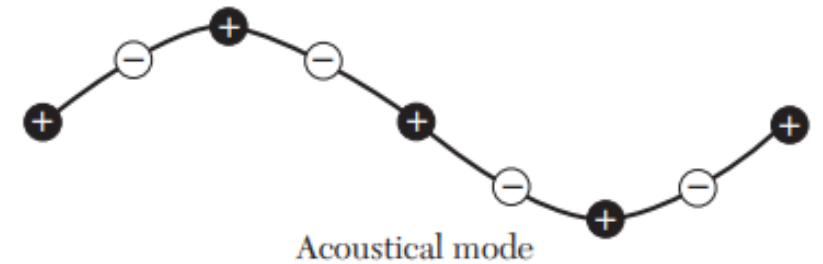# DATA-DRIVEN UNDERSTANDING OF INTERATOMIC INTERACTIONS IN SOLIDS

DYLAN SOH AND YI XIA, PHD.

https://news.mit.edu/2010/explained-phonons-0706

A BRIEF HISTORY OF PHONONS

- Phonons are quantized vibrations within a crystal.

- They correspond to the behavior of heat and sound in lattice systems.

C. Kittel, in Introduction to Solid State Physics, 8th ed.   https://www.sciencedirect.com/science/article/pii/S2666647221000142
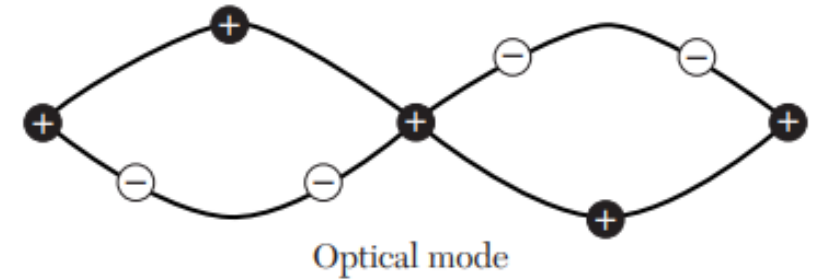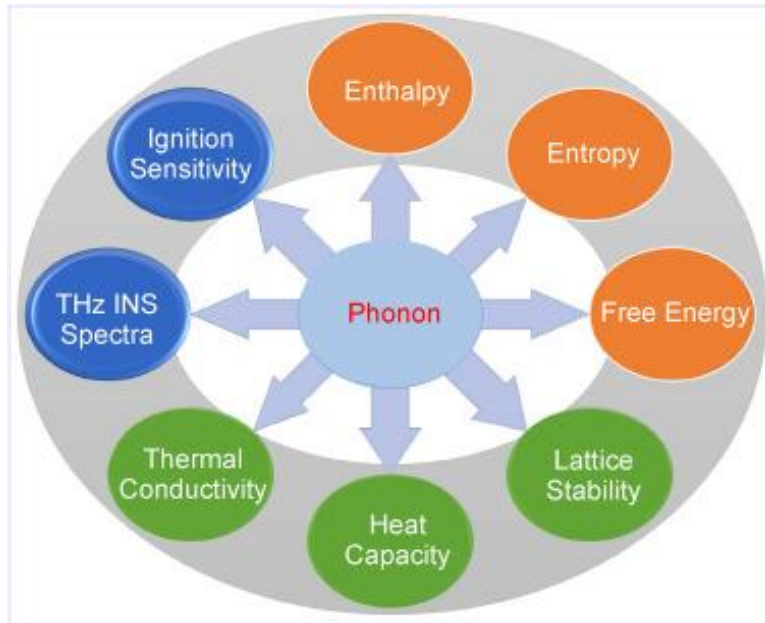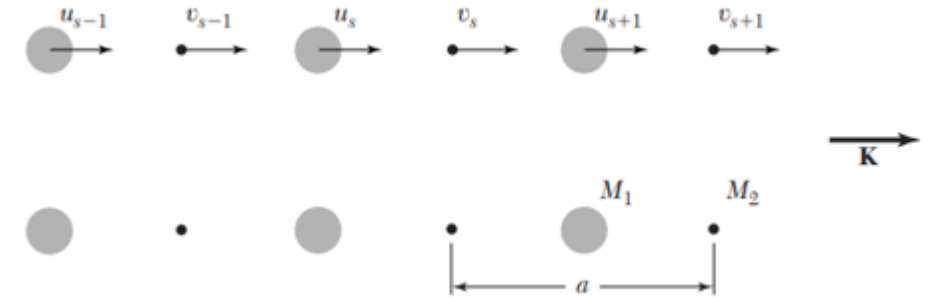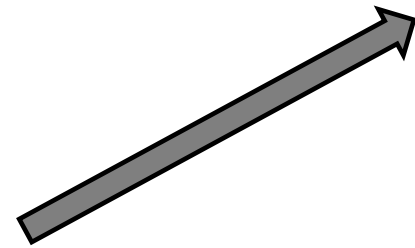
PHONONS TO BONDING STRENGTH

- Bonds between atoms act similar to simple harmonic oscillators:

    - Vibrations between these bonds represent phonons

    - Allows the calculation of force constants between atoms

- Through Hooke's law, force constants are synonymous with bonding strength.

- Although software calculation of force constants is commonplace given a lattice, there's little research on how these force constants depend on distances and elemental properties for many different lattices.
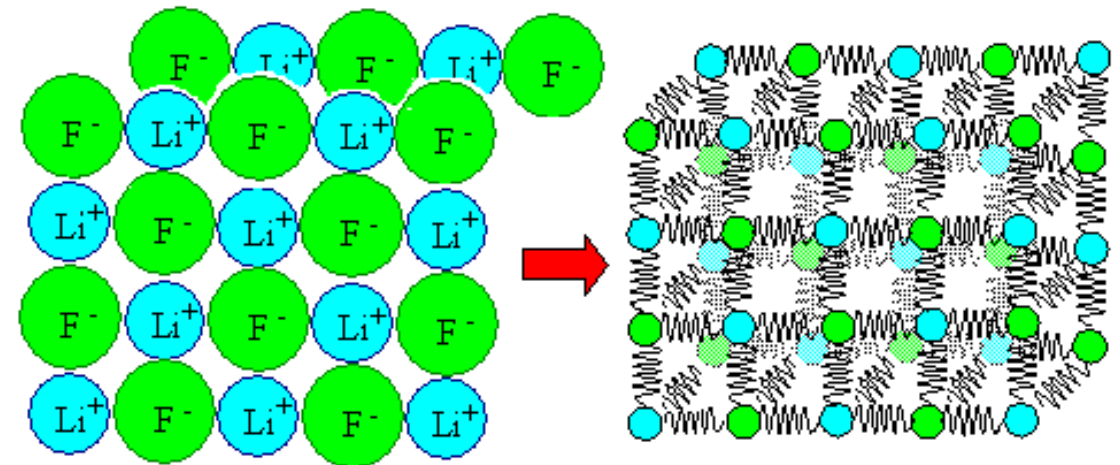
https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/s4_1_2.html

PHONON CALCULATIONS

u_{s-1} v_{s-1} u_s v_s u_{s+1} v_{s+1}

M_1 M_2

a

C. Kittel, in Introduction to Solid State Physics, 8th ed.

- Bonds between atoms in a crystal act and are modeled as simple harmonic oscillators (e.g. springs)

- The crystal's potential energy is expanded with respect to the atomic displacements.

