EST: Project 1

Exam No; B139340

August 21, 2025

1 Introduction

Hydrogen sulfide (H_2S) decomposes under pressure into H_3S and pure sulphur. This exercise utilizes the Quantum Espresso density functional theory package (DFTP) to investigate the high critical temperature (Tc) superconductivity (if existent) from the specific 3D, highly symmetric, high pressure phase of H_3S .

A basic calculation involves the creation of a Slurm job, written in Bash, which links with the Quantum Espresso input file and outputs a file based on the inputs specifications, e.g. cell parameters, atomic positions and size of atoms and k grid magnitude. The Slurm jobs can also be modified using a sed to loop over the input files to replace a desired parameter and iterate over how many parameters required instead of running each job for one different parameter. Output files produce valuable data such as the total energy of the unit cell, Fermi energies and stress tensor component values.

Quantum Espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials. This project used QE k-point grids. In computational material area, various properties of materials are determined by integrals over the Brillouin zone in reciprocal space. K-points are a set of discrete points to approximate these integrals, the k-grids effectiveness tested using DFT (Density Functional Theory)[1]. Also used were QE q-points, which specifies the q points used to sample the Brillouin zone. This file is used in the context of phonon dispersion calculations. The format is the same as the KPOINTS file.

For the density of states (DOS), first to define the number of electronic states as $\rho(E)dE$ within energy intervals of $E, E + dE$. The DOS requires the performance of a fixed-ion SCF calculation. In DFT plane wave calculations, the energy is $E = \frac{\hbar^2 * k^2}{2m}$. The DOS also depends on creating a non-self consistent field calculation (nscf) where in general one should find a large number of k points to achieve convergence as the DOS depends on the integration of k space. Dense k points are also necessary to remove numerical noise and minimise total run time.

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Attributed to *F. Marsiglio*[2], Eliashberg theory is a theory of superconductivity that describes the role of phonons in providing the attractive interaction between two electrons. When phonon dynamics are considered, retardation effects that impact the electrons occur in the form of a frequency-dependent electron self-energy. In the superconducting state, this means that the order parameter, generally considered to be a static quantity in the Bardeen-Cooper-Schrieffer (BCS) theory becomes frequency-dependent [2]. A major part of Eliashberg theory (as opposed to BCS theory) is the presence of the electron-phonon propagator...

$$\lambda_{\mathbf{k}\mathbf{k}'}(z) \equiv \int_0^\infty \frac{2\nu\alpha^2_{\mathbf{k}\mathbf{k}'}F(\nu)}{\nu^2 - z^2} d\nu$$

with $\alpha^2_{kk'}F(v)$ the spectral function of the phonon Green function. This function can be written as $\alpha^2F(\omega)$ to emphasize that the coupling part α^2 can have significant frequency dependence. This spectral function is often called the Eliashberg function [2].

Superconductivity gives way to conduction with no loss in energy, however if a current is added to such a device a lot of energy is used to allow it to cool. A device which worked without cooling would be significant in its development. To create Cooper pairs from phonons and electrons, superconductivity requires a strong coupling. This coupling breaks at high temperatures, at these temperatures and at high frequencies - phonons are predicted to couple. From this dense atomic hydrogen would be expected to be a room temperature superconductor, however the challenge exists where pure atomic hydrogen forms at very high pressures.

H_2s when decomposed into H_3S and sulphur a high pressure phase is expected to produce high superconductivity at high Tc [3]. In an experiment published in 2015, a group of researchers from Germany showed that compressed hydrogen disulfide, H_2S, is a superconductor up to $Tc = 203K$ – but at a pressure of around 150 GPa or 1.5 Mbar [4].

To conclude this project aims to investigate the transition temperature (Tc) of H_3S via DFPT phonon calculations, the real force space constants, the Eliashberg function, the mode-averaged electron-phonon coupling parameter and with the use of the McMillan-Allen-Dynes equation's screened Coulomb interaction $\mu*$ where Tc depends significantly on, to further explore through different values of $\mu*$ with different q point grids to determine this dependence for H_3S and to finally conclude a description of Tc for the Im3m phase of H_3S.

