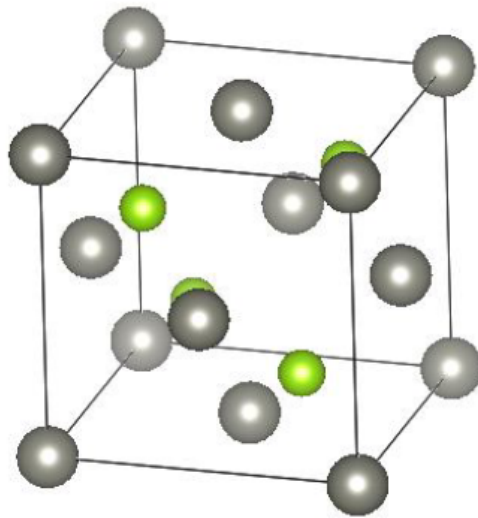


UNIVERSITY OF LA LAGUNA
FACULTY OF SCIENCES, PHYSICS SECTION

Trabajo de Fin de Grado

Study of thermodynamical properties
of materials with quantum-mechanical
methods

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Resumen (Español)

Este trabajo de fin de grado ha consistido en el aprendizaje sobre el empleo de herramientas de simulación computacional en el marco de la mecánica cuántica para poder estudiar las propiedades de los materiales físicos, que son sistemas constituidos microscópicamente por muchos átomos, donde cada átomo estaría formado por un núcleo y una nube de, a priori, muchos electrones. Este es un problema que podría parecer formidable por su constitución, no obstante, se puede abordar a través de simulaciones computacionales, que consisten en la resolución de un determinado problema a través de un ordenador que obtiene soluciones numéricas de las ecuaciones que describen el problema según un modelo determinado. Aunque esta forma de investigación pueden ser de gran utilidad para analizar situaciones que no se pueden estudiar experimentalmente, por ejemplo, debido a la imposibilidad de replicar ciertas condiciones extremas en un laboratorio, las simulaciones que se aplicaron en este proyecto obtienen resultados que pueden ser replicados desde el punto de vista experimental. De hecho, en esta investigación se utilizan los resultados experimentales que pueden ser consultados en la literatura para comprobar la veracidad de las simulaciones realizadas. El principal propósito de este trabajo ha consistido en obtener las propiedades termodinámicas y vibracionales de un cierto compuesto sólido y cristalino, a través de una simulación mecano-cuántica partiendo desde primeros principios. Esto implica que el estudio del material se realiza partiendo desde cero de los postulados de la física cuántica y construyendo un modelo satisfactorio del sistema que pueda ser resoluble desde el punto de vista computacional, lo cual puede implicar realizar algunas aproximaciones, aunque sin tener en cuenta ningún aporte experimental. En la práctica, esto se traduce en la resolución de la ecuación de Schrödinger sin más consideraciones que los números atómicos de los átomos implicados en el material, aparte de la forma en la que se encuentran distribuidos en el cristal.

La primera parte del trabajo comprende la descripción de la teoría que hay detrás del procedimiento que fue aplicado durante la investigación. Se fundamenta principalmente en la Teoría del Funcional de la Densidad, que está sostenida por los teoremas de Hohenberg y Khon, que nos permiten obtener un modelo en el que las propiedades del sistema solo dependen de la densidad electrónica en el estado fundamental del cristal. También se presentarán el resto de consideraciones que hay que tener en cuenta para poder obtener un modelo resoluble que permita encontrar las propiedades ya mencionadas, por ejemplo, la expansión de la función de onda en una base con un número finito de ondas planas, elegido a partir de criterios como la selección de una energía de corte que tenga en cuenta únicamente

las contribuciones más importantes y que, al mismo tiempo, nos permita obtener una buena convergencia para el desarrollo. Una vez obtenidas las propiedades del estado fundamental y la estructura cristalina relajada, se pueden estudiar las vibraciones en el interior del cristal a partir de la consideración de desplazamientos individuales sobre cada átomo, la obtención de una matriz dinámica que responda a las fuerzas generadas por dichos desplazamientos y su diagonalización que resultará en la obtención de los distintos fonones o vibraciones colectivas internas del cristal, que a su vez servirán de base para obtener las propiedades termodinámicas con las técnicas de la mecánica estadística.

En este trabajo, el compuesto que fue analizado fue el seleniuro de zinc (ZnSe), un cristal semiconductor que, en condiciones normales, presenta una estructura zinc blenda (grupo espacial 216 F-43m) y que, típicamente, se utiliza o bien en la construcción de diodos emisores de luz, o bien en la construcción de ventanas y lentes ópticas en las que su alta transparencia frente al infrarrojo pueda ser provechosa. Esta propiedad lo hace muy útil en espectroscopia de infrarrojos.

Tras analizar el compuesto, el trabajo se centra en presentar las herramientas computacionales necesarias para la consecución de las simulaciones mecano-cuánticas. El software aplicado fue el *Vienna Ab-initio Simulation Package* (VASP), que permite analizar el material con la aplicación de la Teoría del Funcional de la Densidad y el método de los pseudopotenciales, así como el paquete *phonopy*, que es el que permite aplicar el método del fonón congelado, procedimiento por el cual se obtiene la matriz dinámica y se diagonaliza para hallar los fonones en el punto Γ de la zona de Brillouin.

Finalmente, se dedica la última parte del trabajo a presentar los resultados obtenidos por la simulación mecano-cuántica. Una vez aplicados los métodos mencionados con anterioridad, se puede calcular el volumen de la estructura relajada. Con dicha estructura, al aplicar el método del fonón congelado a superceldas $2 \times 2 \times 2$, se obtienen las frecuencias de los fonones en el punto Γ , así como sus representaciones irreducibles. En este caso, se puede mejorar el modelo aplicando correcciones no analíticas, descritas en detalle en la sección de análisis de resultados del trabajo, con la finalidad de producir un desdoblamiento en las ramas ópticas de los fonones, que facilita el análisis de cómo varían las vibraciones del material al aplicar cambios de presión. Este desdoblamiento se obtuvo para distintos valores de presión, alcanzando valores de hasta $P = 12$ GPa. Para finalizar, se obtiene la energía interna, la entropía, la energía libre de Helmholtz y la capacidad calorífica para distintos valores de presión y temperatura, a partir de la densidad de estados previamente estimada en el cálculo de los fonones. Se concluye que los resultados son

satisfactorios porque las propiedades termodinámicas están en concordancia con leyes muy importantes de la física, como la tercera ley de la termodinámica o la ley de Dulong y Petit.

Abstract

This final degree project has consisted on the attempt to apply computational simulation methods on a physical system with crystalline nature and constituted by many atoms, that is, by many nuclei and electrons. The purpose of these methods consists on resolving the system in order to obtain its thermodynamical and vibrational behaviours by using a first principles quantum-mechanical approach, which basically consists on resolving the Schrödinger equation without any experimental input, just the atomic numbers of the atoms involved along with their positions inside the crystal. While simulational computations are particularly useful on researches that require non feasible conditions due to the unviability to recreate them on a laboratory, this particular research has already been performed with experimental methods so we will show some comparisons between the results achieved with the simulations and the ones predicted and obtained by other scientists in the literature.