- Using classical physics, phonons can be calculated by diagonalizing the harmonic Hamiltonian.

- Computation of all bonds in a lattice as harmonic oscillators are done through computation utilizing DFT and periodic boundary conditions.

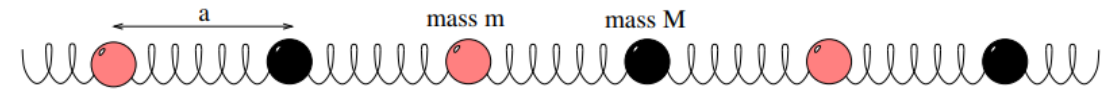$$-kx = m\frac{d^2x}{dt^2}$$

$$U = \frac{1}{2}kx^2$$

$$F(x) = -kx$$

a mass m   mass M

https://www.damtp.cam.ac.uk/user/tong/aqm/aqmfour.pdf

$$\omega = \sqrt{\frac{k}{m}}$$

A

B
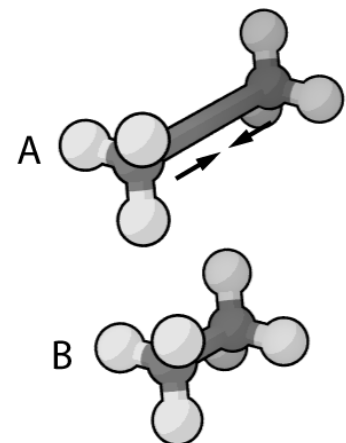
Rest of Images cited from Wikipedia

CALCULATE FORCE CONSTANTS FROM PHONOPY

$$\Phi_{ij}(M\mu, N\nu) \simeq -\frac{F_i[M\mu; \Delta r_j(N\nu)]}{\Delta r_j(N\nu)}$$
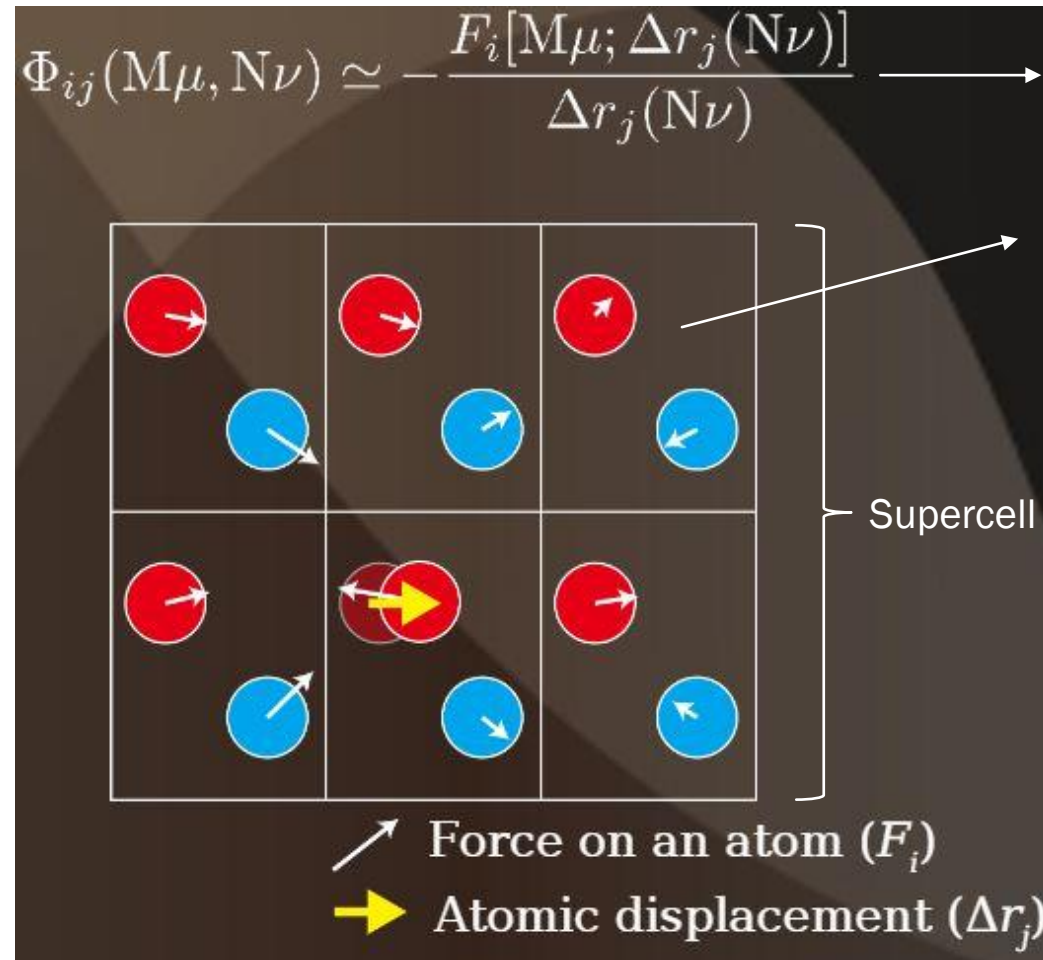
The Finite Difference Method

Primitive Cell

Supercell

Force on an atom (F_i)

Atomic displacement (Δr_j)

"Introduction to phonopy" Available: https://docplayer.net/174700706-Introduction-to-phonopy.html.

BRIEF INTRO TO THE PHONON DATABASE

- Each compound within the database gives a download link containing the compound's:
    - Unitcell (POSCAR)
    - k-point mesh (KPOINTS)
    - Pseudopotentials & Exchange functionals (POTCAR)
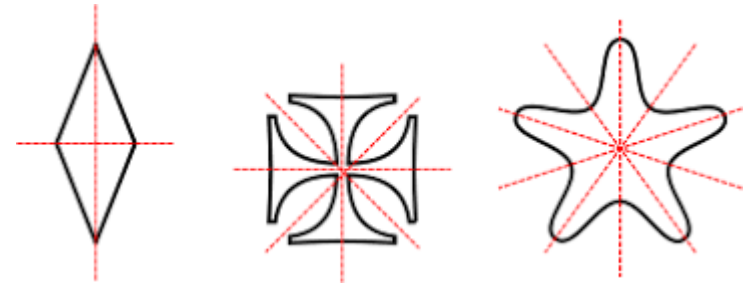   - Control parameters for Phonopy or VASP (INCAR)

○ Materials id 25 / N2 / Pa-3 (205)

○ Materials id 39 / Tl / Im-3m (229)

○ Materials id 111 / Ne / Fm-3m (225)

○ Materials id 147 / Se / R-3 (148)

○ Materials id 149 / Si / Fd-3m (227)

○ Materials id 154 / N2 / P2_13 (198)

○ Materials id 160 / B / R-3m (166)

Material ID Number

Symmetry Number

SPACE GROUPS

https://mathstat.slu.edu/escher/index.php/Introduction_to_Symmetry

- The symmetry number for each compound details the respective numerical index of the corresponding space group that the material is classified in.

- Each numerical index details the usage of different rotational and translational matrices and vectors to create the given lattice defined.

- The space groups can be further divided into sub-groups that determine the type of lattice symmetry (Triclinic, trigonal, orthorhombic, cubic, etc...)