2 Method

For the &system settings from [5], the experimental lattice constant was found to be 2.98 Ang and converted to bohr, 5.63 b. a.u, set as 'celldm(1) in the QE scf dos input file. For H_3S the number of the type of atoms was set to 2 as defined in ntyp and ibrav - the bravais lattice index, set to 3 in QE for Im-3m [6]. The occupations was set to smearing which represents gaussian smearing for metals. The option > la2f was set to .true. for the eigenvalues on the dense > k-point grid. The space group (denoted space_group) was set to 229 for the $Im\bar{3}m$.

For the &electrons settings, the conversion threshold , 'conv_thr', is used to set the default value of the threshold (ethr) for iterative diagonalization, for this purpose it was set to $1.0d-8$. The mixing factor for self-consistency, $mixing\_beta$, was set to 0.7.

ATOMIC SPECIES:

H 1.008 H.pbe-van_bm.UPF

S 32.06 S.pbe-van_bm.UPF

ATOMIC POSITIONS: The atomic positions of H and S atoms are in Cartesian coordinates, in units of the lattice parameter.

ATOMIC_POSITIONS crystal_sg

H 0.00 0.50 0.50

S 0.50 0.50 0.50

The K grid sizes specified by (K_POINTS) which are special k-points in the irreducible Brillouin Zone were increased 2 2 2 for each of the cut-off energies.

2.1 SCF Calculation

To determine a cut off energy where total energy converges at 10meV/atom, the QE SCF input file, 'ecutwfc', was changed to 25, 50, 75, 80, 95 and 100 Ry and ran via a sed loop written in the job script.

To investigate convergence, k grids were chosen; 6, 8, 10, 12, 24 and 36 (where these integers are identical to each of the three components, e.g. k point value 6 = 6 6 6 in QE input file). The output SCF files provided values for the total energy of the unit cells in Ry. They were divided by 4 (4 atoms in the H_3S [6]) to obtain energy per atom which was converted to eV. To define convergence, the data points were chosen with such k grid and a variety of cut off energies to find the difference between data points energy equal to or below 10 meV. This in similarity to the variance and standard deviation of each data set allows a closer look into the spread of energies. Each cut off energies data sets were plotted independently.

From post processing data, the resulting total energies per atom for each cut off energy were plotted together to determine point of convergence. This value subsequently used for DOS and further steps in the DFPT calculations.

2.2 Density of States (DOS)

SCF convergence tests were run on various k-point grid sizes (Nk, Nk, Nk) to obtain a well converged DOS. Post processing QE output files were sent via an scp command to a local computer and plotted through python. The cut off energy was 80 Ry and degauss set for Gaussian smearing set to 0.05.

```python
import matplotlib.pyplot as plt
from matplotlib import rcParamsDefault
import numpy as np

# load data
energy, dos, idos = np.loadtxt("dos8.dat", unpack=True)

# make plot
plt.figure(figsize = (12, 6))
plt.plot(energy, dos, linewidth=0.75, color='red')
plt.yticks([])
plt.xlabel('Energy (Ry)')
plt.ylabel('DOS')
plt.axvline(x=17.7611, linewidth=0.5, color='k', linestyle=(0, (8, 10)))
plt.xlim(-20, 100)
plt.ylim(0, )
plt.fill_between(energy, 0, dos, where=(energy < 17.7611), facecolor='red', alpha=0.25)
plt.text(17.6, 0.03, 'Fermi energy', rotation=0)

plt.show()
```

Figure 1: As an example DOS plot with python, in this case with k grid 8 8 8 at 80 Ry cut off energy

2.3 Stress Tensor

Stress is defined as force per unit area. If we take a cube of material and apply some pressure we can measure the stress on it in various directions. These measurements will form a second rank tensor; the stress tensor.

