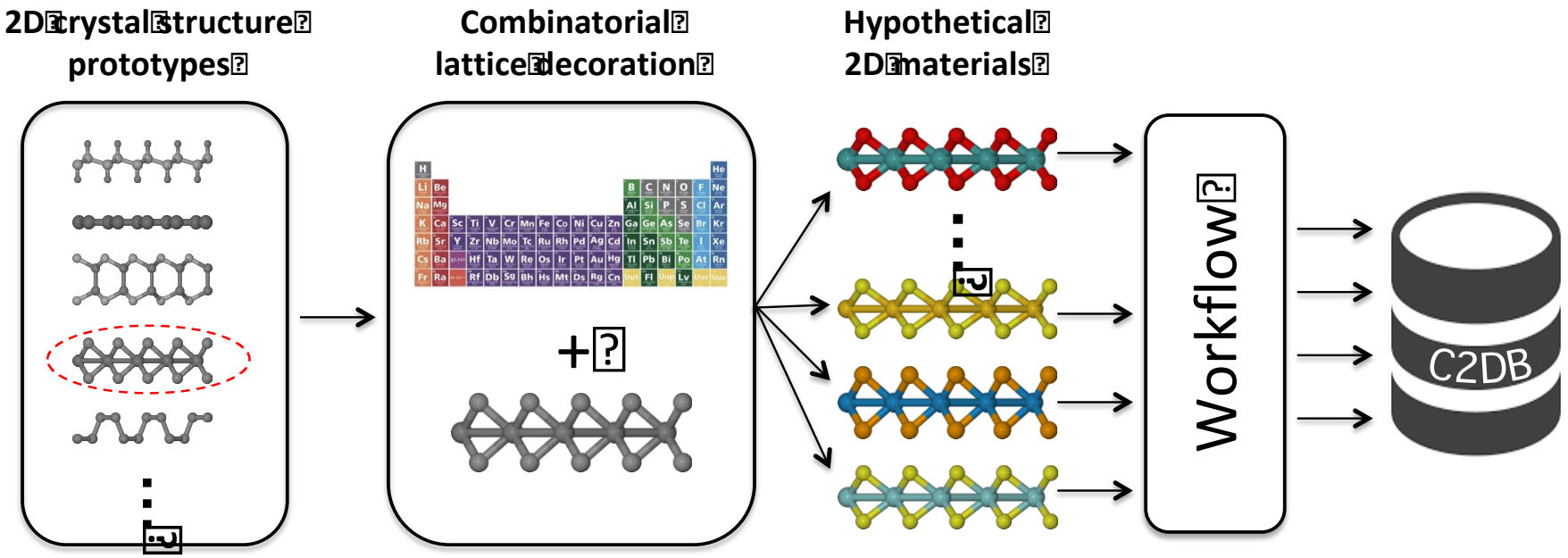
C2DB

The Computational 2D Materials Database

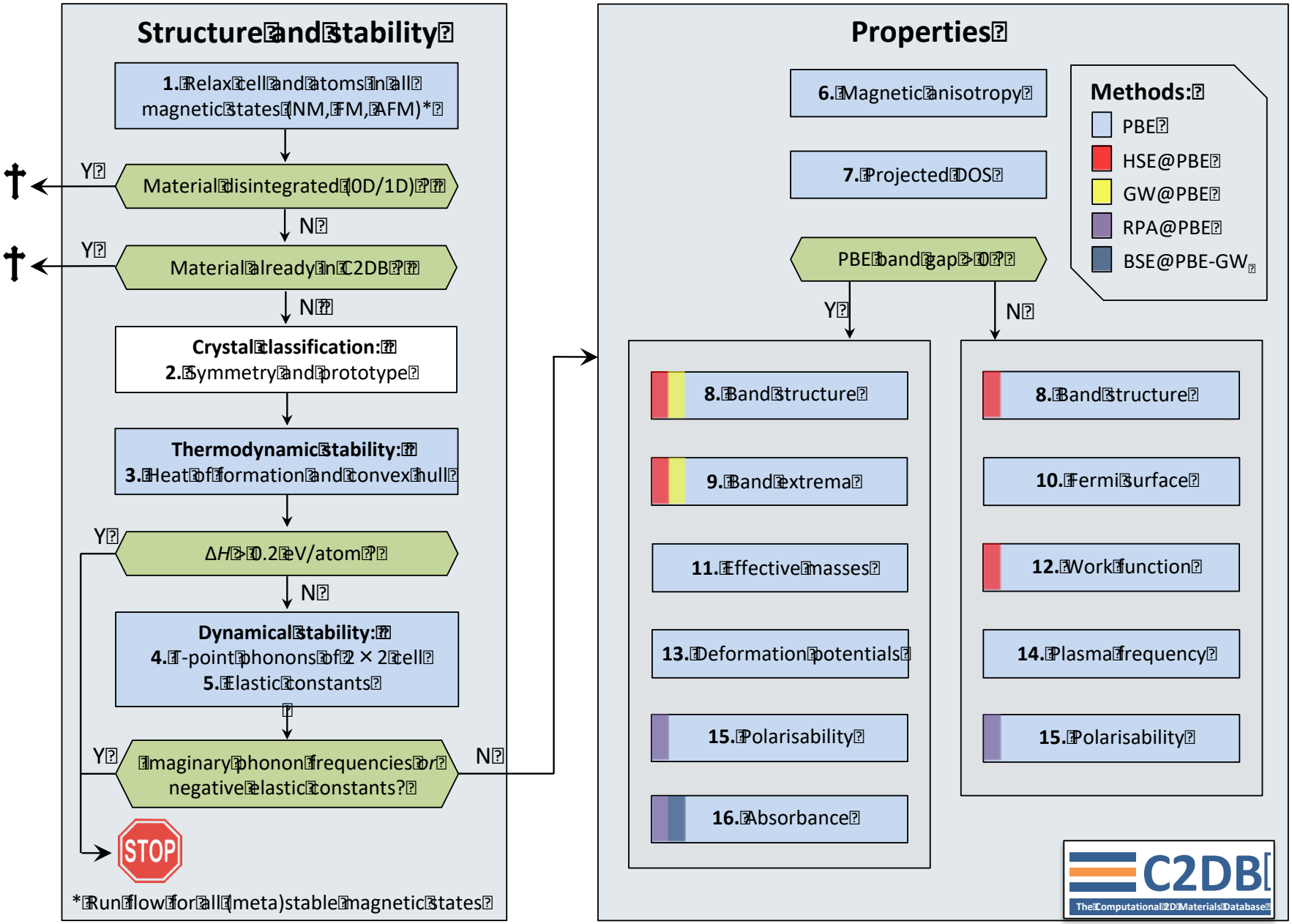
http://c2db.fysik.dtu.dk

Haastrup *et al.* 2D Materials **5** 042002 (2018)

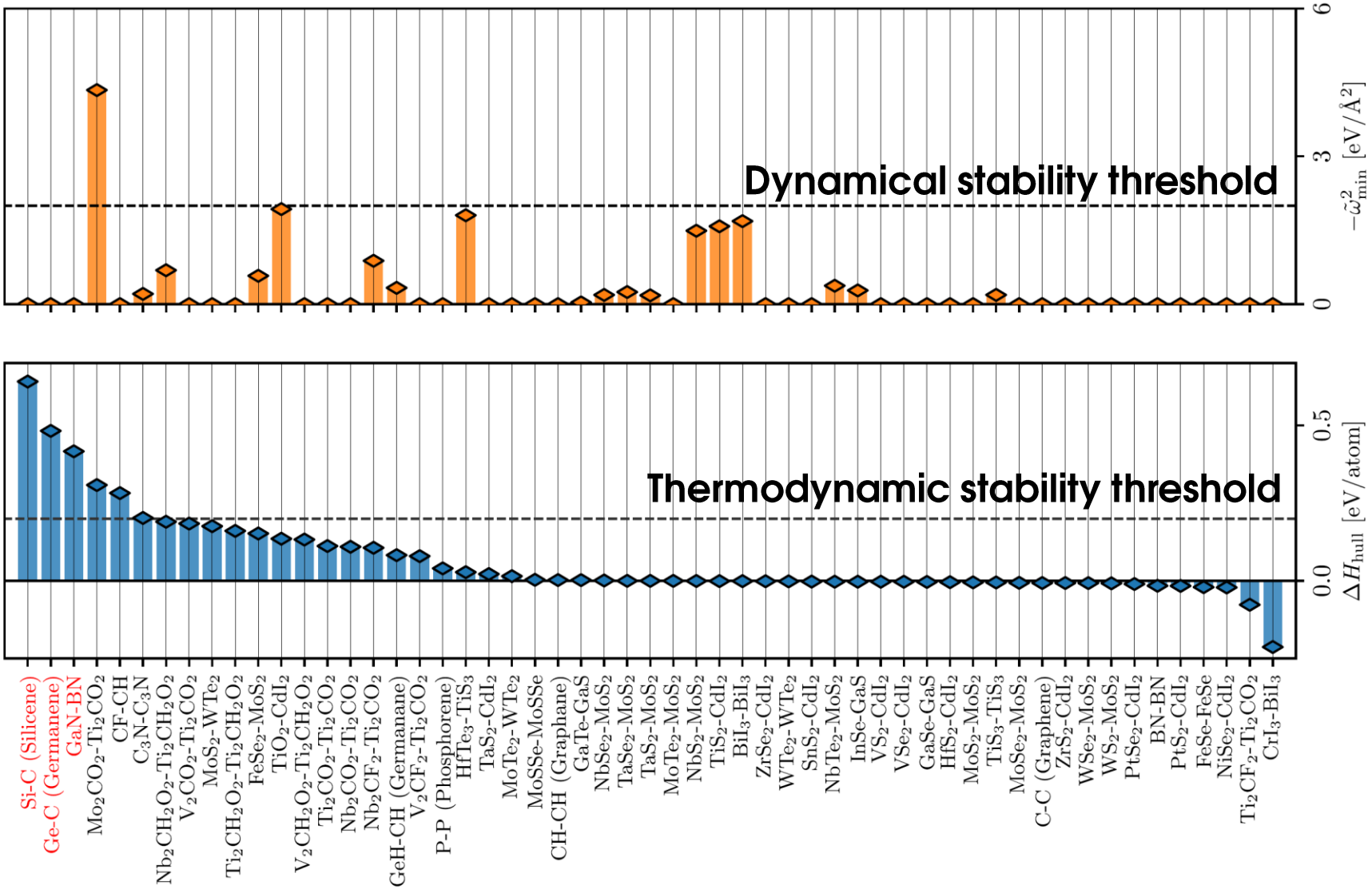
Organizes structural, thermodynamic, elastic, electronic, magnetic, and optical properties of 4000 monolayers distributed over 40 different crystal structures



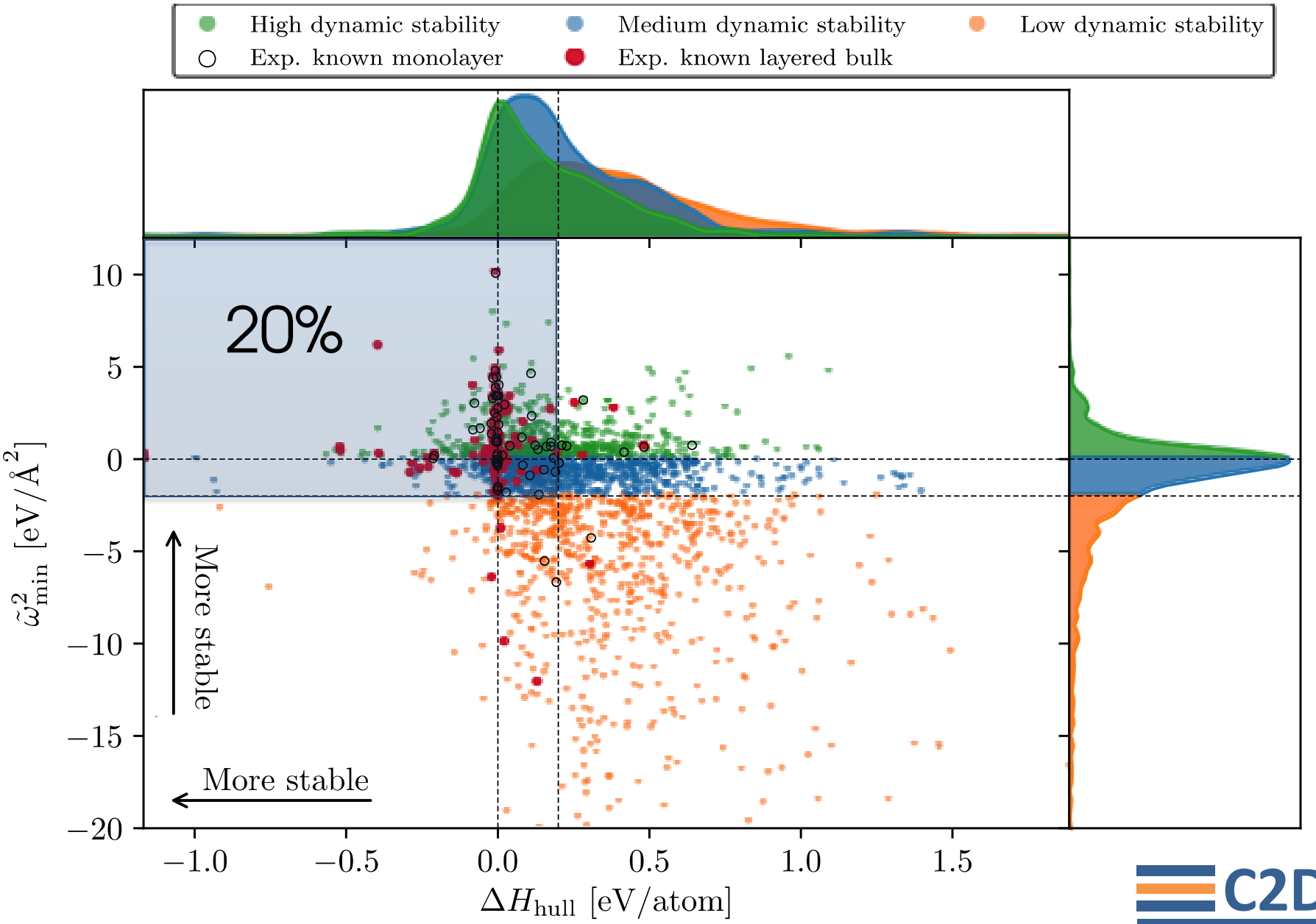
The workflow



When is a material stable?