Frequency in Symmetry Groups in the Database
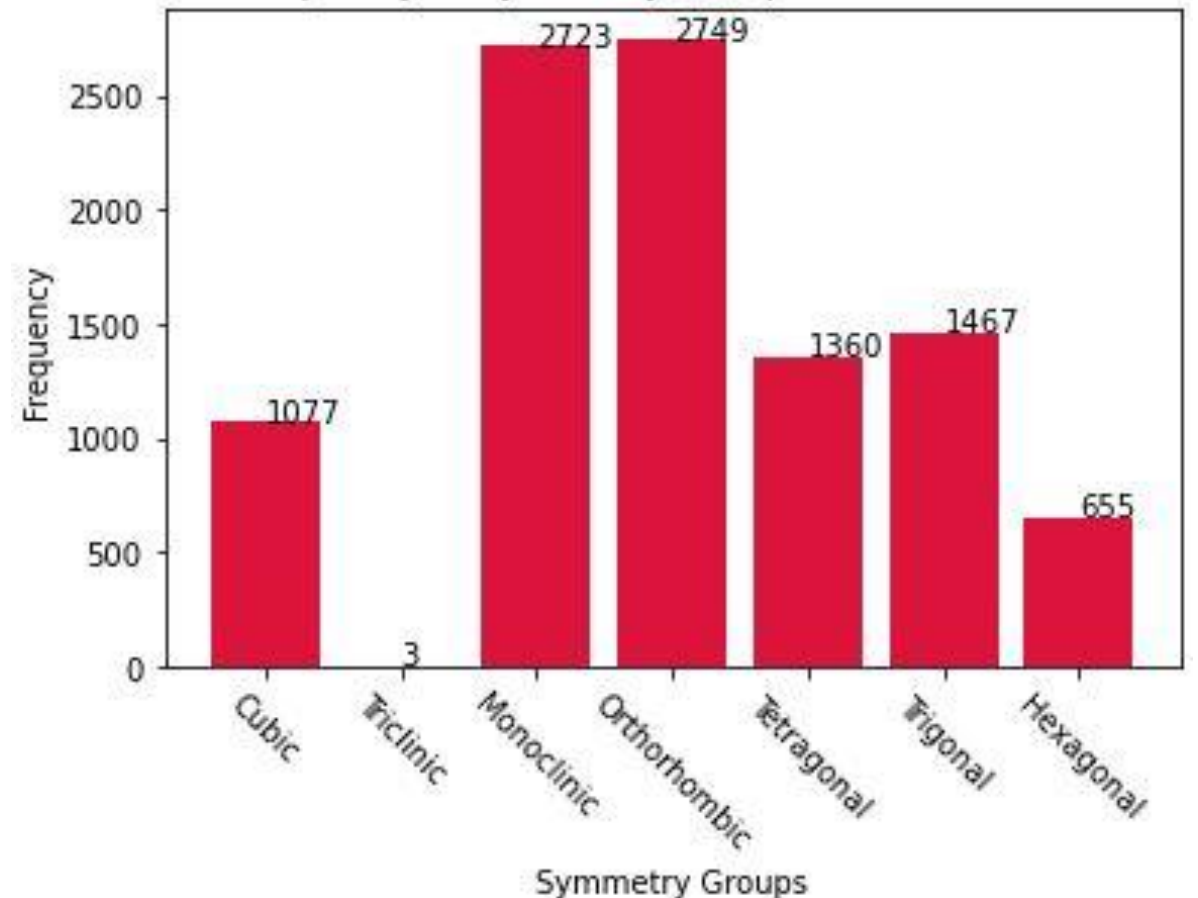
FORCE CONSTANTS IN THE FORM OF TRACES

- One major flaw: Multiple rotational-symmetry transformations for each atomic pair impact the atoms' displacement.

- Foreman-Lomer Theorem resolves this by stating that traces of the force constant matrices remain unchanged since the phonon values uniquely determine them.

- These traces represent bond strengths!

$$tr\left(\begin{bmatrix} 5 & 3 & 5 \\ 4 & -1 & 2 \\ -3 & 8 & 7 \end{bmatrix}\right) = 5 - 1 + 7 = 11.$$

TRACE VS. DISTANCE CALCULATIONS OF A SINGLE COMPOUND:

The coordinates detailing each atom's position in the supercell are given in SPOSCAR (one of the outputs of Phonopy).

SPOSCAR (Supercell):

```
1 generated by phonopy
2     1.0
3       12.0841852099999993      -0.0000008800000000       0.0000000000000000
4       -6.0420918300000004      10.4652118099999996       0.0000000000000000
5        0.0000000000000000       0.0000000000000000      17.6977176199999988
6 S Tl
7    27    54
8 Direct
9     0.3427570600000000   0.0096004200000000   0.3132409100000000  ──→ Atom 1 Position
10    0.6668433600000000   0.6572429399999999   0.3132409100000000  ──→ Atom 2 Position
11    0.9903995799999999   0.3331566400000000   0.3132409100000000  ──→ Atom 3 Position
12    0.3420215500000000   0.3432314300000000   0.0274373900000000
```

The force constants on the supercell are given in the matrix notation of each atom pair.

FORCE_CONSTANTS:

```
1   81    81
2 1 1
3        3.338608993564256      -0.088317732719219      -0.16976300772684
4       -0.088375828417551       3.670307464981150      -0.106096182347630  ──→ Matrix
5       -0.169546500000000      -0.105701500000000       3.039746500000001
6 1 2
7       -0.036068500433537       0.012552496817580      -0.023802499901175
8       -0.005953344647274      -0.043701086156114       0.001357063556748
9        0.009184500000000      -0.009109500000000       0.092346500000000
10 1 3
11      -0.038941999686435      -0.014201502973125       0.003277000910548
12       0.004305881168271      -0.040827034550722       0.012503674534059
13       0.010708500000000      -0.021294000000000       0.092347000000000
14 1 4
15      -0.023626496438090       0.057361001330862      -0.061611497344097
16       0.048912250497742       0.018275441197555       0.036470932343866
17      -0.059592500000000       0.066981500000000      -0.116296500000000
```
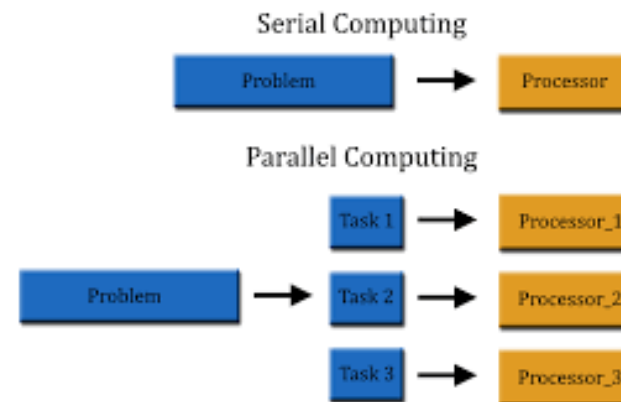
Atom 1 & Atom 2 Pair

Atom 1 & Atom 3 Pair

BRIDGES-2 SUPERCOMPUTER

- Used supercomputer for data analysis calculations

- Simply create a bash script and paste in code and parameters to use the supercomputer.

- Utilize parallel computing for faster computation times throughout.

- Out of over 10034 compounds from the database, over 1077 cubic compounds extracted and 2774451 bonds analyzed.

