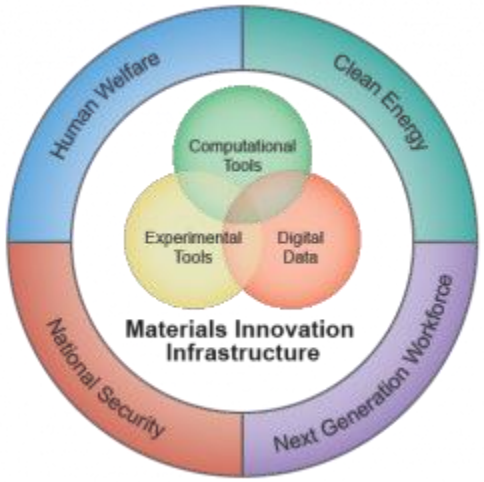


JARVIS-DFT

High-throughput Identification and Characterization of Two-dimensional Materials using Density functional theory

By

Kamal Choudhary

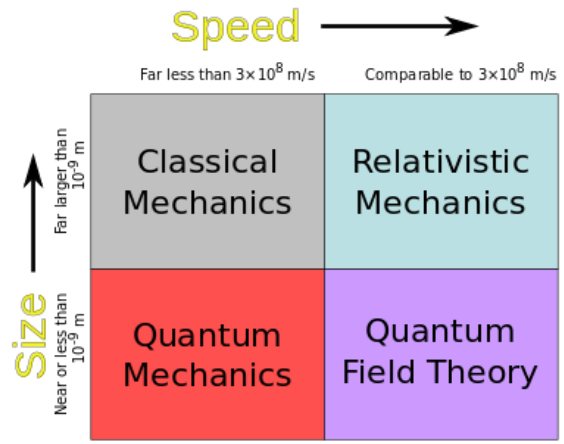
Acknowledgments: Francesca Tavazza, Arunima Singh, Ryan Beams, Irina Kalish

NIST Materials Genome Initiative
Gateway to Materials Genome Information

Outline

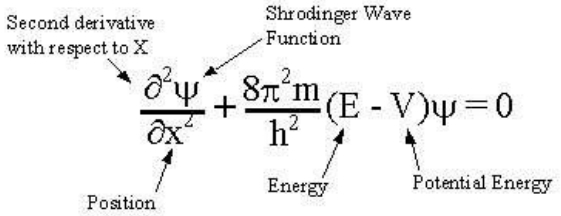
- Introduction to DFT
- Introduction to 2D materials
- Webpage
- Applicabilty and validation
- Workflow
- Conclusions

Intro: Density Functional Theory



- Classical Newton's laws not applicable for electrons (**very fast, very tiny**);
- Schrödinger equation: mathematical equation that describes the evolution over time of a physical system in which quantum effects, such as **wave–particle duality**, are significant (such as electrons)

$$H\psi = E\psi$$



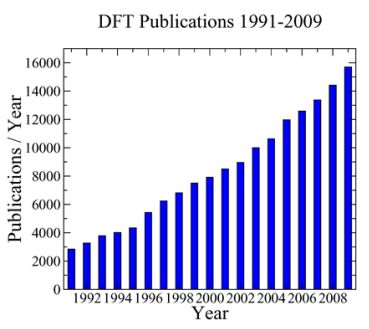
- Schrödinger equation of a **fictitious system** (the "Kohn–Sham system") of non-interacting particles (typically electrons) that generate the same density as any given system of interacting particles

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Eff}(r)\right]\psi_i(r) = E_i(r)\psi_i(r) \qquad V_{Eff} = T + V_{Ne} + V_{ee} + V_{XC}$$

- XC discussion: "I still don't understand why DFT works"-**Lt. Walter Kohn**

Hohenberg, Pierre; Walter Kohn (**1964**). "Inhomogeneous electron gas". *Physical Review*. **136** (3B): B864–B871

- **Different Functionals: LDA, GGA (PBE, PW91, optB88), HSE06 etc.**



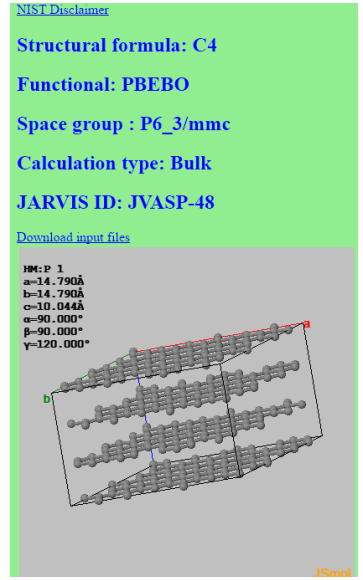
https://en.wikipedia.org/wiki/Classical_mechanics
http://www.psi-k.org/Update3.shtml
http://www.physlink.com/Education/AskExperts/ae329.cfm

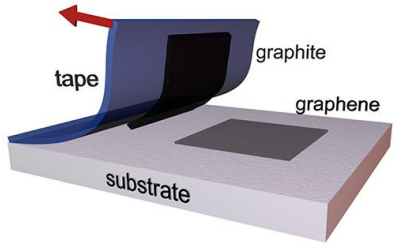
Intro: Two-dimensional materials

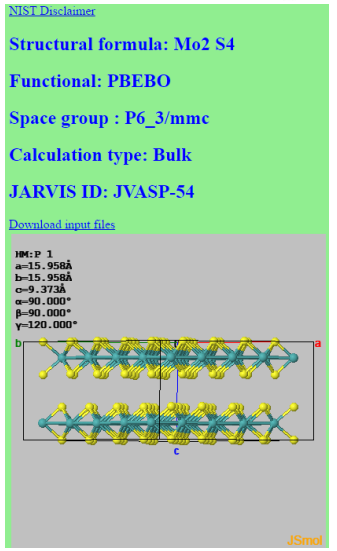
- Vander-Waal bonding in z-direction, covalent bonding in x, y-directions,e.g. Graphene,MoS_2

