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Quantum Nuclear Motion in Density Functional Theory

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Abstract

Ab-initio methods such as density functional theory (DFT) can accurately solve the many-body interactions of the electrons of up to hundreds of atoms. This has allowed for the prediction of material properties over a wide range of conditions. As DFT relies on the Born-Oppenheimer approximation, the motion of atomic nuclei must be solved for with additional calculations, as often done for in molecular dynamics simulations or the calculation of the phonon spectrum of a crystal structure. In this thesis, we will focus on the effects of quantum nuclear motion; in many systems, it is safe to assume the nuclei behave classically, however, the quantum nature of the nucleus becomes more significant as we look at systems with lower atomic mass, temperatures and pressures. In the extreme, this leads to novel phenomenon such as superfluids, but can also have significant effects even in semi-classical phases.

This thesis will detail a systematic study of these highly quantum materials using ab-initio techniques, with a particular focus on systems where quantum nuclear motion significantly affects a material’s equation of state (EOS). While it is common to include the zero-point energy calculations where relevant, we find that many ab-initio studies do not take into account the effect the zero-point contributions have on the pressure due to the extra calculations involved. While this effect is insignificant in most situations, under certain conditions with light elements, many important properties cannot be accurately calculated without considering it.

We first find the limits of the quasi-harmonic density functional perturbation theory (DFPT), in the highly quantum regime of low-pressure, < 1 GPa solid helium. We find that the systematic error due to the choice of functional is the limiting factor in the accuracy of the resulting equation of state. We attempt to account for the known an-harmonic properties of the He-He interaction with the Self-Consistent Ab-initio Lattice Dynamical
method (SCAILD) [1]), which assumes the system is at a temperature above the Debye limit. We found that this limited the method’s accuracy, as under 1 GPa the helium melt line is below the Debye limit. PIMD is a fully quantum mechanical approach to modelling nuclear motion, however, the computational expensiveness of this technique means a fully converged calculation is not possible. This investigation not only acts as a starting point for future DFT studies in low pressure helium but also serves as a test of these methods in a highly quantum regime.

Having established the highly quantum mechanical limit at low pressures, this sets the stage for answering open questions that have, until now, not been addressed in the literature involving H-He and Be-He systems.

Typically, simulations of H$_2$-He mixtures have focused on high pressures and temperatures due to the interest in planetary dynamics. In experiments at lower pressures, < 15 GPa, the vibrational frequency of hydrogen molecules has been observed to increase strongly with He concentration in H$_2$-He fluid mixtures. This has been associated with H-He interactions, either directly through chemical bonding [2], or indirectly through increased local pressure [3].

Here we demonstrate that coupling between hydrogen molecules in the pure hydrogen fluid decreases the frequency of the hydrogen molecule vibron and that the increase in the Raman frequency seen in the mixture is due to a decrease in the number of H$_2$ molecules participating in the mode. We find no evidence of chemical bonding between He and H atoms, with helium acting only to separate the hydrogen molecules. The variety of possible environments for H$_2$ gives rise to many Raman active modes, which causes the broadening of the vibron band. As the Raman active modes tend to be the lower frequency vibrons, these effects work together to produce the majority of the shift seen in experiment. DFT also reveals that the pressure in the H$_2$-He mixture is primarily due to quantum nuclear effects.

Another area of active research where quantum nuclear motion plays a significant role is in the formation of defects in the beryllium lattice. Beryllium’s interaction with both helium and hydrogen is of particular interest due to beryllium’s potential use as a key component in fusion reactors [4, 5, 6, 7, 8]. Due to the high neutron flux, radiation-induced defects appear in these metals. One example is voids created from vacancies which are a primary defect created by irradiation; Voids which are exposed to helium often form He bubbles, weakening the material [5, 9, 10, 11, 12]. Therefore, it is important to understand the mechanisms behind the nucleation of these bubbles.
While the current literature does include the zero-point energy contributions to defect formation [11, 13, 14, 15], by accounting for the zero-point contributions to the pressure, we are able to analyse how the behaviour of the defects change over a range of pressures up to 20 GPa. We calculate the enthalpy of formation and binding of a number of interstitial defects and vacancy structures. We find substitutional defects transition from binding to each other to repulsing at a pressure of \( \sim 18.6 \). To our knowledge, this change in behaviour has not been described in the literature and could be relevant to future studies looking to combat the formation of helium defects in beryllium.

Recent experimental studies have found evidence of beryllium hydride structures forming on the surface layer of beryllium crystals when they are bombarded with hydrogen isotope ions, but only above an areal density of \( 2.0 \times 10^{17} \text{cm}^{-2} \) [16, 17]. We performed the first ab-initio study into the interaction of complex beryllium hydride chains with the beryllium surface [18, 19, 20, 21], showing that these chains are unstable with respect to hydrogen atoms bound to the beryllium surface but stable with respect to free hydrogen molecules. Thus, these calculations predict, that while there are hydrogen absorption sites available, the beryllium hydride chains will be absorbed into the beryllium bulk. However, when the beryllium surface is fully saturated with hydrogen, the beryllium chains will spontaneously desorb from the beryllium surface. This provides a theoretical explanation for the formation of beryllium hydride crystals seen in experiments.
Lay Summary

Quantum mechanics is the physics of the small. Unlike in the classical physics we are used to in everyday life, a particle’s position and velocity cannot be exactly known. This means the nucleus of an atom trapped in place will always be in motion, even at zero Kelvin (K). This quantum nuclear motion has an associated energy we call zero-point energy. Pressure can be defined in terms of how much the energy of a system changes as the volume changes. In this thesis, we focus on the effect quantum nuclear motion has on pressure when calculating the properties of materials using Density Functional Theory (DFT).

DFT is a method by which we can efficiently calculate the interactions between the electrons of a group of atoms. This allows us to predict the properties of materials from first principles, simulating systems of over a hundred atoms. DFT is regularly used to simulate materials under conditions where the chemistry we are used to in our day-to-day breaks down, such as at extreme pressures, temperatures and magnetic flux. This allows for the identification of new materials and their potential use in new technologies. DFT is also vital to developing our understanding of extreme environments around us, such as those found in the interiors of planets throughout the universe, including our own. Many of the calculations carried out in this study will be in the gigapascal (GPa) range. This will include pressures similar to those of at the bottom of the Mariana Trench, which experiences pressures over a thousand times that of our atmosphere or \( \sim 0.1 \) GPa. Some calculations exceed pressures found at the centre of the earth, which is thought to experience around 350 GPa.

It is common for DFT studies to include calculations of the zero-point energy; however, they are less likely to include the effects of quantum nuclear motion on a system’s pressure. This is a perfectly reasonable thing to do in most situations, as the effect on pressure is small, and the additional calcula-
tions can be computationally expensive. However, quantum nuclear motion becomes increasingly significant as you look at systems with lower pressure, temperature and atomic mass. With this in mind, Chapter 3 of our study into quantum nuclear motion in DFT involves a methodological study of existing techniques. To do this, we use these techniques to calculate the relationship between the pressure, volume and energy, otherwise known as the equation of state (EOS), of helium at low pressures (< 1 GPa) and temperatures (< 10 K). We can then compare this with experimental measurements and quantify the limits of current techniques. Helium is the ideal test case as its low atomic mass and weak inter-atomic interactions mean that, under these conditions, its EOS is dominated by quantum nuclear effects. In this study, we find that systematic error due to the choice of functional (a parameterization of the DFT calculation) introduces uncertainty into the accuracy of DFT predictions. We also highlight the break down of certain methods that don’t use the quasi-harmonic assumption, which assumes that all interactions between atoms can be approximated as simple springs.