To calculate the stress tensor and forces, the QE SCF input files &control section was modified to include the lines;

tstress = .true.,

tprnfor = .true.

Post processing SCF output files give 3x3 arrays of the stress tensor components.

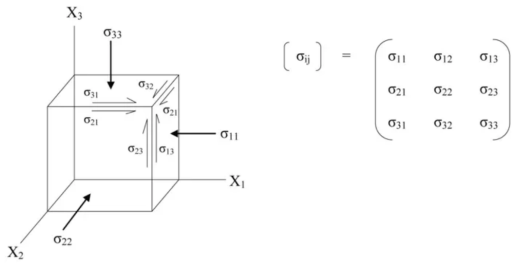

Figure 2: Right: stress tensor components

2.4 Postprocessing of the DFPT

2.4.1 Job Script

srun pw.x < h3s.scf-dos.in > h3s.scf-dos.out: Perform a DOS-quality SCF calculation to obtain all eigenvalues on dense k grid

srun dos.x < h3s.pp_dos.in > h3s.pp_dos.out: run postprocessing to extract eigenvalues and write DOS file

srun ph.x < h3s.elph.in > h3s.elph.out: Phonon calculation to calculate phonon frequencies, displacement patters, tensors and charges

srun q2r.x < h3s.q2r.in > h3s.q2r.out: calculates Interatomic Force Constants (IFC) in real space from dynamical matrices produced by ph.x on a regular q-grid

srun matdyn.x < h3s.matdyn.in > h3s.matdyn.out: Finds dynamical matrix on a denser q grid and calculates Eliashberg function

lambda.x: similar to matdyn.x with the exception it finds Tc for superconductivity using the McMillan formula

2.4.2 Determining Tc

The crystal structure were added to an input file along with the plane wave and k-grid parameters. An input file was prepared for the phonon calculation that used DFPT to determine the mode-dependent electron-phonon coupling parameters on a regular grid of q-points. Another input file containing the q-grid (q, q, q) of the DFPT phonon calculations was created. The real-space force constants were prepared in an input file and ran via q2r.x. The Eliashberg function $\alpha^2F(\omega)$ calculation input file was prepared and ran using matdyn.x. The mode-averaged electron-phonon coupling parameter λ calculation was prepared in an input file also containing settings for $\mu*$ and ran via lambda.x, its resulting output was a .dat file containing a series of Tc estimates that are obtained with different Gaussian broadening values for the electron-phonon coupling integration over the Brillouin zone. The input file for the DFPT q grids were modified increasing the q points and the process was repeated. The input file λ setting $\mu*$ was changed and the entire process repeated including changing the q point grids.

3 Results

3.1 SCF Convergence

Table below shows the k grids (Nk Nk Nk) represented by a single number which is equal to each Nk, total energy per atom in Ry and eV, the corresponding kinetic cut off energies and the standard deviation of each cut-off energy data set.

Table 1

K grid	Total Energy (Ry)	Cut off (Ry)	Total Energy/atom (eV)	Standard Deviation (meV)
6	-5.863653778	25	-79.77913752	0.786979444
8	-5.861140043	25	-79.74493638	
10	-5.86111038	25	-79.7445328	
12	-5.860986365	25	-79.74284549	
24	-5.861087603	25	-79.7442229	
36	-5.861087635	25	-79.74422334	
6	-5.864548838	50	-79.79131544	0.850016504
8	-5.86204995	50	-79.75731631	
10	-5.862000435	50	-79.75664263	
12	-5.861878508	50	-79.75498372	
24	-5.861982515	50	-79.75639881	
36	-5.861981933	50	-79.75639089	
6	-5.864824255	75	-79.79506269	0.795904744
8	-5.862310743	75	-79.76086458	
10	-5.862275445	75	-79.76038433	
12	-5.86215387	75	-79.75873022	
24	-5.862257905	75	-79.76014569	
36	-5.862257275	75	-79.76013712	
6	-	80	-	
8	-5.862278965	80	-79.76043222	0.000666626
10	-5.862297228	80	-79.7606807	
12	-5.862175535	80	-79.75902499	
24	-5.862279598	80	-79.76044083	
36	-5.862278965	80	-79.76043222	
6	-5.864854098	95	-79.79546871	0.85080704
8	-5.86235573	95	-79.76147667	
10	-5.86230575	95	-79.76079665	
12	-5.862184025	95	-79.7591405	
24	-5.862288083	95	-79.76055627	
36	-5.862287443	95	-79.76054757	
6	-5.864853653	100	-79.79546266	0.982038788
8	-5.862355283	100	-79.76147058	
10	-5.862305298	100	-79.7607905	
12	-5.862183573	100	-79.75913434	
24	-5.86228763	100	-79.76055012	