DIMENSIONALITY ==PERIODICITY

- Easily exfoliated, scotch-tape type, potential candidate for sub-nanometer technology, Si-replacement, flexible electronics, and other applications
- **For DFT calculation on 2D materials**: position of atoms (r) obtained from XRD and other experiments, ICSD database and other DFT databases
- DFT databases (**Materials Project, AFLOW, OQMD**) took structures from ICSD and used PBE functionals consistently for all structures, JARVIS-DFT took from them
- **Catch**: PBE functionals overestimate lattice constants (the r's in PBE-DFT are not correct)
- **JARVIS-DFT**: Using REST API at Materials-project got all the crystal structures with ICSD and PBE data and calculated relative error $\delta = \frac{|c_{PBE} - c_{ICSD}|}{c_{ICSD}}$
- If the error is more than **5%,** we predict them to be 2D materials; at least 521 such materials Found, recalculate with better optB88 functionals, tight DFT convergenece





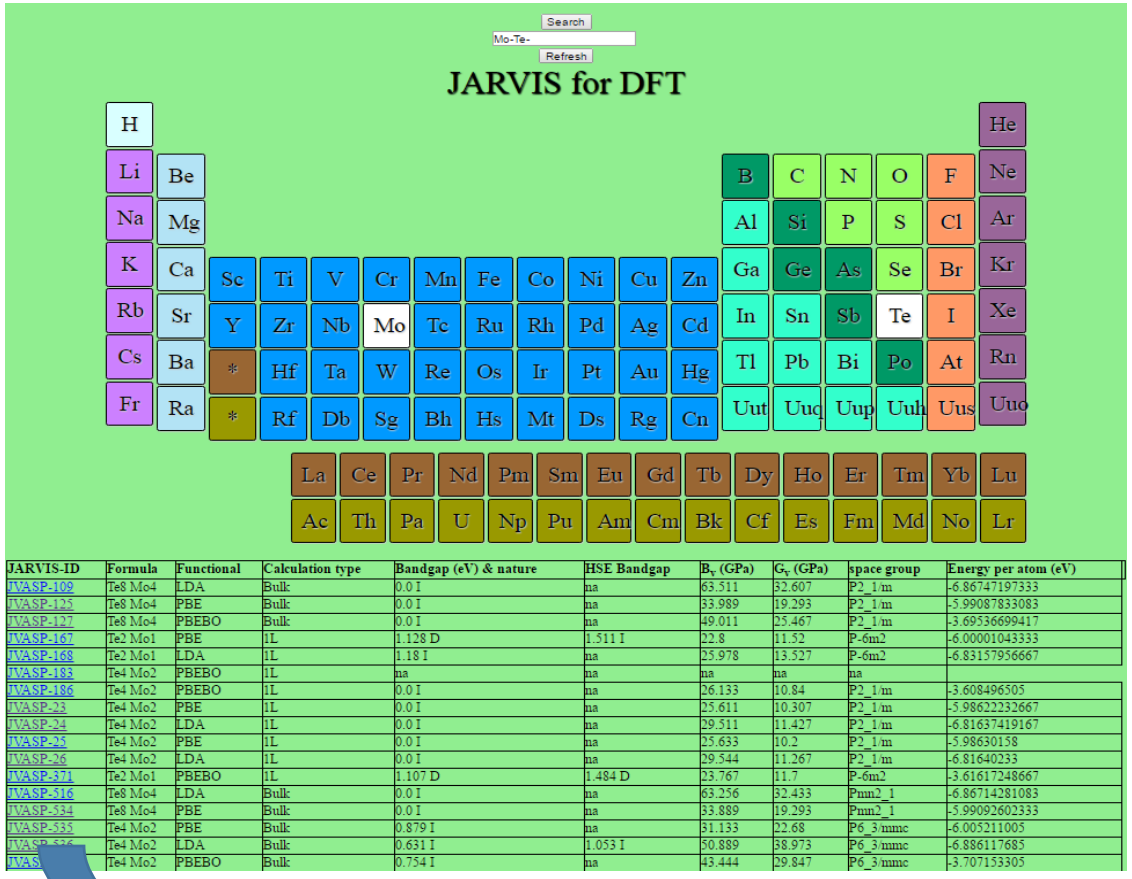


http://ammcttwtht.tumblr.com/post/101405895438/a-miracle-material-can-take-the-world-to-the

Webpage

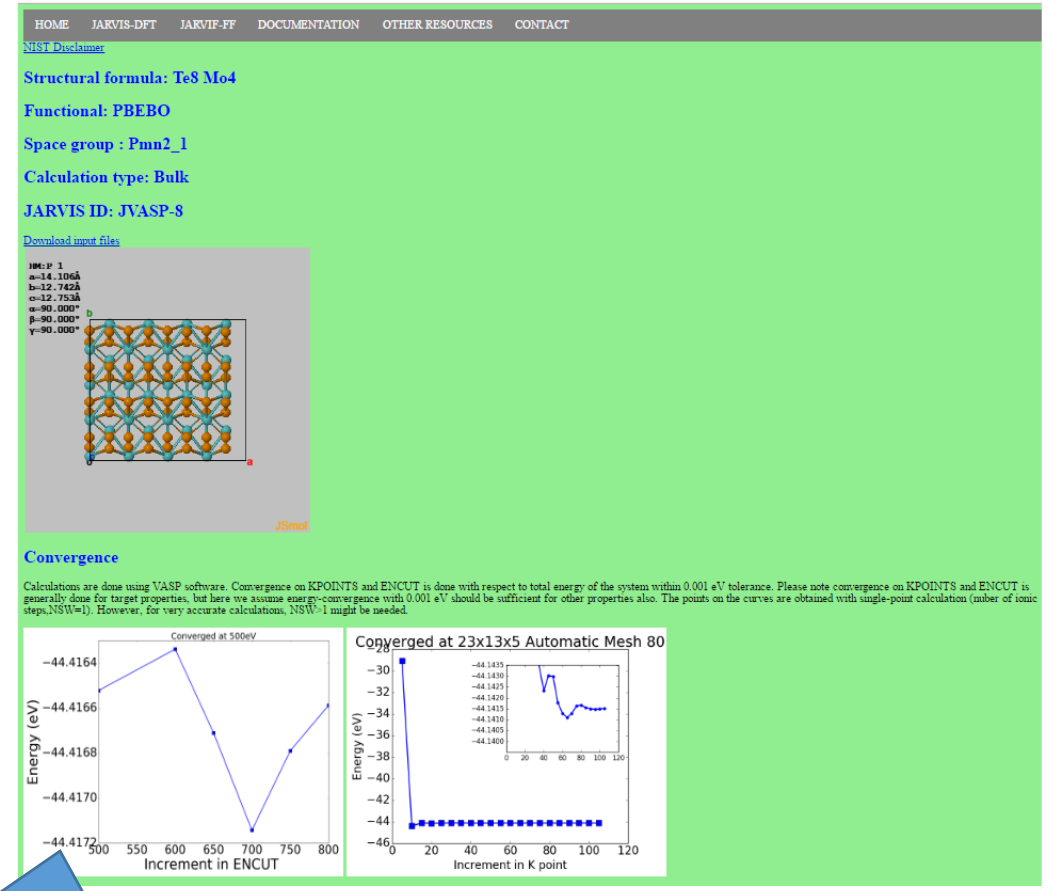
http://www.ctcms.nist.gov/~knc6/JVASP.html