On the first part of this report we will introduce the theory behind these simulation methods, which basically consists on Density Functional Theory (DFT), along with the different assumptions that need to be considered in order to obtain the sought properties. Secondly, we will explain the methodology used to apply the simulations to our system and to make all the calculations required. Finally, we will carefully examine all the results and highlight the most important conclusions that can be extracted from them.

The physical system used in this work was the zinc selenide semiconductor crystal (ZnSe). This compound, which typically presents a zincblende structure (space group 216 F-43m), is usually used on light emitting diodes due to its dynamical controlled electric conductance or even in infrared spectroscopy as it presents infrared transparency.

The software used on the quantum-mechanical calculations was the *Vienna Ab-initio Simulation Package* (VASP) as well as the *Phonopy* package to simulate the atomic displacements with an harmonic approximation and find the phonons frequencies at Brillouin's Γ point. After having obtained this data, it was easy to get a prediction of the partial and total density of states, the entropy, the Helmholtz free energy, the heat capacity and the internal energy as well as their variations with the temperature. Furthermore, different pressures analysis were made including those with high pressure values up to 12 GPa.

1- Theory Introduction

1.1 Quantum description for the system

It is a well known fact that baryonic matter is made up of atoms and it can present itself under different physical states. From the point of view of the condensed matter, some of the most interesting materials are the crystalline solids. Due to the intensity of the interatomic forces, they consist on a system of atoms organized around definite equilibrium positions which are defined forming up a grid with a certain periodicity. Therefore, the properties of the system will not only depend on the nature of the atoms that constitute it, but also in the configuration in which they are distributed inside the grid.

We will focus our attention on studying this crystalline structure from a first principles approach. In practice, this requires us to start off from the most generic postulates of the formalism of quantum mechanics. However, we will need to make some assumptions and approximations in order to obtain a consistent model that could be solved computationally on a reasonable time span. This does not present any conflict as first principles methods are free from any experimental input, but are not exempt of some theoretical approximations.

According to all that has been exposed, our quantum-mechanical study requires us to solve the stationary Schrödinger equation:

$$\hat{\mathbf{H}}\Psi(\mathbf{R}_I; \mathbf{r}_i) = E\Psi(\mathbf{R}_I; \mathbf{r}_i)$$

We can identify $\Psi = \Psi(\mathbf{R}_I; \mathbf{r}_i)$ as the wave function of the system that must have a dependence with the position of the different nuclei coordinates (noted by the I index) and the electrons coordinates (noted by the i index). The total energy is represented by E and $\hat{\mathbf{H}}$ is the Hamiltonian of a system of nuclei and electrons interacting by electrostatic forces. Using the appropriated unit system, this operator takes the form:

$$\hat{\mathbf{H}} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{I,J(I \neq J)} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} +$$

$$+ \frac{1}{2} \sum_{i,j,(i \neq j)} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|}$$

We can recognize some of the properties of the nuclei, such as the mass M_I and the atomic number Z_I , as well as the mass of the electrons m_e . After obtaining this expression we should be able to solve the Schrödinger equation. However, this many-body problem is formidable and not feasible without making some approximations.

The first consideration that should be made is the adiabatic approximation, also called the Bohr-Oppenheimer approximation. This is justified in the fact that the electrostatic forces on the nuclei and electrons are of the same order of magnitude and at the same time the atomic cores have much higher masses than the electrons. This means that the electrons move with much more higher speed than the cores, so we could consider that the system consists on the set of electrons moving inside an effective external potential $V_{ext}(\mathbf{r})$ created by the static atomic cores. This simplifies the problem substantially as this external potential will be time-independent.

After applying this first adiabatic approximation, the Hamiltonian of the system is reduced to the one associated with a problem of many electrons with mutual interactions moving in an external potential $V_{ext}(\mathbf{r})$:

$$\hat{\mathbf{H}} = - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i,j,(i \neq j)} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{ext}(\mathbf{r}_i)$$

1.2 Density Functional Theory

After obtaining the previous form for the Hamiltonian, it is justified that we should apply a second consideration to solve this problem. This implies that we will employ the Density Functional Theory (DFT), which was first formulated by Hohenberg and Kohn [1] and it is used to describe a system of

interacting particles moving in an external potential. This theory is based on the two Hohenberg-Kohn theorems that can be summarized as follows [2]:

1. For any system of particles interacting inside and external potential $V_{ext}(\mathbf{r})$, this potential is determined uniquely by the ground state particle density $n_0(\mathbf{r})$ (up to an additive constant). Since $\hat{\mathbf{H}}$ is determined by $V_{ext}(\mathbf{r})$, it follows that the properties of the system, including the total energy, are determined only by $n_0(\mathbf{r})$.
2. For any $V_{ext}(\mathbf{r})$, the energy is a unique functional, $E[n]$, of the particle density $n(\mathbf{r})$. By minimizing this functional with respect to variations in $n(\mathbf{r})$, one finds the energy and the density of the ground state. The ground state energy of the system is the minimum of this functional and the density that minimizes it is the ground state density $n_0(\mathbf{r})$.

Therefore, DFT does not require the many-body Schrödinger equation or the corresponding wave function, instead, it allows us to obtain any property of the system as a functional of the electron density $n(\mathbf{r})$. We can write this functional for the energy of the ground state of the system (using atomic units: $e = \hbar = 1/(4\pi\epsilon_0) = 1$) as it follows:

$$E[n] = \int V_{ext}(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + F[n]$$

Moreover, this functional satisfies the condition $\int n(\mathbf{r}) d\mathbf{r} = N$, where N is the total number of electrons inside the crystal. $F[n]$ is an unknown universal functional which does not depend on the external potential, but it has some dependence with the kinetic energy of the system and the electron-electron interactions, also including the Hartree energy term:

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

While these theorems do not provide any way to construct this functional, Kohn and Sham [3] used this formalism to derive a procedure that provides a set of equations that could be resolved with a self-consistent method. Kohn and Sham noted that in a system of N non-interacting electrons inside an external potential, $F[n]$ is just the kinetic energy functional. Consequently, the

energy functional for a system of N interacting electrons inside an external potential could be written as:

$$E[n] = \int V_{ext}(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + T_S[n] + E_{exc}[n]$$

where $T_S[n]$ is the kinetic energy functional and $E_{exc}[n]$ is an exchange-correlation energy functional.

We should stop momentarily to analyze the meaning of this exchange-correlation energy. Basically, what Kohn and Sham were trying to do here was to obtain the solution of the real interacting electronic problem by resolving an auxiliary non-interacting electronic problem and then adjusting the energy to the real problem by adding the Hartree energy term and this $E_{exc}[n]$ term. If we knew with precision the form of this exchange-correlation functional, then we could obtain an exact solution of the real problem with the auxiliary solution. However, this exchange-correlation energy term is unknown and it can only be estimated with approximations.

