

Electronic Structure Theory Superconducting Hydrogen Disulfide

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1 Introduction

Superconductors are materials that, when cooled below a critical temperature, conduct electricity with zero resistance. Most superconducting materials do so at extremely low temperatures, limiting their usefulness. However the immense potential applications of high temperature superconductors has motivated much research into potential materials. [1] have found that hydrogen disulfide is a conventional (described by BCS theory) superconductor at 203 K, however at a pressure of roughly 150 GPa. While this high pressure limits direct applications, this breakthrough in high temperature superconductivity may lead onto more discoveries. This is consistent with a prior theoretical prediction by [2] that hydrogen disulfide would superconduct at pressures around 200 GPa. At such high pressures, [2] predict that hydrogen disulfide decomposes to pure sulfur and H_3S , which has the structure shown in figure 1. They believe the H_3S is responsible for the superconductivity. In this report, I confirm their claims of BCS superconductivity at 203 K and 200 GPa, by using Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) on the structure shown in figure 1, implemented in the Quantum Espresso software suite.

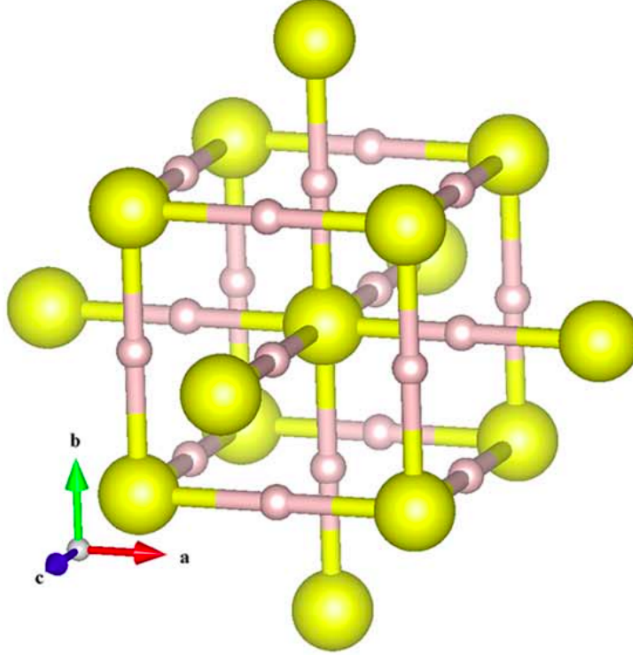


Figure 1: Hydrogen sulphide structure with $Im\bar{3}m$ symmetry. Large spheres represent S, small H. Taken from [2]

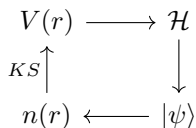
2 Methodology

2.1 Density Functional Theory

DFT is a broad term for theories of electronic structure, as well as computational methods of implementing these theories, that rely on an electron density formulation of quantum mechanics. In particular, modern DFT is based on the Hohenberg-Kohn theorems, the first of which states that there is a bijection between ground state potentials (V_0) and ground state electron densities (n_0), in the non degenerate case. A useful result of this is that the ground state expectation value of any observable is a functional of the ground state density (e.g. $E_0 = E[n_0]$). The second HK theorem states that the minimum of $E[n]$ occurs at the true ground state electron density n_0 . These statements can be generalised to degenerate systems, spin polarised systems and finite temperatures, although they do not offer any obvious way to implement them.

The Kohn-Sham equations remedy this, by providing a mapping from a set of interacting electrons and ions to a set of non-interacting quasi-particles immersed in an effective potential. This is analogous to the Hartree-Fock method for interacting quantum mechanical systems. This transfers all the hard work into calculating the effective potential, at which point some approximations are made. This scales nicely with system size, unlike some more direct wavefunction based methods, which has lead to Kohn-Sham DFT being a very commonly used modelling tool in condensed matter physics.

The common first step in DFT calculations is a self consistent field (SCF) loop. The potential already uniquely defines the Hamiltonian, which uniquely defines the state, which in turn defines the electron density. The Hohenberg-Kohn theorem shows that the electron density defines the potential, closing the loop. SCF calculations work by initialising the electron density with a reasonable guess, then from the resultant Hamiltonian computing a new electron density. This is repeated until the electron density converges to a steady self consistent state. A diagram of the SCF loop is shown below.