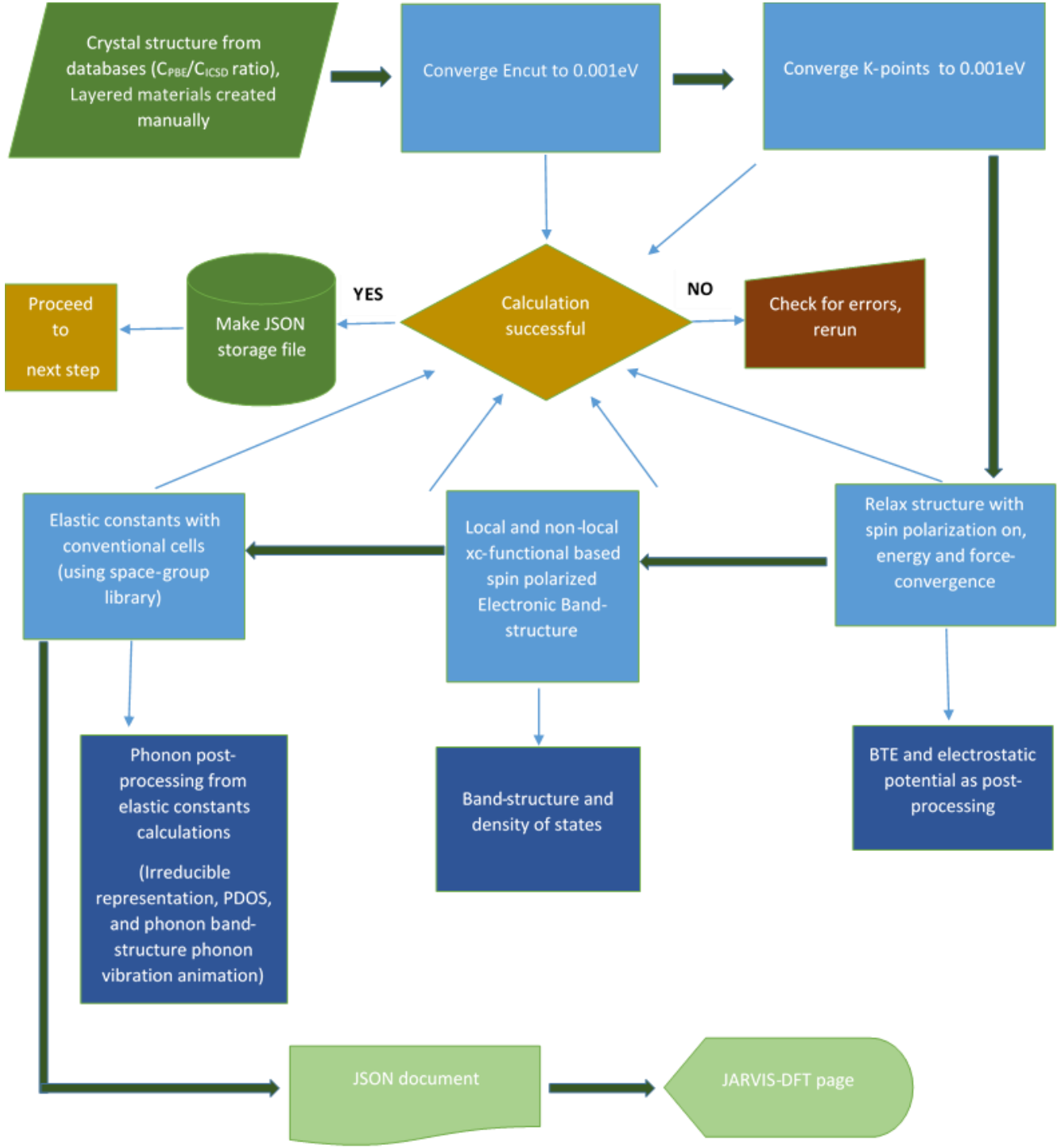
- Click on elements, click search, click JARVIS-ID



JARVIS-ID	Formula	Functional	Calculation type	Bandgap (eV) & nature	HSE Bandgap	B_T (GPa)	G_V (GPa)	space group	Energy per atom (eV)
JVASP-109	Te8 Mo4	LDA	Bulk	0.0 I	na	63.511	32.607	P2_1/m	-6.86747197333
JVASP-125	Te8 Mo4	PBE	Bulk	0.0 I	na	33.989	19.293	P2_1/m	-5.99087833083
JVASP-127	Te8 Mo4	PBEBO	Bulk	0.0 I	na	49.011	25.467	P2_1/m	-3.69536699417
JVASP-167	Te2 Mo1	PBE	1L	1.128 D	1.511 I	22.8	11.52	P-6m2	-6.00001043333
JVASP-168	Te2 Mo1	LDA	1L	1.18 I	na	25.978	13.527	P-6m2	-6.83157956667
JVASP-183	Te4 Mo2	PBEBO	1L	na	na	na	na	na	
JVASP-186	Te4 Mo2	PBEBO	1L	0.0 I	na	26.133	10.84	P2_1/m	-3.608496505
JVASP-23	Te4 Mo2	PBE	1L	0.0 I	na	25.611	10.307	P2_1/m	-5.98622232667
JVASP-24	Te4 Mo2	LDA	1L	0.0 I	na	29.511	11.427	P2_1/m	-6.81637419167
JVASP-25	Te4 Mo2	PBE	1L	0.0 I	na	25.633	10.2	P2_1/m	-5.98630158
JVASP-26	Te4 Mo2	LDA	1L	0.0 I	na	29.544	11.267	P2_1/m	-6.81640233
JVASP-371	Te2 Mo1	PBEBO	1L	1.107 D	1.484 D	23.767	11.7	P-6m2	-3.61617248667
JVASP-516	Te8 Mo4	LDA	Bulk	0.0 I	na	63.256	32.433	Pmn2_1	-6.86714281083
JVASP-534	Te8 Mo4	PBE	Bulk	0.0 I	na	33.889	19.293	Pmn2_1	-5.99092602333
JVASP-535	Te4 Mo2	PBE	Bulk	0.879 I	na	31.133	22.68	P6_3/mmc	-6.005211005
JVASP-536	Te4 Mo2	LDA	Bulk	0.631 I	1.053 I	50.889	38.973	P6_3/mmc	-6.886117685
JVASP-537	Te4 Mo2	PBEBO	Bulk	0.754 I	na	43.444	29.847	P6_3/mmc	-3.707153305

