Room temperature superconductors of H_3S at high pressure within the BCS theory.

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I. INTRODUCTION

Superconducivity is a unique property of materials such as metals, ceramics, organic materials, or heavily doped semiconductors that conduct electricity without resistance and energy loss, and their respective magnetic flux fields are expelled from the material. But current superconducting devices use significant amounts of energy for one purpose - cooling. CERN, for example, uses more energy cooling the magnets than accelerating the protons. Superconductors are crucial in many application ranging from medical, engineering to computers[1]. In recent years, many interests and investments have been poured into the research of quantum computing. One of the popular types of quantum computer works based on superconducting electronic circuits known as Superconducting Quantum Computer. It uses Cooper pairs in which the total spin of a Cooper pair is an integer number, hence making the Cooper pairs bosons. Cooled bosons, contrary to cooled fermions, are allowed to occupy a single quantum energy level, in an effect known as the Bose-Einstein condensate which forms the basis behind the technology of Superconducting Quantum Computers.[2]

In this paper, the superconducting critical temperature T_c of H_3S is examined using SCF (self-consistent field) calculation and DFPT (density field perturbation theory) calculation. These calculations are simulated using QE (Quantum Espresso), which is a first-principles electronic-structure calculations and materials modeling software based on density-functional theory, plane wave basis sets, and pseudopotentials.

The input data for the calculations used in this paper is obtained from the paper by Duan, Liu, Tian and et.al.[3]. The objective of this paper is to carry out computations of H_3S through running simulations using Density Functional Theory and Density Functional Perturbative Theory methods using Quantum Espresso and McMillan-Allen-Dynes equation to compute the critical temperature T_c of H_3S. The results of this simulation are then compared against the results from the paper by Duan, Liu, Tian and et.al.

II. METHODOLOGY

A. Density Functional Theory

Quantum Espresso calculations are based on Density Functional Theory and Density Functional Perturbation theory. Therefore we shall delve into the concepts and theorems behind DFT and DFPT.

The fundamental equation of quantum mechanics is the Schrödinger equation and it is used for the calculations of the electronic structure of many-electron systems begin with. The time-independent non-relativistic Schrödinger equation for many-body system is given as[4]:

$$\hat{H}\Psi = E\Psi \tag{1}$$

where $\hat{H}$ is the molecular Hamiltonian operator, E is the total energy of the system and Ψ is the many body/electron wave function.

The corresponding Hamiltonian for such a system can be written as[4]:

$$\hat{H} = T_e + T_n + V_{en} + V_{nn} + V_{ee} \tag{2}$$

where T_e is the kinetic energies of the electrons, T_n is the kinetic energies of the nuclei, V_{en} is the electron-nuclei coulomb interaction, V_{nn} is the nuclei-nuclei coulomb repulsion and V_{ee} is the electron-electron coulomb repulsion.

The solution of many-body Schrödinger equation which can only be solved by considering certain approximations required for simplifying the Hamiltonian. Since the masses of nuclei are much greater than that of electrons, so with the use of Born-Oppenheimer approximation we can simplify molecular Hamiltonian as given in Equation 2. The Born-Oppenheimer approximation is primarily based on the following assumptions[4];

1. The electronic wave function depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.

2. The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the fast moving electrons.

Under this approximation, the nuclear kinetic energy is neglected and repulsion between the nuclei is considered as constant. The molecular Hamiltonian (Equation 2) is then reduced to the electronic Hamiltonian H_e contains only electronic part is written as[4];

$$\hat{H}_e = T_e + V_{ee} + V_{ext} \tag{3}$$

where V_{ext} is the external potential which accounts for the electron-nuclei coulomb interaction term.

Finding the solution of the Schrödinger equation with the Hamiltonian in Equation 3 is too complex due to having $3N$ variables of the many-electron wave-function, where N is the number of atoms per unit cell. Therefore, for solving many-electron problems require the use of other methods such as the Thomas-Fermi theory and Hartree-Fock method.