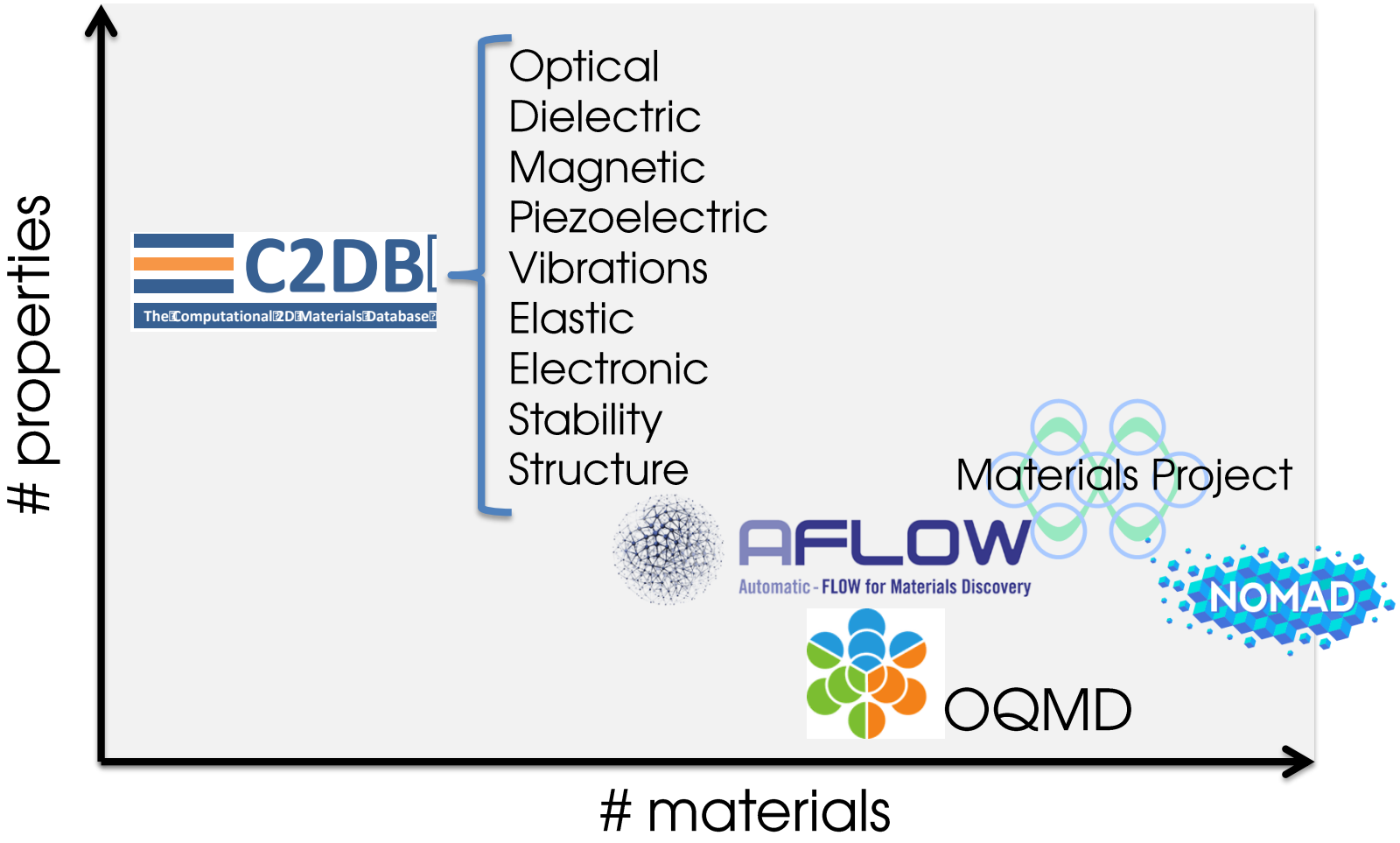


Stability of all materials in the C2DB



C2DB
The Computational 2D Materials Database

Exploring the *property dimension* of materials space



Computational 2D materials databa

c2db.fysik.dtu.dk -> click browse

Computational 2D materials database

Search formula e.g. MoS2

Structure prototype: -

Class of material: -

Dynamic stability: - - -

Thermodynamic stability: - - -

Magnetic state: -

Band gap range [eV]: - PBE

Help with constructing advanced search queries ...

Toggle list of keys ...

Displaying rows 1-25 out of 3712

Rows: 25 | Add Column

Formula	Prototype	Magnetic state	Space group	Heat of formation	Band gap (PBE)	Work function
Ag_2O_2	AuSe	NM	Pm	-0.046	0.164	-
Ag_2S_2	AuSe	NM	Pm	0.064	0.962	-
Ag_2Se_2	AuSe	NM	Pm	0.022	0.751	-
Ag_2Te_2	AuSe	NM	Pm	0.059	0.478	-
Au_2O_2	AuSe	NM	P2/m	-0.010	0.175	-
Au_2S_2	AuSe	NM	Pm	-0.091	1.218	-
Au_2Se_2	AuSe	NM	Pm	-0.116	0.957	-
Au_2Te_2	AuSe	NM	Pm	-0.105	0.622	-
Co_2O_2	AuSe	FM	Pm	-0.557	0.000	6.263
Co_2S_2	NiSe	FM	Pm	-0.266	0.000	5.350

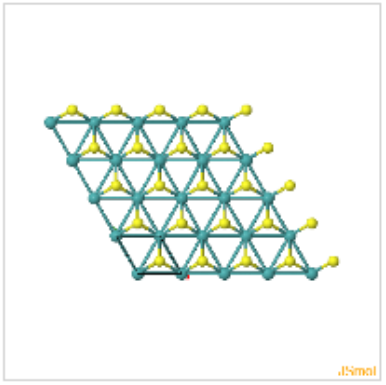
MoS_2

Basic properties

Property	Value
Structure prototype	MoS2
Class of material	TMDC-H
Space group	P-6m2
Band gap (PBE)	1.58 eV
Magnetic state	NM
ICSD id of parent bulk structure	26401
Dynamic stability	HIGH
Thermodynamic stability	HIGH
Monolayer DOI	10.1103/PhysRevLett.105.136805

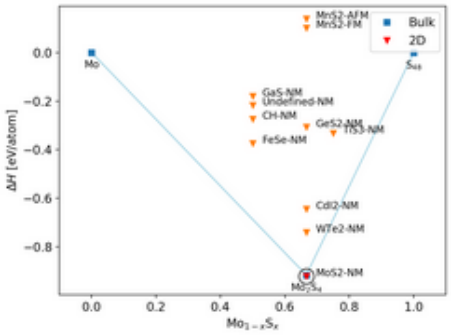
Axis	x	y	z	Periodic
1	3.164	0.000	0.000	True
2	-1.582	2.757	0.000	True
3	0.000	0.000	15.127	False

Lengths:	3.164	3.164	15.127
Angles:	90.000	90.000	120.000



Download - Unitcell -

Stability



Property	Value
Heat of formation	-0.92 eV/atom
Energy above convex hull	-0.01 eV/atom
Minimum eigenvalue of Hessian	-0.00 eV/Ang^2

Monolayer formation energies

Mo2S4 (MnS2-AFM)	0.135 eV/atom
Mo2S4 (MnS2-FM)	0.102 eV/atom
Mo2S2 (GaS-NM)	-0.150 eV/atom
Mo2S2 (Undefined-NM)	-0.215 eV/atom
Mo2S2 (CH-NM)	-0.274 eV/atom
Mo2S2 (GeS2-NM)	-0.307 eV/atom
Mo2S6 (TiS3-NM)	-0.333 eV/atom
Mo2S2 (FeSe-NM)	-0.374 eV/atom
Mo2S2 (CdI2-NM)	-0.645 eV/atom
Mo2S4 (WTe2-NM)	-0.740 eV/atom