- Kpoint, Energy cut-off and force convergence (N/A in other DFT databases, but very important!)
- Both bulk and single-layer materials available





JARVIS-DFT workflow

- Written in python language
- Separate calculation for mono-layer and bulk materials
- Mono-layer created by adding additional vacuum (20 Angstrom) in z-direction
- c-lattice constant not-optimized for mono-layer (custom compilation of VASP)
- Example:

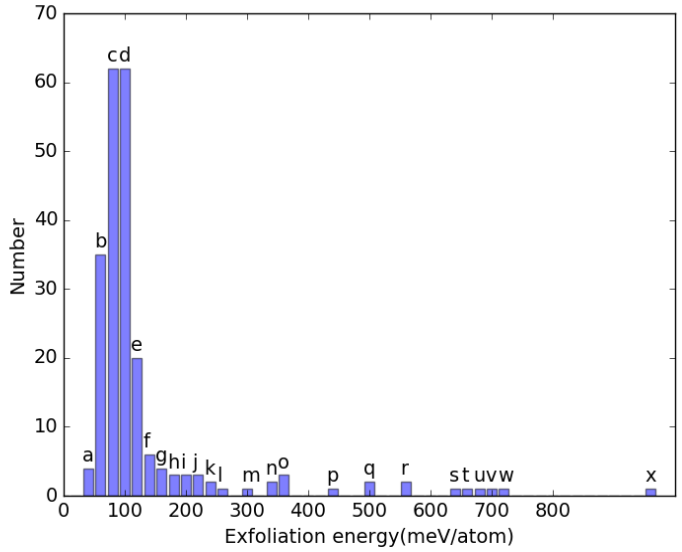
```
bulk@mp_48
   1.00000000000000
     1.2325005105744926   -2.1347529556398626    0.0000000000000000
     1.2325005105744926    2.1347529556398626    0.0000000000000000
     0.0000000000000000    0.0000000000000000    6.6962686124617425
   C
     4
Direct
  0.0000000000000000  0.0000000000000000  0.2500000000000000
  0.0000000000000000  0.0000000000000000  0.7500000000000000
  0.3333330000000032  0.6666669999999968  0.2500000000000000
  0.6666669999999968  0.3333330000000032  0.7500000000000000
```

```
Surf-mp-48
   1.00000000000000
     1.2320971008984494   -2.1340542301747005    0.0000000000000000
     1.2320971008984494    2.1340542301747005    0.0000000000000000
     0.0000000000000000    0.0000000000000000   30.8030730000000013
   C
     2
Direct
  0.0000000000000000  0.0000000000000000  0.0633300000000006
  0.3333330000000032  0.6666669999999968  0.0633300000000006
```

Exfoliation energy calculations

- Exfoliation energy:

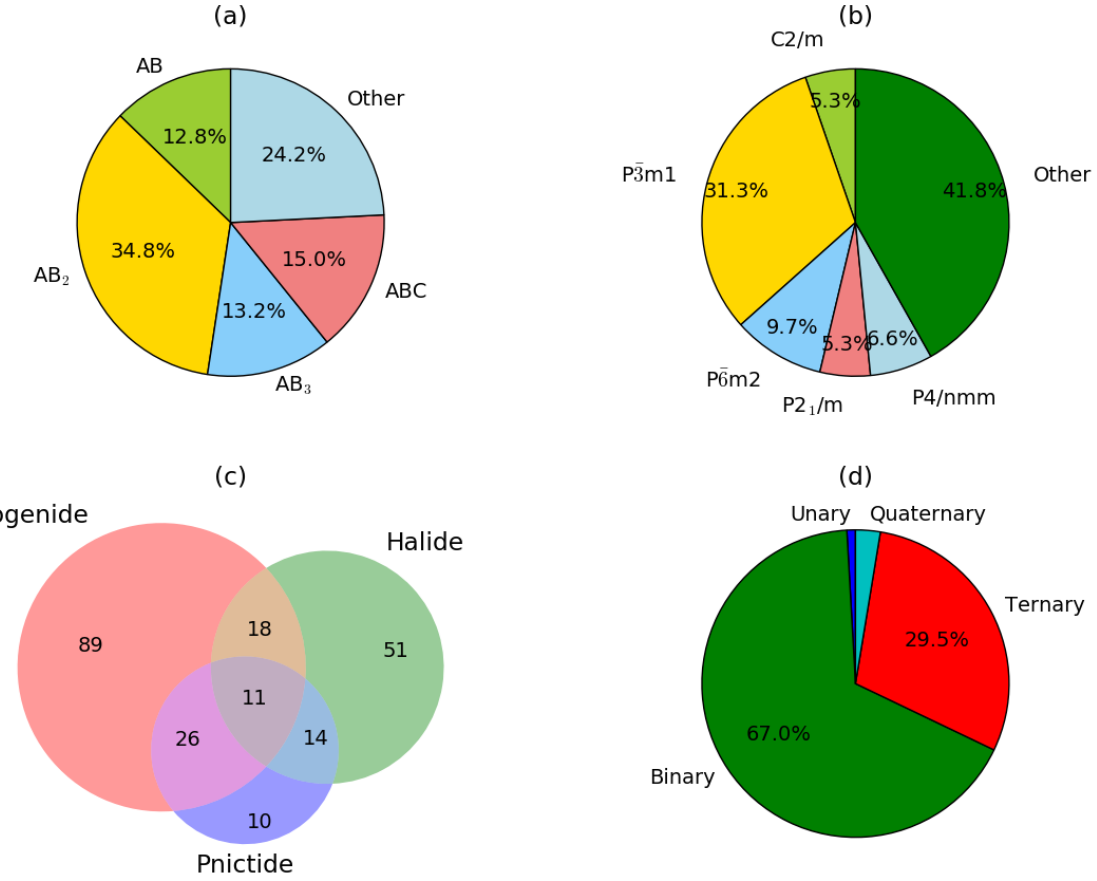
$$E_f = \frac{E_{1L}}{N_{1L}} - \frac{E_{bulk}}{N_{bulk}}$$