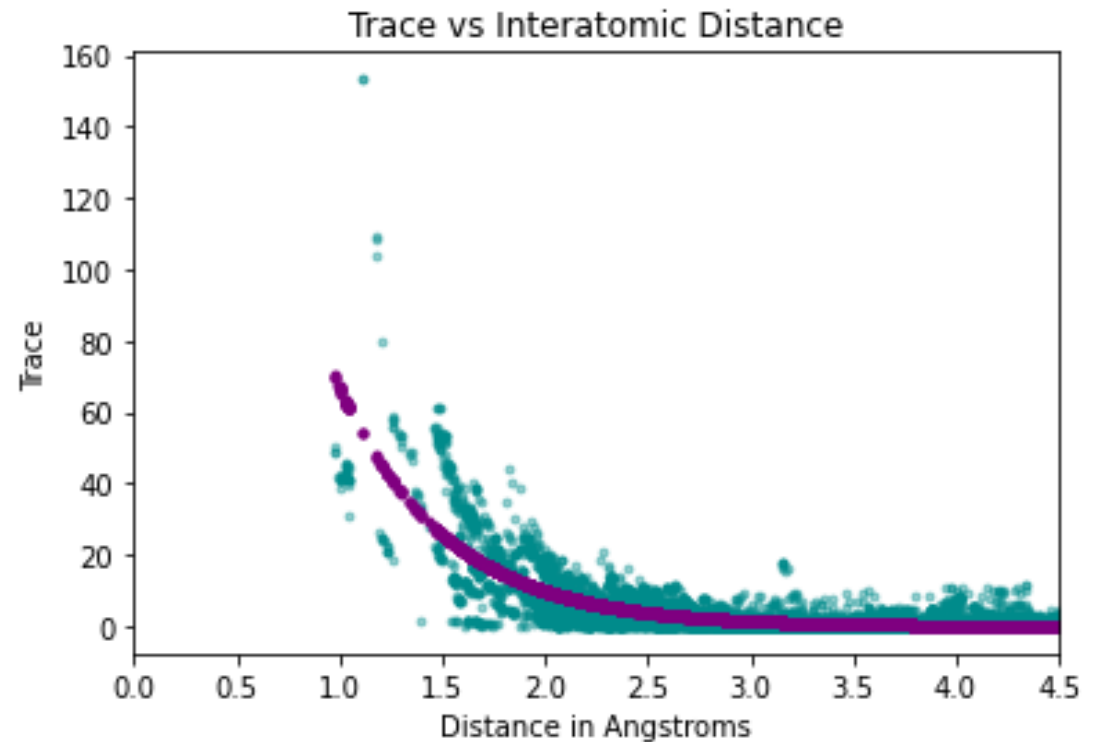- Through symmetry analysis using the supercomputer, 103181 bonds were used for results.

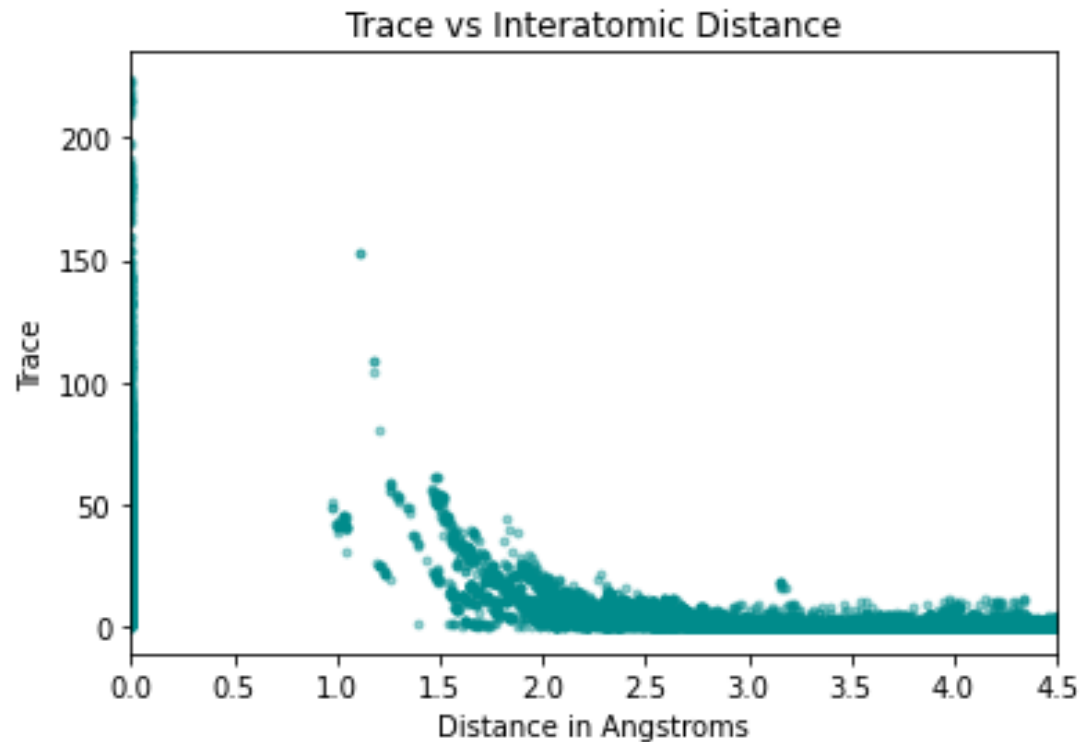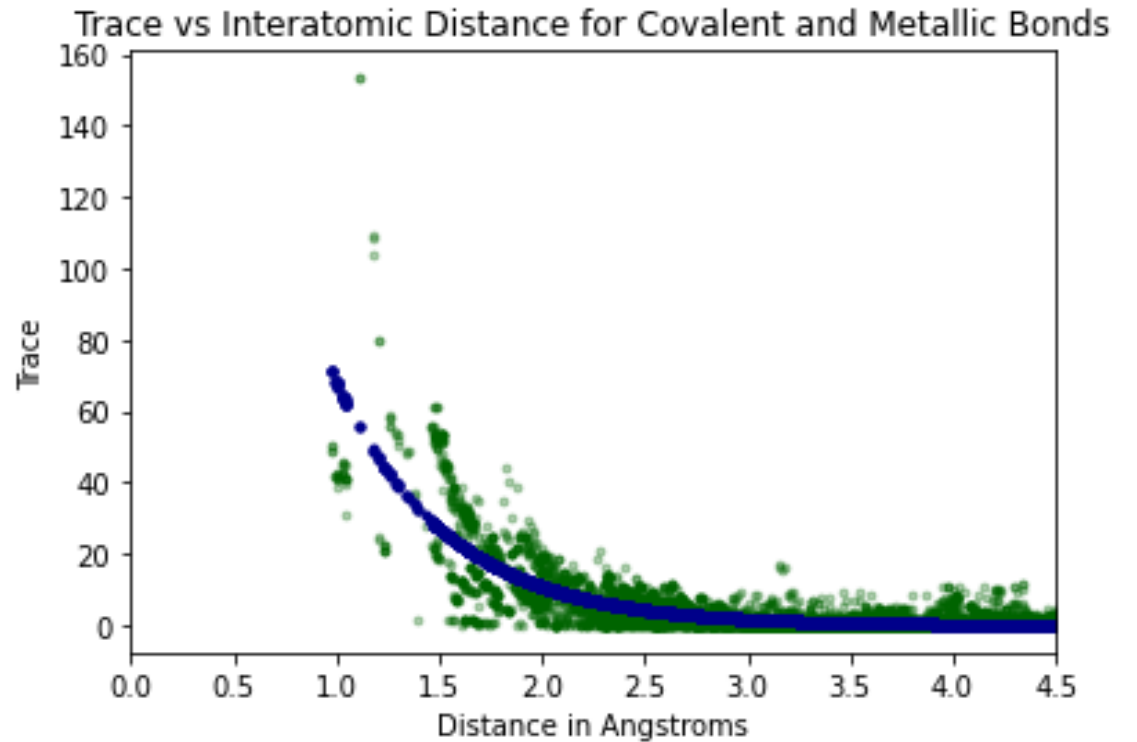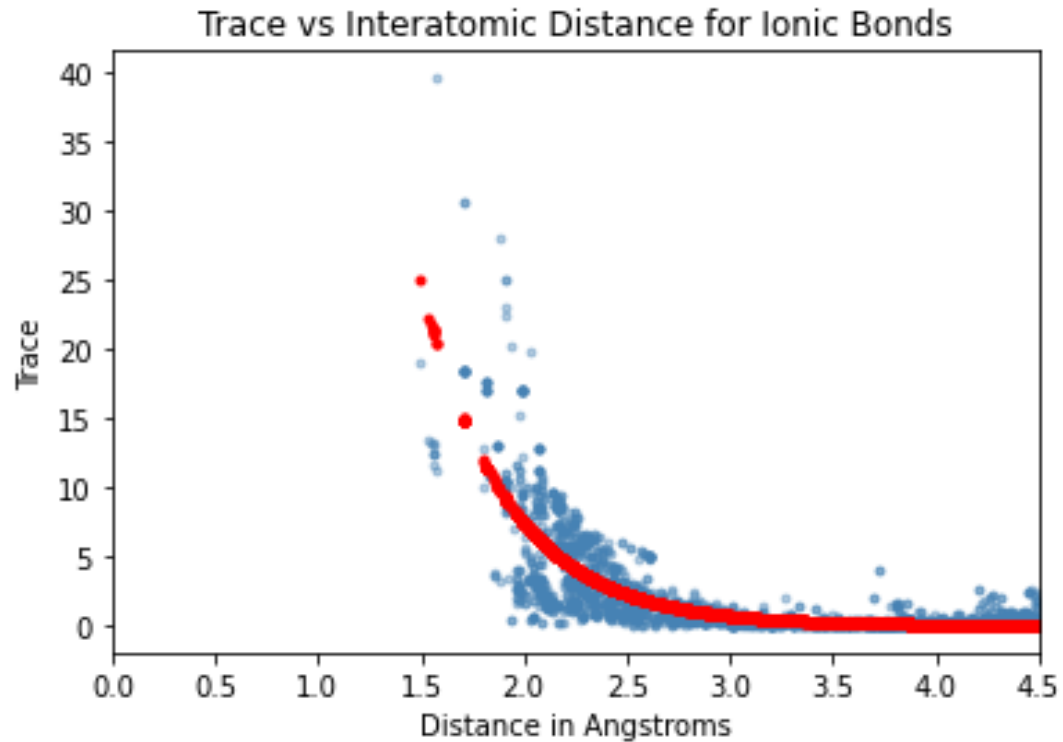https://www.hpcwire.com/off-the-wire/bridges-2-begins-production-operations/