Therefore, if we include all potential terms inside an effective potential:

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{exc}(n(\mathbf{r}))$$

with:

$$\mu_{exc}(n(\mathbf{r})) = \frac{\delta E_{exc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Using this effective potential, we could find the ground state of the system by resolving the following set of one-particle equations that have the same form as the Schrödinger equations associated to the non interacting auxiliary case:

$$\left\{ -\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad ; \quad i = 1, \dots, N$$

With this set of equations, which are called the Kohn-Sham equations, we can find the electronic density for the ground state of the system with $n(\mathbf{r}) =$

$\sum_{i=1}^N |\psi_i(\mathbf{r})|^2$. As we previously discussed, the exact exchange-correlation energy functional is unknown and must be estimated with reasonable assumptions. We could begin by considering that the electron density $n(\mathbf{r})$ varies slowly, so we could adopt a *local density approximation* (LDA) with the form:

$$E_{exc}(\mathbf{r}) = \int n(\mathbf{r})\varepsilon_{exc}(n(\mathbf{r})) d\mathbf{r}$$

This approximation allows us to consider the exchange-correlation density $\varepsilon_{exc}(\mathbf{r})$ as the same as that of an homogeneous electron gas, which does not have an analytical expression, nevertheless there is a widely used expression for it, which was obtained by Alder and Ceperley [4] through quantum Monte Carlo simulations. While this approximation works remarkably well and it was the simplest approximation proposed by Hohenberg and Kohn on their original article about DFT [1], if we desire to obtain a more accurate results on our research, then we should use a more refined approximation called the *generalized gradient approximation* (GGA), which includes not only the dependence with the electronic density, but also the dependence with its gradient.

1.3 Solutions for the Khon-Sham equations

Now, we must solve the Khon-Sham equations which describe an electron moving inside the effective potential considered before. This will require to expand the wave functions in an advantageous basis set. There are three main approaches to perform this expansion, each of them with certain advantages and disadvantages that need to be taken into account:

- Plane wave basis set: It is a really simple basis to implement with first principles methods. It implies the use of the Fourier transform between the real and reciprocal spaces, and there already exist numerous efficient algorithms to perform this task. However, the main downside is that it requires a large number of plane waves to recreate the wave functions and potentials with enough accuracy.
- Lineal combination of atomic orbitals (LCAOs): As these orbitals are only important in regions of the space near the atoms, the number of

orbitals required to obtain the wave functions and potentials are very low, nonetheless it usually presents bad convergence.

- Atomic sphere methods: This consists on dividing the space into regions near each nuclei where all the magnitudes present atomic-like properties with a smooth variation of said properties in the regions between the atoms. This method provides the best benefits from both the plane wave and the LCAOs but the computational cost is high on average and it is difficult to implement on the algorithms.

Due to its simplicity, we will stick with the plane wave basis set method to solve the Kohn-Sham equations, but we will implement another approximation to reduce the number of plane waves required. As we know, solids are composed of nuclei bounded together through valence electrons which are the ones that determine most of the properties of the system. Therefore, as the valence electrons undergo a smooth potential in contrast to the internal electrons that remain localized around the atoms because of the strong atomic potential, we will replace the Coulomb potential created by the atomic cores with a first principles pseudopotential which removes the radial nodes for the wave function as well as conserves the real behaviour of both the wave function and the Coulomb potential in the region outside the core, where valence electrons are located. The pseudopotentials that were required on this research were projector-augmented wave pseudopotentials (PAWs), which tend to improve the accuracy of the simulation and reduce the computational time devoted to them. They have analytical expressions that can be found in the literature for each atom and position [5].

As the crystal has its atoms repeated periodically in space, the electrons will feel a periodic potential and this property will then translate itself into the wave function. We could then apply Bloch's theorem to each electronic wave function. As we know, Bloch's theorem implies that in solids that present periodicity, each wave function could be constructed by a product between a plane wave and a periodic function with the periodicity of the crystal. This wave function could be expressed as it follows:

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

where the sum runs for all the reciprocal lattice vectors \mathbf{G} , n is the electronic

band number and \mathbf{k} refers to a vector in the first Brillouin zone that identifies the state. To simplify the problem of computing all these wave functions we can take into account that the electronic wave functions that are close to each other are almost identical, consequently we can restrain ourselves to methods that use only a finite small number of \mathbf{k} points, called “special \mathbf{k} -points” within the Brillouin zone. One of these methods is the Monkhorst-Pack scheme which is the one that was implemented on the simulations. The reason behind it was that for semiconductors such as the zinc selenide (ZnSe), which was the material that was actually researched on this project, this method would only require just a few special \mathbf{k} points to simulate it correctly as we will discuss later in future sections.

Nonetheless, the plane wave series for a certain \mathbf{k} point would still be infinite but we can truncate it to a finite number due to the fact that the coefficients $C_{n,\mathbf{k}+\mathbf{G}}$ are more important for plane waves with small kinetic energy, $\frac{\hbar^2}{2m_e}|\mathbf{k} + \mathbf{G}|^2$ than at higher energies, so it is possible to just include these more important terms and ignore the others by cutting the series with the condition:

$$\frac{\hbar^2}{2m_e}|\mathbf{k} + \mathbf{G}|^2 < E_{cutoff}$$

This defines a cutoff energy E_{cutoff} that must be adjusted by analyzing and reducing the error that it introduces on the simulations. A higher cutoff energy will produce a higher convergence on the sum of the plane waves. We will explain this in further detail in future sections as this was part of the initial research.

After the special \mathbf{k} points and the cutoff energy E_{cutoff} have been carefully selected, we could finally solve the Kohn-Sham equations with a self-consistent method. Firstly, we must choose the pseudopotential V_{eff}^{pseudo} determined by the type of atoms and their positions in the crystalline grid, but we must also make an initial guess for the electronic density $n_{in}(\mathbf{r})$ that we want to introduce in the equations through the calculation of the effective potential. We then solve the Kohn-Sham equations with computational methods and we obtain the eigenstates that will allow us to obtain a new electronic density $n_{out}(\mathbf{r})$, which we will use as the new $n_{in}(\mathbf{r})$ that will be utilized to solve the equations again. After several times repeating this process, we should reach self-consistency between the $n_{in}(\mathbf{r})$ and $n_{out}(\mathbf{r})$ and we could use this

solution as our electronic density from which we could calculate the system properties.

Nevertheless, after obtaining the self-consistency value of $n(\mathbf{r})$, we should check if the results corresponds to the optimized relaxed geometry of the crystalline structure, which would require that the forces on the atoms must be zero. We can obtain this forces through the Hellmann-Feynmann theorem [6] and if they do not correspond to the relaxed structure, a minimization algorithm that changes the atomic positions would be required just before repeating the process again.

1.4 Phonons

After having obtained the relaxed structure with DFT, we can now shift to study the vibrational properties of the crystal. Many physical characteristics of the system respond to the microscopic vibrations inside it, specially related to thermal, electrical and mechanical behaviours.

To study these properties in detail, let us consider an infinite periodic crystal with N (typically in the order of Avogadro's number) unit cells and n atoms per cell. The j atom in the cell, characterized by a certain lattice vector \mathbf{L} (represented by the lattice index L), will vibrate around the equilibrium position $\mathbf{r}_0(jL)$, so we could define its displacement vector as:

$$\mathbf{u}_{jL} = \mathbf{r}_{jL} - \mathbf{r}_{0jL}$$

This allows us to define a set of $3nN$ atomic coordinates. We could then expand the total energy of the crystal in a Taylor series using the atomic displacements around the equilibrium geometry. As this geometry is the most stable, dynamically talking, it will produce a minimum for the total energy and consequently, the first order term on the Taylor expansion will be zero.

$$E = E_0 + \frac{1}{2} \sum_{jj'LL'} \mathbf{u}_{jL}^T \mathbf{D}_{jLj'L'} \mathbf{u}_{j'L'} + \dots$$

E_0 is the static energy at the equilibrium (we will consider this as the zero

pressure value), \mathbf{u}_{jL}^T is the transpose of \mathbf{u}_{jL} and $\mathbf{D}_{jLj'L'}$ is the 3x3 matrix that contains the second derivatives of the energy with respect to the atomic displacements \mathbf{u}_{jL} and $\mathbf{u}_{j'L'}$ of the atoms, which could be represented by:

$$(\mathbf{D}_{jLj'L'})_{\alpha\beta} = \frac{\partial^2 E}{\partial(\mathbf{u}_{jL})_{\alpha} \partial(\mathbf{u}_{j'L'})_{\beta}}$$

where α and β run over the cartesian coordinates (x , y and z).