Each k grid was changed from 8 - 36 which provided total energies per atom. The plots below show each cut-off energy data set where the energies per atom were plotted against k grid.

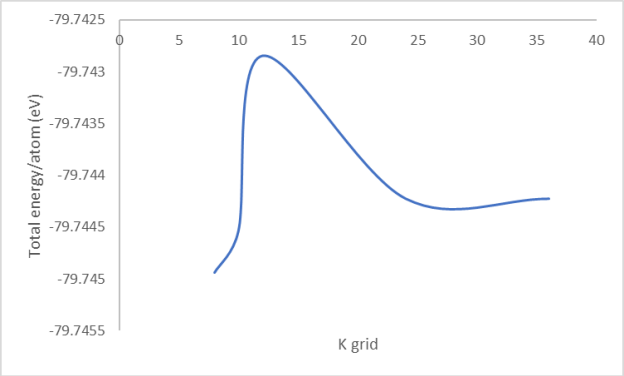

Figure 3: Total energy/atom vs k grid for 25 Ry kinetic cut off energy

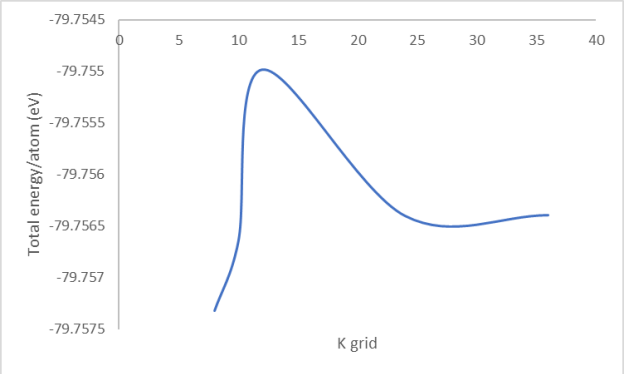

Figure 4: Total energy/atom vs k grid for 50 Ry kinetic cut off energy

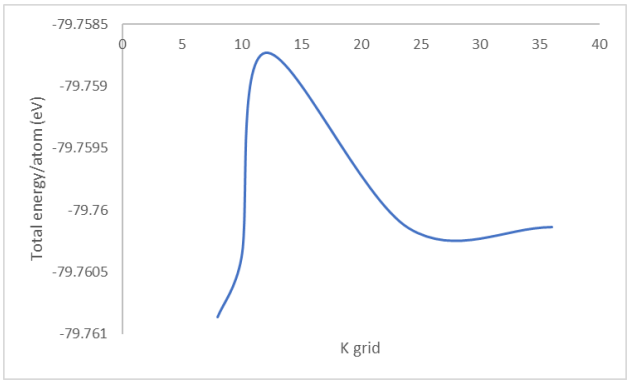

Figure 5: Total energy/atom vs k grid for 75 Ry kinetic cut off energy

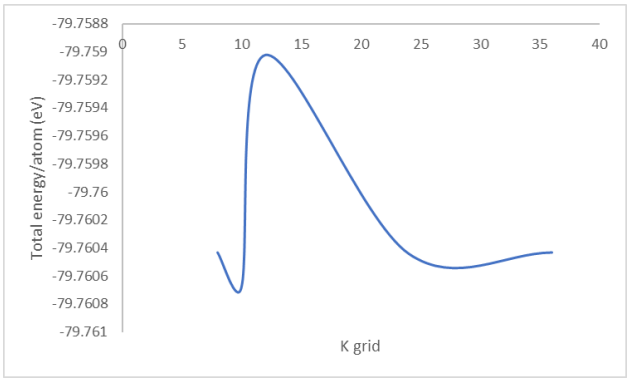

Figure 6: Total energy/atom vs k grid for 80 Ry kinetic cut off energy

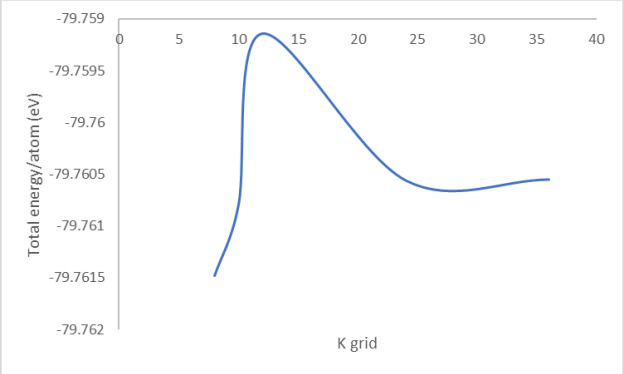

Figure 7: Total energy/atom vs k grid for 95 Ry kinetic cut off energy

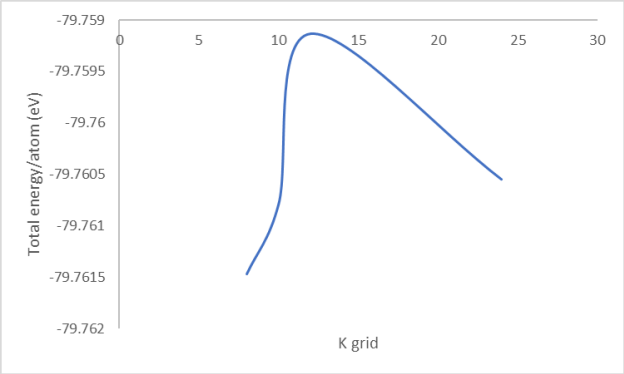

Figure 8: Total energy/atom vs k grid for 100 Ry kinetic cut off energy