Having explored the limits of what is possible with DFT, we then apply these methods to other highly quantum systems, allowing us to address questions previously unexplored in the literature.

Chapter 4 describes calculations on hydrogen and helium under pressures of up to 15 GPa. These calculations were carried out with a focus on explaining two phenomenon seen in experimental measurements: evidence of chemical bonding between hydrogen and helium, and the unusual change in hydrogen molecule vibration seen in mixtures. Recent experiments have claimed to discover a new compound with chemical bonding between hydrogen and helium in the solid regime [2]. This would be a dramatic departure from the previously understood behaviour of hydrogen and helium, particularly because of the supposed chemical bonding between the elements. Our calculations find no evidence of chemical bonding or even mixing in the solid regime, supporting the hypothesis of other experiments suggesting that the signals seen in the original experiment can be better explained by nitrogen contamination rather than the formation of a new compound [22, 23].

Next, we investigate the vibration of the H$_2$ molecule in the H$_2$-He fluid regime. The frequency of the vibrating H$_2$ molecule is a unique signal often used to identify the different phases of hydrogen and its compounds. In H$_2$-He mixtures, this frequency has been found to depend on He concentration, increasing as the He concentration increases [2, 3, 22]. We are the first to reproduce this effect using DFT and explain the mechanism behind this be-
haviour. We find that in pure hydrogen, the oscillations of the H$_2$ molecules couple, which lowers the frequency of the oscillations. When introduced, helium atoms separate the hydrogen atoms, weakening the coupling between H$_2$ molecules and increasing the frequency of the oscillations. As this behaviour is not caused by a direct interaction between the H$_2$ molecules and the helium atoms, it could occur in any mixture or compound containing H$_2$ molecules. Now this mechanism is understood, the change in hydrogen signal can be used to identify these materials in experiment.

In Chapter 5, we look at helium defects in beryllium to understand how the zero-point contribution to pressure affects defects. Beryllium has been proposed as a key component of tritium breeding blankets which look to provide a source of tritium for future fusion reactors [4, 5, 6, 7, 8]. Fusion reactors are attempting to use the same process that fuels the sun to provide a cheap, clean energy source. The reaction works by fusing deuterium and tritium to produce helium and excess energy. While deuterium is easily accessible, tritium is more difficult to come by. Tritium breeding blankets aim to overcome this obstacle by reacting lithium-6 with the neutrons released by the fusion reactor to produce tritium on-site. The beryllium in the breeding blanket increases the number of neutrons which react with the lithium-6, however, in the process decays into helium isotopes. The formation of helium bubbles is one of the leading practical causes of degradation in the beryllium [5, 9, 10, 11, 12].

An accurate model of the behaviour of the helium defects is, therefore, an active area of interest. We carry out the first DFT study of the effects of pressure on helium defects in beryllium. As well as mapping out the change in formation cost up to 20 GPa, we find a dramatic change in the interaction between helium atoms trapped in vacancies. Below 18.6 GPa, these helium defects bind to one another contributing to the formation of helium bubbles, however, above this pressure, they repel. This is caused by the competition between the crystal attempting to maximise the number of Be-Be bonds, pushing the defects together, and trying to minimise the volume, driving them apart. We also show that the inclusion of zero-point contributions to the pressure strongly influences the calculated binding strength. Highlighting the importance of accounting for all effects of quantum nuclear motion. This discovery opens up a possible method of combating the formation of helium bubbles in the beryllium lattice.

As beryllium is a candidate for the plasma-facing layer of the tritium breeding blanket, the interaction of the beryllium surface with hydrogen and
its isotopes is another area of active research. Hydrogen readily binds to absorption sites on the beryllium surface [12, 24, 25, 26, 27, 28, 29], making the rate at which hydrogen isotopes escape the beryllium bulk a non-trivial question. Experiments that simulate the environment in the fusion reactor core have found that deposits of beryllium hydride crystals begin to form when the beryllium surface is bombarded with deuterium ions. These crystals are only seen above a certain ion flux and act to decrease the rate at which hydrogen ions escape the beryllium bulk, lowering the efficient of the tritium breeding blanket. Motivated by this, we simulate the interaction of beryllium hydride molecules with the beryllium surface. We find that the most energetically favourable configuration is for hydrogen ions to be absorbed on to the beryllium surface. However, once the beryllium surface is saturated with hydrogen ions, the beryllium hydride molecule is the next most energetically favourable configuration. This suggests that they will spontaneously form after all hydrogen absorption sites are occupied. We can therefore understand that the formation of beryllium hydride deposits seen in the experiment is the result of the saturation of the beryllium surface with hydrogen ions.
Declaration

I declare that the thesis has been composed by myself and that the work has not been submitted for any other degree or professional qualification. I confirm that the work submitted is my own, except where work which has formed part of jointly-authored publications has been included. My contribution to this work and those of the other authors have been explicitly indicated below. I confirm that appropriate credit has been given within this thesis where reference has been made to the work of others.

The work presented in Chapter 4 was previously published in Physical Review B as Localization effects on the vibron shifts in helium-hydrogen mixtures by Sam B. Ramsey, Miriam Pena-Alvarez, and my supervisor Graeme J. Ackland. This study was conceived by all of the authors. I, Sam B. Ramsey, carried out all density functional theory calculations and the analysis of the results.
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Chapter 1

Introduction

Density functional theory is a technique which provides an accurate approximation of the quantum mechanical effects of electrons’ behaviours in atomic systems whilst being efficient enough to allow for large-scale, > 100 atom, simulations to be carried out. These two properties make it perfect for simulating high-pressure systems where unfamiliar electronic properties can occur and large simulation cells are needed to understand complex structural behaviours. For elements with lighter atomic nuclei, such as hydrogen and helium, quantum nuclear effects can become significant. Whilst DFT does not account for quantum nuclear motion, standard techniques used to calculate phonon behaviour can capture these effects. However, we find that many ab-initio studies do not consider the effect the zero-point contributions have on pressure. In this study, we will look to address this gap in the literature by focusing on systems where quantum nuclear motion contributes significantly to the equation of state of a material.

We start with a methodological study which probes the current limits of ab-initio techniques in modelling these quantum materials. Due to the combination of its weak inter-atomic interaction as well as its low mass, helium’s EOS is particularly sensitive to contributions due to quantum nuclear motion. To date, no ab-initio studies have been carried out in the low-pressure, < 1 GPa, solid helium phase. Therefore, our investigation of this phase will act as an ideal test case for the limits of ab-initio techniques in these highly quantum materials and expand the current phase space probed by ab-initio methods. This allows us to use these techniques to address open questions that exist in the literature. We will demonstrate how proper modelling is necessary to calculate the properties of these quantum materials.
In the following chapters, we will show how this can influence calculations ranging from phonon behaviour, enthalpy of mixing, defect formation and binding energies. The first highly quantum system we expand these methods to will be hydrogen-helium mixtures. Much of the studies which exist in the literature on hydrogen-helium mixtures focus on pressures and temperatures relevant to the Jovian planets. As such, there is a lack of ab-initio studies which address behaviour in lower pressures, < 15 GPa, where the quantum nuclear motion dominates. We will show that ab-initio techniques can accurately reproduce experimental results in this regime. This allows us to address, until now, unexplained Raman signal behaviour seen in experiments [2, 3, 22], and provide insight into recent claims of hydrogen-helium chemical bonding seen in experiments [2].

Next, we look at the formation and behaviour of helium defects in the beryllium lattice. By using the methods developed in previous chapters, we expand our understanding of the behaviour of these helium defects up to a pressure of 20 GPa. Motivated by experimental measurements of beryllium hydride deposits on the beryllium surfaces [16, 17, 30] in high hydrogen ion flux environments, we carried out the first ab-initio simulations of complex beryllium hydride chains with beryllium surface. We produce a description of the absorption and desorption of these molecules with the (0001) crystal surface.