From now on, we will adopt an harmonic approximation, which considers that the atoms inside the crystal vibrate inside an harmonic well around fixed positions. In practice, this means that this energy expansion must be truncated on second order. Therefore, it can be shown that the equation of motion for each atom will be given by:

$$m_j \frac{d^2 \mathbf{u}_{jL}}{dt^2} = \mathbf{F}_{jL} = - \sum_{j'L'} \mathbf{D}_{jLj'L'} \mathbf{u}_{j'L'}$$

where m_j is the mass of the j atom, and \mathbf{F}_{jL} is the force acting over the atom on the jL position. There will be $3nN$ equations of motion, one for each cartesian coordinate for each atom. If we impose boundary conditions for this system, it could be shown that the solutions will have the form of plane waves, where there would exist a \mathbf{k} index, which would represent a \mathbf{k} vector of the first Brillouin zone:

$$\mathbf{u}_{jL} = \boldsymbol{\varepsilon}_{\mathbf{k}\nu j} e^{i(\mathbf{k}\mathbf{L} - \omega_{\mathbf{k}\nu} t)}$$

For a periodic system with N primitive cells, there would be N permissible \mathbf{k} vectors that could be used as solutions of the equation of motion. However, we must also introduce a ν index that allows us to counter the number of solutions for a given \mathbf{k} vector, and it will run from 1 to $3n$. $\boldsymbol{\varepsilon}_{\mathbf{k}\nu j}$ is the displacement vector and it shows the space direction for the propagation of the wave of collective atom displacements.

This atomic vibrational waves showed by this last equation is what we call *phonons*, which are usually represented by their wave frequencies $\omega_{\mathbf{k}\nu}$. Phonons are also considered to be quasiparticles that carry the vibrational energy and the vibrational momentum through the crystal.

We will now substitute this last solution into the equation of motion for the atomic displacements in $\mathbf{L} = 0$ (reference unit cell). This will result in:

$$m_j \omega_{\mathbf{k}\nu}^2 \boldsymbol{\varepsilon}_{\mathbf{k}\nu j} = \sum_{j'} \left(\sum_{L'} \mathbf{D}_{j0j'L'} e^{i\mathbf{k}\mathbf{L}'} \right) \boldsymbol{\varepsilon}_{\mathbf{k}\nu j'}$$

Next, we must apply a transformation in order to remove the atomic masses from the equation. We define $\boldsymbol{\eta}_{\mathbf{k}\nu j}$ as:

$$\boldsymbol{\varepsilon}_{\mathbf{k}\nu j} = \frac{1}{\sqrt{m_j}} \boldsymbol{\eta}_{\mathbf{k}\nu j}$$

This allows us to replace the matrix on the right hand side of the equation of motion with:

$$\mathbf{D}_{jj'}(\mathbf{k}) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{L'} \mathbf{D}_{j0j'L'} e^{i\mathbf{k}\mathbf{L}'}$$

resulting in the equation:

$$\omega_{\mathbf{k}\nu}^2 \boldsymbol{\eta}_{\mathbf{k}\nu j} = \sum_{j'} \mathbf{D}_{jj'}(\mathbf{k}) \boldsymbol{\eta}_{\mathbf{k}\nu j'}$$

All of the 3x3 matrices for the n atoms in the unit cell can be collected to form a square $3n \times 3n$ matrix $\mathbf{D}(\mathbf{k})$. This matrix is called the *dynamical matrix* and its Fourier transform to real space would result in a matrix really similar to the second derivatives matrix $\mathbf{D}_{j0j'L'}$ but weighted on the atomic masses. This real matrix is called the *force-constant matrix*:

$$\mathbf{C}(\mathbf{L})_{j\alpha j'\beta} = \frac{1}{\sqrt{m_j m_{j'}}} \frac{\partial^2 E}{\partial(\mathbf{u}_{j0})_\alpha \partial(\mathbf{u}_{j'L'})_\beta}$$

We will then merge all the atomic coordinates in the displacement vector $\boldsymbol{\eta}_{\mathbf{k}\nu}$. This will result in the eigenvalues equation:

$$\omega_{\mathbf{k}\nu}^2 \boldsymbol{\eta}_{\mathbf{k}\nu} = \mathbf{D}(\mathbf{k}) \boldsymbol{\eta}_{\mathbf{k}\nu}$$

This eigenvalues equation allows us to diagonalize the dynamical matrix which will result in the calculation of the phonon frequencies $\omega_{\mathbf{k}\nu}$ and the eigenvectors $\boldsymbol{\eta}_{\mathbf{k}\nu}$, which are called the polarization vectors or normal modes. Therefore, we have modeled the vibrational properties of the system by a set of normal modes that represent all the vibrations in the inside of the crystalline structure. Actually, we have also improved our model by introducing the microscopic effects of the temperature in the system, as we should not forget that the adiabatic approximation neglected the atomic cores movement, limiting the initial study to the $T = 0$ K case.

There are several computational methods to obtain the solution for the diagonalization of the dynamical matrix. This project employed the *frozen-phonon method*, also called the direct method, to study the frequencies of the phonons under different pressure conditions. We will develop this method in further detail in a later section.

1.5 Thermodynamic Properties

As we have already discussed, the crystal vibrations could be represented as a set of normal modes from harmonic oscillators, which could be interpreted as quasiparticles called phonons. It is a well known fact that phonons are particles with an integer spin quantum number, therefore, phonons are boson particles and we could modelize the crystal as a Bose-Einstein gas and apply the knowledges from statistical mechanics to obtain the thermodynamical properties.

Bose-Einstein gases satisfy the property that there is no limitation on the number of particles that could be asociated with a determined quantum state. If we define the number of occupation $n_{\mathbf{k}\nu}$ as the number of bosons that, in this case, have the same energy $\hbar\omega_{\mathbf{k}\nu}$, then we could express the total vibrational energy for a certain j quantum-mechanical state configuration of the system as:

$$E_{vib,j} = \sum_{\mathbf{k}\nu} \left(n_{\mathbf{k}\nu} + \frac{1}{2} \right) \hbar\omega_{\mathbf{k}\nu}$$

The index j will define all the different possible quantum-mechanical configurations for the system. This allows us to obtain the canonical ensemble partition function as the sum:

$$\mathcal{Z} = \sum_j e^{-\beta E_{vib,j}}$$

where:

$$\beta = \frac{1}{K_B T}$$

If we consider E_0 as the total ground state of the system, then it is easy to show that:

$$\mathcal{Z} = e^{-\beta E_0} \prod_{\mathbf{k}\nu} z_{\mathbf{k}\nu}$$

This means that the canonical ensemble partition function can be separated into a product of individual normal modes contributions $z_{\mathbf{k}\nu}$, defined as the convergent sum:

$$z = \sum_{n=0}^{\infty} e^{-\beta \hbar (n+1/2)\omega} = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}}$$

from which:

$$-\ln \mathcal{Z} = \beta E_0 + \sum_{\mathbf{k}\nu} \left[\frac{\beta \hbar \omega_{\mathbf{k}\nu}}{2} + \ln (1 - e^{-\beta \hbar \omega_{\mathbf{k}\nu}}) \right]$$