https://www.teldat.com/blog/parallel-computing-bit-instruction-task-level-parallelism-multicore-computers/
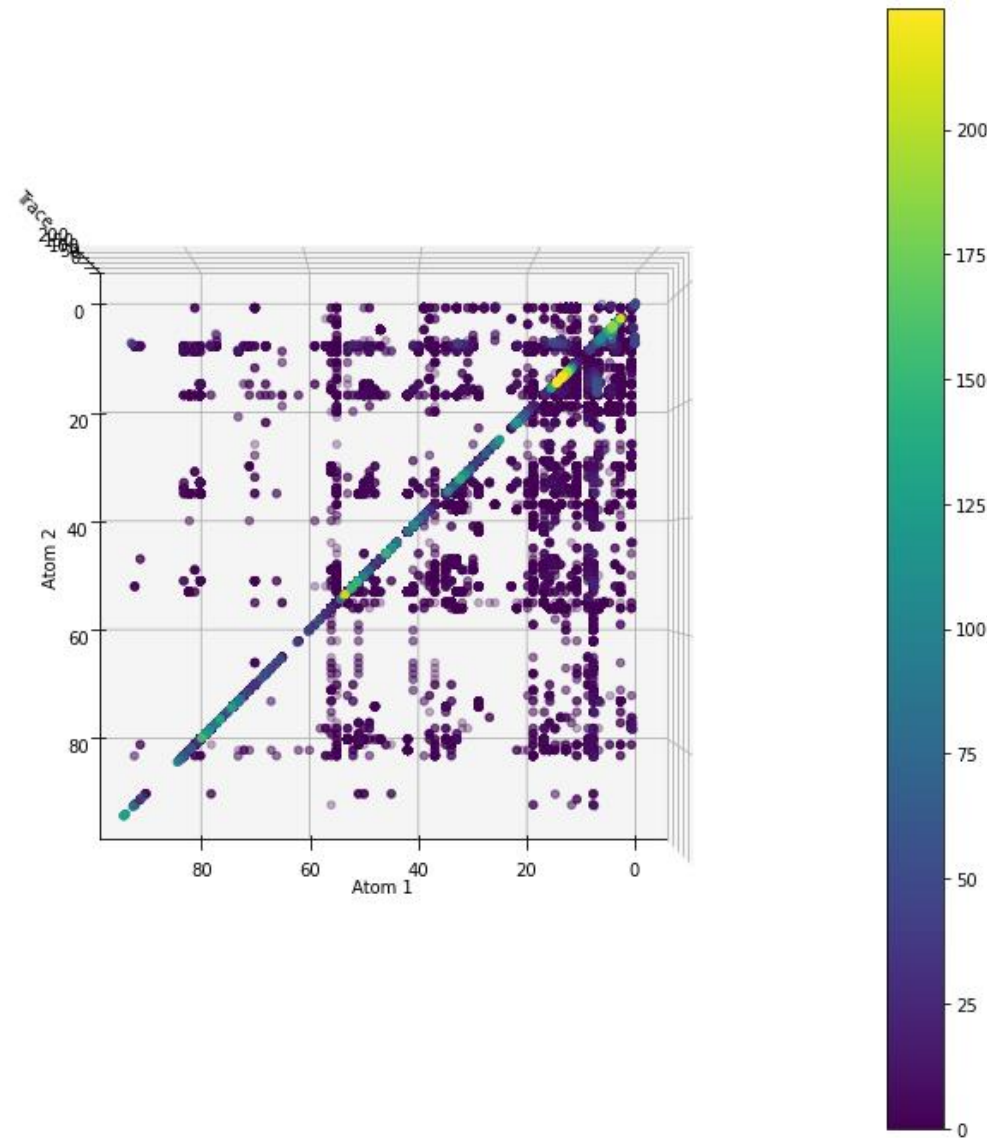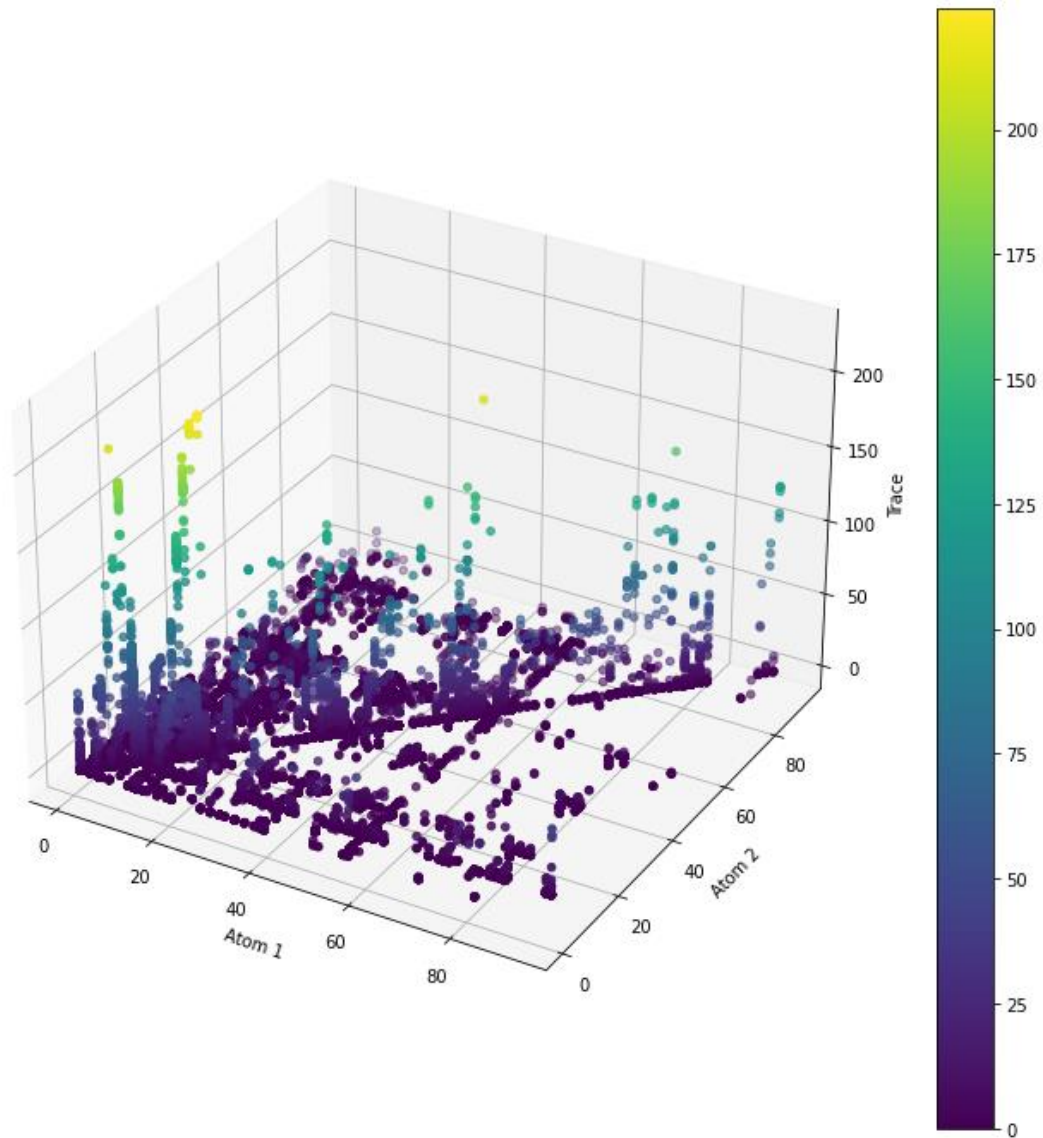
BOND DISTANCE VS. BOND STRENGTH FOR ALL CUBIC COMPOUNDS