Table shows total energy per atom with k grids at different cut off energies.

k grid	Cut off (Ry)	Total Energy/atom (Ry)
24	25	-5.861087603
24	50	-5.861982515
24	75	-5.862257905
24	80	-5.862279598
24	95	-5.862288083
24	100	-5.86228763

The plot below shows the energies per atom plotted against cut-off energy in Ry to investigate the optimum cut-off energy at k grid 24 24 24.

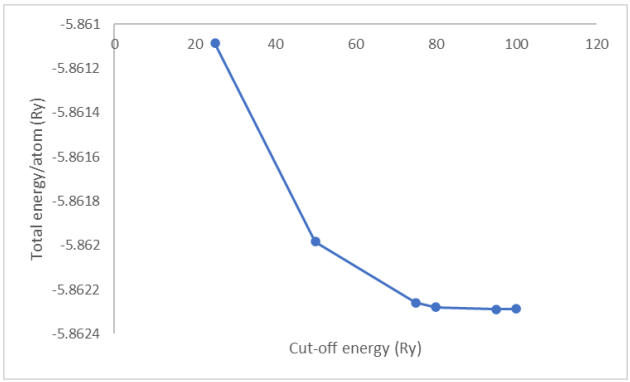

Figure 9: Total energy per atom vs cut off energy in Ry (ecutwfc in QE input setting)

From the previous figure, it can be seen that at around 80 Ry in cut-off energy, the total energy starts to converge (level out). Take the difference between the 95 Ry and 80 Ry data points for instance gives a value of 0.115 meV which indicates convergence happens before these points and less so before 75 Ry cut off energy.