This allows us to calculate the Helmholtz free energy as:

$$F = -K_B T \ln \mathcal{Z} = E_0 + \sum_{\mathbf{k}\nu} \left[\frac{\hbar \omega_{\mathbf{k}\nu}}{2} + K_B T \ln (1 - e^{-\frac{\hbar \omega_{\mathbf{k}\nu}}{K_B T}}) \right]$$

On the considered limit for the volume $V \rightarrow \infty$, the sum is replaced with an integral of the phonon density of states $g(\omega)$:

$$F = E_0 + \int_0^\infty \left[\frac{\hbar\omega}{2} + K_B T \ln(1 - e^{-\frac{\hbar\omega}{K_B T}}) \right] g(\omega) d\omega$$

We should not forget that the phonon density of states is normalized on $3nN$:

$$\int_0^\infty g(\omega) d\omega = 3nN$$

We have finally obtained our theoretical model. After calculating the phonons, the computational tools that were used on this project allowed the obtainment of the phonon density of states from the dispersion curves.

Therefore, all thermodynamic properties could be obtained from the Helmholtz free energy F through derivatives. The entropy of the system satisfy:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V$$

The total internal energy could then be trivially calculated through:

$$U = TS + F$$

Another magnitude that we should take into account would be the heat capacities at constant volume. This quantity can be estimated through:

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

2- Objectives

This work has the purpose of learning the use of quantum computational simulation techniques, similar to those described in the previous section, to predict the vibrational and thermodynamical properties of a selected material.

The chosen system for this research was the zinc selenide ZnSe semiconductor, which adopts a crystalline zincblende structure that belongs to the space group 216 F-43m at normal conditions. It is widely used in the construction of certain light emitting diodes due to the possibility to control dynamically its electric conductance, but it is also used for the construction of optical lens, as it presents transparency for the infrared range, which also makes it a relevant material on infrared spectroscopy.

Using VESTA, a tridimensional visualization program that could be applied for obtaining structural models and crystalline morphologies, we get a visual model of the ZnSe structure:

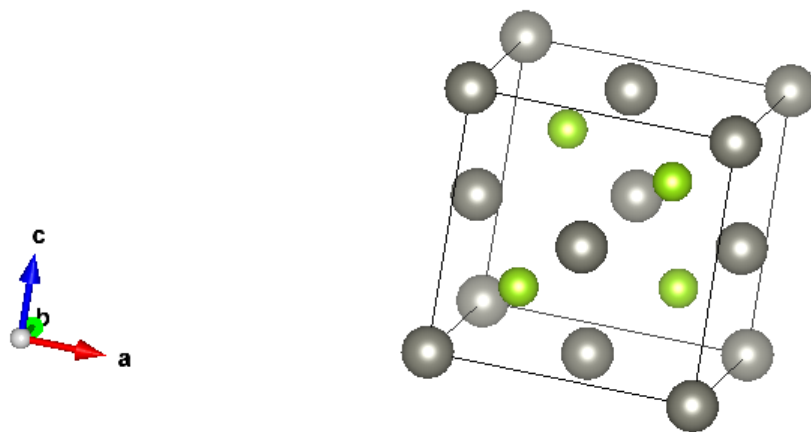


Figure 1: ZnSe zincblende structure.

where the gray spheres represent the zinc atoms and the green ones represent the selenium atoms.

3- Methodology

3.1 Procedure description

The first step of the research was to find the parameters for the relaxed structure of the ZnSe at temperature $T = 0$ K and pressure $P = 0$ GPa. This was achieved by the use of the *Vienna Ab-initio Simulation Package* (VASP), a software that allows first principles studies for materials by applying DFT and the pseudopotentials theory. This simulation package allows us to use a plane wave basis set for the quantum-mechanical description of the material researched. There is more information about VASP on its website [7].

In a summarized way, VASP performs the quantum-mechanical simulations after the configuration of four files:

1. POSCAR file: this is the file that contains the structure of the material that is being researched. This could be generated from a .cif file obtained from the ICSD data base via VESTA.
2. POTCAR file: this is the file that contains the pseudopotentials which describe the atoms in the POSCAR.
3. KPOINTS file: this file gives the integration grid for the integrals that VASP must perform on the first Brillouin zone, which are approximated by a set of special \mathbf{k} points, as it was explained in previous sections.
4. INCAR file: this is the file which contains all the instructions and information about the parameters of the simulation that VASP is about to carry out. This allows us to set the convergence energy criteria, the type of GGA that we want to apply to our simulation, the energy cutoff, etc.

Therefore, the starting point for the simulation would be a set of data about the structure that, for simplicity, will be experimental values for the material that could be found in the ICSD data base [8]. The cell that was used was the cubic primitive cell for the ZnSe, and its volume could easily be calculated through $V = a^3/4$, being a the lattice parameter of the grid. This primitive cell has two atoms, where the Zn atom will be in position $(0, 0, 0)$ and the Se atom will be in position $(1/4, 1/4, 1/4)$.

The procedure to obtain the relaxed structure was very simple. This consisted of compressing the cell at different pressures, through the selection of different volumes. VASP would then apply its algorithms to resolve the system and would give back the values of volume, ground state energy and pressure associated with each compression. The relaxed structure volume could then be estimated as the case associated with the approximated zero value for the pressure which, by the way, it would display the minimum energy for the system. This process was preceded by an initial study on the convergence with different values for the cutoff energy and \mathbf{k} points. This is explained in further detail in the next subsection, which verses about the computational details that were taken into account for the simulations.

After the relaxed volume was obtained, the next step was to find the phonons through the frozen-phonon method. This procedure allows us to obtain the frequencies of the phonons from the relaxed structure by applying small displacements on the atoms, then calculating the forces associated with every frozen configuration through the Hellmann-Feynmann theorem and finally diagonalizing the resulting dynamic matrix associated to the resultant forces. This method is applied with the *phonopy* package [9].

However, the primitive cell (1x1x1 supercell) does not allow us to find the phonons in all the points of the reciprocal space, it just gives the values for the Γ point. This will result in the need to apply larger supercells to have a bigger picture. In this case, a 2x2x2 supercell was applied to the system with the same initial conditions. As the displacement of the 16 atoms that constitute this supercell have the positive and negative orientations for the three space directions, symmetry properties were incorporated to the algorithm as a way of reducing the number of simulations and the computational time required.

With the dynamical matrix, the PHONON software [10] would then diagonalize it and give back the frequencies of the phonons, the dispersion curves and also the partial and total phonon density of states $g(\omega)$. This process was repeated for different values of the pressure, including high pressure values up to 12 GPa as it would allow us to then fit the results with a polynomial, that would give us the variation of the phonon frequencies with the pressure.

As it was previously discussed, the phonon density of states would then allow us to obtain the thermodynamic properties such as the internal energy U , the entropy S , the Helmholtz free energy F and the heat capacity C_v with their variations with the temperature T . This procedure was repeated for

different values of pressure P and the results obtained were compared in plotted graphs.