The Hartree-Fock (HF) method provides the approximate solution for the many-body Schrödinger equation in the

ground state. HF method suggests that the motion of each electron can be described with the single-particle function and this particle function does not depend explicitly on instantaneous motions of other electron. The electron-electron interaction is approximated through the Hartree approximation where n number of electron wave-function Ψ is considered as the product of single-particle orbitals $\psi_i(\mathbf{r}_i\sigma_i)$:[4]

$$\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_n\sigma_n) = \frac{1}{n!}\psi_1(\mathbf{r}_1\sigma_1)...\psi_n(\mathbf{r}_n\sigma_n) \quad (4)$$

The Hartree approximation does not account for the exchange interaction under the interchange of particle coordinates but was rectified by Fock with the Hartree-Fock approximation. This approximation assumes that electron exchange interaction can be written by the wave-function Ψ_{HF} which is defined as an antisymmetrised product of orbitals. $|Psi_{HF}$ can be represented with N×N determinant which is defined as the Slater determinant[4]:

$$\Psi_{HF} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\mathbf{r}_1\sigma_1) & \psi_1(\mathbf{r}_2\sigma_2) & ... & \psi_1(\mathbf{r}_N\sigma_N) \\ \psi_2(\mathbf{r}_1\sigma_1) & \psi_2(\mathbf{r}_2\sigma_2) & ... & \psi_2(\mathbf{r}_N\sigma_N) \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ \psi_N(\mathbf{r}_1\sigma_1) & \psi_N(\mathbf{r}_2\sigma_2) & ... & \psi_N(\mathbf{r}_N\sigma_N) \end{vmatrix} \quad (5)$$

The full Hartee-Fock equation with Hartree-Fock wave function is given as[4]:

$$E[\Psi_{HF}] = (-\frac{\nabla^2}{2} + V_{ext})\psi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \frac{|\psi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r})$$

$$- \sum_j \delta\sigma_i\sigma_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_j(\mathbf{r}') \quad (6)$$

Here, $\psi(\mathbf{r}\sigma)$ is represented as $\psi(x)$ for the simplification of the above equation. The Hartree-Fock equation consists of four terms; the first term represents the kinetic energy of electrons while the second term includes the electron-ion potential contribution. The third term, which is known as Hartree potential, is an electrostatic potential, appears due to the charge distribution of N-electrons. The last term, known as the exchange term, arises due to the inclusion of the Pauli principle and determinant form of the wavefunction.

Thomas-Fermi method is used to find the solution of the many-electron problem where the electron density $\rho(r)$ is considered as a central variable rather than the wavefunction. The total energy is defined as a functional as[4];

$$E_{TF}[\rho(r)] = A_k \int \rho(r)^{\frac{5}{3}} dr + \int \rho(r)V_{ext}(r)dr + \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|\mathbf{r}-\mathbf{r}'|}drdr' \quad (7)$$

The first term of the above equation represents the kinetic energy of a non-interacting electron system, A_k the coefficient which is defined as $A_k = \frac{3}{10}(3\pi^2)^{2/3}$ The next term corresponds to the classical electrostatic interaction energy term between the nuclei and the electrons. The static coulomb potential term $V_{ext}(r)$ arises due to nuclei. The last term of the above equation represents the electron-electron interaction energy, known as Hartree energy. The Thomas-Fermi method provides a rough description of electrostatic potential and charge density but could not explain the binding mechanism of atoms. However this theory is essential in the development of DFT.

Density functional theory is a powerful method to predict the electronic properties of molecule/clusters and materials due to accuracy and high computational efficiency[4]. In this method, the electron density is treated as a central variable instead of many-electron wavefunction. The implementation of electron density leads to a significant reduction in the level of difficulty as well as the computational cast. In other words, 3N variables (in the case of many-electron wavefunction) are reduced to only three variables (three Cartesian directions) with the use of density, which shows that variables do not depend on the number of electrons.

Walter Kohn and co-workers established the theoretical foundation of density functional theory. They postulated two theorems[5]:

Theorem I: The electron density $n_0(r)$ determines the external potential V_{en} (to within an additive constant)

where $n_0(\mathbf{r}) = \sum_i |\psi_i|^2$.

Theorem 2. The energy functional $E[n]$ has its minimum at the true ground state density $n_0(\mathbf{r})$, i.e. that density that corresponds to the actual Hamiltonian H.

An approximation of the ground-state energy by minimizing the total energy functional, is given by (Course note p29 eq. 3.24 3.25)[6]:

$$E[n] = V_{ee} + T_{en} + \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad (7)$$

The Hohenberg-Kohn theorems and their consequences are significant but do not offer any practical use.Kohn and Sham would later develop a workable implementation of the energy minimisation principle. They proposed the use of auxiliary system of non-interacting electrons, while incorporating the complicated electron-electron interaction into an exchange-correlation functional.