ASE Modules used

```
File Edit Options Buffers Tools Python Virtual Envs Elpy Flymake YASnippet Help
from ase.optimize import BFGS  # Relax structure
from ase import phonons  # Calculate phonons and diagonalize dynamic matrix
from ase.dft.band_structure import BandStructure  # Make band structure
from ase.formula import Formula  # Data type for chemical formulas
from ase.lattice import HEX2D  # Bravais lattice knows band path
from ase.db import connect  # Connect or create a new ASE database
```

```
-UUU:----F1  ase-modules.py   All L7     (Python WS || Flymake[0 6] Elpy) ------
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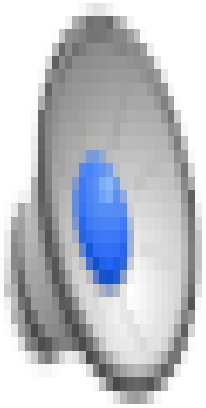
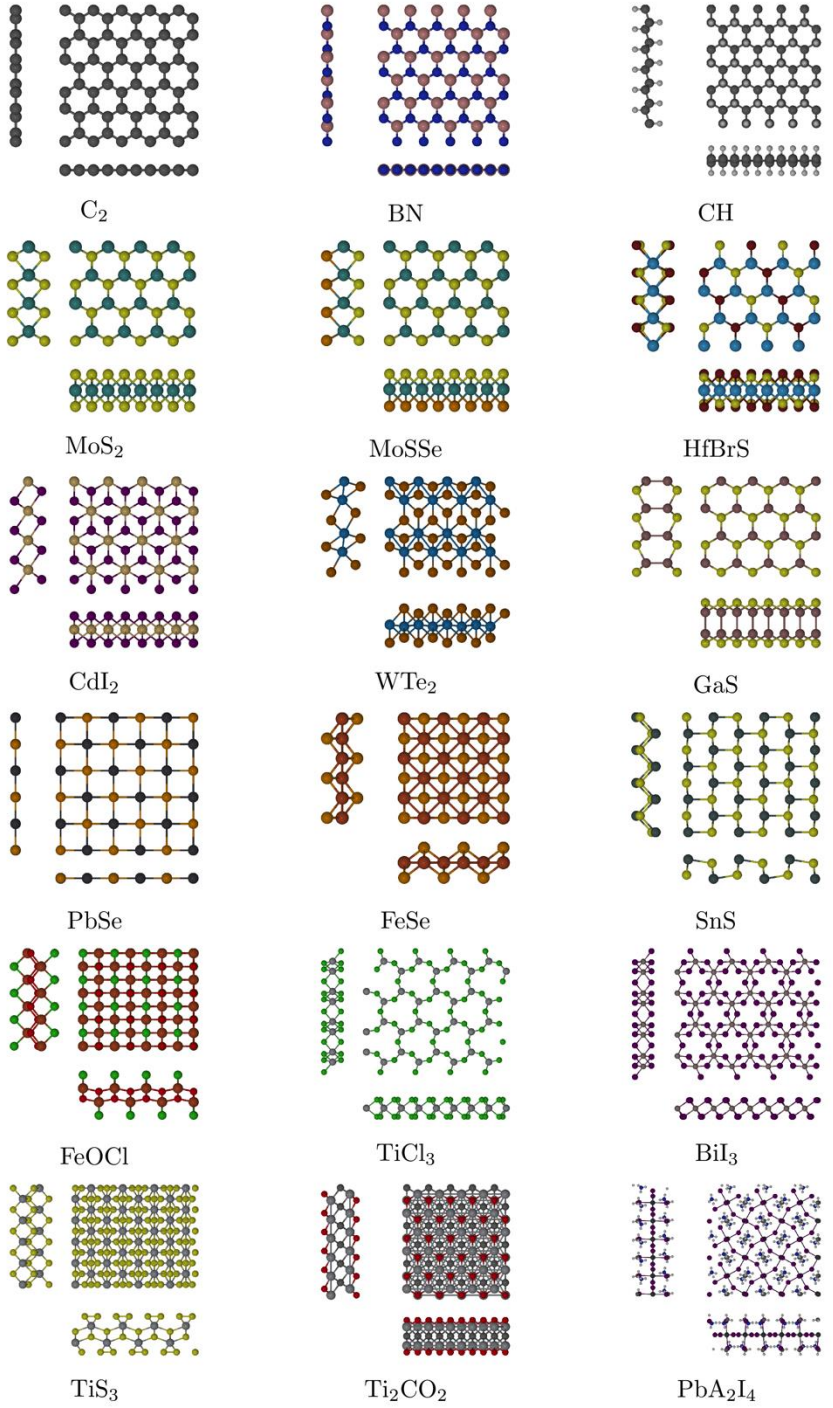
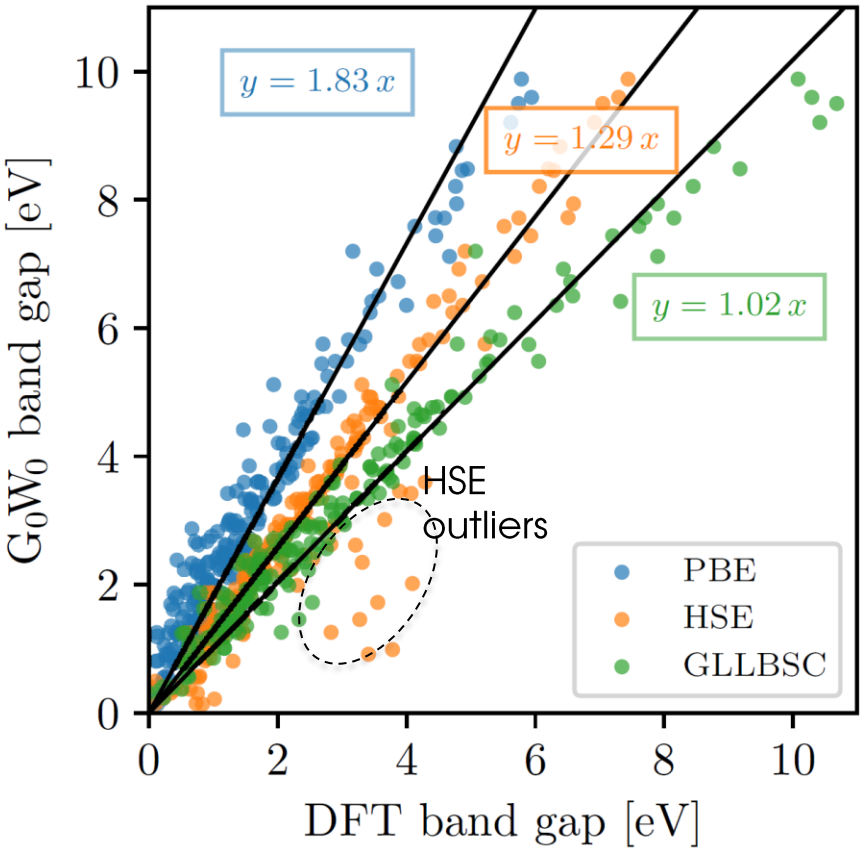
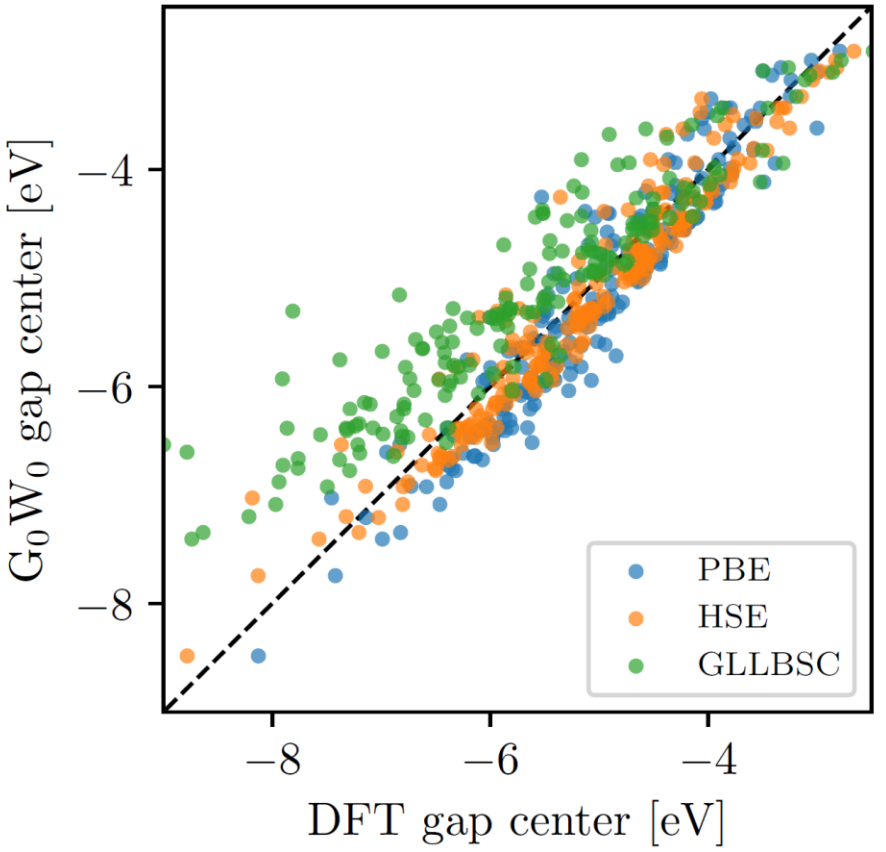


CORRELATIONS & MODEL VALIDATION



Evaluating band gaps



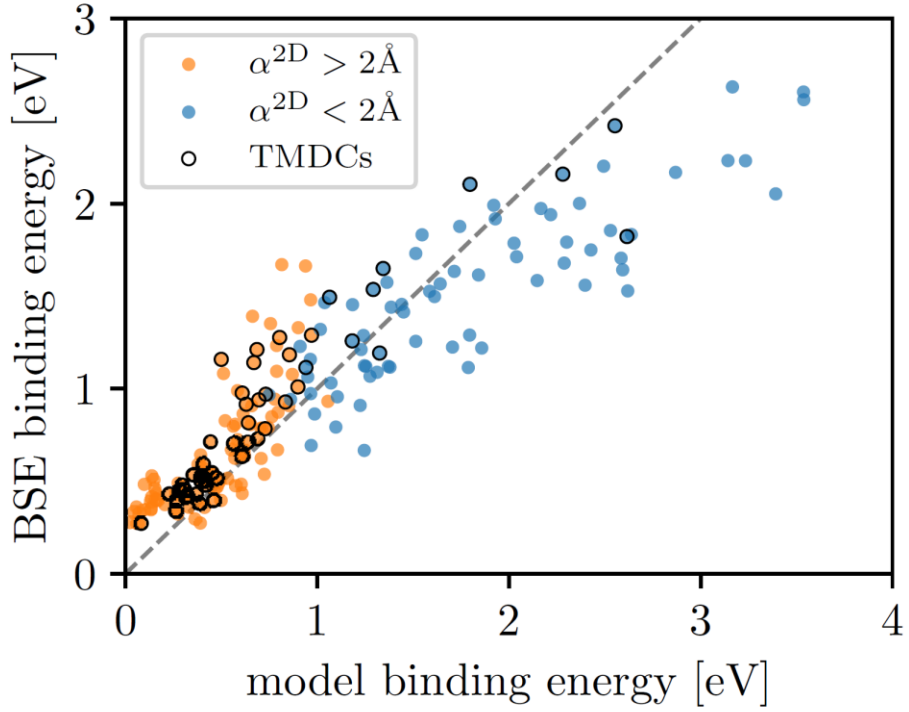


	PBE	HSE06	GLLBSC
MAD w.r.t. G_0W_0 (band gap)	1.49	0.82	0.38
MAD w.r.t. G_0W_0 (gap center)	0.37	0.32	0.76

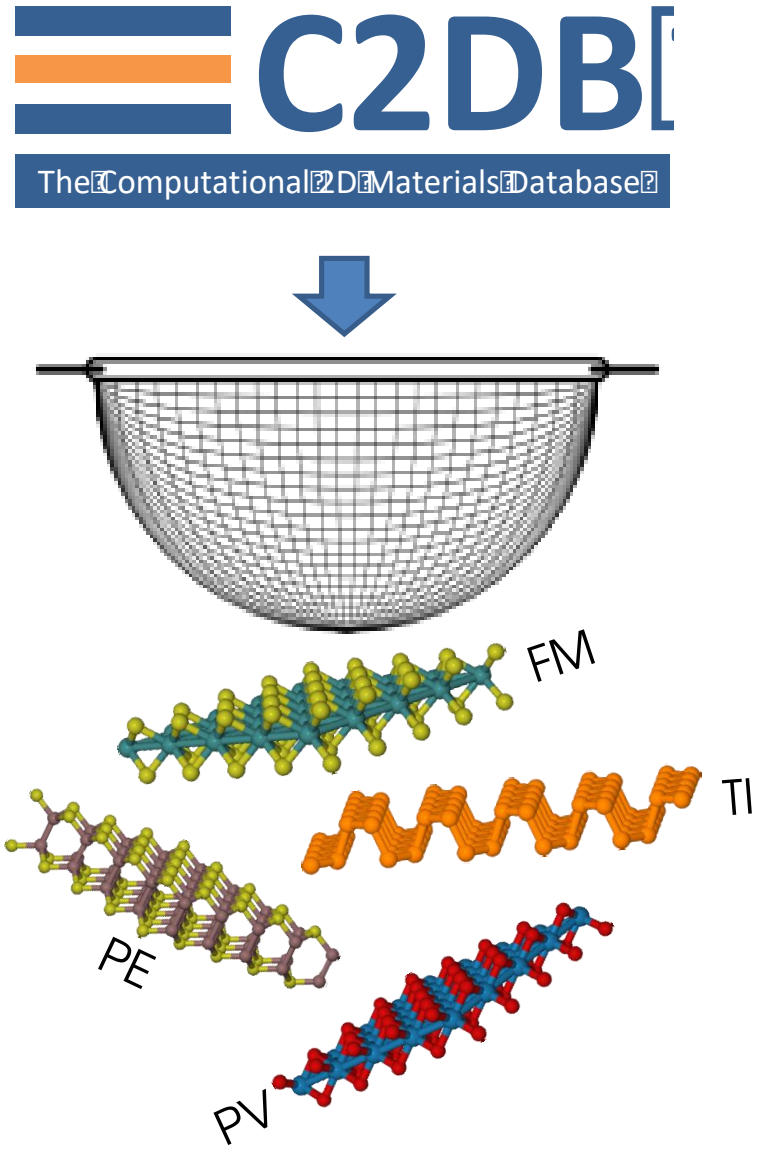
C2DB
The Computational 2D Materials Database

Modelling exciton binding energies

$$E_{\mathrm{B}} = \frac{8\mu_{\mathrm{ex}}}{(1+\sqrt{1+32\pi\alpha^{2\mathrm{D}}\mu_{\mathrm{ex}}/3})^2}$$



SCREENING FOR NOVEL 2D MATERIALS



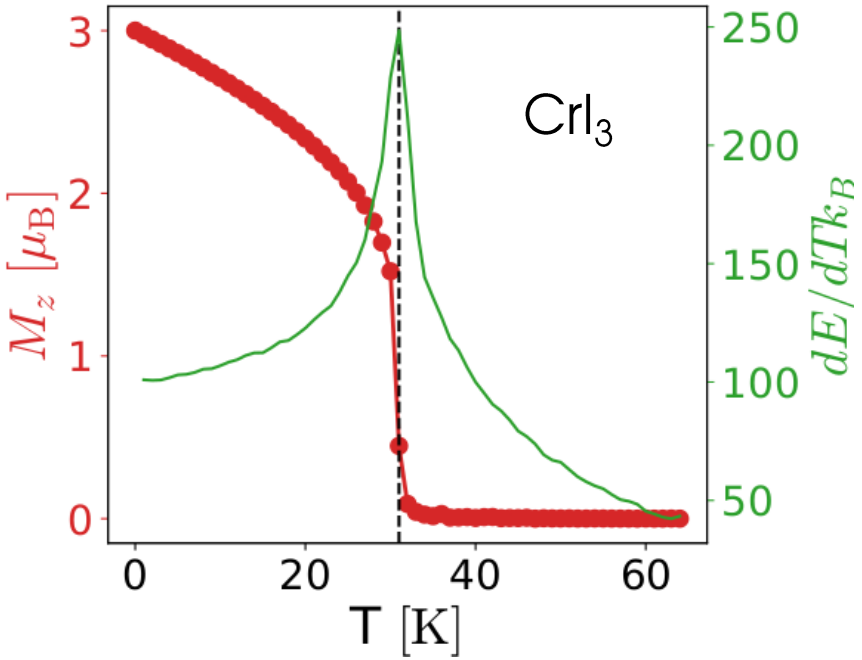
Ferromagnetic 2D semiconductors

Heisenberg Hamiltonian:

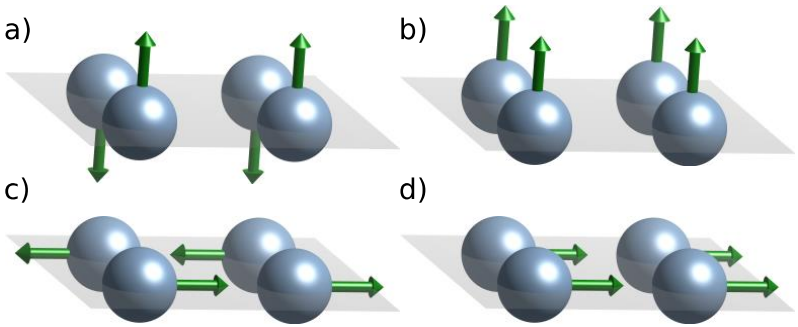
Anisotropy terms

$$H = -\frac{1}{2}\sum_{i\neq j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j - \sum_i A_i (S_i^z)^2 - \frac{1}{2}\sum_{i\neq j} B_{ij} S_i^z S_j^z$$

Classical Monte Carlo simulations:



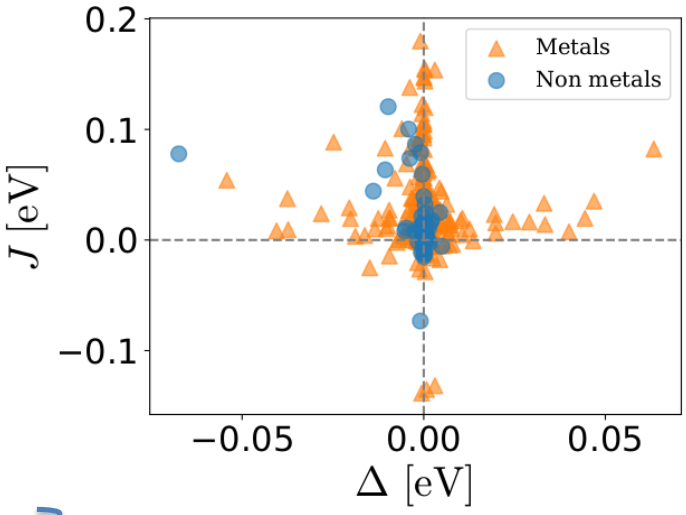
Parameters from total energy of different spin configurations:



D. Torelli *et al.* arXiv:1903.11466

Ferromagnetic 2D semiconductors

Screening 550 ferromagnetic materials.
spin-wave gap (Δ) >0 → out-of-plane easy axis



Most interesting compounds:

Formula	Structure	J [meV]	Δ [meV]	S [$\hbar$]	T_C [K]
MnO_2	CdI_2	6.37	0.125	1.5	81
CrI_3	BiI_3	3.95	1.280	1.5	50
$CrBr_3$	BiI_3	2.82	0.185	1.5	24
$CrCl_3$	BiI_3	2.19	0.016	1.5	10
$CoCl_2$	CdI_2	0.26	0.249	1.5	8
MnI_2	CdI_2	0.05	0.081	2.5	4
$MnBr_2$	CdI_2	0.05	0.024	2.5	3
$NiCl_2$	CdI_2	1.18	$\sim 10^{-4}$	1.0	2
$FeBr_3$	BiI_3	0.04	0.124	2.5	2
CoO	FeSe	106.54	0.199	1.5	520
FeS	FeSe	28.99	0.591	2.0	413

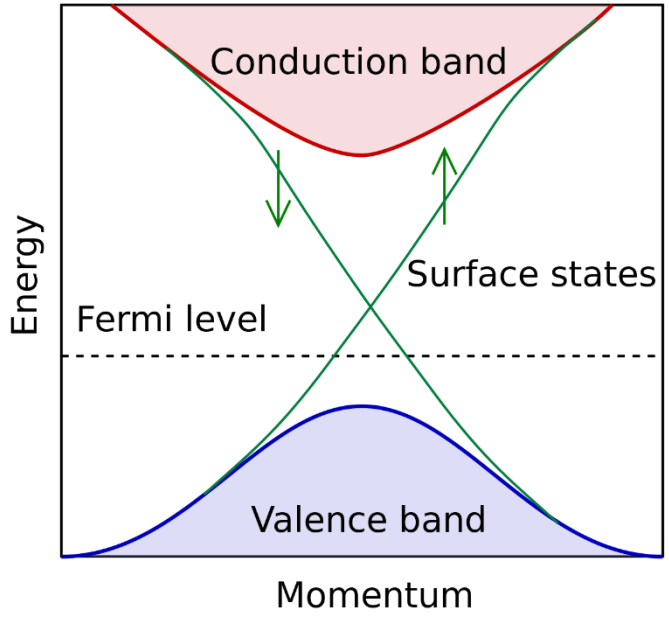
Predicted stable

Predicted unstable

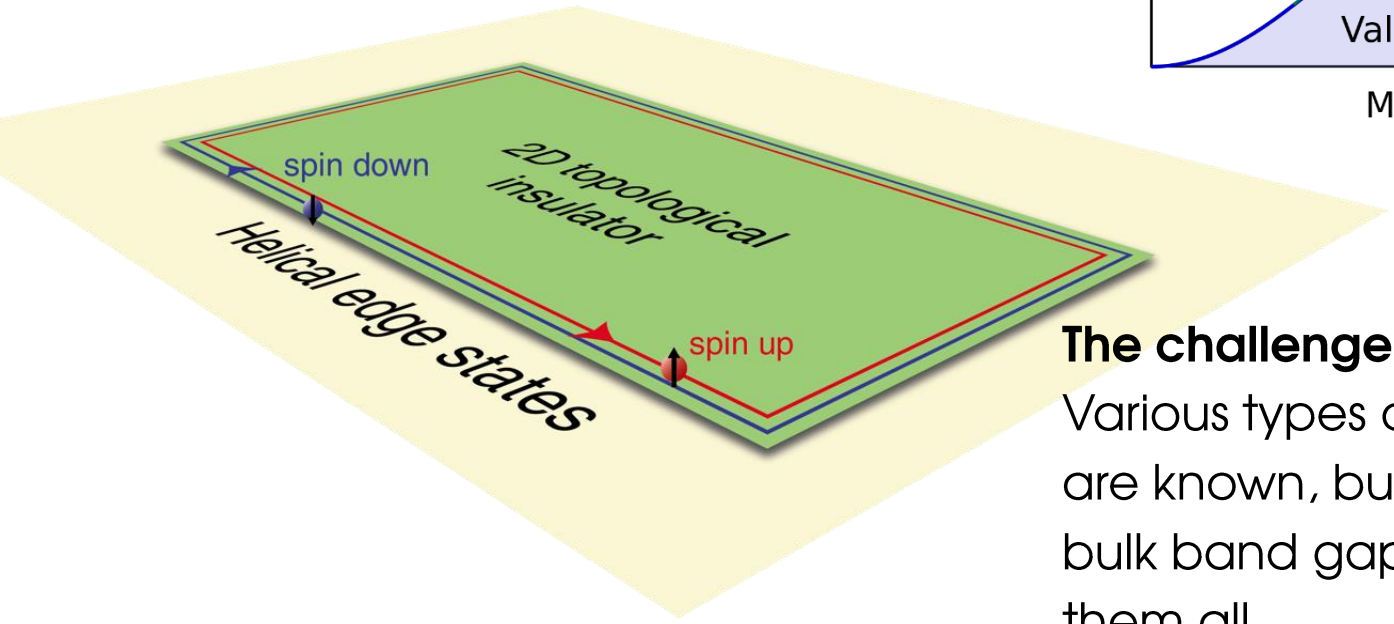
D. Torelli *et al.* arXiv:1903.11466

Topological insulators

Topological insulator:
Material with non-trivial symmetry-protected topological order. The bulk is an insulator, but symmetry-protected conducting states exist at the edges.

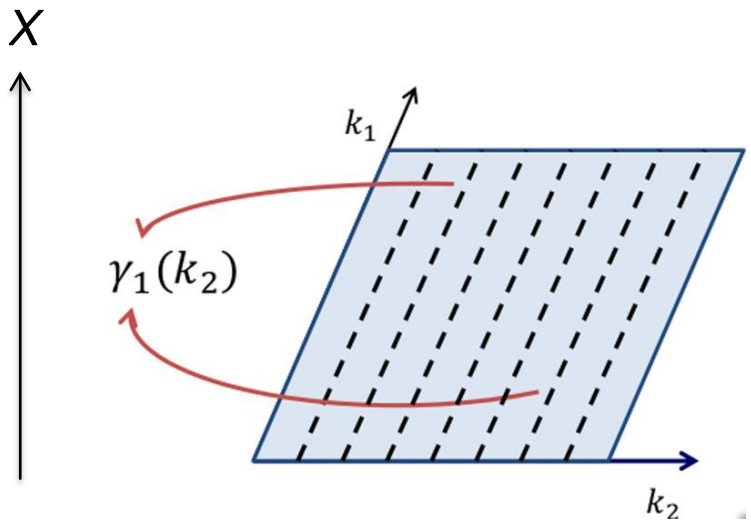


(Wikipedia)



The challenge:
Various types of topological classes are known, but the small size of the bulk band gap remains an issue for them all.