- 427 bulk, 252 Single layer, 227 common, calculations still running (thousands of processors needed)

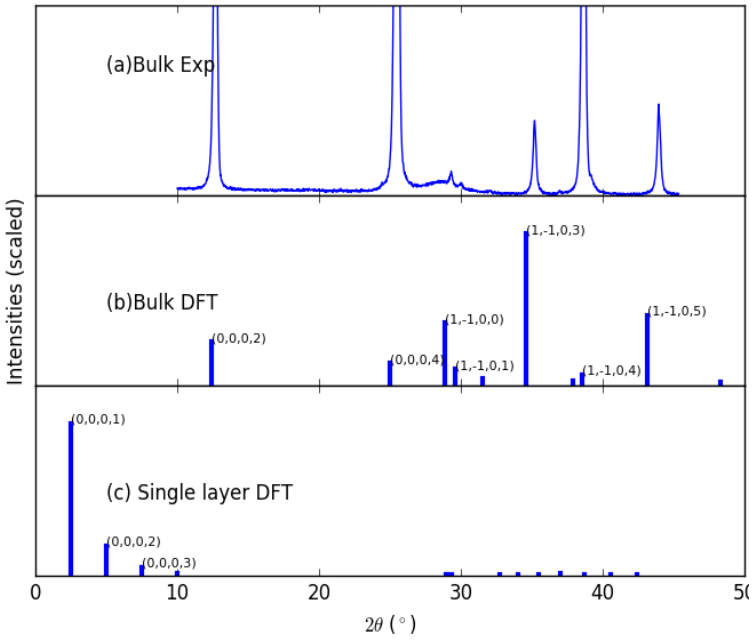
	Energy range (meV)	Materials
a)	0-40	$TiNCl$, SiH_4, $HfBrN$, $Mg(AlSe_2)_2$
b)	40-60	$GaSe$, CrS_2, ZrS_3, NiO_2, GaS, $ZrSe_3$, $NdTe_3$, US_3, TiS_3, $PrIO$, $DySI$, Sc_2CCl_2, $ThIN$, $TiBrN$, $InClO$, $LuSBr$, $SrHI$, $BiIO$, $BiBrO$, $KMnP$, $TiIN$, Sc_2NCl_2, $TlSbO_3$, $ZrCl$, $SmTe_3$, $PrTe_3$, As_2O_3, Nb_2CS_2, $RbMnAs$, SiH, Bi_2TeI, $ScCl$, $TbBr$, $Ge(BiTe2)_2$, GaS
c)	60-80	WSe_2, WS_2, MoS_2, C, SnO_2, PtO_2, $CdBr_2$, $ReSe_2$, $CrSe$, $MgCl_2$, $CoBr_2$, $ZrCl_2$, $MgBr_2$, TcS_2, $FeCl_2$, $MnCl_2$, $MnBr_2$, $InSe$, $CrBr_3$, VCl_3, USe_3, $IrCl_3$, $ScCl_3$, $RhCl_3$, TaI_2O, $DySBr$, $ErSeI$, $ErSCl$, $BiClO$, $OsCl_2O$, $CdCl_2$, BN, $Nb(SCl)_2$, Bi_2Te_2S, $ThBrN$, $HfCl_4$, Bi_2Te_2Se, $MgPSe_3$, $CdPS_3$, $ScPS_4$, $PPdS$, $TmAg(PSe_3)_2$, $ScAg(PSe_3)_2$, $ErAg(PSe_3)_2$, $ScAg(PS_3)_2$, Nb_3Cl_8, Nb_3TeCl_7, $InAg(PSe_3)_2$, Hf_3Te_2, $SNCl$, Sr_3Si_2, $TiCl_2$, $HfFeCl_6$, $GaTe$, CS_2, $Nb(SeCl)_2$, $CrCl_3$, BiI, $TiBr_2$, $GaAg(PSe_3)_2$, $CdPS_3$, TiS_2
d)	80-100	NbS_2, $MoSe_2$, $NbSe_2$, WTe_2, $MoTe_2$, VSe_2, ZrS_2, HfS_2, $HfSe_2$, MoS_2, PtO_2, PtS_2, SnS_2, $SnSe_2$, TiO_2, TiS_2, $TiSe_2$, $ZrSe_2$, TaS_2, $SiTe_2$, $TaSe_2$, VS_2, $TaSe_2$, MgI_2, SbI_3, PbI_2, GeI_2, SiS_2, MnI_2, CaI_2, $RhBr_3$, BiI_3, $MoBr_3$, $RuBr_3$, PCl_3, AuI, BPS_4, $IrBr_3$, $Re(AgCl_3)_2$, $AlPS_4$, $AlSiTe_3$, $PPdSe$, $CrSiTe_3$, Nb_3TeI_7, NdI_2, Al_2Te_3, S_5N_6, $AlTeI_7$, $AlSeBr_7$, CdI_2, PSe, Ta_3TeI_7, TmI_2, $SbBr_3$, P_4S_5
e)	100-120	$HfTe_2$, $PtSe_2$, $TiTe_2$, WO_2, SnO, BCl_3, Te_2Br, Te_2I, PBr_3, TiI_3, $BiTeCl$, $BiTeI$, $TlPt_2S_3$, $AlBr_3$, $BiSBr$, CaN, Mn_2Bi, HgI_2, $SrThBr_6$, P
f)	120-140	BBr_3, AlI_3, $TlTe_3Pt_2$, $SbSBr$, $TlPd_2Se_3$, P_2Se_5
g)	140-160	PdS_2, Te_2Pt, BI_3, $Ta(ICl)_2$
h)	160-180	$PdSe_2$, $NiTe_2$, NbI_5
i)	180-200	ZrS, PI_3, $BaBrCl$
j)	200-220	Te_2Pd, Te_2Ir, $BiSe_2$
k)	220-240	$SbSeI$, $BiSI$
l)	240-260	Bi_2Te_3
m)	260-300	VS_2
n)	300-340	$CaSn$, $KAuSe$
o)	340-360	$KAuS$, $RbAuS$, $RbAuSe$
p)	360-440	Sc_2C
q)	440-500	GaN, $TiSe_2$
r)	500-560	Sr_2H_3, Ca_2H_3
s)	560-640	AlN
t)	640-660	$TiTe_2$
u)	660-680	$CrSe_2$
v)	680-700	$ZrTe_2$
w)	700-720	$CoAs_2$
x)	720-960	Ti_2O