The Kohn-Sham equation (Course slides, W3 pg 17) is given as[6]:

$$\left[-\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{xc}\mathbf{r}) + V_{en}\mathbf{r})\right]\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r}) \quad (8)$$

where V_{xc} is the exchange-correlation potential and V_H is the Hartree energy given by:

$$V_H = \frac{1}{2}\int\int d(\mathbf{r})d(\mathbf{r}')\frac{n((\mathbf{r})n(\mathbf{r}')}{|(\mathbf{r}) - (\mathbf{r}')|} \quad (9)$$

B. Density Functional Perturbation Theory

The first approach for calculation of phonons was based on response functions, since all harmonic force constants, elastic constants, etc. involve only second derivatives of the energy, they can be derived using second-order perturbation theory.

Generally, the perturbation of the first order density response is (Course note sec 6.4, eq. 6.14) is given as[6]:

$$\Delta n(\mathbf{r}) = 2\sum_i f_i \phi_i^* \Delta\phi_i(\mathbf{r}) \tag{10}$$

The perturbation in the single particle wave functions, $\Delta\phi_i$ itself, can be written from first-order perturbation theory as:

$$[H_e - \epsilon_i]\Delta\phi_i = -(\Delta v_{KS}\phi_i \tag{11}$$

where

$$\Delta V_{KS}(\mathbf{r}) = \Delta V_{en}(\mathbf{r}) + \int \frac{\Delta n(\mathbf{r}')}{|(\mathbf{r}) - (\mathbf{r}')|} d^3(\mathbf{r}') + \int \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \Delta n(\mathbf{r}' \tag{12}$$

$$\Delta\epsilon_i = \phi_i \Delta V_{KS} \phi_i \tag{13}$$

Equation 10 - 13 are the central object in DFPT and are carried out in the phonon calculations in Quantum Espresso.

III. RESULTS AND DISCUSSION

A. Structure of H_3S

The SCF calculation for the energy cut-off convergence test uses the data supplied from the paper by Duan, et. al. For the *Im3m* structure, the space group number is 229 with the lattice constant a = 2.984 with two formula unit cell. The atomic positions for H; x = 0.0, y = 0.5, z = 0.5, and S; x = 0.5, y = 0.5, z = 0.5 are taken from the paper by Duan and et. al[3]. These data is used in the SCF calculation for the density of state.

B. Convergence Test

Fig. 1 shows that the convergence tests on the plane wave energy to converge within total energies of 10 meV per atom is achieved at around 30 Ry.

Subsequently, convergence tests on the k-point grid size K × K × K is carried out to obtain a well-converged DOS. Refer to Fig. 2 and Fig.3.

The Fermi energy obtained for K-point 8 at 30 Ry is shown on Fig. 3 to be about 17.65 meV. As indicated in the DOS plot, the point at the Fermi energy shows non-zero value of density of states for all K-points. No band gap is present hence indicating that H_3S is a metal.

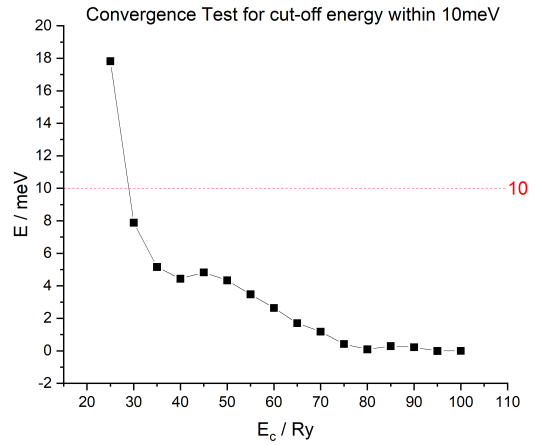

Fig. 1. SCF convergence tests on the plane wave energy.

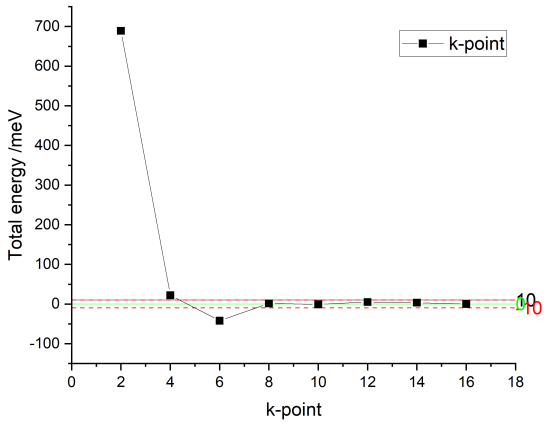

Fig. 2. SCF convergence tests on the k-point grid size

From Fig. 3, observe that the K-point starts to converge at K = 8. Using the energy cut off at 30 Ry and K-point = 8 to calculate the the stress tensor components and then compare the pressure to the ideal value, P = 200 GP.