Topological invariants



Hybrid Wannier function of band *n* localized along *x*

$$\left|W_{njk_2}\right\rangle = \int_0^1 dk_1 e^{-i\mathbf{k}\cdot(\hat{\mathbf{r}}+\hat{\mathbf{R}}_j)}\left|\tilde{u}_{n\mathbf{k}}\right\rangle$$

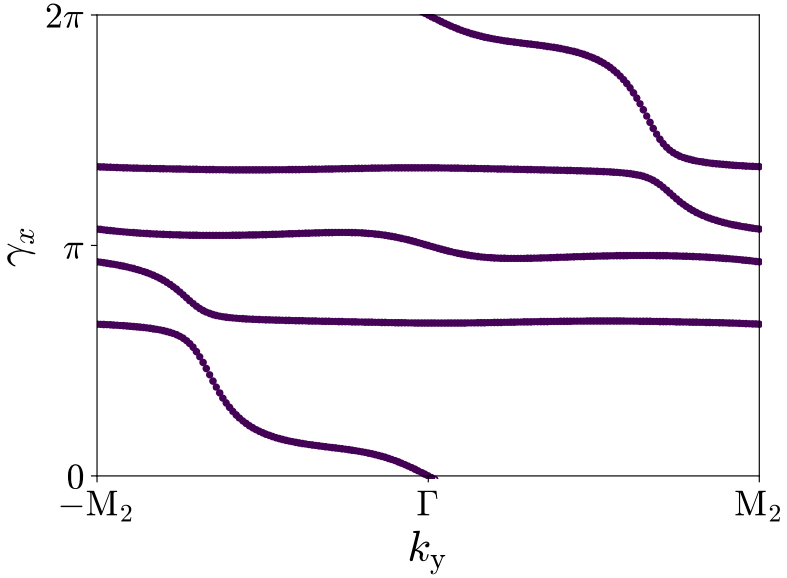
Center of Wannier function

$$x_{1,n}(k_2) \equiv \left\langle W_{n0k_2}\left|\hat{x}_1\right|W_{n0k_2}\right\rangle = \gamma_{1,n}(k_2)/2\pi$$

Berry's phase

$$\gamma_{1,n}(k_2) = i\int_0^1 dk_1\left\langle\tilde{u}_{n\mathbf{k}}\left|\partial_{k_1}\tilde{u}_{n\mathbf{k}}\right\rangle\right.$$

Berry phase diagram



Topological invariants determined by the number of Berry phases crossing any horizontal line.

Equivalently: The amount of charges shifted by one unit cell when k_2 is cycled.

Topological insulators: New materials

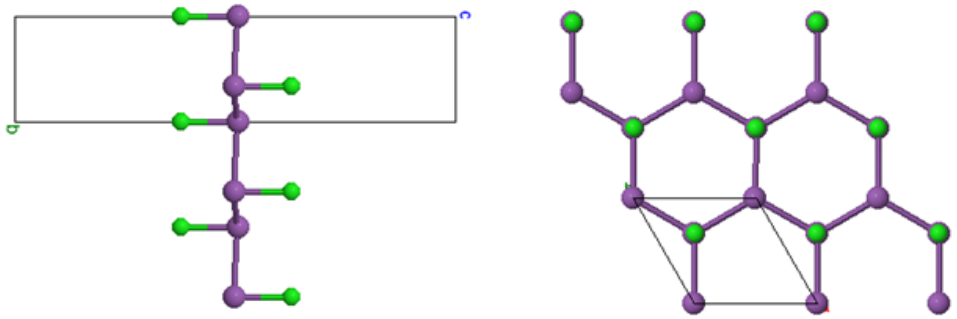
New quantum spin Hall insulators (from screening of 3331 materials)

Material	Prototype	Topology	KS gap (meV)	HOF (eV)	EACH (eV)
AuCl	FeSe	$\nu = 1$	20	0.10	0.30
CrAsBi	BiTeI	$\nu = 1$	35	0.31	0.46
IrSe	GaSe	$\nu = 1$	134	0.18	0.45
TiTe	GaSe	$\nu = 1$	109	−0.08	0.63
ZrTe	GaSe	$\nu = 1$	207	−0.28	0.65
AuI_3	BiI_3	$\nu = 1$	109	0.10	0.10
TiIN	FeOCl	$\nu = 1$	62	−1.18	−0.26
TlClSe	FeOCl	$\nu = 1$	27	−0.36	0.32
TiS	CH	$\nu = 1$	54	−1.13	0.31
TiCl	CH	$\nu = 1$	13	−0.64	0.45
ZrS	CH	$\nu = 1$	132	−1.16	0.26
ZrSe	CH	$\nu = 1$	20	−0.91	0.25
ZrCl	CH	$\nu = 1$	37	−0.59	0.73
ZrBr	CH	$\nu = 1$	45	−0.34	0.68
SbCl	CH	$\nu = 1$	434	−0.46	0.13
SbBr	CH	$\nu = 1$	442	−0.31	0.10
SbI	CH	$\nu = 1$	584	−0.12	0.13
HfS	CH	$\nu = 1$	158	−0.89	0.43
HfSe	CH	$\nu = 1$	42	−0.64	0.54
ReS	CH	$\nu = 1$	309	0.10	0.54
HgCl	CH	$\nu = 1$	129	−0.37	0.23
HgBr	CH	$\nu = 1$	188	−0.25	0.22
PbF	CH	$\nu = 1$	116	−1.43	0.45

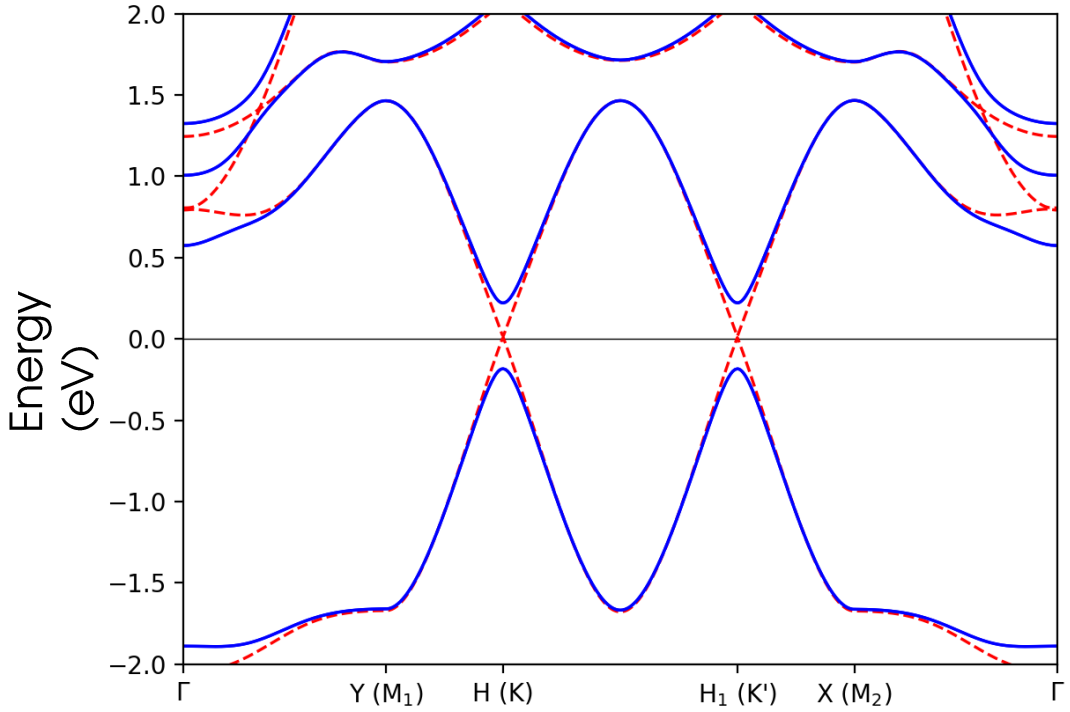
Dynamically stable materials in bold

Olsen *et al.* Phys. Rev. M **3**, 024005 (2019)

Topological edge states on SbCl



Atomic structure of SbCl monolayer.
(graphane crystal structure)



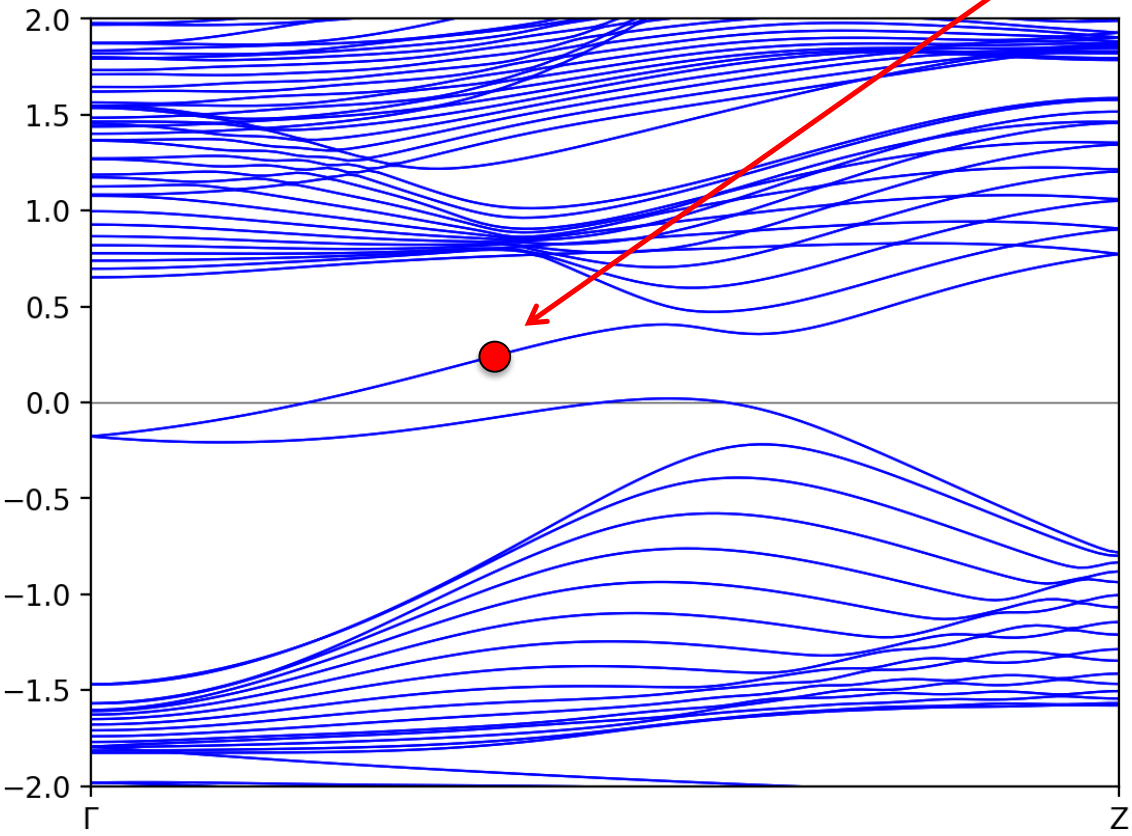
Band structure of infinite SbCl sheet.

Gap is due to spin-orbit coupling.

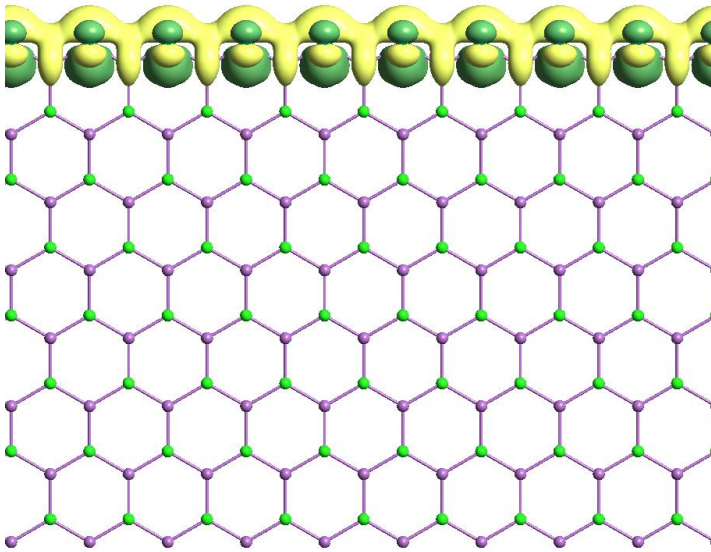
Work by Luca Vanucci, CAMD

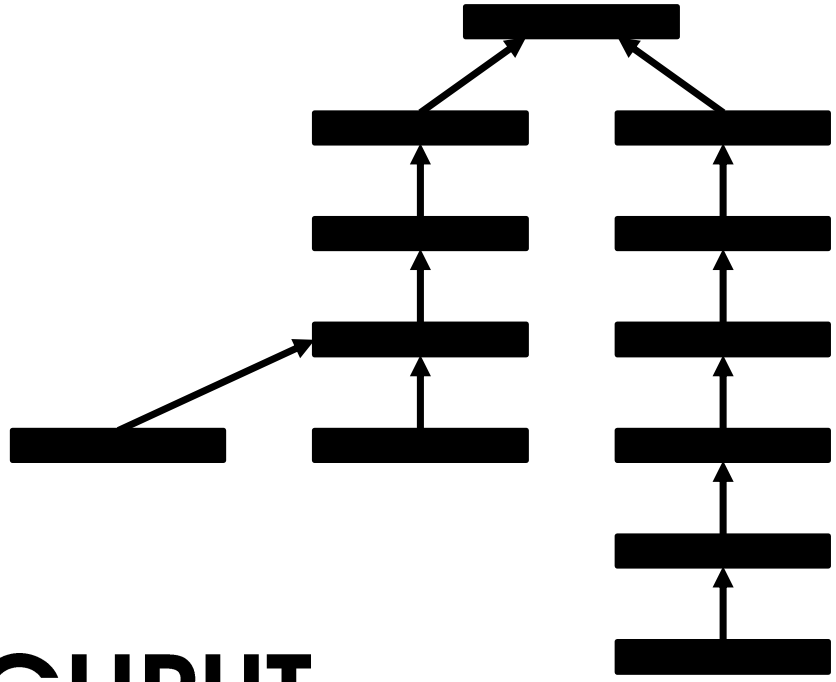
Topological edge states on SbCl

Band structure of SbCl nanoribbon:

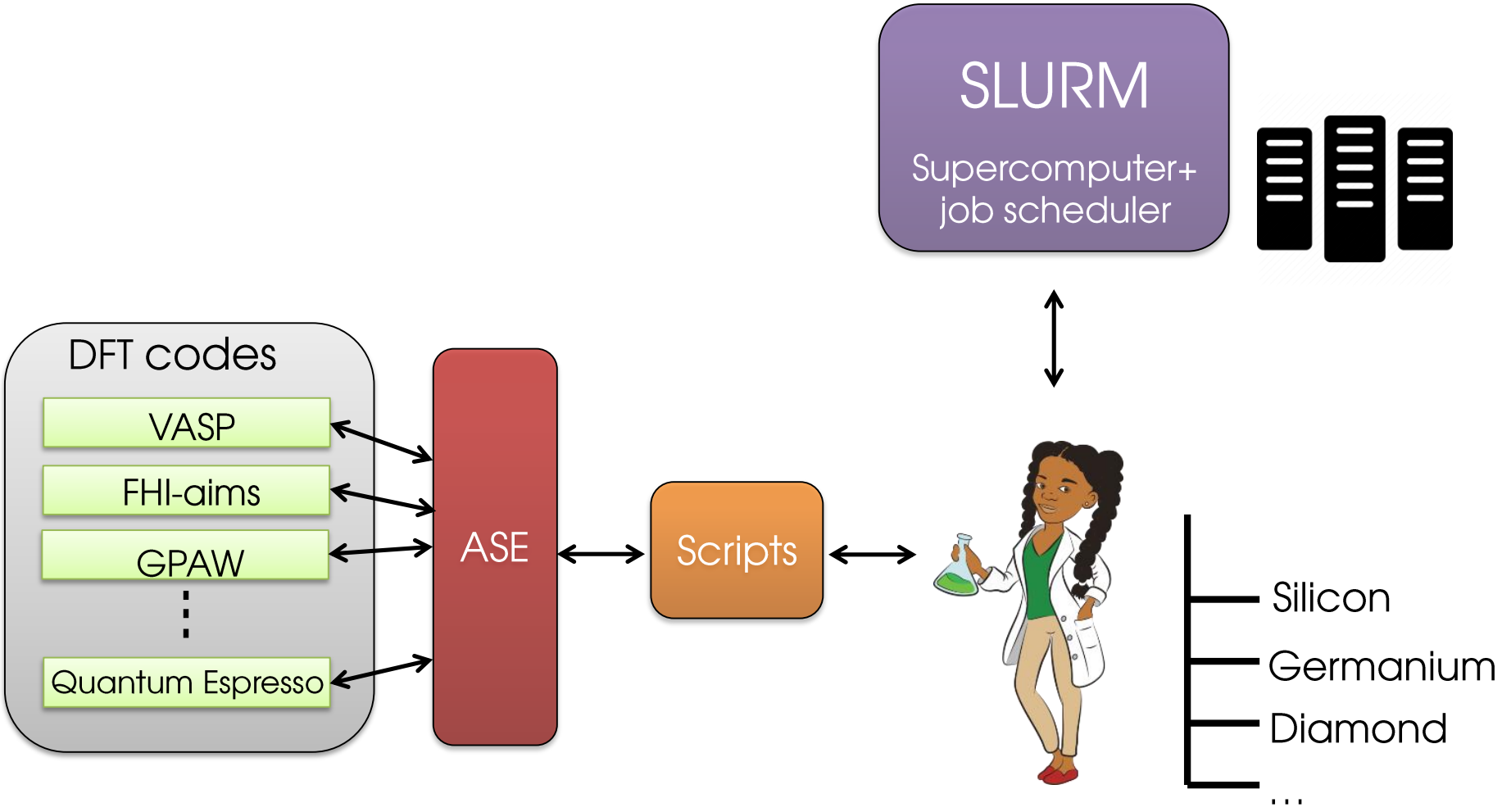


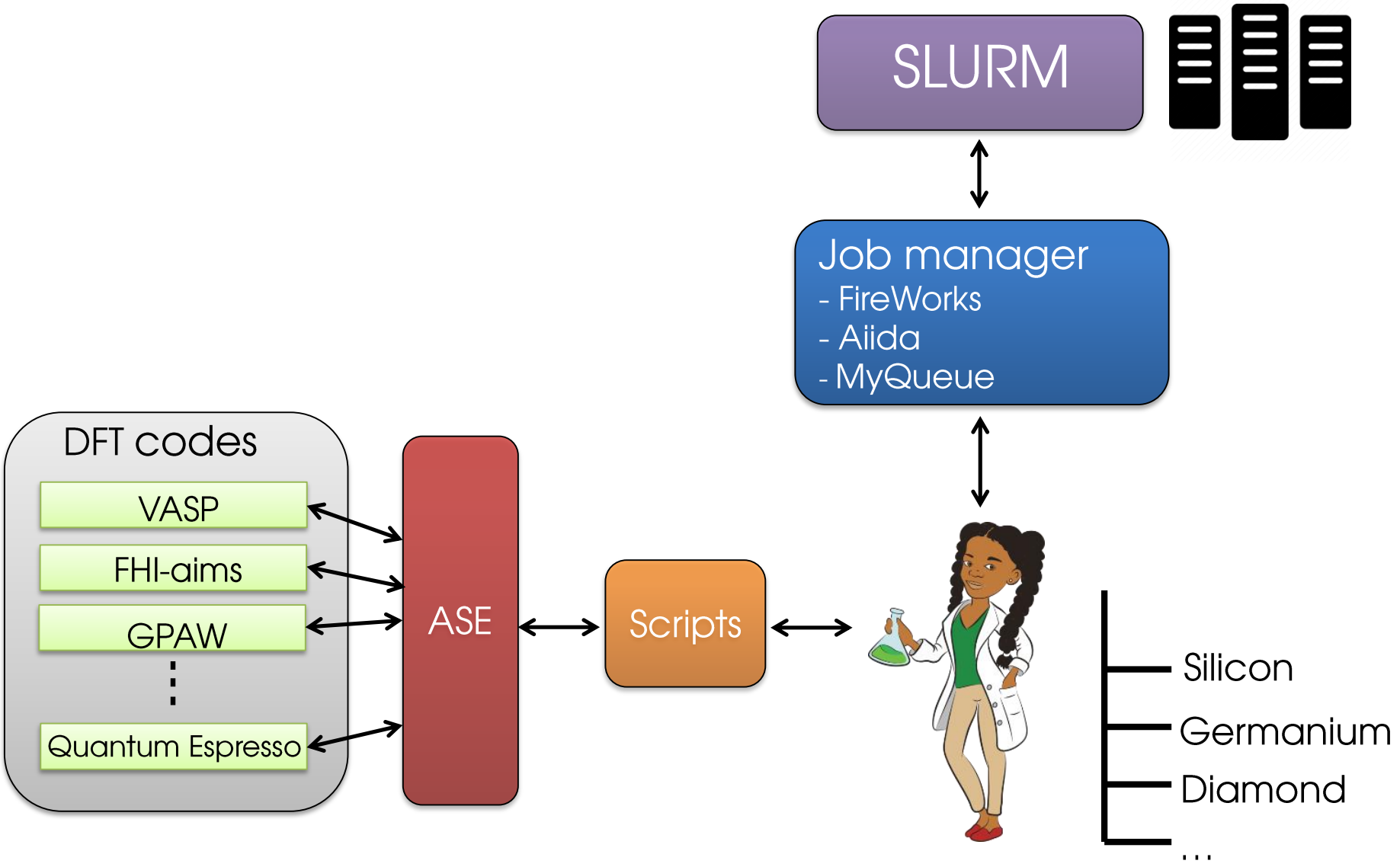
Topologically protected metallic edge state





HIGH-THROUGHPUT IN PRACTICE (@CAMD)


SLURM
Supercomputer+
job scheduler
DFT codes
VASP
FHI-aims
GPAW
Quantum Espresso
ASE
Scripts
Silicon
Germanium
Diamond
...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- MyQueue
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VASP
FHI-aims
GPAW
Quantum Espresso
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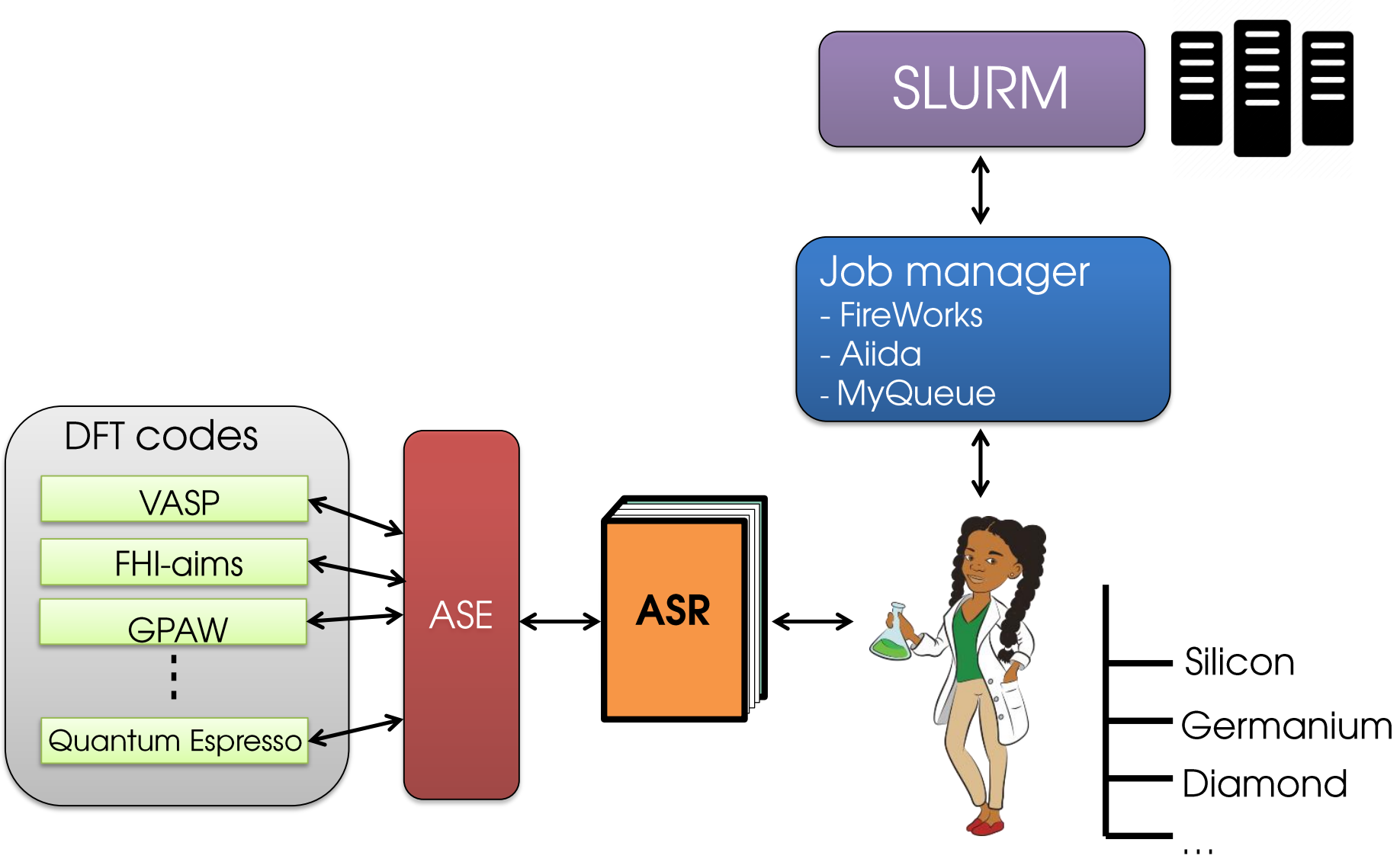
MyQueue