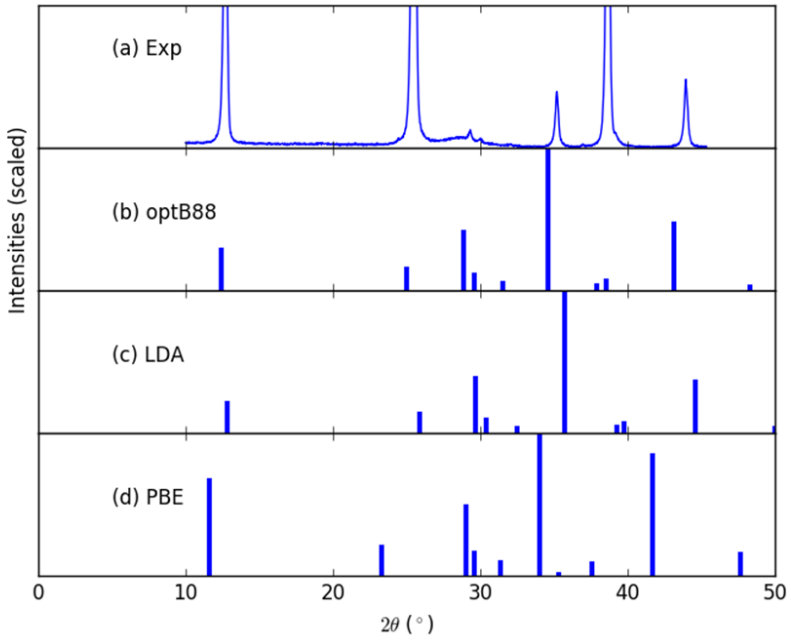
Classification of database



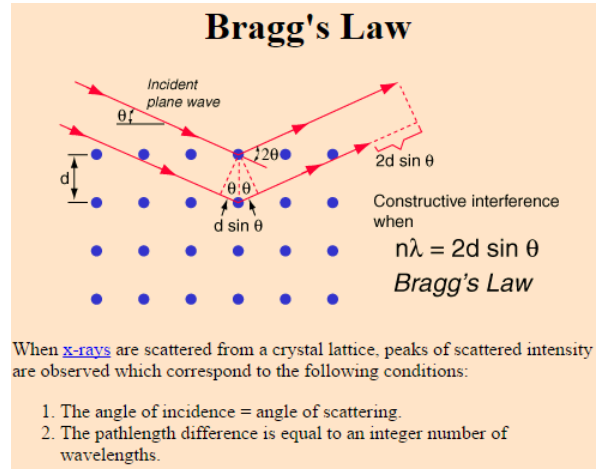
- 2D materials are not just AB2
- More than *2H* ($P\bar{6}m2$) and *1T* ($P\bar{3}m1$) prototype
- Venn diagram
- Majority of 2D materials are binary

Validation and Applicability





- Computational X-ray diffraction:

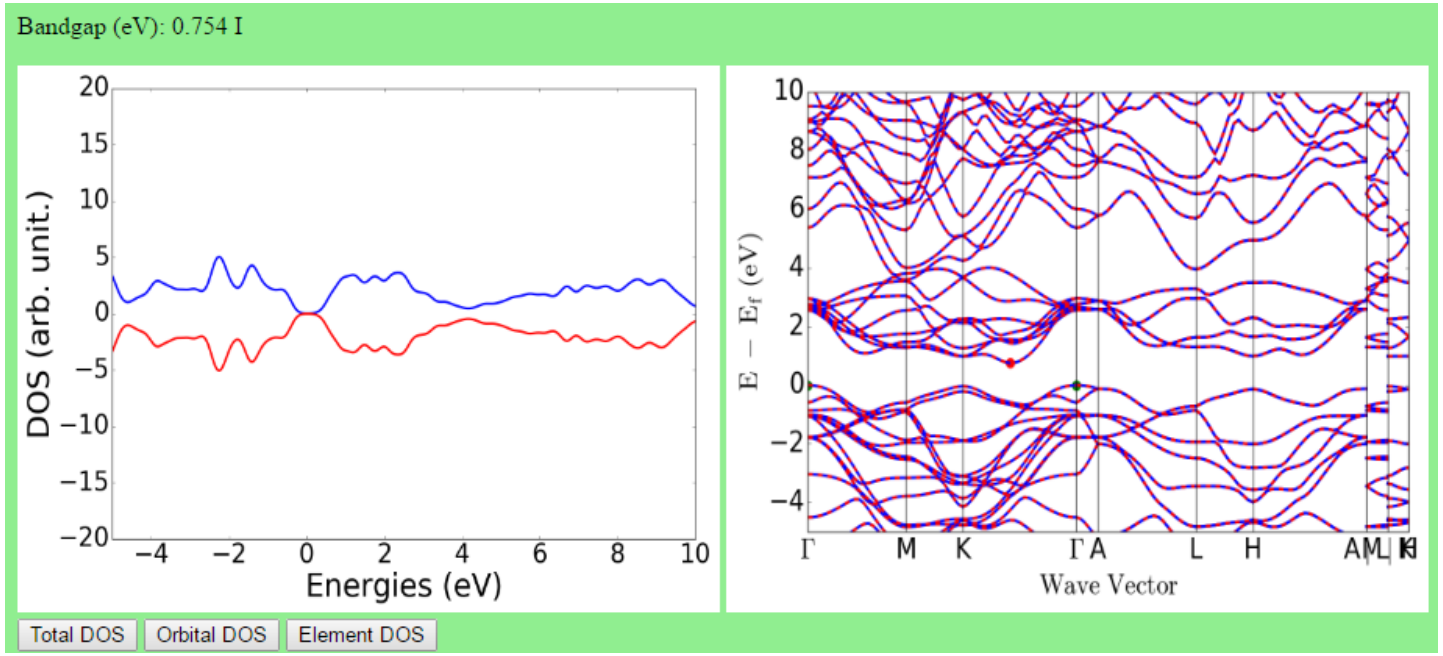


- Experimental data from Irina Kalish (MoTe2-2H)
- Computational XRD implemented in pymatgen
- Excellent agreement of optB88 and experiments
- PBE gives erroneous peaks
- Single-layer XRD also available