In Chapter 2, we carry out a comprehensive review of the existing literature. Establishing the current state of the art in ab-initio techniques and covering the primary computational methods that will be relied on in the subsequent chapters. This also includes discussions on the experimental methods used to create the extreme conditions that are of interest to the condensed matter community, as well as the types of measurements that experimentalists can take. These are the experimental measurements we will both attempt to explain and use to evaluate our calculations’ accuracy. We then move on to outlining the current areas of active research for the two elements that are the focus of this thesis, hydrogen and helium. We give an outline of the current phase diagram of the helium isotopes and the computational methods used to study them. Highlighting the lack of low pressure ab-initio studies. We also cover the currently understood high pressure hydrogen phases as well as the physical mechanisms that drive each phase transition. These lay the basis for talk about current ab-initio studies on hydrogen-helium mixtures. Again this review highlights the lack of low pressure ab-initio studies.

In the first section of Chapter 3, we begin our systematic study of helium
at low pressures, < 1 GPa, using DFPT. The existing literature on helium at these pressures uses simple pairwise interaction potentials to model electron interactions. This allows for computationally expensive techniques such as Path Integral molecular dynamics (PIMD) or Quantum Monte Carlo (QMC) methods to be used to model the quantum behaviour of the nuclei. At higher pressures, many-body interactions become important, and recent progress has been made in extending techniques using three-body potentials fitted to DFT calculations [31]. We carried out DFT calculations and compared a number of different functionals. The LDA functional is the least accurate, with hybrid and GGA functionals producing better fits to experimental results. As well as this, we find that our predictions improve when Van der Waals effects are taken into account.

After comparing these functionals, we find that there is still a systematic error due to the choice of GGA functional at low enough pressures. A difference exists between the EOS of each helium isotope driven by the zero-point energy (ZPE) contribution to the pressure [32, 33]. We can therefore determine the accuracy of a given method to model quantum nuclear motion by reproducing this difference. Our calculations show that helium is not stable at volumes seen in experiments without including ZPE. PBE-based functionals with Van der Waals corrections are the most accurate in reproducing the pressure gap and modelling the phonon behaviour. However, the quasiharmonic approximation in DFPT eventually leads to imaginary modes, resulting in unrealistic ZPE contributions.

The resulting imaginary modes from DFPT indicate the breakdown of the harmonic approximation. In the next section, we attempt to account for an-harmonic effects known to be present in helium-helium interactions [34, 35]. The Self-consistent ab initio lattice dynamical method (SCAILD) [1] can be used to approximate the effect of an-harmonic modes on the in a solid. In the second section of Chapter 3, we attempt to use the SCAILD method to reproduce the helium isotope equation of states. However, the SCAILD method requires approximations that assume calculations are carried out above the Debye limit. Solid helium exists below the Debye limit at certain regions of the phase diagram, challenging the applicability of SCAILD in the pressure regime of interest. Unfortunately, at the pressures we are interested in for this study, the melt line exists below the Debye temperature. High-temperature calculations above the Debye limit encounter stability issues and erratic jumps in the ZPE, leading to softer phonon modes and lower volumes for a given pressure when compared to DFPT calculations.
Low-temperature calculations below the Debye limit experience noise and breakdown of the approximation used in SCAILD, especially in the quantum regime of lower densities and Helium-3 isotope calculations. Despite the noise and poor parameterization of the equation of state, an improvement is observed in the predicted equation of state compared to DFPT, indicating the contribution of an-harmonic modes to the error seen in previous sections.

In the next section, we look at using PIMD to account for quantum nuclear motion in ab-inito calculations of low pressure helium. Path integral molecular dynamics (PIMD) approximates the fully quantum solution by using parallel instances of classical molecular dynamics simulations connected by harmonic oscillators. In theory, this method approaches a fully accurate model of the quantum nuclear effects as the number of classical molecular dynamics simulations, or beads approaches infinity. As PIMD is a molecular dynamics calculation, it already accounts for an-harmonicity in the helium potentials. PIMD simulations incur high computational costs due to the increased number of simulations required to approximate quantum behaviour accurately. Converging the bead number in PIMD for the pressure regime of interest is computationally expensive and impractical. Increasing the bead number beyond $\sim 128$ beads leads to a deviation from experimental values in the predicted equation of state. This suggests that either the simulation cell size was not adequately converged or the formulation of PIMD lacking quantum nuclear exchange terms is unsuitable for describing solid helium below 1 GPa.

In Chapter 4, we model hydrogen and helium mixtures at pressures lower than 15 GPa using ab-initio techniques. We will investigate claims made by two experiments based on Raman signal measurements. Yoo et. al. reported evidence of mixing between hydrogen and helium in the solid phase brought about by chemical bonding between the elements [2]. However, Turnbull et. al. have proposed contamination as an alternative explanation for the observed Raman signals [22]. The chapter also investigates the blueshift of the hydrogen vibron in hydrogen-helium mixtures seen in experiments [22, 2, 3]. Previous studies have suggested that a localised pressure effect causes this blueshift. We propose a localization effect due to the separation of hydrogen molecules by helium as the underlying mechanism. By accounting for zero-point effects, we are able to calculate the enthalpy of mixing for both the solid and fluid regimes. Our calculations find that hydrogen and helium do not readily mix, with a hydrogen concentration of $< 0.2\%$ in the helium solid at 300 K. A Mulliken population analysis [36, 37, 38] showed no evidence of
chemical bonding between hydrogen and helium atoms. The weak attraction
between hydrogen molecules in the solid regime is observed, which is weak-
ened further by including zero-point effects. These calculations support the
explanation proposed by Turnbull et. al. [22] and agree with other ab-initio
calculations published since [23]. In agreement with experiments, our cal-
culations suggest that hydrogen and helium readily mix in the fluid regime
below 15 GPa [2, 39, 37, 38].

The behaviour of hydrogen molecules under pressure, including the turnover
of the hydrogen vibron in pure hydrogen and the blueshift observed in hydrogen-
helium mixtures, is poorly understood. The vibron frequency is blueshifted
in mixtures, and the magnitude of the shift depends on the relative con-
centration of the mixture, with a lower hydrogen concentration leading to a
larger blueshift. After correcting for changes to pressure due to zero-point
effects, DFPT calculations of Raman signals at various concentrations show
good agreement with experimental results [22, 2, 3]. These calculations also
suggest that the change in local pressure on a hydrogen molecule is not suf-
ficient to induce the change in frequency seen in experiments. Along with
this, we show a correlation between the observed vibron shift and the lo-
calisation of the hydrogen vibron. This supports the hypothesis that the
change in hydrogen vibron frequency is due to a reduction in coupling be-
tween hydrogen molecules. We also carry out calculations of a lone hydrogen
molecule in a helium pressure medium. In these calculations, we see that the
hydrogen vibron does not undergo the turnover seen in the pure hydrogen
crystal without the coupling effect between hydrogen molecules. Therefore,
we conclude that the hydrogen vibron’s turnover is caused by an increase in
coupling between hydrogen molecules as proposed by [40].