IONIC AND COVALENT-METALLIC BONDS
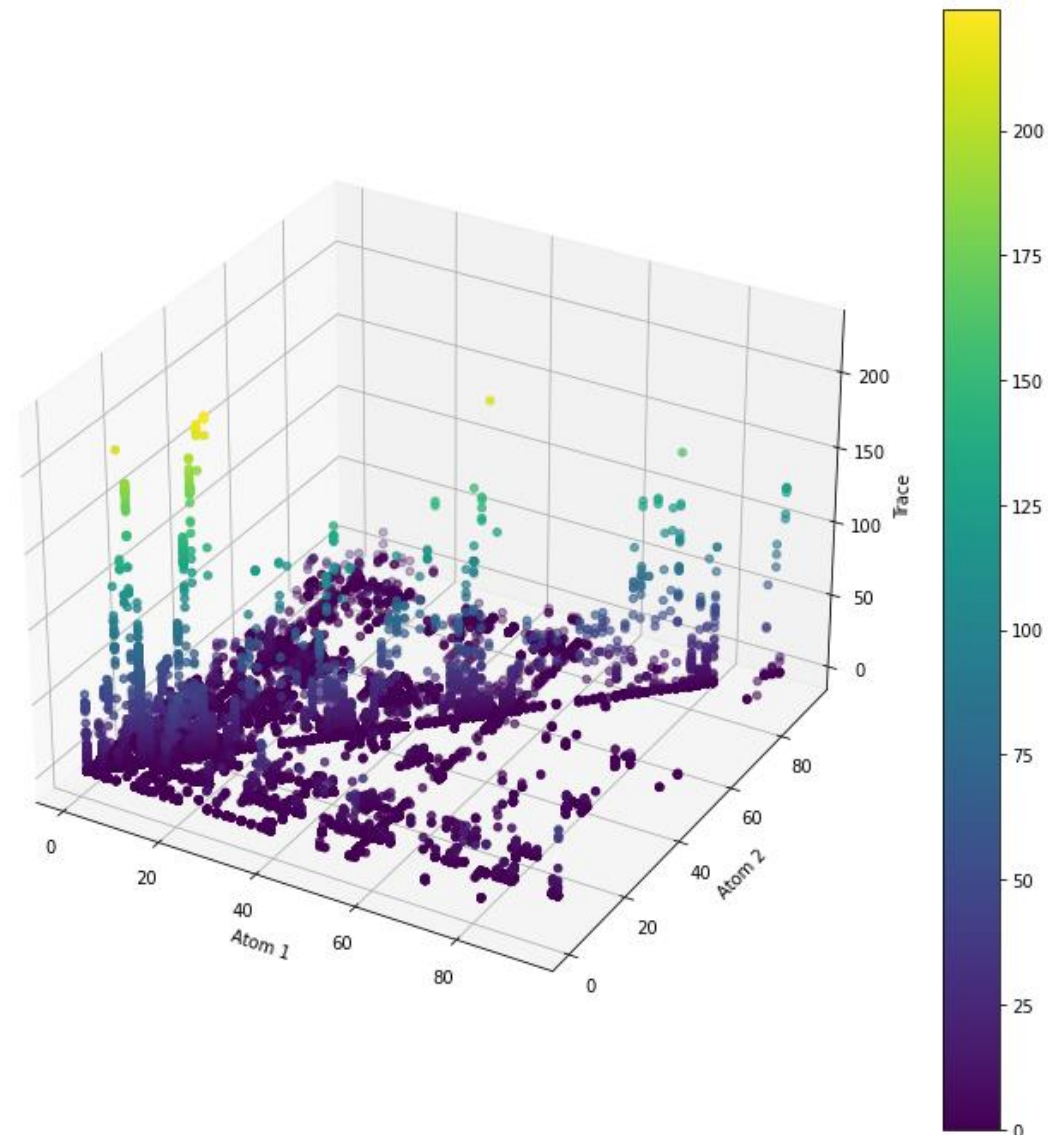
BOND STRENGTH VS. ATOMIC NUMBERS
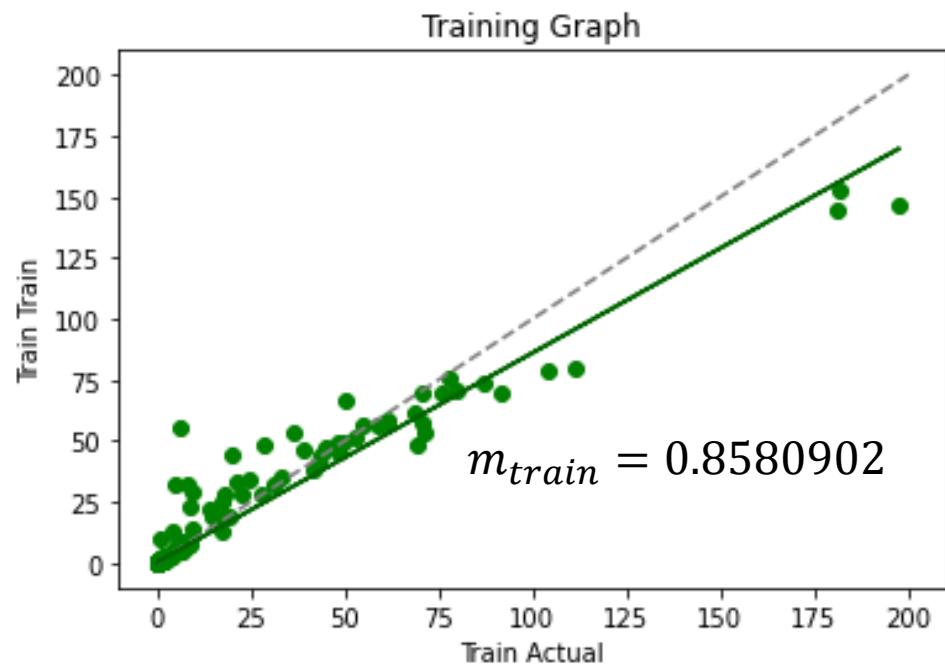
COMPARISON OF PREVIOUS FORCE CONSTANTS RESEARCH