Listing 1. The h3s.scf-dos.out output pressure as calculated using Quantum Espresso.

```
[s2256510@cirrus-login3 Project-1]$ grep
    "kbar" h3s.scf-dos.out
          total   stress  (Ry/bohr**3)
          (kbar)     P=    1997.15
```

Referring to Listing 1, the stress tensor for the converged crystal is diagonal, with $\sigma_{11} = \sigma_{22} = \sigma_{33} = 1997.15$ kbar, for the value obtained with the K point and energy cut-off. After conversion from kbar to GPa, the pressure is 199.7 GPa and is within 0.15% accuracy compared to the ideal pressure.

For metals, the Gaussian smearing parameter in Quantum espresso can be used to improved convergence. Referring to Fig. 4, by using K-point = 8 and energy cut off at 30 Ry, the

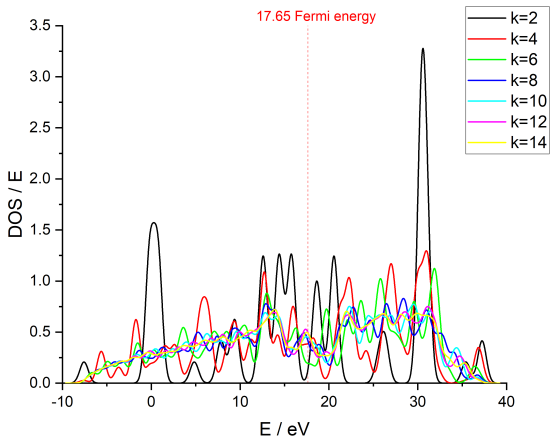

Fig. 3. K-Points convergence of the DOS (Density of state)

Gaussian smearing parameter degauss = 0.07 yields a pressure of 200.02 GPa which matches very closely to the value from the paper.

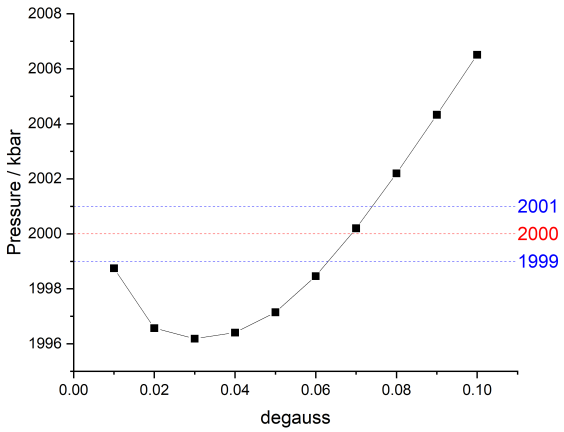

Fig. 4. Gaussian Smearing parameter vs pressure of H_3S

C. DFPT and Critical Temperature T_c

After calculating the pressure, the phonon calculation using DFPT is calculated to determine the mode-dependent electron-phonon coupling parameters on a regular grid of Q-points. The Q-point needs to be chosen such that for each wave vector K in the DOS K-point and every wave vector q in the q-point and must be commensurate as these two parameters are not independent.

A different sets of K-point and Q-points are used in the here in order to converge the critical temperature T_c against the values from the paper. Three sets of K and Q points values are used here namely: K = 8 with Q = 2, 4; K = 12 with Q =2, 3, 4, 6; K = 16 with Q = 4, 8. Refer to Fig. 5, it is quite obvious that Q = 8 and K = 16 yielded the closest T_c against the paper by Duan and et. al., hence all calculations from this point onward use K= 16 and Q = 8.

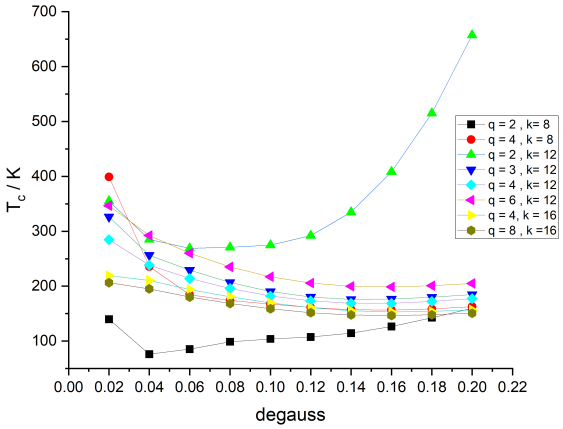

Fig. 5. K and Q point convergence against T_c. Note that μ^* used for this computation is 0.1