3.2 Computational details

We will take a moment to specify and review all the characteristics employed by the simulations. As it was mentioned earlier, the INCAR and KPOINT files control many of their parameters. At the beginning of the research, it was crucial to analyze the convergence with respect to the cutoff energy and the number of \mathbf{k} points. This was done by obtaining the energies of the ground state for two different volumes and then analyzing how the energy difference for those two configurations evolve with the cutoff energy or with the number of \mathbf{k} points selected. This was actually plotted on graphs:

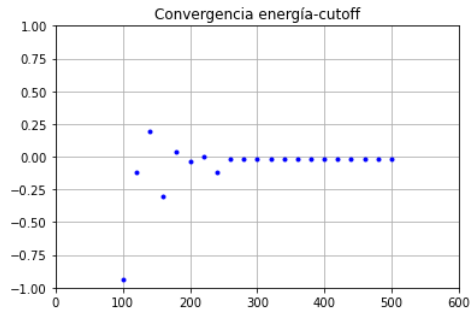


Figure 2: Energy difference with the cutoff energy.

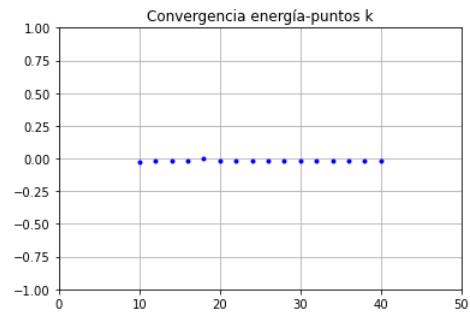


Figure 3: Energy difference with the number of \mathbf{k} points.

As it is shown on the graphs, we can assure that the convergence is reached up to 300 eV for the cutoff energy and 20 for the number of special \mathbf{k} points.

Therefore, the energy cutoff selected for the rest of the study was set to 400 eV and the number of \mathbf{k} points was set to 20, which is associated to the $6 \times 6 \times 6$ grid configuration. For both of this parameters, we obtain a highly accurate convergence of 1 meV.

After obtaining the relaxed structure, it satisfied that the forces on the atoms were less than 10^{-6} eV/Å. Also, the exchange-correlation energy was described in the GGA approximation with the Armiento-Mattson (AM05) functional. This gave more accurate results for the simulations than the Perdew-Burke-Ernzernhof (PE) functional and the Perdew-Burke-Ernzernhof prescription for solids (PS) functional, al least with respect to the experimental value that was provided.

4- Results Discussion

4.1 Crystalline relaxed structure

The first set of results were the crystalline relaxed structure parameters. After the first simulations were carried out, I was able to obtain a value for the equilibrium volume, which could be compared with the one given in the literature. Both quantities are given in this next table, along with the lattice parameter associated to it. It must be noted that the literature provides the X-ray diffraction experimental value $a = 5.668 \text{ \AA}$ for the unit cell [11]. The primitive cell is four times smaller than the unit cell (ZnSe is a face centered cubic structure) so its volume would be $V_p = a^3/4 = V_u/4$. This allows us to obtain the volume of the simulated unit cell as $V_u = 4V_p = 180.800 \text{ \AA}^3$.

	Experimental data	Simulation data
Volume (\AA^3)	180.091	180.800
a (\AA)	5.668	5.655

Table 1: Simulated values against experimental values for the volume of the unit cell and the lattice parameter.

As we can see, both values are very close to each other. This reveals to us that the simulation that was performed with DFT was really accurate, so our model hypothesis fits well to the reality.

4.2 Phonons at zero pressure

After simulating the small displacements on the atoms and diagonalizing the dynamical matrix with a 2x2x2 supercell, we obtain the values for the phonon frequencies on Brillouin's Γ point, along with the density of states and the dispersion curves.

Table 2 presents the different phonons that appear at Γ point and at zero pressure. As we can see, the system presents three acoustic phonons (TA) which are theoretically zero on this zone center as well as three transversal optical phonons (TO) with the same frequency. The simulation also gives the irreducible representations of the phonons which are in concordance with the

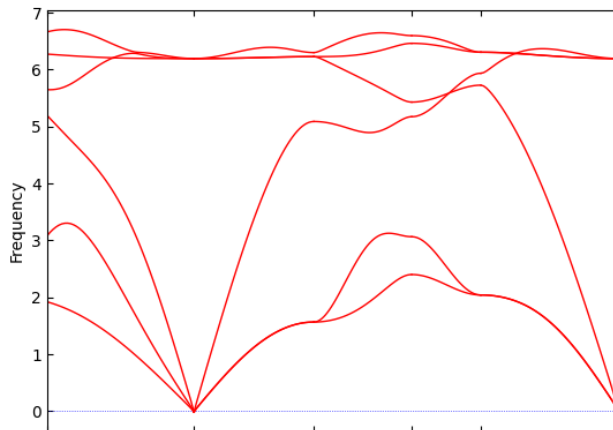


Figure 4: Dispersion relations for ZnSe at $P = 0$ GPa.

theoretical results. This could be checked up on the Bilbao Crystallographic Server [12]. The dispersion curve associated with these results is displayed in Figure 4, where the frequencies values are given in THz, but could be transformed to cm^{-1} through the relation $1 \text{ THz} = 33.356 \text{ cm}^{-1}$.

While this has allowed us to obtain a first view on the phonon frequencies, the optical phonons appear triply degenerate where, in reality there exist two different values for the optical frequencies on the neighborhood of Γ , the transversal optical (TO) phonon being doubly degenerate, as well as the longitudinal optic (LO) phonon that is not degenerate and have higher energy than the TO phonons. The reason behind this inability to visualize the LO-TO splitting is the existence of the large range Coulomb potential, which goes with $1/r$, so its Fourier transform goes with $(4\pi)/k^2$, which diverges for $\mathbf{k} \rightarrow 0$ (Brillouin's Γ point). This could be solved up by introducing

Type	Degeneracy	Frequency (cm^{-1})	Irreducible representations
TA	3	0	T2 (Raman/Infrared)
TO	3	206.574	T2 (Raman/Infrared)

Table 2: Phonons for ZnSe at Γ point for $P = 0$ GPa.

the *non-analytical corrections* (NAC), which would allow us to obtain this splitting on a very close region to Γ . To apply these corrections, it was necessary to obtain the Born effective charges, as well as the dielectric constant. The effective charges are the net positive charges that electrons feel due to the screening effect that the internal electrons produce in the electrostatic interaction with the atomic core. It is defined as $Z^* = Z - S$, where Z is the atomic number and S the screening constant [13]. These effective charges and the dielectric constant were estimated by analyzing how the system does respond to an electric field and their values for the zero pressure case are displayed on Table 3. The results obtained for the LO-TO frequencies are summarized in Table 4, and the dispersion relations with the LO-TO splitting are displayed in Figure 5.

Born charge 1	Born charge 2	Dielectric constant
2.152	-2.152	8.788

Table 3: Born effective charges and dielectric constant for $P = 0$ GPa.