TABLE XIV. Force constants of covalent bonds.[a]

	LiLi	BB	CC	NN	OO	HH 5.76 FF
Single bond:	0.147; 0.255	1.835; 2.65	3.4; 4.5; 4.9; 6.6	4.73	5.84	4.453; 7.145
Double bond:			9.6	9.46	11.765	
Triple bond:			15.8	14.19 (22.962)	17.90	

	NaNa	AlAl	SiSi	PP	SS	ClCl
Single bond:	0.106; 0.172	0.27	1.0; 1.42	1.852	2.69	3.286
Double bond:				3.704	4.96	
Triple bond:				5.556	7.23	

	KK	GaGa	GeGe	AsAs	SeSe	BrBr
Single bond:	0.054; 0.099	0.24	0.80; 1.29	1.356	1.91	2.458
Double bond:				2.712	3.61	
Triple bond:				4.068	5.31	

	RbRb	InIn	SnSn	SbSb	TeTe	II
Single bond:	0.046; 0.082	0.15	0.33; 0.57	0.87	1.25	1.72
Double bond:				1.74	2.368	
Triple bond:				2.61	3.49	

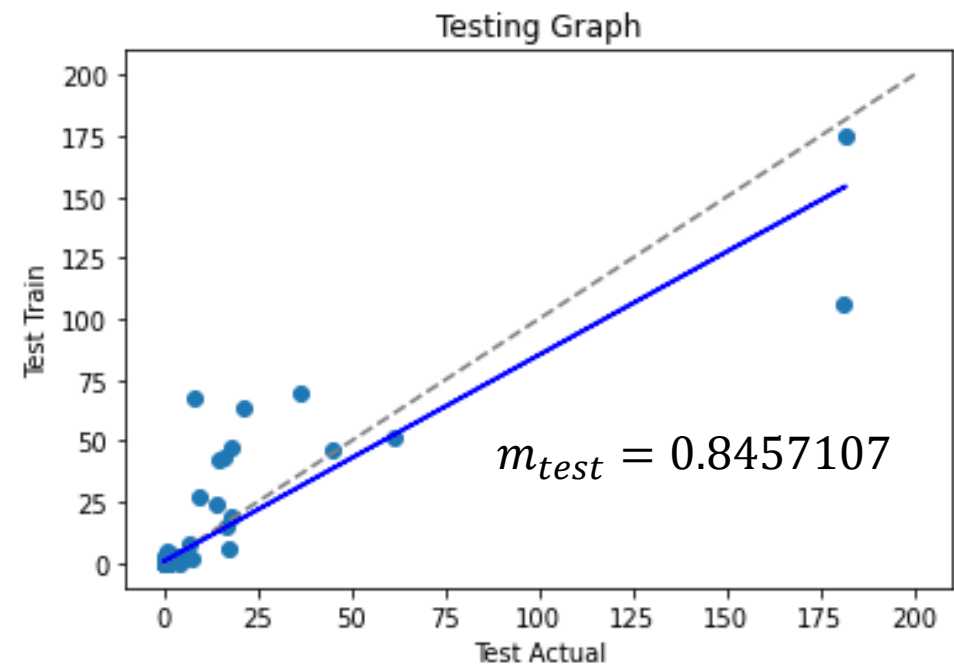|	CsCs	TlTl	PbPb	BiBi		
Single bond:	0.038; 0.069	0.10	0.31	0.44		
Double bond:				...		
Triple bond:				1.836		

[a] About force constants for the single bonds:
For alkali metals two values have been recorded for the single bonds; the lower value corresponding to $s-s$ bond and the higher value to $s-p$ bond.
The lower value for BB corresponds to $p-p$ bond while the higher value corresponds to sp^2-sp^2 bond. The single bond force constants of AlAl, GaGa, InIn, and TlTl correspond to $p-p$ bonds.
Under CC four values have been recorded for the single bonds. They correspond in order of magnitude to $p-p$, tetrahedral, trigonal, and digonal bonds. For SiSi, GeGe, and SnSn the lower value corresponds to $p-p$ bond while the higher value corresponds to tetrahedral bond.
The single bond force constants of NN, PP, AsAs, SbSb, BiBi, OO, SS, SeSe, TeTe, ClCl, BrBr, II correspond to $p-p$ bonds. The $p-p$ bond force constant of FF has not been ascertained.

G. R. Somayajulu , "Dependence of Force Constant on Electronegativity, Bond Strength, and Bond Order. VII", J. Chem. Phys. 28, 814-821 (1958).

MACHINE-LEARNING MODEL

Training Graph

$m_{train} = 0.8580902$

$R^2 = 0.934088$

Testing Graph

$m_{test} = 0.8457107$

$MSE = 38.014786$

SUMMARY

- Calculating phonon frequencies in many cubic compounds enables one to understand bond strengths, representing traces of the force constant matrices within solids.

- Data optimization shows the simple physics that relates distance to bond strength.

- Analysis of elemental properties lines up with previous research on the force constants on bonds with the same element.

- As with machine learning, the model can fit and potentially predict bond strengths.