Using the McMillan-Allen-Dynes equation (course note equation 6.31 page 72)[6] to compute T_c, given as:

$$T_c = \frac{\omega_{log}}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right] \tag{14}$$

$$\lambda = 2\int \frac{\alpha^2 F(\omega)}{\omega} d\omega \tag{15}$$

$$\omega_{log} = \exp\left[2\lambda \int_0^\infty \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega)\right] \tag{16}$$

where λ is the Fermi-surface averaged electron-phonon coupling parameter and ω_{log} is the weighted logarithmic average phonon frequency and μ^* is the screened Coulomb interaction ranging from 0.1 to 0.3.

With the T_c obtained from the computation of K-point = 16 $\times$ 16 $\times$16 and Q-point = 8 $\times$ 8 $\times$ 8, a set of calculations using McMillan-Allen-Dynes equation is computed with a range of μ^* from 0.1 to 0.3. Referring to Fig. 6, it is evident that the value of μ^* significantly affects the value of T_c.

As illustrated in Fig. 6, T_c for $\mu^* = 0.1$ gives a value ranging from 146.5 K of 206.3 K. Comparing against the paper[3] by Duan et. al used the Q-point of 8 $\times$ 8 $\times$ 8 and K-point of 32 $\times$ 32 $\times$ 32 with a range of T_c from 191 K to 204 K. One can infer that the K-points, Q-points and μ^* play an important role in obtaining a good range of T_c.

In conclusion, this result gives a promising sign towards achieving practical room temperature superconductors. However, H_3S will only exhibit superconducting properties when it is subjected to a high pressure of about 200 GPa, at a temperature not too near "room" temperature, which renders it

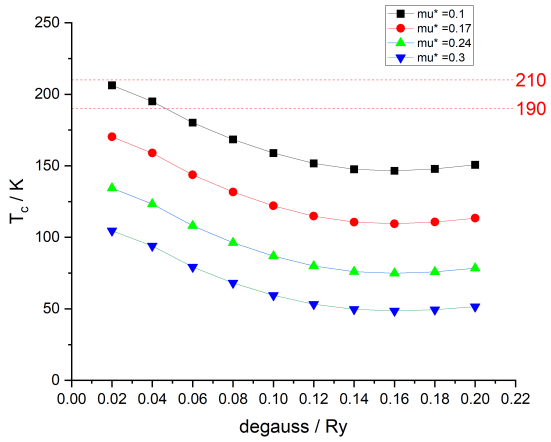

Fig. 6. T_c of different μ^* versus degauss

impractical for wider application. Nevertheless, such results demonstrate the possibilities of testing the superconductivity of different materials using similar methods as outlined in this report.

IV. REFERENCES

[1] *Superconducting magnets of the future in the making at CERN*, en. [Online]. Available: https://home.cern/news/news/accelerators/superconducting-magnets-future-making-cern (visited on 04/26/2022).

[2] *Superconducting quantum computing*, en, Page Version ID: 1083361594, Apr. 2022. [Online]. Available: https://en.wikipedia.org/w/index.php?title=Superconducting_quantum_computing&oldid=1083361594 (visited on 04/26/2022).

[3] D. Duan, Y. Liu, F. Tian, *et al.*, "Pressure-induced metallization of dense (H2S)2H2 with high-Tc superconductivity," en, *Scientific Reports*, vol. 4, no. 1, p. 6968, Nov. 2014, ISSN: 2045-2322. DOI: 10.1038/srep06968. [Online]. Available: https://www.nature.com/articles/srep06968 (visited on 04/23/2022).

[4] A. K. Kushwaha, "A Brief Review of Density Functional Theory and Solvation Model," en, Mar. 2022. DOI: 10.26434/chemrxiv-2022-vlhm0. [Online]. Available: https://chemrxiv.org/engage/chemrxiv/article-details/6231c8042c5010f92a7d0bd6 (visited on 04/26/2022).

[5] *3.1 Density-functional theory*. [Online]. Available: https://www.tcm.phy.cam.ac.uk/~pdh1001/thesis/node17.html (visited on 04/26/2022).

[6] G. A. a. E. Santos, *Electronic Structure Theory*, University Learn Page. [Online]. Available: https://www.learn.ed.ac.uk/webapps/blackboard/content/listContent.jsp?course_id=_85563_1&content_id=_5937454_1&mode=reset (visited on 04/26/2022).