Some numerical considerations are worth mentioning. Convergence times can be significantly improved by using pseudopotentials, at some small accuracy cost. As most of the interesting behaviour in condensed matter is due to the valence electron wavefunctions away from the core, the complexities of both valence and inner electron wavefunctions near the core can be removed, by approximating them with much simpler functions. These are known as pseudopotentials - they are numerically more pleasant, but still capture all the relevant physics of chemical bonding and interesting collective electronic behaviour. The pseudopotentials used here are constructed from a plane wave basis set (more specifically Vanderbilt type ultrasoft potentials), which allows for efficient Fourier transforms. This introduces the plane wave cutoff energy parameter, which represents the highest energy plane wave function that can be used. Higher cutoffs yield more accurate results, at increased computational cost.

Calculations can be further optimised by exploiting the symmetries that result from the periodic structure of crystal systems. By working in reciprocal space (k-space), much of the work in solving the Kohn-Sham equations and extracting observables can be reduced to integrals over the Brillouin Zone. As such, the resolution with which one samples the BZ is a further parameter in calculations, again with higher values leading to more accuracy at increased cost. For any SCF calculation the cutoff and k-space values need to be chosen, and by increasing both until the SCF results converge sufficiently with respect to a very high accuracy SCF calculation, a decent trade-off between accuracy and speed can be achieved.

Once the SCF calculations have converged, a series of post processing steps can be done to extract useful information. This will vary significantly depending on the task at hand, but the steps used in this project will be described. Firstly the plane wave cutoff and k-space sampling had to be determined. The crystal structure of H_3S at 200 GPa was taken from [cite here later]. The cutoff energy was varied between 25-100 Ry, with convergence being when the total energy of the system was within 10 meV per atom of the total energy at 100 Ry. Once this had been achieved, the necessary k-space sampling was determined by calculating and inspecting the density of states.

Once sufficient k-space sampling and cutoff energies had been determined, the SCF calculations were repeated to generate a stress tensor, from which the pressure of the system was calculated. This checked that the calculations reproduced the pressures claimed in [cite here later]. As BCS superconductivity relies on electron-phonon coupling, DFPT is needed.

2.2 Density Functional Perturbation Theory

In DFT the energy of the Kohn-Sham system can be represented (in a harmonic approximation) with a force constant matrix, describing the forces acting on each atom due to every other atom. As there are lots of atoms in a typical system, this is necessarily huge and is typically not computed directly. By exploiting periodicity, the force constant matrix can be represented (up to a phase factor) by the dynamical matrix \mathcal{D} . This leads to a linear algebra problem, from which the eigenvectors and eigenvalues correspond to phonon modes and frequencies respectively. DFPT then explores how this system reacts to perturbations, by working with the dynamical matrix in reciprocal space. In the case of electron-phonon coupling, periodic perturbations are used. Typically only phonons with wavevectors close to the fermi surface couple with electrons. This is then used to approximate the Eliashberg function $\alpha^2F(\omega)$, which is a frequency dependant measure of electron-phonon coupling strength. From this the superconducting temperature can be estimated from the McMillan-Allan-Dynes equation:

$$T_c = \frac{\omega_{log}}{1.2} \exp \left[\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (1)$$

where:

$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad \omega_{log} = \exp \left[\frac{2}{\lambda} \int_0^\infty \frac{\alpha^2 F(\omega) \ln(\omega)}{\omega} d\omega \right] \quad (2)$$

and the integral for λ is over the fermi surface. The parameter μ^* is a quasi-free parameter that represents the screened Coulomb interaction. The last few steps of post processing were then repeated with varying k-sampling and μ^* values, from which the superconducting transition temperature T_c was calculated.

3 Results

Figure 2: Energy per atom difference from results at 100 Ry. Shown are results for k-point samplings ranging from 4-10, all behaving very similarly.