In Chapter 5, we expand the investigation of these highly quantum ma-
terials to include there Beryllium is widely used in industrial applications,
including nuclear and potential fusion reactors. Tritium breeding blankets
aim to address the shortage of tritium by using fusion reactions to irradiate
lithium-6 and use beryllium as a neutron multiplication source [4, 5, 6, 7, 8].
Helium bubble formation in beryllium is a limiting factor in the longevity
of materials with high neutron flux [5, 9, 10, 11, 12]. Un-
derstanding the formation and behaviour of helium defects in α-Beryllium is
crucial for modelling helium bubble formation. Ab-initio studies have exam-
ined helium defects in beryllium, but none have investigated the role of ZPE
in defect behaviour. This study explores the influence of ZPE on helium
defects in beryllium up to 20 GPa. The inclusion of ZPE does not quali-
tatively change defect formation. However, it is required to determine how the behaviour of defects changes as pressure increases. We find that up to a pressure of 20 GPa, substitutional defects remain preferred over interstitial defects, and the basal plane split dumbbell defect is preferred among interstitial sites. Interstitial defects show increased attraction to vacancies with increasing pressure. At around 18.6 GPa, substitutional defects transition from experiencing an attractive force between each other to experiencing a repulsive force. This is driven by the competition between minimising volume and increasing the number of Be-Be bonds. This opens up the possibility that inducing pressure on the beryllium lattice could be used to combat helium bubble formation in beryllium components. Further studies should investigate pressure effects on helium trapping in larger vacancy clusters to understand the effects on helium bubble formation better.

Interactions between hydrogen and the beryllium surface are important in understanding the viability of beryllium materials in plasma-facing environments. A number of Ab-initio studies have provided insights into the interaction of hydrogen molecules with the beryllium surface [12, 24, 25, 26, 27, 28, 29]. However, until now no ab-initio study has investigated how complex beryllium hydride chains, which take the form of \((\text{BeH}_2)_n\) [18, 19, 20, 21], interact with the beryllium surface. Molecular dynamics simulations and DFT calculations were performed to study the interaction of the \(\text{Be}_3\text{H}_6\) chain with the \((0001)\) beryllium surface. The \(\text{Be}_3\text{H}_6\) chain was chosen to limit the size of the simulation cell. The absorption profiles of both the \(\text{Be}_3\text{H}_6\) chain and lone hydrogen molecules are obtained. We find that the chain readily bonds with the beryllium surface. However, it is unstable with respect to hydrogen atoms absorbed to the surface. We also find that an absorbed hydrogen atom causes a larger reduction in surface energy than an absorbed beryllium molecule on the same site. This suggests in the presence of a beryllium surface saturated with absorbed hydrogen atoms, beryllium chains would readily desorb from the beryllium surface. Computational limitations prevented this study from accounting for ZPE or modelling longer \((\text{BeH}_2)_n\) chains, but due to the energy scales involved, the qualitative behaviour is not expected to change. In experiment, the beryllium hydride deposits are present in beryllium crystals bombarded with high hydrogen isotope ion flux [16]. Our calculations suggest that the deposits form because the hydrogen isotopes are deposited onto the beryllium surface faster than they are desorbing. This leads to the absorption sites of the beryllium surface being saturated and the desorption of beryllium hydride molecules. This suggests that the formation of these
beryllium hydride crystals can be combated by ensuring the surface of the beryllium lattice is not saturated with hydrogen ions.
Chapter 2

Background

The theory of quantum mechanics has been around in some form or another for almost 100 years. Despite this, solving for the behaviour of any more than a handful of interacting particles is not an easy task. As the number of particles increases, so the computational time taken to simulate the system grows prohibitively large. This many-body interaction problem is still one of the largest issues in condensed matter physics. Much of the work done in this field is on improving our approximations to the exact quantum theory. This issue is particularly important in the study of elements which exhibit highly quantum behaviour for their nuclei. Hydrogen and helium are two such elements. As they are so light, accounting for nuclear quantum effects such as zero-point motion is vital to properly understand their properties and crystal structure. Each exhibits unique properties when placed under extreme conditions, making them the subject of intense research from the condensed matter community.

Hydrogen was first predicted to turn metallic under high pressures in 1935 by Wigner and Huntington [41]. The predicted density accords well with modern estimates, but the pressures it was predicted to occur at were at least an order of magnitude too small. Regardless of this, it has been one of the most sought-after states of matter in high-pressure condensed matter physics. Impressive properties are predicted to manifest themselves in metallic hydrogen, the most exciting being room temperature superconductivity: one of the greatest ambitions in condensed matter physics [42]. We are just now beginning to reach the pressures needed to make metallic hydrogen with controversial claims of observations already being made [43, 44]. Recently progress has been made in lowering the pressure needed to metallize hydrogen.
through the use of high-pressure hydrides, which now hold the current record for the highest superconducting critical temperature [45, 46, 47, 48, 49]. However, much is still not known about hydrogen’s crystal structure, even in the phases that can be reached experimentally.

Helium’s unique behaviour is most prevalent at extremely low temperatures where the zero-point motion of the atoms dominates any other interaction forces. This zero-point motion is so extreme that even at zero Kelvin, it remains a liquid. At extremely low temperatures, approximately 2 K, helium enters a phase known as a superfluid [50]. The atoms in this Bose-Einstein condensate phase act as one indistinguishable object, flowing without resistance even through solid objects. However, helium can become a solid under pressure. Some have even suggested that this solid may share properties with the superfluid phase, flowing without resistance as the atoms exchange between sites on the crystal lattice. A series of experiments claiming to detect evidence of this behaviour in solid helium drew much attention to the subject. However, these experiments were later found to be measuring a classical signal due to the elasticity of the crystal structure [51]. To this day, the existence of supersolidity in helium or another other material is still an open question.

My work will attempt to further our understanding of these elements by through a methodological study using current simulation techniques. The aim of these will not only be to investigate the behaviour of these highly quantum materials but also to better understand the limitations of the tools used to simulate their behaviour. We go on to demonstrate the importance of accounting for the quantum nuclear effects of hydrogen and helium in a number of complex systems which have not been addressed in the literature.

2.1 Methods

2.1.1 Density Functional Theory

This thesis will focus, by and large, on simulations using the density functional theory (DFT) method. DFT is currently one of the most widely used techniques, in part due to an impressive speed relative to other electronic structure methods whilst maintaining accuracy in systems where many-body interactions are significant. Instead of solving the Hamiltonian for \( N \) interacting electrons, DFT reduces the problem to solving for the density function
of a single electron. This is made possible through a theorem put forward by Hohenberg and Kohn which states that there always exists a functional of the electron’s density that if minimized, uniquely describes its ground state energy configuration \[52\]. Unfortunately, the exact functional is not known. Finding good approximations to this functional is an ongoing task for the DFT community.

The majority of DFT applications in condensed matter start from the Born-Oppenheimer approximation, which makes the assumption that nuclear and electron motion are decoupled, and as such only the electrons are solved for quantum mechanically \[53\]. The electron Hamiltonian is often split into four main parts: the kinetic energy, the electrons’ interaction an external potential, the electrons’ interaction with the electron charge density, and an exchange-correlation term.

\[
E[n(r)] = \int V_{\text{ext}}(r) n(r) \, dr + \frac{e^2}{2} \int \int \frac{n(r) n(r')}{|r - r'|} \, dr \, dr' + T[n(r)] + E_{xc}[n(r)]
\]  

(2.1)

Where \( n \) is the electron charge density, \( T \) is the kinetic energy and \( E_{xc} \) is the exchange-correlation term. In practice, most methods reintroduce wavefunctions of non-interacting electrons in order to calculate the kinetic energy and band structure. From this, we can define an effective potential acting on each electron as

\[
V_{\text{eff}}(r) = V_{\text{ext}}(r) + \frac{e^2}{|r - r'|} \int \frac{n(r')}{|r - r'|} \, d^3r' + \frac{E_{xc}[n(r)]}{\delta n(r)}
\]  

(2.2)

This allows us to construct a self-consistent cycle which will converge on the ground state electron charge density and involves only solving a series of single electron Hamiltonians. The steps of this self-consistent cycle are:

1. Construct an initial density.

2. Solve the Hamiltonian for an electron under the effect of the effective potential given in equation 2.2 for each electron.