```
$ mq submit relax.py -R 8:1h Si/ Ge/ C/
```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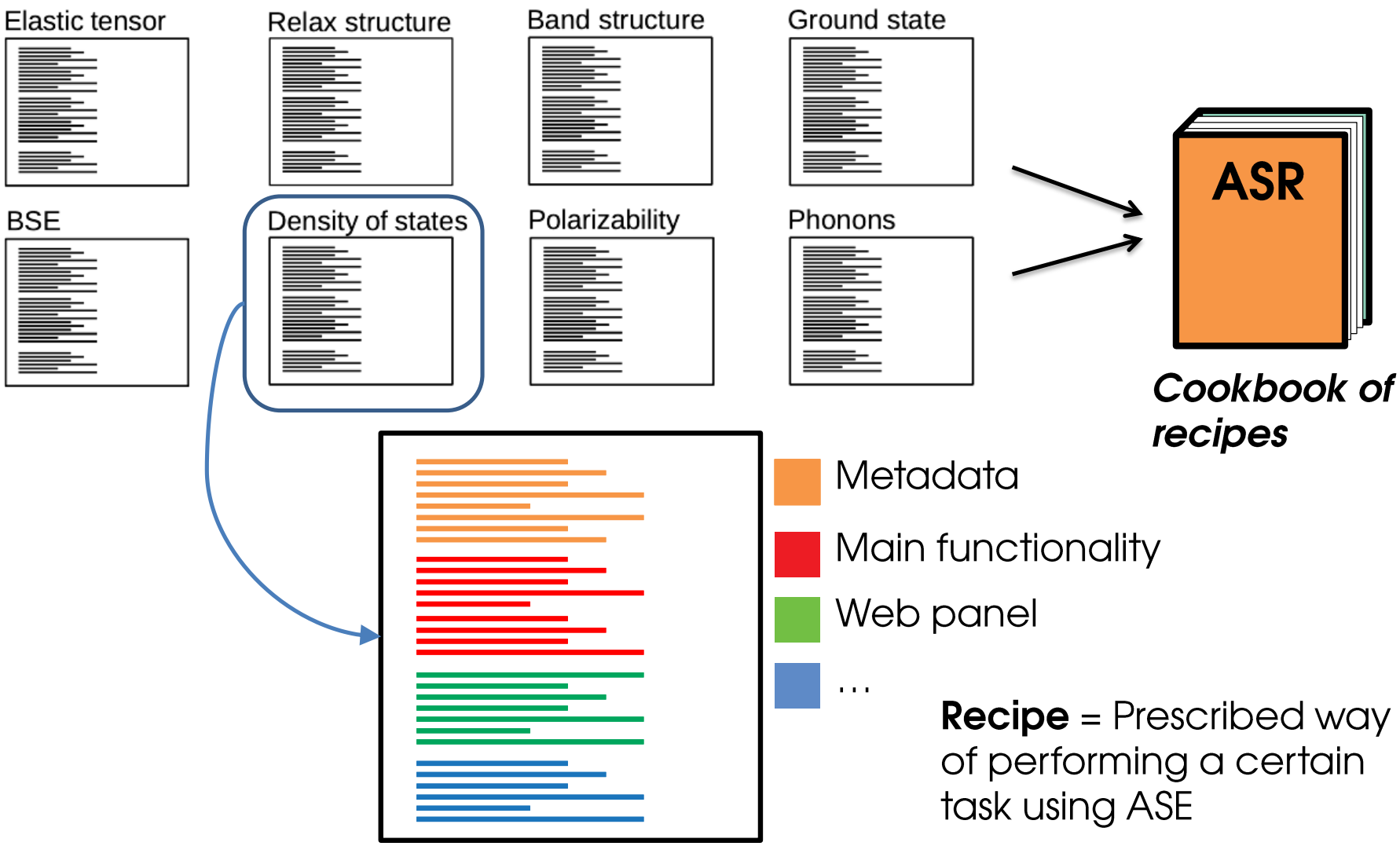
Atomic Simulation Recipes (ASR)



Recipe = Prescribed way of performing a certain task using ASE

Dependencies

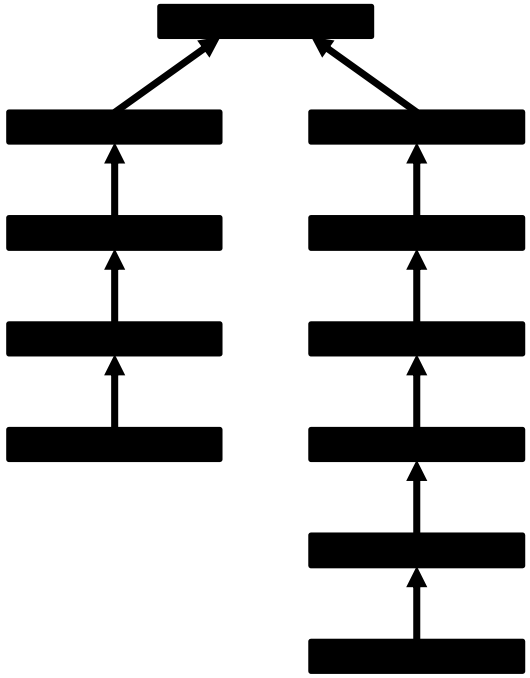
```
def main():
    ...