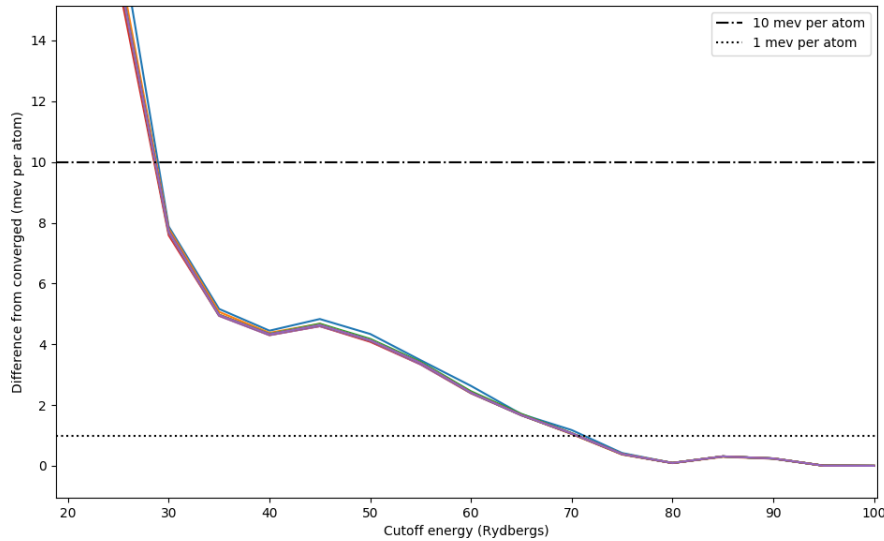


Figure 2 shows how the total energy per atom of H_3S varies with plane wave cutoff energy. A cutoff energy of 30 Ry was enough to result in convergence within 10 mev per atom, and as such was used throughout the rest of this project. If more accuracy is needed, a cutoff of 75 Ry results in convergence within 1 mev per atom.

Figure 3: DOS for varying low resolution k-point sampling values. Left side is over a broad range of energies, right side is zoomed in around the fermi energy.

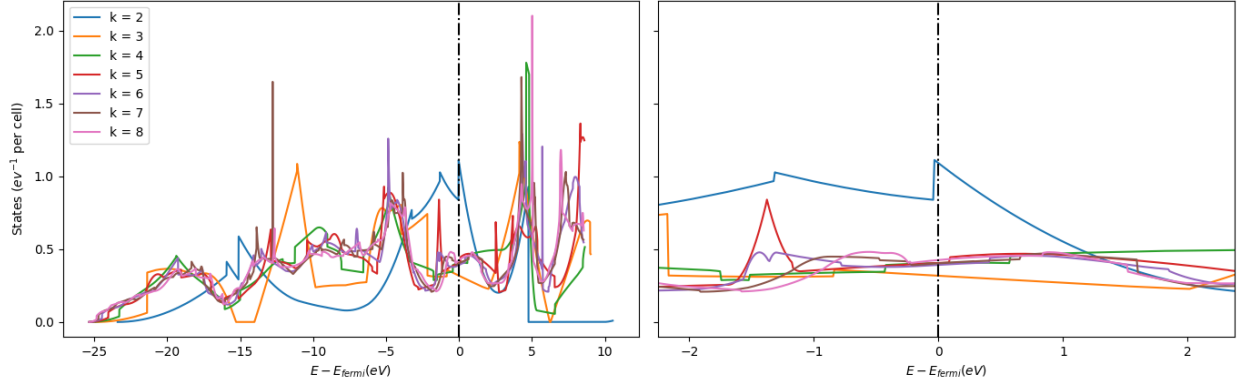
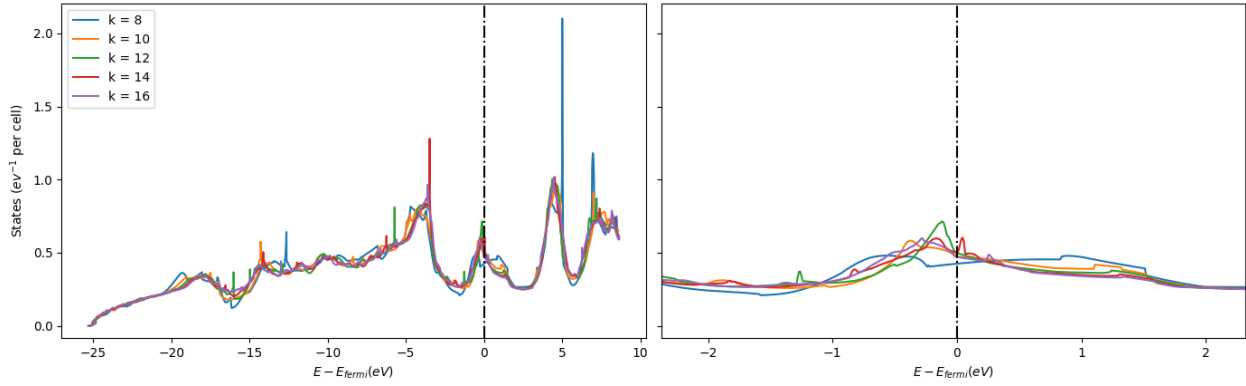