3.2 DOS

From the QE output files the Fermi energies were recorded for each k grid at 80 Ry cut off energy

Fermi (Ry)	Fermi (eV)	K grid
17.7611	241.6523	8
17.8045	242.2428	10
17.7338	241.2808	12
17.761	241.6509	24
17.7611	241.6523	36

The plots below show the different DOS at a chosen optimal cut-off energy of 80 Ry with different k point grids; (8 8 8) (24 24 24) and (36 36 36) with occupied bands filled indicated by red filling.

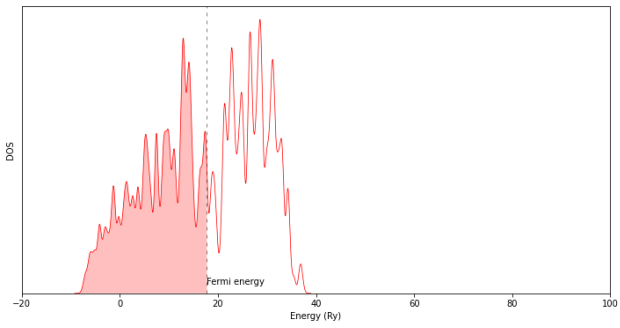

Figure 10: Density of states (DOS) at 8 8 8 k grid showing Fermi energy at 17.7611 Ry

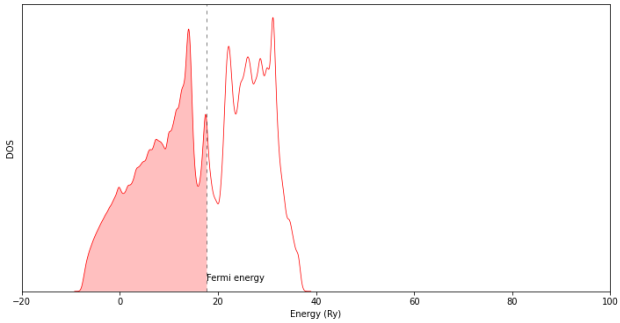

Figure 11: Density of states (DOS) at 24 24 24 k grid showing Fermi energy at 17.7611 Ry

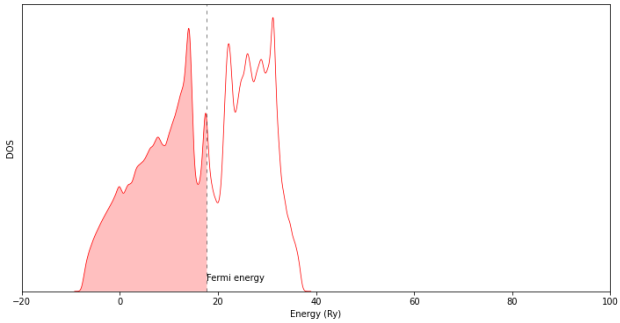

Figure 12: Density of states (DOS) at 36 36 36 k grid showing Fermi energy at 17.7611 Ry

3.3 Stress Components

With a k grid value of 24 24 24 and plane wave cut off energy of 80 Ry, the stress tensor components were produced in the QE output file, they were found to be 2051.09 kbar to give a value of 205.109 GPa. This is 0.109 GPa from the experimental value [3].

kbar			Gpa		
2051.09	0	0	205.109	0	0
0	2051.09	0	0	205.109	0
0	0	2051.09	0	0	205.109

3.4 H_3S Im3m; Tc, q points and $\mu*$

At q grid 4 4 4 with dense q grid 10 10 10, Gaussian Broadening of 0.02 Ry and $\mu*$ at 0.1.