def collect_data():
    ...

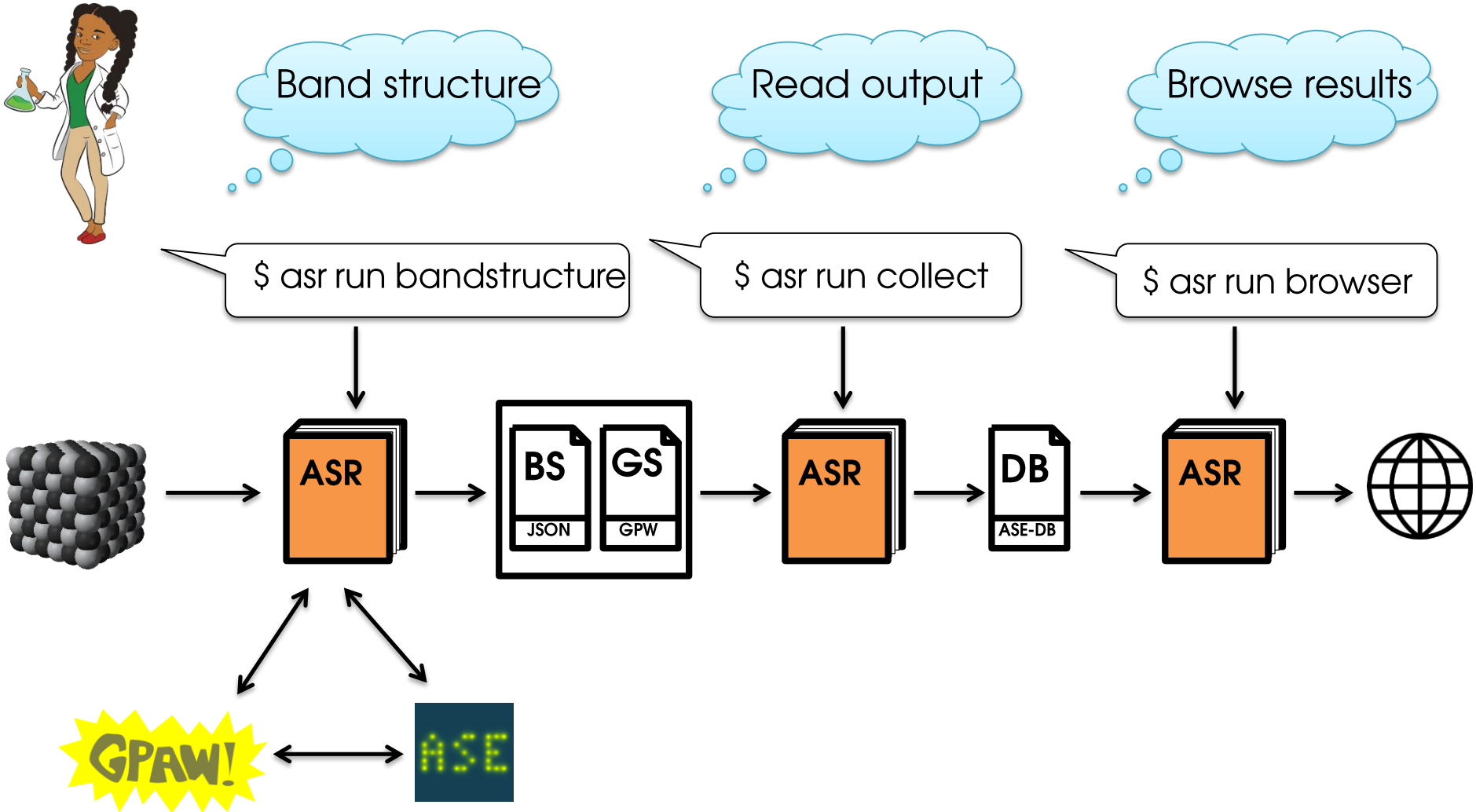
def webpanel():
    ...