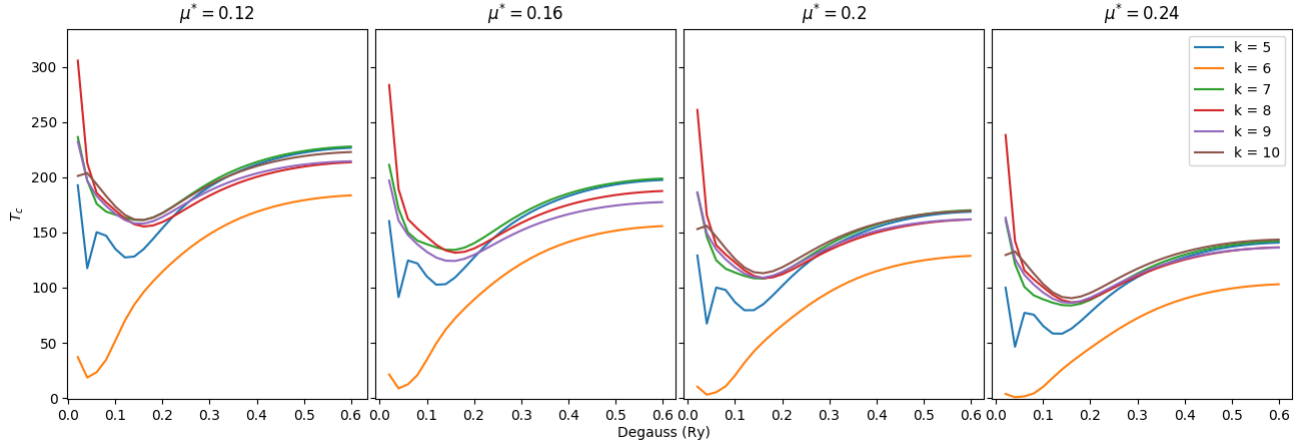
Figure 4: DOS for varying high resolution k-point sampling values. Left side is over a broad range of energies, right side is zoomed in around the fermi energy.



As electron-phonon coupling that leads to BCS superconductivity is mostly at the fermi surface, convergence of the DOS is most important around the fermi energy. From these plots(figures 3 and 4), a k-point sampling of 8 was determined to be sufficient. With the converged values, an SCF calculation to find the stress tensor was run. This had 201.49 GPa along the diagonals, and 0 everywhere else. This agrees well with the 200 GPa described in [2].