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/backbone/r4_1_3.html
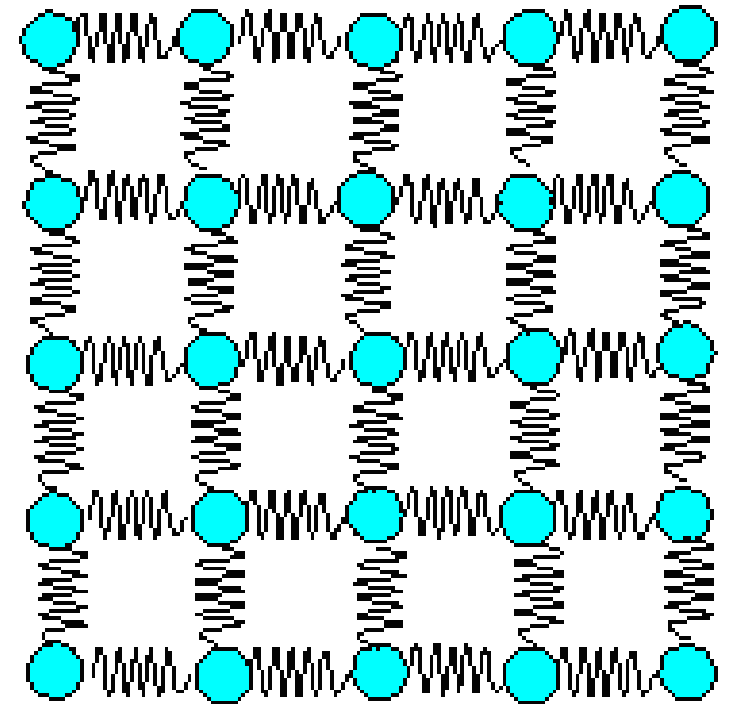
TAKEAWAYS AND FUTURE EFFORTS

- One should add new information to or clean the dataset to improve model efficiency

- Expand to other space groups for more data and check to see if the model can predict the traces from these groups.

- For the three-dimensional plots, ignore traces with zero distance.

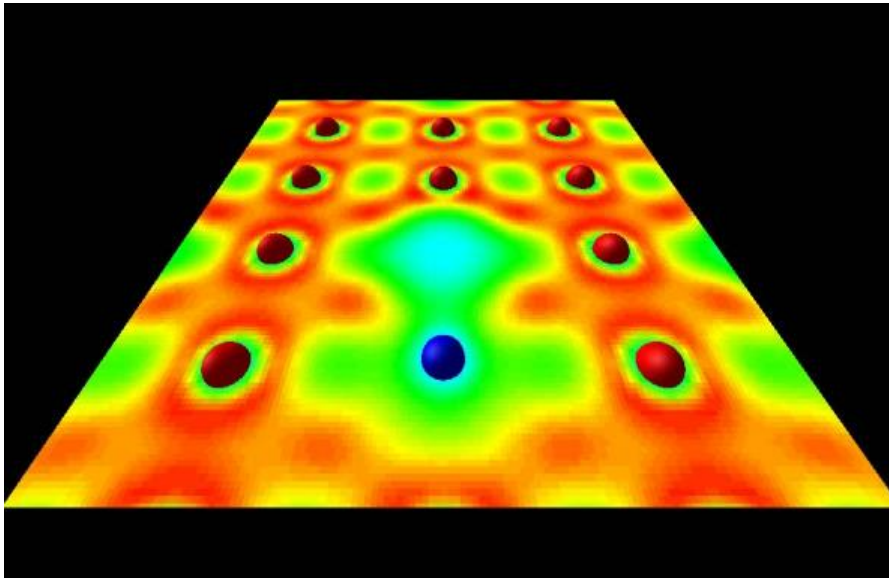- Revise all code for unforeseeable errors.

ACKNOWLEDGEMENTS

DENSITY-FUNCTIONAL THEORY (HOHENBERG-KOHN)
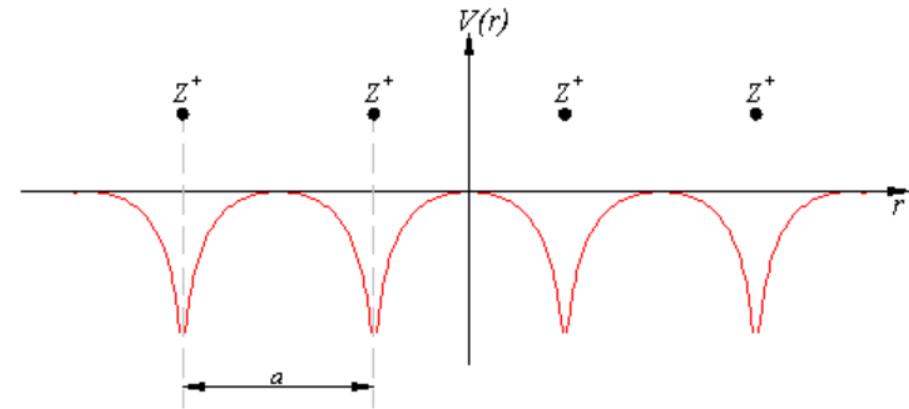
Schrödinger equation:

$$\hat{H}\Psi\left(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M\right) = E\Psi$$

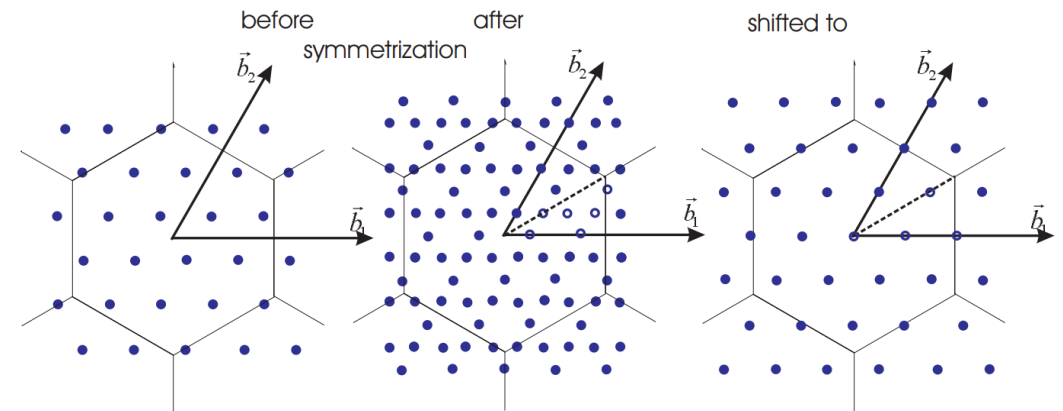DFT allows the ground-state energy E from the Schrödinger equation to be a functional of the electron density:

$$\rho(\boldsymbol{r}) = \sum_i^N |\psi_i(\boldsymbol{r})|^2 \rightarrow E = E[\rho(\boldsymbol{r})]$$

Bloch's Theorem in Solids (Periodic Cells):

$$\psi(x + a) = e^{i(\vec{k} \cdot a)} \psi(x)$$

before symmetrization   after   shifted to

Result: one can create an equally-spaced "mesh," which allows one to calculate $\rho(\boldsymbol{r})$

Wolverton, C., "MSE 458 Atomic-Scale Computational Materials Science." Northwestern University.

Oses, C., "Introduction to DFT: VASP." Duke University