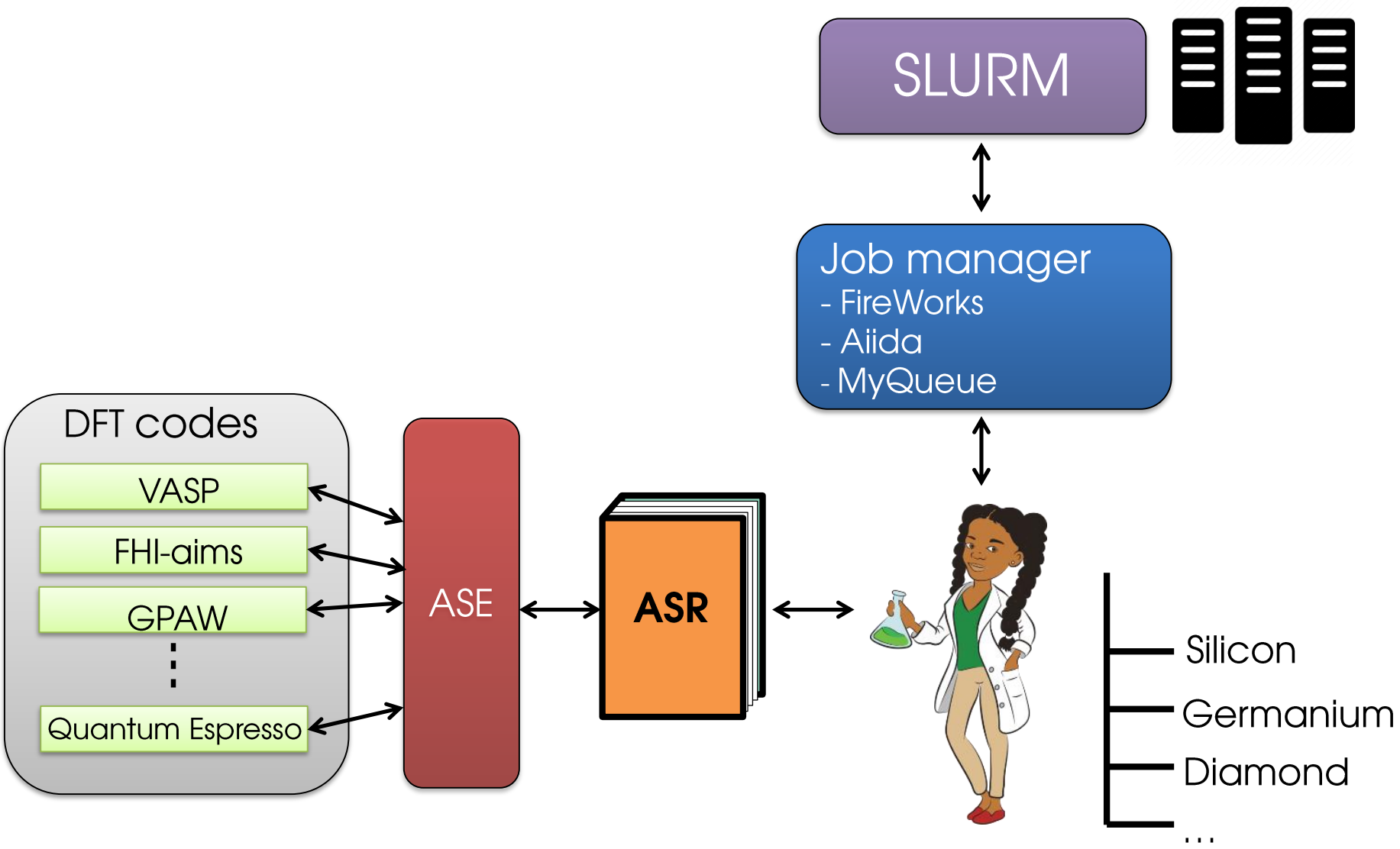
creates = ['something.json']  # what files are created
dependencies = ['asr.other_recipe']  # any dependencies?
resources = '1:10m'  # 1 core for 10 minutes
diskspace = 0  # how much diskspace is used
restart = 0  # how many times to restart
```

Sample recipe



Command line mode

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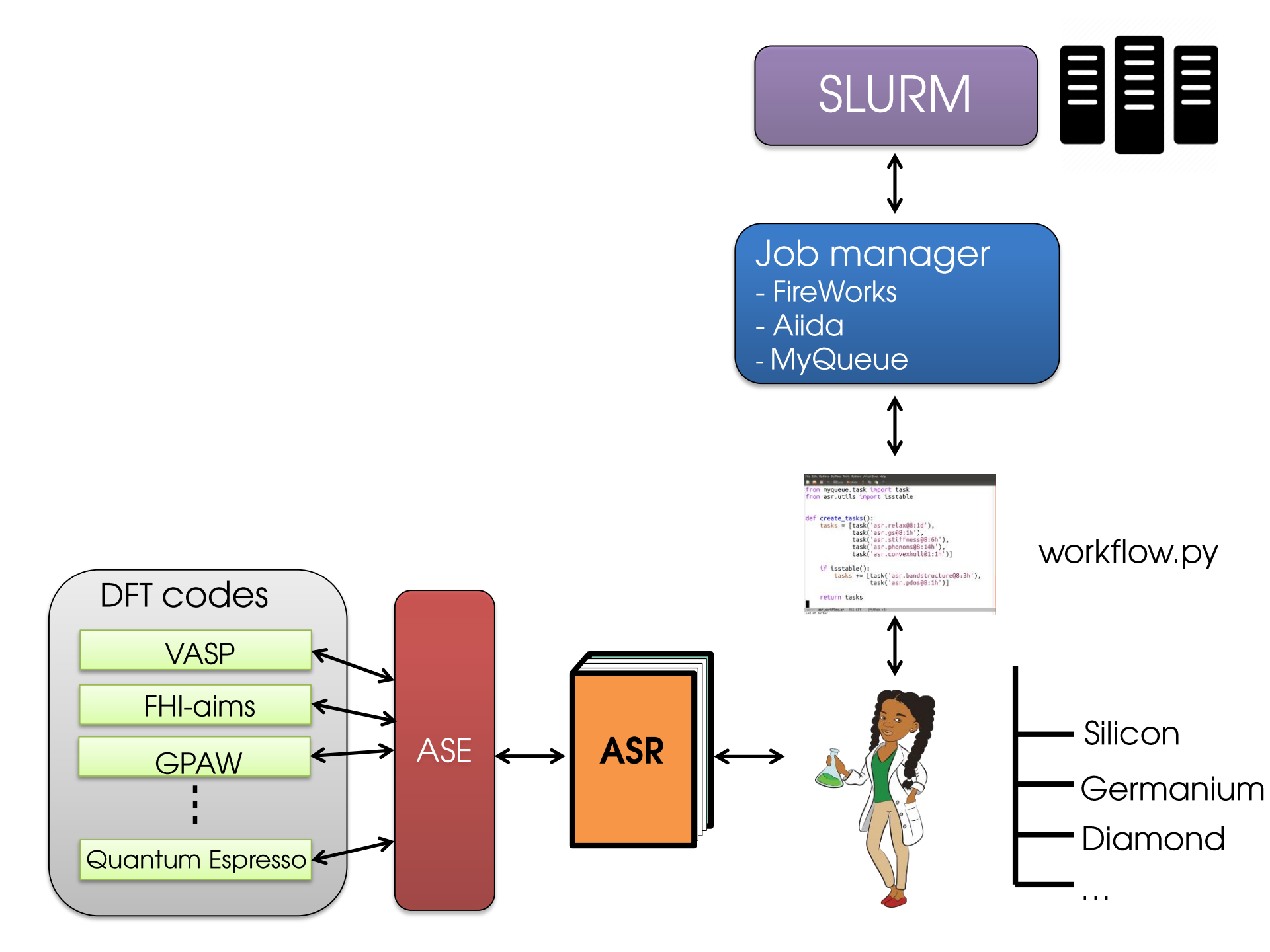
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...

MyQueue workflow example

File Edit Options Buffers Tools Python Virtual Envs Help

Save Undo