Tables below show the post processing values of lambda, ω_log, Tc, Alpha 2F from Eliashberg Function and Degauss - Gaussian spreading. As the values of lambda vary greatly with changing Degauss, convergence has not been reached.

lambda	omega_log	Tc
-1.10563	1487.39	1129.404
-0.12983	1000.577	1124.661
0.16133	1624.553	0
0.27235	4005.802	0
0.31367	3119.339	0
0.33283	2837.061	0
0.3503	2653.907	0
0.37182	2507.49	0
0.39623	2394.908	0.001
0.42048	2308.845	0.007

Alpha 2F	Omega_log	lambda	Degauss
-1.04	1487.39	-1.10563	0.02
-0.279754	1000.577	-0.12983	0.04
0.02403	1624.553	0.16133	0.06
0.1454	4005.802	0.27235	0.08
0.186667	3119.339	0.31367	0.1
0.203366	2837.061	0.33283	0.12
0.21869	2653.907	0.3503	0.14
0.23891	2507.49	0.37182	0.16
0.26314	2394.908	0.39623	0.18
0.288688	2308.845	0.42048	0.2

At an attempt to investigate the Tc and λ dependence of predictive models [7], Tc, ω_log was plotted against lambda using the Allen-Dynes equation for λ.

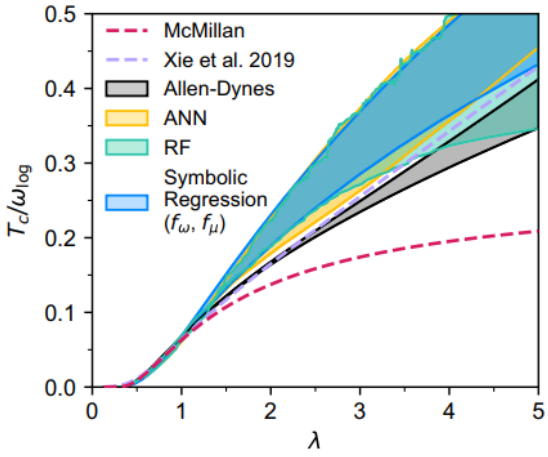

Figure 13: Selective models where the Allen–Dynes formula and the ANN, RF, and symbolic regression machine learning corrections from this work are plotted. All models behaved similarly for low to moderate values of λ. For larger values of λ, the ANN, RF, and symbolic regression corrections deviate significantly from the Allen–Dynes equation as well as the previous symbolic regression equation. The RF regression exhibits discontinuities due to its piecewise-constant form, credit *Xie et al* [7] .

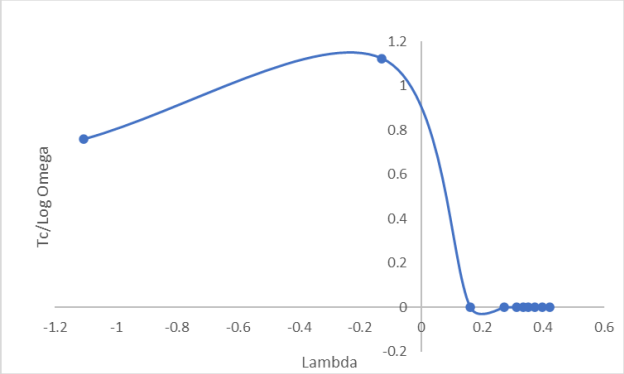

Figure 14: At q grid 4 4 4 with dense q grid 10 10 10, Nk 26 26 26 k grid, Gaussian Broadening of 0.02 Ry and $\mu*$ at 0.1, $\frac{Tc}{\omega_log}$ vs λ. This plot far from Figure 13s expected trajectory for the Allen Dynes model.