3. Calculate a new density from the resulting wavefunctions.

4. Check for convergence, if not converged input new density back into the second step.
5. If converged output values, and calculate physical properties.

It is the exchange-correlation term that contains most of the non-trivial quantum mechanical and many-body interactions between the electrons. As the actual form of this part of the functional is unknown, it must be treated with approximations. The simplest approximation is the local density approximation (LDA). This formulation is given as

$$E_{xc} = \int \epsilon_{ex} [n(r)] n(r) \, dr$$

(2.3)

where $\epsilon_{ex}$ is the exchange-correlation density of a homogeneous electron gas of density $n$. This is fitted to near-exact quantum Monte Carlo (QMC) simulations. As all electron wavefunctions contribute to the density without the exchange-correlation term in the functional, each electron interacts with itself through the electron density. The surprising effectiveness of LDA can be attributed to it correctly replicating the exchange-correlation hole which should exist in the exact form of the functional. LDA works well in systems that have relatively homogeneous electron densities, however, this is often not safe to assume particularly outside of metallic systems.

In an attempt to improve on this, the generalised gradient approximation (GGA) has been formulated. In its general form, GGA takes not only the magnitude of the electron density into account, but also the gradient. This is particularly important in hydrogen as the electron density is mostly concentrated around the molecules and can be fairly inhomogeneous, particularly at high pressures. GGAs have the general form

$$E_{xc} = \int f [n(r), \Delta n(r)] \, dr$$

(2.4)

Multiple forms of the functional $f [n(r), \Delta n(r)]$ have been proposed. One of the most popular is that of Perdew Burke and Ernzerhof (PBE) [54]. PBE manages to explicitly maintain the exact exchange-correlation hole while being fitted to a suite of molecular systems which can be more exactly calculated using quantum chemistry. Throughout most of this study, we will use a variant of the PBE functional. However, other formulations of GGA’s are used, each performing better in different regimes. Some which will be investigated in this thesis include PBEsol [55], a revised parameterisation of PBE specifically designed to improve performance in describing solids,
and BLYP \cite{56, 57} which uses an exchange functional fitted to Hartree-Fock exchange energies and a correlational functional fitted using LDA.

There also exist formulations that use the exact Hartree-Fock exchange energy of short-range interactions in conjunction with GGA. These techniques are known as hybrid methods. Selecting the correct functional can be an area of contention in DFT studies. The extra degree of freedom allowed by the exchange-correlation term can allow simulations to give reasonable results for the wrong reasons. In response to these worries, it is commonplace for studies to present results from a broad range of functionals. Along with this, it is also important to explain, when the functionals do differ, why some give a more accurate description of that particular system. This should act to minimize fears that a particular functional is favoured only because it performs well, rather than because it accurately describes the system.

Both LDA and GGA functionals depend only on the local electron density, while longer-range effects are ignored. One of the most prominent of these effects is Van der Waals (VdW) interactions. In the classical picture, Van der Waals forces are caused by correlations in fluctuations of electron densities at long range and are often much weaker than short-ranged interactions. Due to this, it is often safe to average out these long-range interactions, particularly in high-pressure systems in which the electron density is fairly uniform, and other interaction terms increase more rapidly as volume decreases. However, there are cases where Van der Waals interactions are significant either in describing particular dynamics or because other interactions are particularly weak \cite{58}. Helium, with its electrons comfortably filling the lowest energy orbitals, falls into this second category. There are many techniques for incorporating Van der Waals interactions into DFT. The simplest of these corrections take the form

\begin{equation}
E_{\text{disp}} = \sum_{a,b} f(r_{ab}, i, j) \frac{C_{6ab}}{r_{ij}^6}
\end{equation}

where A and B index different atoms, the $1/r^6$ term replicates the leading order term of the long-range Van der Waals attractions, and $f(r_{ab}, a, b)$ is a damping term to stop the $1/r^6$ contribution blowing up at short-range. The pairwise interaction depends only on a single coefficient characterised by experimental data or ab initio simulations of interactions between different atomic dimmers. These methods fail to take into account that these coefficients depend on the polarisability of the atom, which changes depending on
the conditions they are in. These conditions change dramatically under high pressures as more atoms are forced together. These effects are taken into account in formulations put forward by Grimme et. al. [59] and Tkatchenko-Scheffler [60]. Here we use the DFT-D2 dispersion correction described by Grimme in 2006 [59], it uses a semi-empirical method to parameterise how the polarisation of an atom depends on its neighbours. Tkatchenko and Scheffler [60] attempt to provide a method that requires less parameterisation. This is done by relating the polarisability to the volume an atom occupies in a solid or molecule. The volume each atom occupies is determined from DFT calculations using Hirshfeld partitioning [61] of the electron density. Grimme et. al. has since proposed a more complex correction known as DFT-D3 [62], however they have yet to be implemented in CASTEP [63] and so are not used in this study. Instead of using a simple pairwise correction term DFT-D3 accounts for many-body interactions with the inclusion of an additional term of the order of giving a correction term of $1/r^6$ giving the equation

$$E_{\text{disp}} = \sum_{ab} \left[ f_{d,6}(r_{ab}, a, b) \frac{C_{6ab}}{r_{ab}^6} + f_{d,8}(r_{ab}, a, b) \frac{C_{8ab}}{r_{ab}^8} \right]$$ \hspace{1cm} (2.6)$$

Unlike the DFT-D2 method both the damping functions ($f_{d,6}(r_{ab}, a, b)$ and $f_{d,8}(r_{ab}, a, b)$) and the coefficients ($C_{6ab}$ and $C_{8ab}$) depend on the local environment of the two atoms. Specifically, their coordination number, which is estimated by their distance to the surrounding atoms. Van der Waals interactions can be included in the exchange functional itself, rather than taken into account afterwards. These methods are known as vdW-DFT and have functionals with terms of the form

$$E_{\text{disp}} = \int \int n(r) K_{xc}(r, r') n(r') d\mathbf{r} d\mathbf{r}'$$ \hspace{1cm} (2.7)

Where the interaction between distant fluctuations in the electron charge density is mediated by the linear response kernel $K_{xc}$. Even more computationally expensive methods include many-body interaction and screening effects. Screening is particularly important in extended systems such as solids. The random-phase approximation has the advantage of automatically including all orders of interactions, not just the $C_6$ term [64]. However, this method is often prohibitively computationally expensive. Another method based on Tkatchenko-Scheffler accounts for many-body screening using less computationally expensive methods [65].
Other simplifications can be made to decrease DFT calculation time. Treating each electron individually in simulations with heavier atoms can make the system prohibitively large. As such, it is common practice to only explicitly simulate valence electrons using DFT; the other electrons are taken into account through the interaction potential. This pseudopotential is fitted to reproduce all electron calculations outside a cutoff radius. This also allows us to ignore high energy interactions between the nucleus and the electrons at short distances which would lead to infinitely high cut-off energies. Pseudopotentials are split into two categories depending on how the potential within the cutoff radius is modelled. Either they conserve the norm of the wavefunction within the radius (norm-conserving pseudopotentials), or they do not (ultrasoft pseudopotentials).