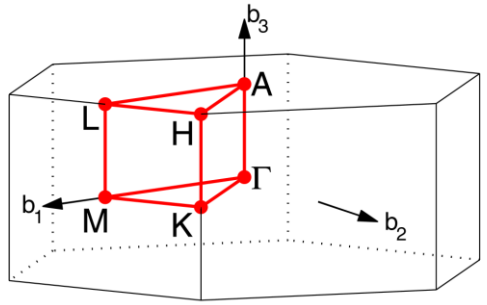
http://faculty.gvsu.edu/majumdak/public_html/OnlineMaterials/XRay.pdf
http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html

Validation and Applicability

- Density of states and Band-structures:



- optB88 bandgaps
- Few LDA, PBE and HSE06 bandgaps



HEX path: Γ-M-K-Γ-A-L-H-A|L-M|K-H

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

Brillouin zone for hexagonal system

Read WARNINGS!

Validation and Applicability

- Elastic-constants and Gamma-point phonons:

Elastic Tensor C_{ij} GPa

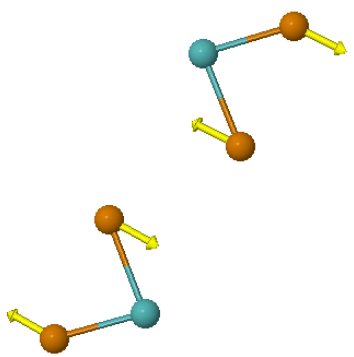
119.5	32.8	11.3	0.0	0.0	0.0
32.8	119.5	11.3	0.0	0.0	0.0
11.3	11.3	41.2	0.0	0.0	0.0
0.0	0.0	0.0	43.3	0.0	0.0
0.0	0.0	0.0	0.0	15.5	0.0
0.0	0.0	0.0	0.0	0.0	15.5

Point group

point_group_type: 6/mmm

Visualize Phonons here

Phonon mode (cm^{-1})	Representation
-0.0465217481	None
-0.0362848079	None
0.0136711726	A2u I
22.1183439196	E2g R
35.3915249465	B2g
112.721031921	E2u
114.212804132	E1g R
166.789595244	B1u
170.535305026	A1g R
226.002625615	E1u I
226.037033636	E2g R
275.946925877	A2u I
279.963912554	B2g



Read WARNINGS!

DFT Phonon mode 1x1x1 cell (cm^{-1})	DFT 1x1x1 Representation	Experimental modes	Experimental Representation	DFT Phonon modes for 2x2x2 cell	DFT 2 Represe
-0.13	Bu I			-0.58	Bu
-0.06	Au I			-0.04	Bu
-0.04	Bu I			0.06	Au
7.36	Bu I			6.08	Bu
25.80	Au I			24.65	Au
31.04	Bu I			26.09	Bu
76.66	Ag R			74.09	Ag
84.86	Ag R	80.56	Ag R	81.54	Ag
88.03	Bg R			87.63	Bg
90.32	Bg R			89.60	Bg
103.28	Bg R	96.54	Bg R	102.36	Bg
104.17	Bg R	108.32	Bg R	102.95	Bg
107.55	Au I			106.61	Au
108.54	Ag R			107.12	Ag
109.91	Au I			108.66	Au
112.03	Ag R	112.8	Ag R	111.10	Ag
114.06	Bu I			115.46	Bu
122.27	Bu I			121.19	Bu
124.29	Ag R			121.90	Ag
126.27	Ag R	129.2	Ag R	123.58	Ag
129.64	Bu I			126.25	Bu
134.19	Bu I			130.53	Bu
151.35	Ag R			150.19	Ag
156.27	Ag R	163.32	Ag R	153.05	Ag
175.28	Au I			176.42	Au
175.94	Au I			176.93	Au
184.24	Bg R			181.76	Bg
186.30	Bg R	191.64	Bg R	185.04	Bg
190.81	Bu I			189.22	Bu
190.93	Bu I			189.61	Bu
236.52	Ag R			234.90	Ag
239.60	Ag R	248.45	Ag R	239.42	Ag
252.88	Ag R	258.61	Ag R	250.04	Ag
253.04	Ag R	263.34	Ag R	252.26	Ag
264.26	Bu I			264.26	Bu
265.13	Bu I			264.73	Bu