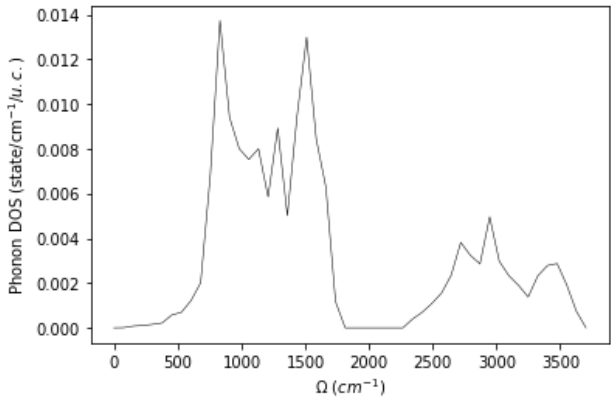

Figure 15: Phonon DOS Im3m for q grid 4 4 4 and Nk 26 26 26

4 Discussion

The total energy per atom vs cut off energy indicated convergence occurring at 80 Ry, this cut-off subsequently used for further calculations.

The stress tensor was found to be 0.109 GPa from the experimental value, this is likely due to a lack of convergence in the k grid 24 24 24, however the convergence in the DOS indicates convergence in k grids at around 26 26 26. The Fermi energies for all three DOS found to be around 17.7611 Ry.

For chapter 3.2, the series of DOS calculations showed convergence after 24 24 24 K grids. To minimise further noise 26 26 26 k grid was thus chosen for the DFPT calculations.

With q point 4 4 4 and Nk 26 26 26, Tc was found at a maximum of 1129.404 K at Gaussian Broadening of 0.02 Ry and $\mu*$ at 0.1. As this is far from converged where Tc is 929 K from experimental value, $\mu*$ was further increased due to its strong dependence on Tc.

The calculation was then repeated for a denser q point grid 8 8 8 and higher $\mu*$.

5 Evaluative Discussion

During scf calculations, bad convergence can be a result of a mixing_beta (mixing factor above self consistency) above 0.3. The setting mixing_mode can also be adjusted to suit convergence. In this case mixing_beta was initially set 0.7 with a run time of around 14hrs, it was then decreased to 0.3 which decreased run time significantly.

For the initial SCF calculations during convergence tests a k grid of 6 6 6 produced unwanted noise.

During the DFPT calculations, q grid at 4 4 4 with 26 26 26 k grids, Tc was not converged at 1000 K. Literate values found convergence at 32 32 32 k point grid with 8 8 8 q point [3]. .

Cirrus Limitations;

To run all simulations, Cirrus was used. Cirrus is a HPC system designed to solve computational, simulation, modelling, and data science challenges. The converged Tc simulation was the longest running job with over 24 hours of wall time. Many factors lead to these simulations being obstructed such as the disk quota being exceeded, using too many K or nK points and jobs being killed for using too many nodes (in this case 10). Ideally one should find an output of the lambda files to give a maximum Tc in its data of 200 K to illustrate the convergence of Tc. The $\mu*$ parameter, K point grid and q points should be noted.

References

[1] W. Wan et al., "Efficient generation of k-point grids for quantum espresso and catalytic role of cop (101) for electrochemical hydrogen evolution compared with pt (100) and pt (111)", PhD thesis (Johns Hopkins University, 2018).

[2] F Marsiglio, "Eliashberg theory: a short review", Annals of Physics **417**, 168102 (2020).

[3] D. Duan et al., "Pressure-induced metallization of dense (h2s) 2h2 with high-t c superconductivity", Scientific reports **4**, 6968 (2014).

[4] A. Drozdov et al., "Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system", Nature **525**, 73–76 (2015).

[5] A. Bussmann-Holder et al., "Structure and composition of the 200 k-superconducting phase of h2s under ultrahigh pressure: the perovskite (sh-)(h3s+).", SUPERSTRIPES, 300 (2016).

[6] R. Akashi, "Archetypical "push the band critical point" mechanism for peaking of the density of states in three-dimensional crystals: theory and case study of cubic h 3 s", Physical Review B **101**, 075126 (2020).

[7] S. Xie et al., "Machine learning of superconducting critical temperature from eliashberg theory", npj Computational Materials **8**, 14 (2022).