In norm-conserving pseudopotentials, the integral over the square of the wavefunction within the cut-off radius is constrained to match the integral over the square of the wavefunction in the exact solution. This is equivalent to constraining the occupancy of each pseudo-wavefunction to one electron. A number of methods exist for generating pseudopotentials which meet these constraints. In order to reduce the computational cost of DFT calculations it can be useful to optimise the pseudopotential in a way that reduces the cut-off energy. The scheme used to generate the norm-conserving pseudopotentials in CASTEP is based on the work of Lin et. al. [66] and Lee et. al. [67]. In this scheme, the pseudopotential is based on a set of spherical Bessel functions as shown below

\[
\psi_{l}^{ps}(r) = \sum_{a=1}^{4} \alpha_a \psi_l(k_a r) , \tag{2.8}
\]

\[
\frac{j_l(k_a r_c)}{j_l(k_a r_c)} = \frac{\phi_l(r_c)}{\phi_l(r_c)} \tag{2.9}
\]

Here \( j_l(k_a r) \) are the spherical Bessel functions with \( (a - 1) \) zeros between \( r = 0 \) and \( r = r_c \). The coefficients \( \alpha_i \) are then varied to minimize the kinetic energy outside of a cut-off vector of length \( k_c \). This process automatically satisfies the need to normalisation and continuity of the first two derivatives of the pseudo-wavefunctions at \( r_c \). The accuracy and efficiency of the resulting pseudopotential by tuning \( k_c \) for a given \( r_c \).

Ultrasoft pseudopotentials relax the norm-conserving constraint in favour of reducing the cut-off energy of the pseudopotential, resulting in improve-
ments in the computational costs. However, many calculations become significantly more complex to implement without the norm-conserving constraint. This means that it is common to rely on norm-conserving pseudopotentials for calculations which involve linear response implementations of phonon calculations or nonlocal exchange-correlation functionals.

Blocks theorem states that a periodic system can be described fully by wavefunctions $\psi_k$, where $k$ is the crystal momentum, within the first Brillouin zone. This can be expressed as a lattice-periodic factor $\mu_k(r)$ multiplied by a plane-wave

$$\psi_k(r) = e^{i k \cdot r} \mu_k(k) \quad (2.10)$$

It is there for natural when solving DFT calculations in solid-state systems to use a plane-wave basis set to represent the valence electrons. The plane-wave basis set also has the advantage of fitting periodic boundary conditions found in simulation cells and can be easily converted between real and phase space using fast Fourier transforms (FFT). The cut-off energies of the pseudopotentials determine the resulting plane-wave basis set, with only plane-waves with kinetic energy below the cut-off energy being solved for. This means that the computational cost of a given calculation will depend on the cut-off energy used. We, therefore, want to minimize the cut-off energy without sacrificing computational accuracy. To do this we converge the accuracy of the calculation with respect to the cut-off energy. Tolerances of down to 1 meV are regularly achieved. In theory, this accuracy should increase as the cut-off is raised, however, as we have just shown many pseudopotentials are optimised with a specific cut-off energy in mind. This leads to some cases where increasing the cut-off energy can in fact decrease the accuracy of the resulting DFT calculation. In a system with multiple elements, it is important to ensure that the cut-off energy is converged to the hardest pseudopotential in the simulation. Now that we have defined a finite basis set, we must next ensure that we accurately sample the reciprocal space of our simulation cell.

Now that we have defined a finite basis set the next step is to ensure an adequate sampling of the Brillouin zone. In theory, an integral over the entire Brillouin zone is required to calculate the energy of a given system, however, in practice, we can get away with a sum over a finite number of k-points [68]. In high symmetry situations such as we might expect to find in a solid crystal, we can reduce the number of k-point calculations by noticing that many of
the points in the Brillouin zone that we might want to sample are equivalent. Thus by identifying the crystallographic point groups of a simulation cell, we can avoid unnecessary calculations. It is also important to ensure that we choose sample points which are representative of the whole Brillouin zone. As such points of height symmetry such as those on symmetry planes and axes should be avoided. This also has the advantage that when protecting our reduced sampling grid back onto the whole Brillouin zone, grid points do not project onto themselves. There are exceptions to this rule, however, for cases where these high symmetry points are of physical importance. A common sampling grid which is designed to avoid high symmetry points and will be used in much of this work was first described by Monkhorst and Pack [69]. These methods can reduce the number of k-point samples that must be taken, however, it is still important to ensure that the k-point grid is dense enough by converging the number of k-point samples with respect to the physical property being calculated.

At each of the k-points, an energy minimisation of the self-consisted field is carried out. This involves an initial guess at the electron charge density field followed by a minimisation using the variational principle. As with typical minimisation problems there exist a number of schemes which act to speed up and smooth out the convergence process. In particular, a number of mixing schemes are used which mix the electron densities resulting from different self-consistent field calculations. The simplest is known as linear mixing and involves producing the next input density from a linear combination of the previous input density and the current output density. For the majority of calculations in this study, a mixing known as the Pulay method [70] is employed. Rather than relying on only the last two electron densities, the Pulay method keeps track of all previously calculated densities creating a linear combination of each. This linear combination is done in such a way as to reduce the residuals. A number of properties can be tracked to determine the tolerance of the self-consistent field cycle. Typical properties that we are looking to converge are change in the total energy per ion, the magnitude of the force and the position of the atoms.

As well as needing to converge the cut-off energy and the k-point density it is also important to converge the simulation cell size before carrying out calculations of physical properties. The size of the simulation cell is highly dependent on the physical properties which is of interest. If the simulation cell is too small the periodic boundary conditions will lead to self-interactions. The simulation cell must be large enough to minimise the effect of long
range interactions. For isotropic effects, it is important to ensure that the simulation cell is expanded in such a way that the maximises the radius of a sphere that can be fit inside the supercell. Of relevance to this study, these long range interactions are of particular importance in calculations on defects, disordered mixtures and phonons. In simulations with anisotropic effects, as you might expect with surfaces and chains, it can be sufficient to only expand the simulation cell in the direction of the long range effect as long as the other directions have been sufficiently converged. As it is the k-point density that is of importance when sampling the Brillouin zone this can in effect lead to fewer k-points needing to be calculated as the reciprocal space of the simulation cell is reduced as the real space is expanded. This can reduce the calculation time however the effect of increasing the number of ions leads to a significantly greater increase, leading to a net longer calculation, as should be expected.

2.1.2 Phonons and Raman Scattering

Phonons are vital in understanding many interesting properties of a material. As well as understanding the materials’ properties, phonon calculations can account for the zero-point motion inherent in any quantum system. While the effects can be small in heavier particles, in lighter elements such as hydrogen and helium, it can be a significant contributor to the stability of a structure. As well as this, the phonons determine a lattice’s Raman spectrum. Consequently, phonon calculations are of particular interest to this study.