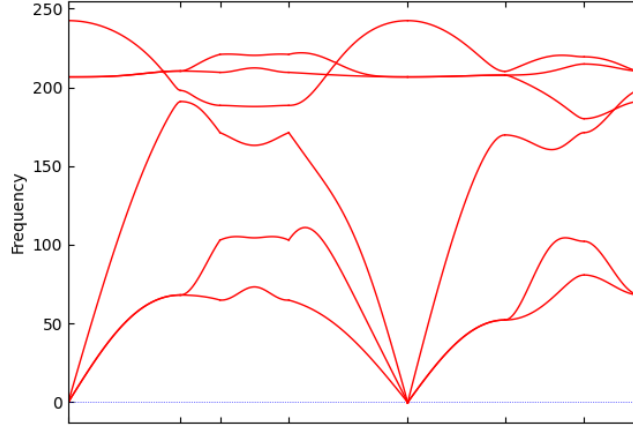


Figure 5: Dispersion relations for ZnSe at $P = 0$ GPa with LO-TO splitting.

Type	Degeneracy	Frequency (cm^{-1})	Irreducible representations
TA	2	0	A1 (Raman/Infrared)
LA	1	0	E (Raman/Infrared)
TO	2	206.574	A1 (Raman/Infrared)
LO	1	242.298	E (Raman/Infrared)

Table 4: Phonons for ZnSe with LO-TO splitting at Γ for $P = 0$ GPa.

There are other results that have been estimated with the simulation. The partial density of states is shown in Figure 6, where the atom 1 represents the zinc and the atom 2 is the selenium. Figure 7 gives us the density of states of the complete compound.

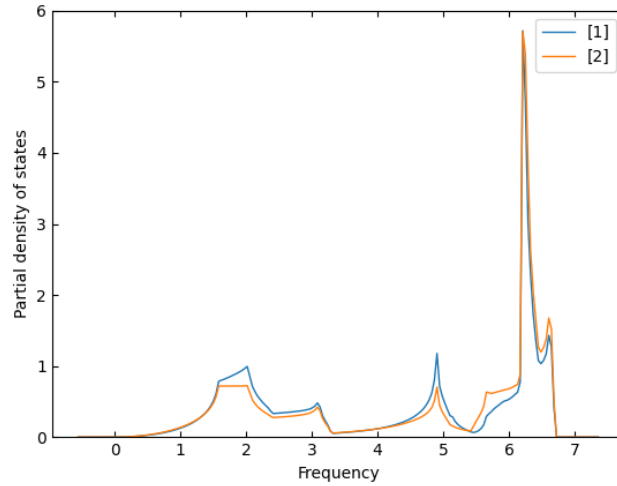


Figure 6: Phonon partial density of states for the ZnSe at $P = 0$ GPa.

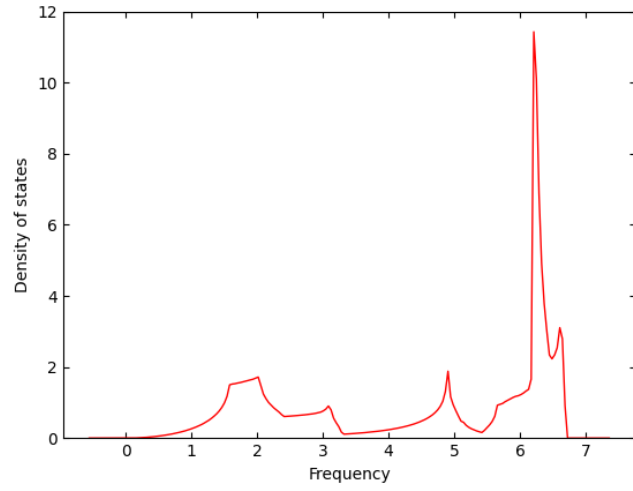


Figure 7: Phonon total density of states for the ZnSe at $P = 0$ GPa.

4.3 Phonons at higger pressures

Next, we will analyze how the phonon frequencies evolve with different pressure conditions. This is an interesting research that occasionally could predict heavy changes for the materials, for instance, a change of phase, although this does not occur within the range of pressures considered in this research. Furthermore, many of the pressure values that we are considering are really difficult to obtain on a laboratory, so the only practical way to analyze the system under this type of extreme conditions is through the simulations.

The calculations that were performed involved obtaining the phonons in Γ on every 1.5 GPa jump of pressure, up to the $P = 12$ GPa value. The LO-TO splitting was specifically considered on this case. Therefore, I obtained the ω_{LO} and the ω_{TO} frequencies for every value of pressure and plotted them against it, before fitting the data with a second grade polynomial $\omega = aP^2 + bP + c$.

The graphs are displayed on Figures 8 and 9. As it could be checked numerically, the bent factor for the polynomial was very low for both cases ($a = -0.093 \text{ cm}^{-1}/\text{GPa}^2$), and it approximately takes the form of a straight line. Consequently, the b coefficient gives us how the frequencies of the vibration changes with the pressure. This is an interesting result as there exist a certain parameter proportional to this derivative that specifies how the vibrational properties of the system changes with the volume. This quantity is called the Grüneisen parameter (γ_{th}) [14]. The values obtained from the simulation are:

$$b_{LO} = \frac{d\omega_{LO}}{dP} \approx 5.092 \text{ cm}^{-1}/\text{GPa} \quad b_{TO} = \frac{d\omega_{TO}}{dP} \approx 5.617 \text{ cm}^{-1}/\text{GPa}$$

This two values are in concordance with the values on the literature. For the LO phonon, it can be found a slightly shifted value of $5.6 \text{ cm}^{-1}/\text{GPa}$ [15], while for the TO phonon, there exist a value of $5.5 \text{ cm}^{-1}/\text{GPa}$ [15] that is almost identical to the simulated value.

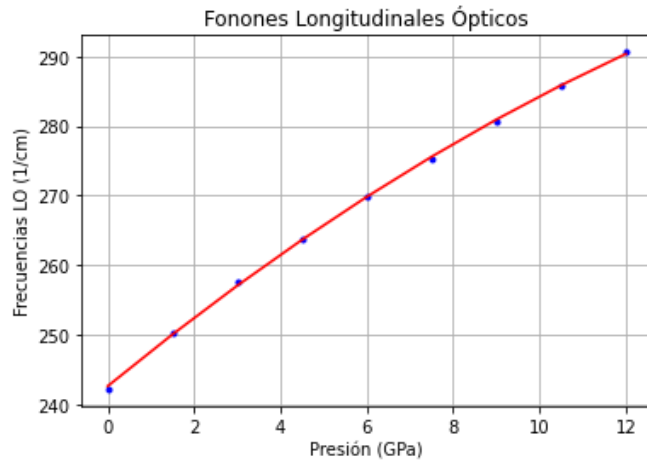


Figure 8: LO phonons frequency change with the pressure in Γ .

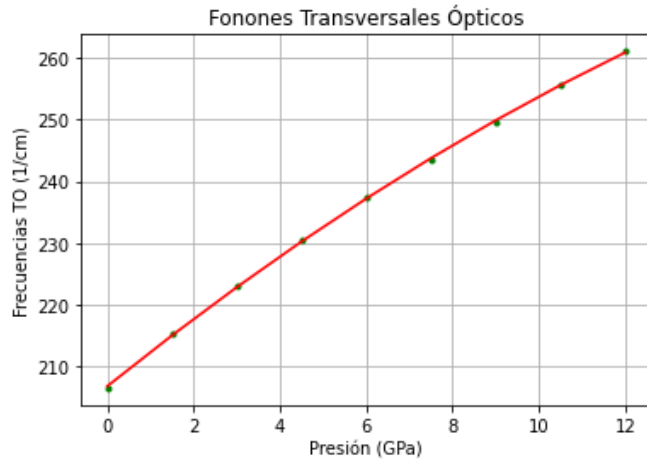


Figure 9: TO phonons frequency change with the pressure in Γ .