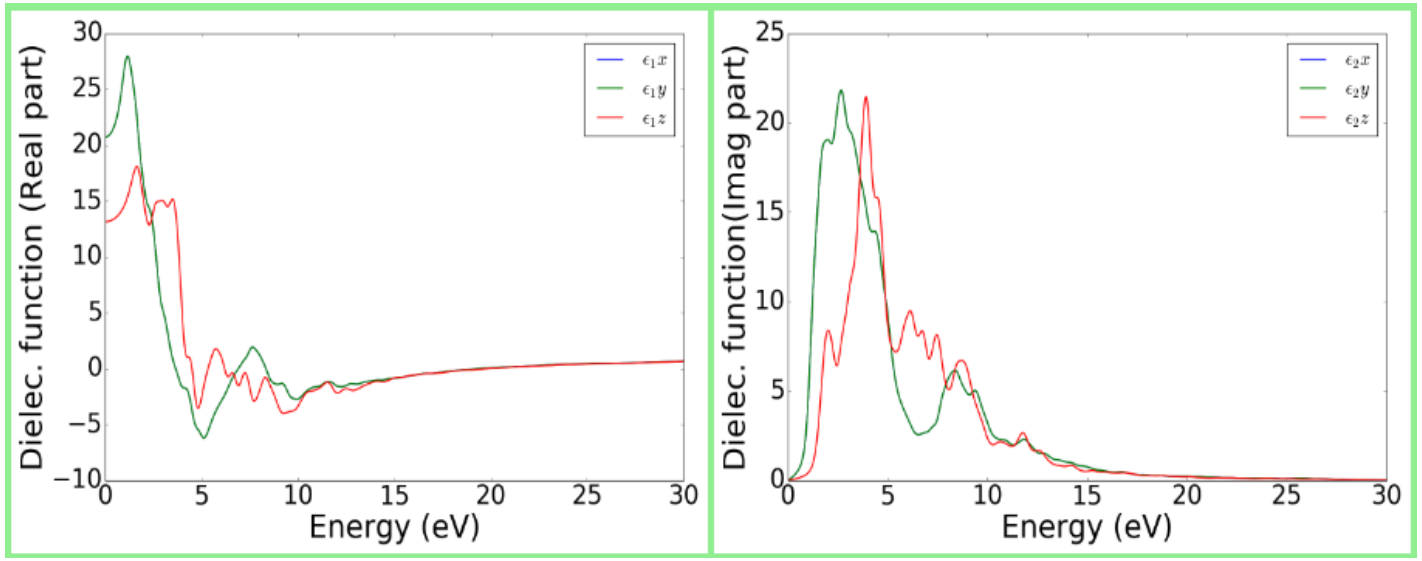
- Experimental data from Ryan Beams, NIST
- <9% error

Validation and applicability

- Optical properties

- Reasonably well for insulating and semiconducting systems
- No intraband contribution
- Absorption coefficient, refractive index, dielectric function, EELS, Optical conductivity

$$\varepsilon^{(2)}_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2w_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega) \times \langle u_{c\mathbf{k}+\mathbf{e}_\alpha q} | u_{v\mathbf{k}} \rangle \langle u_{c\mathbf{k}+\mathbf{e}_\beta q} | u_{v\mathbf{k}} \rangle^*,$$



Read WARNINGS!

Validation and Applicability

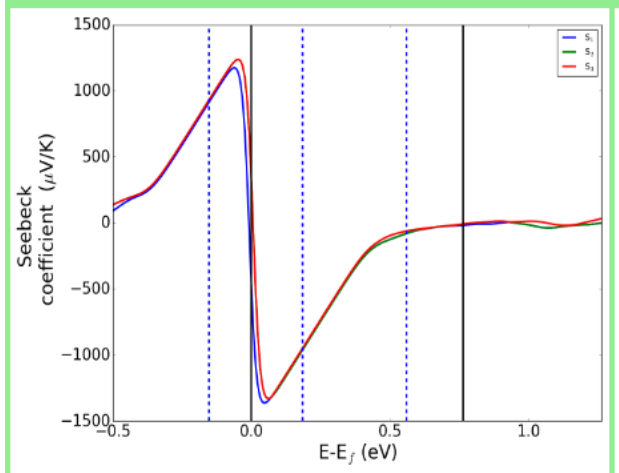
- Thermoelectric properties

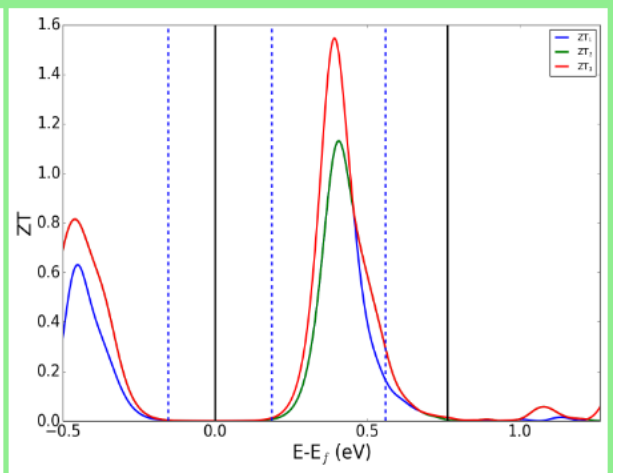
Electron mass tensor (m_e unit)

0.579472673637 -1.9247905275e-18 8.58074633074e-20
-1.9247905275e-18 0.579471339037 6.18803965953e-20
8.58074633074e-20 6.18803965953e-20 0.315280035074

Hole mass tensor (m_e unit)

1.18849079687 1.90402904433e-17 -6.32134631695e-19
1.90402904433e-17 1.18848809009 7.02149023383e-18
-6.32134631695e-19 7.02149023383e-18 1.90003598009





Temp-100 K | Temp-300 K | Temp-600 K

Read WARNINGS!

- BoltzTrap code in pymatgen
- Constant relaxation time approximation
- Only electronic contribution to thermal conductivity
- Perturbation in Fermi-distribution

$$f_0(\mathbf{r},\mathbf{k}) = \frac{1}{1+e^{\frac{E(\mathbf{k})-}{k_B T}}} \qquad f = f_0 + f_1.$$

For a stationary near-equilibrium distribution, the Boltzmann equation is

$$\frac{\mathrm{d}f}{\mathrm{d}t} = 0 = \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \frac{\partial \mathbf{r}}{\partial t} + \nabla_{\mathbf{k}} f \cdot \frac{\partial \mathbf{k}}{\partial t} + \left.\frac{\partial f}{\partial t}\right|_{scat.},$$

$$ZT = \frac{S^2\sigma}{\kappa} T, \quad \kappa = \kappa_e + \kappa_L$$

- Doping dependent properties for:
  Hall tensor, thermal conductivity,
  electronic conductivity tensor, Seebeck tensor

(UNDER CONSTRUCTION)

http://www.diss.fu-berlin.de/diss/servlets/MCRFileNodeServlet/FUDISS_derivate_000000017259/Lukas_Hammerschmidt.Thesis.pdf

Conclusions and Future work

- New publicly available database specially dedicated to 2D materials
- Simple criteria to identify 2D materials, Nanowires and Quantum dots?
- Bulk and layered materials
- Energy of exfoliation, bandgap, work-function, elastic constant values and other data
- Hyperlinked to Materials-Project and AFLOW databases to enable comparison of properties in different databases
- 2D-2L (Francesca),Defects, Machine-learning on data: JARVIS-ML, on the way…
- Baglunch talk on Feb 22

THANKS FOR YOUR ATTENTION !