The two most common methods for phonon calculation are either finite displacement methods or density functional perturbation theory (DFPT). Both seek to solve the lattice dynamics of a crystal structure by using a harmonic approximation [71, 72]. If we assume a nuclei experiences a small perturbation $U$ from its equilibrium position while in an effective potential $V_{\text{nuc}}(R)$ a Taylor expansion of the potential can be written as

$$V_{\text{nuc}}(R_0 + U) = V_{\text{nuc}}(R_0) + \sum_{i\alpha} \frac{\partial V_{\text{nuc}}}{\partial U_{i\alpha}} U_{i\alpha} + \frac{1}{2} \sum_{i\alpha} U_{i\alpha} \frac{\partial^2 V_{\text{nuc}}}{\partial U_{i\alpha} \partial U_{j\beta}} U_{j\beta} + ...$$

(2.11)

where $i$ and $j$ are label the atom number, $\alpha \beta$ and $\gamma$ label the Cartesian coordinates, and $R_0$ is the equilibrium position. The first term is a constant
and as the perturbation is around an equilibrium position the first derivatives cancel. If we ignore the higher-order (anharmonic) terms we can approximate the potential as

\[ V_{\text{nuc}}(R) = \frac{1}{2} \sum_{i,j \alpha \beta} U_{i \alpha} \phi_{ij}^{\alpha \beta} U_{j \beta} \]  

(2.12)

where \( \phi_{ij}^{\alpha \beta} \) is the force constant or Hessian matrix which can be written as

\[ \phi_{ij}^{\alpha \beta} = \frac{\partial^2 V_{\text{nuc}}}{\partial U_{i \alpha} \partial U_{j \beta}} \]  

(2.13)

By taking the Fourier transform of the Hessian matrix we can write the solution to the equations of motion for this potential as an eigenvalue problem.

\[ D_{ji}^{\alpha \beta}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_\gamma \phi_{ij}^{\alpha \beta} e^{-iqR_\gamma}, \]  

(2.14)

\[ D_{ji}^{\alpha \beta}(q) \cdot \epsilon_{i \alpha q} = \omega_q \epsilon_{i \alpha q} \]  

(2.15)

where \( q \) are indices labelling the phonons’ wavenumber, \( \omega_q \) are the phonon frequencies, and \( \epsilon_{i \alpha q} \) the phonon eigenvectors. By letting \( q \to 0 \) we can calculate the phonon frequencies at the \( \Gamma \) point. From this, we can see that all that is needed to calculate phonon properties in the quasi-harmonic approximation is the Hessian matrix. DFPT and the finite displacement theory use different methods to obtain the Hessian. The finite displacement theory populates the matrix directly by carrying out a DFT calculation for a displacement in each of the Cartesian coordinates for each atom. From each of these calculations, the resulting force on each other atom in the unit cell is taken, allowing for the construction of the Hessian matrix. To ensure that the mirror images of the displaced atom do not contribute to the forces experienced by each other atom a supercell is created consisting of repetitions of the unit cell. This supercell size must be converged to ensure an long range interactions are accounted for.

DFPT calculates the Hessian matrix using the Hellmann-Feynman theorem [71] which states that the first and second derivatives of the ground state energy can be written as

\[ \frac{\partial V_{\text{nuc}}}{\partial U_i} = \int \frac{\partial \tilde{V}(\mathbf{R}(\mathbf{r}))}{\partial U_i} n \tilde{R}(\mathbf{r}) d\mathbf{r} \]  

(2.16)
\[
\frac{\partial^2 V_{\text{nuc}}}{\partial U_i \partial U_j} = \int \frac{\partial^2 V_{\tilde{R}}(r)}{\partial \tilde{U}_i \partial \tilde{U}_j} n_{\tilde{R}}(r) \, dr + \int \frac{\partial V_{\tilde{R}}(r)}{\partial \tilde{U}_j} \frac{\partial n_{\tilde{R}}}{\partial \tilde{U}_i} \, dr
\]  

(2.17)

where \( V_{\tilde{R}}(R) \) is the electron-ion interaction potential and \( n_{\tilde{R}}(R) \) is the ground state electron charge density. As it turns out the potential response, \( \frac{V_{\text{nuc}}}{\partial U_i \partial U_j} \), depends linearly on the electron density response, \( \frac{\partial n_{\tilde{R}}}{\partial \tilde{U}_i} \), which itself depends linearly on the wavefunction response. From this, it is possible to construct a set of linearly coupled equations. To solve these equations we simply need to calculate wavefunction response, \( \frac{\partial \psi}{\partial \tilde{U}_i} \), which can be evaluated by first-order perturbation theory in DFT.

In practice, the Hessian matrix is often solved for in reciprocal space. Due to translational invariance a wavevector \( q \) does not induce a force response at any other wavevector \( \tilde{q} \neq q \) simplifying the calculation. This is done by calculating the wavefunction response as is done in the real space but with respect to lattice distortions which correspond to specific wavevectors. Typically phonon frequencies are smooth functions of the wave vector, so Fourier interpolation techniques can be reliably used to obtain finer samplings of the Brillouin zone as might be needed for to calculate phonon dispersions. However, as the real space interactions increase in range more fine samplings of the Brillouin zone are required to produce reliable Fourier interpolations. As such it is important to properly converge the density of q-point samples to ensure the interpolated points are accurate.

Both the finite displacement method and DFPT rely on the quasiharmonic approximation. In situations where the quasiharmonic approximation fails, other methods must be used. In an extreme case, eigenmodes show up with negative energies in the quasiharmonic approximation: they are known as imaginary phonons because if their frequency is taken as the square root of the energy, it is an imaginary number. In reality, this is due to lattice instability in the direction of the phonon mode. If the mode is stable, this is only a local instability with a potential minima either side of the lattice site and a maximum at the lattice site.

Methods have been developed to deal with these situations, with the most broadly used being the self-consistent ab initio lattice dynamical method (SCAILD) [73]. SCAILD takes the initial frequencies calculated in the quasiharmonic approximation and calculates displacements assuming harmonic terms. It then uses ab initio methods such as DFT to calculate forces on atoms at these displacements. Again assuming the mode is anharmonic, a
new frequency is calculated from the second derivative of the energy and checked for self-consistency. This method allows DFT to explore systems that otherwise would appear unstable. The free energy due to phonons is then simply a weighted integration over the phonon density of states. This gives the quantum vibrational energy of the nuclei with a finite temperature being taken into account as $T$ in the equation below.

$$F_{\text{phon}} = \int_0^\infty dw g(w, V) \left[ \frac{\hbar w}{2} + k_B T \ln \left( 1 - e^{-\frac{\hbar w}{k_B T}} \right) \right]$$  \hspace{1cm} (2.18)

The details of the SCAILD method and how they relate to this study are discussed further in Chapter 3.

One of the most common ways to connect ab-initio results directly to experiments is through infrared (IR) and Raman spectroscopy. Both IR and Raman spectroscopy result from photons being absorbed into the crystal structure by exciting higher energy phonon modes. When light is absorbed by a structure’s phonon modes, there are four main responses the lattice can have. Figure 2.1 gives a diagrammatic depiction of each of these behaviours. In IR absorption a phonon at the Γ point is excited into a higher energy mode, as the frequency of the absorbed light corresponds to the frequency of the excited phonon mode the absorption spectra of light passed through a crystal can provide insight into the crystal’s lattice dynamics. The intensity of the IR absorption depends on the change in the electric dipole moment for a given oscillation \[75\]. The first-order infrared intensity of a given mode $q$ can be calculated by evaluating

$$I_{IR}^q = \frac{N \pi}{3c} \left| \frac{\partial \mu}{\partial Q_q} \right|^2$$  \hspace{1cm} (2.19)

where $N$ is the particle density, $c$ is the speed of light, $\mu$ is the electric dipole moment of the system and $Q_q$ is the normal-mode coordinate. The change in the dipole moment can be obtained through both DFPT and the finite displacement method.

$$\frac{\partial \mu_\alpha}{\partial Q_{q_\beta}} = \frac{\partial^2 E(r)}{\partial G_\alpha \partial Q_{q_\beta}} = \frac{\partial F_q}{\partial G_\alpha}$$  \hspace{1cm} (2.20)

where $G_\alpha$ is an external field and $F_q$ are the forces corresponding to the each mode. We can therefore obtain the infrared intensity by calculating the
Figure 2.1: Image take showing the possible outcomes of an absorbed photon of energy $hv_0$ taken from Ref. [74]. In the case where a phonon is excited to a higher energy mode, no photons are emitted resulting in IR absorption with the energy and wavelength of the photon being absorbed corresponding to the difference in the energy between the phonon modes. Otherwise, the photon excites a phonon into a high energy virtual state and quickly decays by emitting a photon. The change in energy and wavelength of the emitted photon corresponds to the difference in energy between the initial and final phonon modes. With a decrease in energy resulting from Stokes Raman scattering, an increase in energy resulting from Anti-Stokes Raman scattering, and no change in energy resulting from Rayleigh scattering.
direct response to an external electric field. This can be calculated as a linear response in DFPT. In the finite displacement method, we must obtain a new relaxation for each field and calculate a new Hessian matrix.