4.4 Thermodynamic properties

Finally, from the results achieved for the phonons, the obtainment of the thermodynamic properties of the system is trivial. Graphs for the Helmholtz free energy (Figure 10), the entropy (Figure 11), the internal energy (Figure 12) and the heat capacity (Figure 13) were plotted for different values of pressure. These properties appear represented against the spectrum of temperatures up to 1000 K.

There are several universal physical results perfectly outlined on this figures. We immediately recognize the typical form for the entropy of a system which decreases with lower temperatures and satisfy the *third law of thermodynamics* ($S \rightarrow 0$ if $T \rightarrow 0$). This is justified in the fact that, as the entropy is a measure of the amount of microscopic configurations that are compatible with the system macroscopic configurations, if there only exist one ground state for the system at $T = 0$ K, then the entropy must be null for that case. Actually, this is also represented in the internal energy graph. In the $T \rightarrow 0$ region, the energy tends to the non degenerate ground state value E_0 , which is a natural consequence in quantum mechanics.

Another law that is definitely outlined is the *Dulong-Petit law*. If we examine the heat capacity, we can identify the $T \rightarrow 0$ case, were it satisfies that $C_v \rightarrow 0$, but if we focus on the higher temperature limit, we obtain a convergence to the value $49.65 \text{ J/K/mol} \approx 6R$, with R being the ideal gas constant. This is a clear manifestation of the Dulong-Petit law, as the heat capacity of all physical systems converge to a certain factor of the R constant, that is related to the number of degrees of freedom for the constituents of the system. In the case of ZnSe, there are two different atoms, each with three degrees of freedom, so it is not surprise that the factor that multiplies R match the six total degrees of freedom on the primitive cell of the crystal.

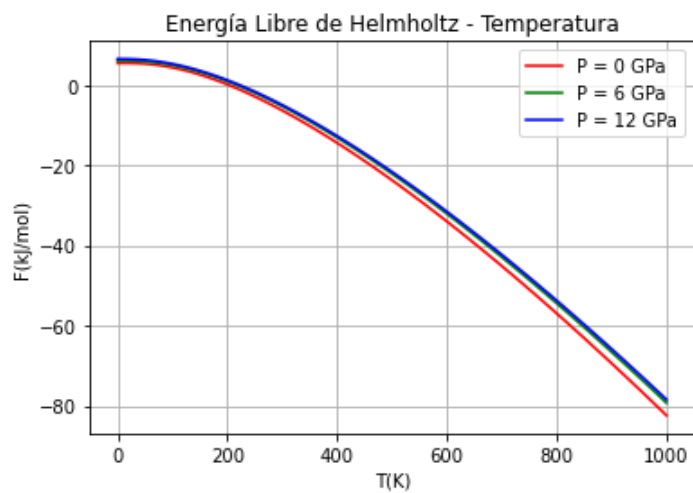


Figure 10: Helmholtz free energy for the ZnSe.

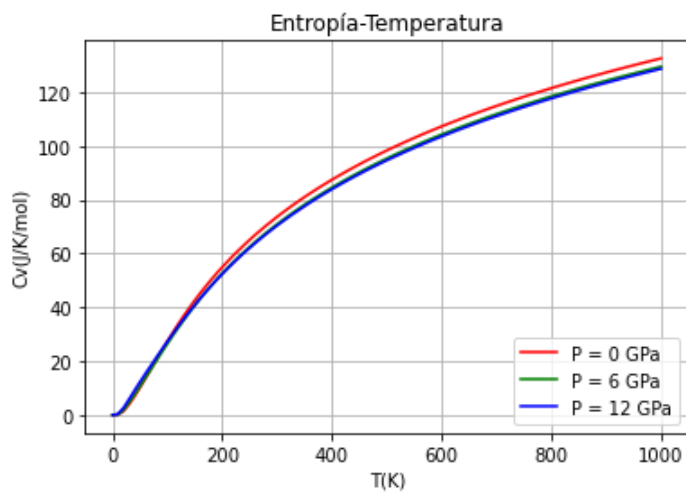


Figure 11: Entropy for the ZnSe.

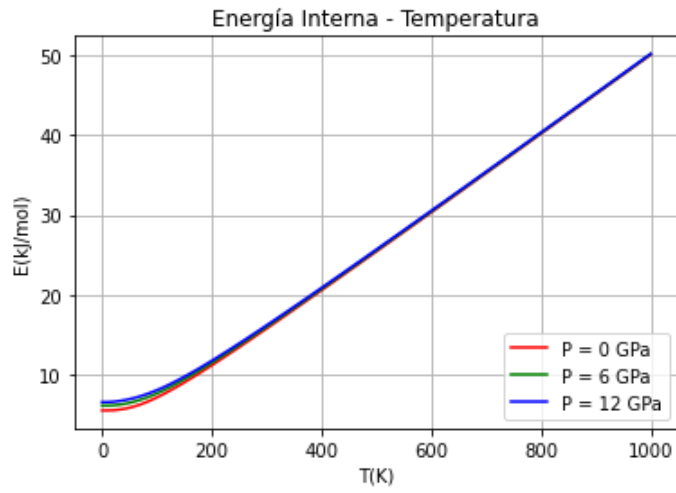


Figure 12: Internal energy for the ZnSe.

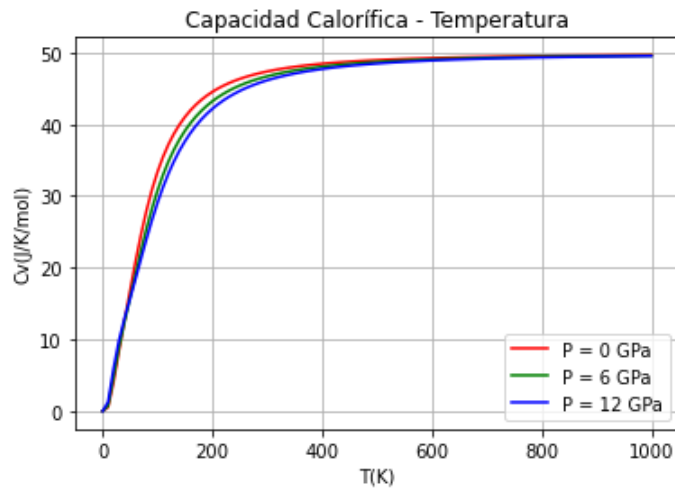


Figure 13: Heat capacity for the ZnSe.

5- Conclusions

We have seen that for a determined crystalline material as the ZnSe, we have been able to obtain its themodynamical properties through a quantum-mechanical perspective, in particular from a first principles perspective. What is more, we have even been able to visualize how a particular system as this semiconductor satisfy the well known universal third law of thermodynamics, as well as the Dulong-Petit law that characterizes the behaviour of the system at the high temperatures limit for any given value of pressure. Furthermore, we also obtained many of the microscopical vibrational properties of the crystal by studying the changes on the frequencies of the phonons with the pressure of the system.

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