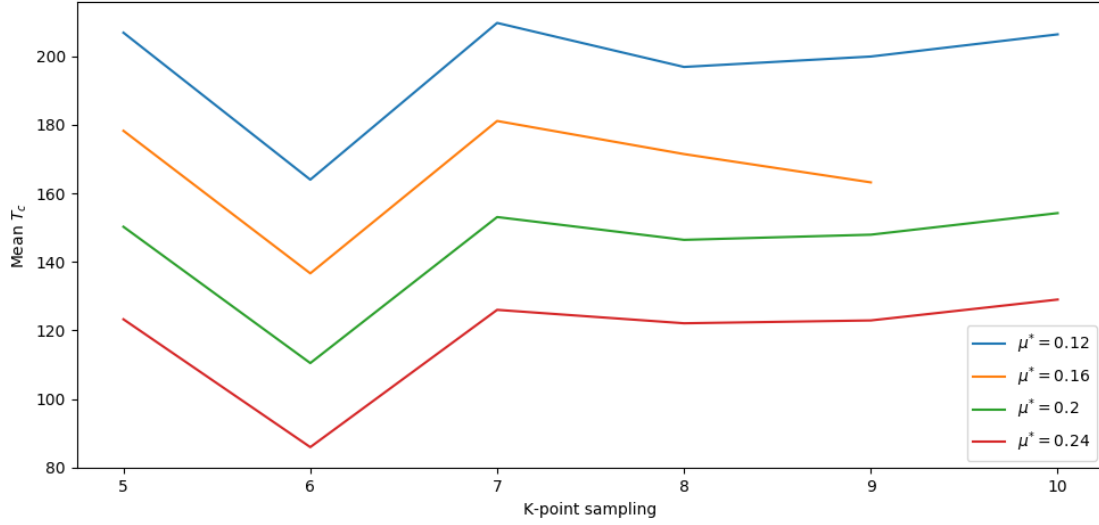
Figure 5 shows how T_c obtained from equation 1 varies with the Gaussian smearing parameter, which affects how the integral for λ is approximated. Multiple plots are shown, with varying k-point sampling and μ^* parameter. The k-point sampling was kept constant through all steps of the calculations - SCF to DFPT post processing - for simplicity. K-point sampling was varied in the range 5-10, as a resolution of 4 lead to the calculations crashing, and any higher than 10 started becoming prohibitively slow.

Figure 5: Superconducting temperatures varying with Gaussian smearing, for various μ^* values and k point sampling.



As T_c varies most before 0.2 Ry, the true value of T_c was estimated by averaging over the range of Gaussian smearing in 0.2 – 0.6 Ry. How these mean T_c values depend on k-sampling and μ^* is shown in figure 6

Figure 6: T_c averaged over Gaussian smearing range 0.2 – 0.6 Ry, for each k-point sampling and μ^* parameter.



At the highest k-point sampling of 10 and $\mu^* = 0.12$, the superconductivity temperature was found to be: $T_c = 206.4$ K. This is agreement with [2], as they used μ^* values in the range 0.1-0.13 to obtain their estimate of $T_c = 203$ K. Figure 6 shows clearly that as k-point sampling is increased, T_c converges. The value for $\mu^* = 0.16$ and $k = 10$ was omitted as the calculations crashed, and were not of high importance as μ^* is not comparable with the results from [2]. $k = 6$ always leads to lower T_c estimates than $k = 5$ or 7, and increased μ^* lowers T_c .

4 Discussion

Hydrogen sulphide has been demonstrated to superconduct at temperatures as high as 203 K, when under extremely high pressure. The results obtained here are in agreement with the theoretical predictions of [2]. As is clear from figures 5 and 6, T_c is strongly dependant on the screened Coulomb potential μ^* . [2] use values in the range 0.1-0.13, stating that these are the commonly accepted values, although values beyond this range significantly lower T_c .

The technique that was used to hypothesise the crystal structure of H_3S at 200 GPa was interesting in it's own right [2]. They combined an evolutionary algorithm with DFT, which allowed them to start from random crystal structures and mutate to 'better' structures - i.e. ones with lower enthalpy. Given how big the space of crystal structures is, an exhaustive search is impossible, so the success of such a method is encouraging.

Following on from this research, lanthanum hydride (LaH_{10}) was found to superconduct at 260 K and 200 GPa [3]. This is near enough room temperature (of Edinburgh student flats during winter) to be a very exciting breakthrough in superconductivity research. Unfortunately none of the recently developed compounds are room pressure superconductors, however the use of *ab initio* methods to simulate these superconductors can elucidate the reasons for such high superconducting temperatures. High frequency phonon modes seem to be a required feature, which can be achieved through large concentrations of hydrogen. It is suspected that pure hydrogen is a superconductor at room temperature, however only at unreachable high pressures [4]. This insight has inspired the recent search for superconducting properties in hydrogen rich compounds, such as the aforementioned LaH_{10} or H_3S . Further study of high pressure high temperature superconductors may reveal possible structures or compounds that superconduct at low enough pressures and high enough temperatures to have potentially revolutionary applications.

References

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