```
from myqueue.task import task
from asr.utils import isstable

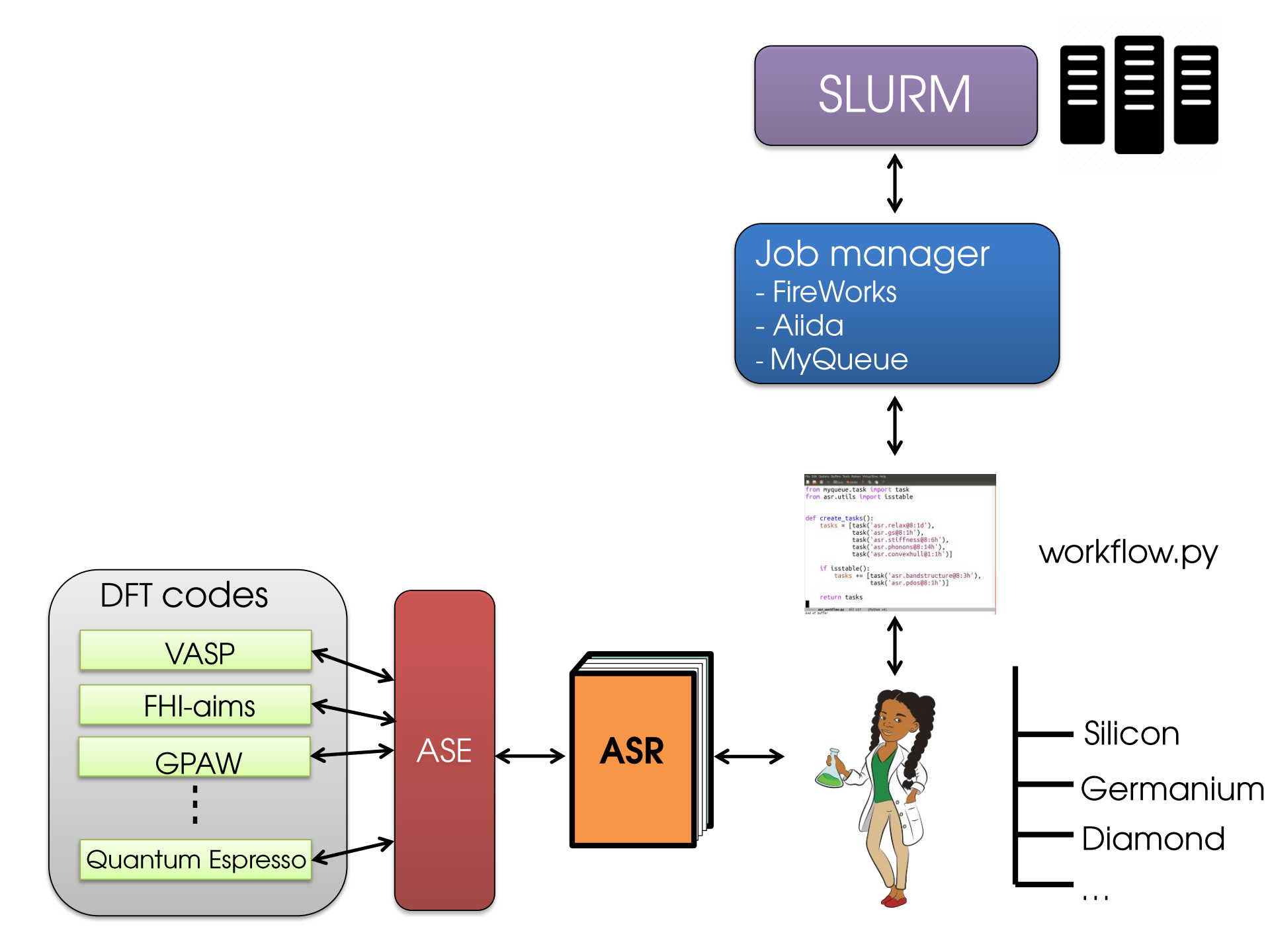

def create_tasks():
    tasks = [task('asr.relax@8:1d'),
             task('asr.gs@8:1h'),
             task('asr.stiffness@8:6h'),
             task('asr.phonons@8:14h'),
             task('asr.convexhull@1:1h')]

    if isstable():
        tasks += [task('asr.bandstructure@8:3h'),
                  task('asr.pdos@8:1h')]

    return tasks
```

-:--- **asr_workflow.py** All L17 (Python +4)

End of buffer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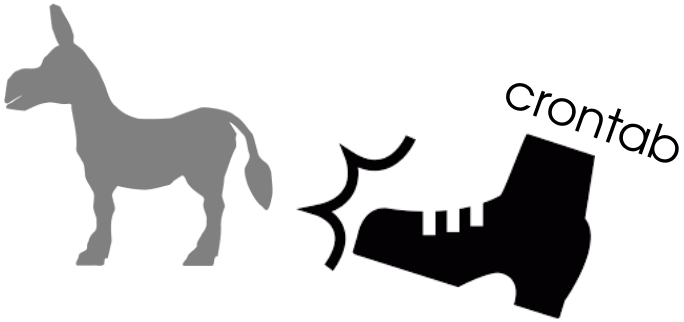
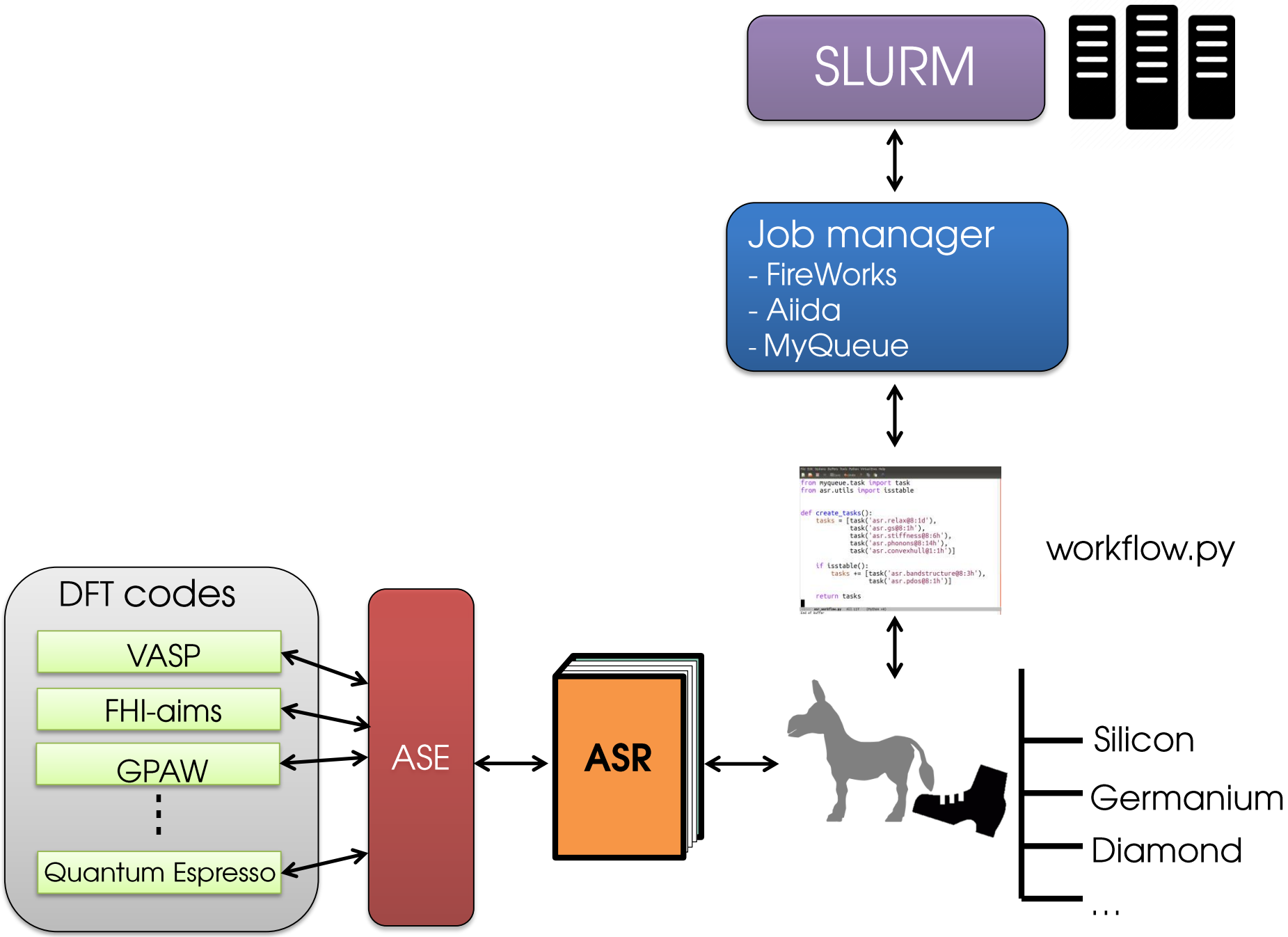
MyQueue workflows

```
$ mq kick; mq workflow workflow.py Si/ Ge/ C/
```

Kick-The-Donkey



5 min interval
(auto)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...

Conclusions

- **Atomic Simulation Environment**
- **Computational 2D Materials Database (C2DB):** A free platform for modeling and discovery of 2D materials
- Data can be used to validate models
- Novel 2D materials discovered.
- **MyQueue:** Simple frontend for SLURM.
- **Atomic Simulation Recipes (ASR):** A new open source Python library for setting up, managing, and analyzing high throughput computations.

Software & Links

- ASE: https://wiki.fysik.dtu.dk/ase/
- GPAW: https://wiki.fysik.dtu.dk/gpaw/
- C2DB: https://c2db.fysik.dtu.dk
- Myqueue: https://myqueue.readthedocs.io
- ASR: https://gitlab.com/mortengjerding/asr/