The other three responses that can be induced in the crystal structure result from a phonon mode being excited into a virtual state before quickly decaying and emitting a photon in the process. These scattering events can be split into two categories, depending on if the scattering is elastic or inelastic. In the elastic case, the phonon decays back into the ground state. This is known as Rayleigh scattering. This results in the emission of a photon of the same frequency as the one that was absorbed. In the inelastic case, the phonon decays to a phonon mode with a different energy than it started in. The photon which is emitted in this process will have its frequency shifted in the process. If the phonon decays to a higher energy mode this is known as Stokes scattering and if it is to a lower energy mode it is anti-Stokes scattering. In practice there is a much higher chance of finding a phonon mode in the ground state and so Stokes scattering dominates the process. By measuring the change in frequency of the light scattered by a crystal a Raman spectrum can be produced.

It is only the phonon modes which change the polarisability of the lattice that produce inelastic scattering. We can use this to calculate the Raman activity of a phonon mode and predict the Raman spectrum produced by a particular structure. The first-order differential of the Raman cross section for the Stokes component of the phonon mode $q$ is given by

$$\frac{\partial \sigma_q}{\partial \Omega} = \left(\frac{2\pi v_s}{c^4}\right)^2 \left|\hat{e}_s \frac{\partial \tilde{\alpha}}{\partial Q_q} \hat{e}_L\right|^2 \frac{h}{8\pi^2 w_q} \left(n^b_q + 1\right).$$

where $v_s$ is the frequency of the scattered light, $\hat{e}_s$ and $\hat{e}_L$ are the unit vectors of the electric field direction for the scattered and incident light, $\tilde{\alpha}$ is the polarisability tensor and $n^b_q$ is the Bose-Einstein statistical factor. The change in the polarisability tensor can be calculated using DFPT and the finite displacement method, however, the process is more complex.

$$\frac{\partial \tilde{\alpha}_{\alpha\beta}}{\partial Q_q} = -\frac{\partial E(r)}{\partial G_{\alpha} \partial G_{\beta} \partial Q_q}$$

$$n^b_q = \left(\frac{\hbar \omega_q}{e^{\hbar \omega_q/k_BT} - 1}\right)^{-1}$$
In the finite displacement method, the phonon eigenvectors must first be calculated, after which the change in the second-order derivatives of the force constants must be calculated for each one resulting in an expensive calculation. In DFPT a linear response method is utilised, this involves an initial calculation of the second-order derivatives with respect to the electric field equation. The change in the polarisability can then be calculated during the initial calculation of each phonon mode [76]. This means that the computational gains made using in using DFPT over the finite displacement method increase along with the size of the simulation cell.

2.1.3 Experimental Techniques

There are two broad categories of high-pressure experiments- dynamic and static compression. Typically, dynamic compression is achieved through shock experiments in which a large impulse is applied to a small sample, rapidly raising its pressure and temperature [77]. These experiments can often reach higher temperatures and pressures than static experiments. There are, however, drawbacks to this type of experiment. The largest problem in the study of solid hydrogen and helium is that only certain parts of the phase diagram can be accessed. As the pressure is increased so quickly, the temperature is also driven well above the melting line of hydrogen. This can be mitigated by ramping the impulse slowly; however, the phase space that can be explored is still limited. As well as this, there is generally a larger uncertainty in the pressure and temperature achieved. Due to the large impulse involved in these experiments, these conditions are only achieved for a short time, and the subsequent samples are destroyed in the process, adding to the difficulty of taking measurements.

Due to the improved control over sample temperature, static experiments are the most relevant for exploring the phase diagram of solid hydrogen. The more complex phases of solid hydrogen can only be created at the extreme limit of pressures available to current static experiments. The highest pressures achieved by static compression are found in diamond anvil cells (DAC) [78]. As their name suggests, DACs work by compressing a small sample between two diamonds with cutlets on the order of 30 \( \text{um}^2 \). The sample is held in place by a metal gasket, typically made of rhenium or tungsten.

DACs also have limited pressure and temperature ranges over which they can explore. Typical experiments involving hydrogen and helium can reach temperatures as high as 1100 K and pressures up to \( \sim 300 \text{ GPa} \) [79]. The
high pressures that can be achieved and the relative cheapness of diamond anvil cells have made them a cornerstone of much of modern high-pressure research.

As with any experiment, DACs have their limitations and problems. Chemical reactions between the sample and the DACs can cause complications at extreme pressures. As well as contaminating the sample, this can weaken the diamonds, causing them to break. Coating the diamonds in gold and aluminium oxide can act as a protective layer mitigating this problem [43, 78]. Defects in the diamond’s surface can also allow the sample to seep into the diamond lattice, increasing the chances of breakage. The polishing and cutting of the diamond is, therefore an important step in determining the range of pressures which can be reached, as this affects the number of defects in the diamond’s surface. The diffusion process through which hydrogen enters the diamond can be dampened by cooling. Liquid helium and nitrogen often being used to achieve this effect.

Diamonds have the advantage of being transparent to a wide range of light frequencies. This has allowed experiments to reach high temperatures through laser heating. This is achieved by using light of an appropriate frequency to bypass the diamond, only heating an absorber embedded in the sample [80]. However, temperature measurements using laser heating are generally not as accurate as those from experiments using resistance heating, as they rely on a sample’s blackbody radiation measurements. Resistance heating can be split into two types, external and internal [81]. External heating has the advantage of not requiring the sample to conduct; however, involves heating diamonds directly. While internal heating avoids this direct heating, any form of heating will increase diffusion and weaken the diamond.

The diamond’s transparency also allows for various types of measurements using light. The most notable are X-ray diffraction, infrared (IR) absorption, and Raman spectroscopy. X-ray scattering utilises scattering angles and intensities to build a 3-dimensional map of the electron density. This is a particularly useful technique in determining the positions of atoms and hence the crystallographic phase of a material. Unfortunately, the electronic density of the hydrogen molecule is fairly isotropic as both electrons occupy the spherical s-orbitals. This means that while the x-ray scattering can reliably determine the position of the hydrogen molecules, it struggles to resolve their orientation [82, 83].

Through X-ray scattering, we are able to determine that the hydrogen molecules remain in an approximately hexagonally close-packed (hcp) lattice
for all molecular phases. To determine the orientations of each molecule, we must rely on IR absorption and Raman spectroscopy. Neither of these methods gives the crystal structure directly. Instead, they give information about the phonon modes of the structure. Thus computational simulations play an important role in the determination of the solid hydrogen crystal structure. Ab-initio techniques such as DFT are used to predict a number of low energy structures. The resulting Raman and IR spectrum of these candidate structures allows for the interpretation of experimental results.

The infrared absorption spectrum is obtained by shining a wide range of frequencies through the sample and observing which frequencies are absorbed. Parts of this light spectrum are absorbed by the vibrations of the same frequency in the lattice structure. Of all the possible lattice vibrations, it is only those which change the dipole moment of the structure that are absorbed in the IR spectrum. This change is only induced in antisymmetric vibrations, and so, in general, the more complex the structure, the more absorption occurs. The normal modes of vibration and their frequency depend on the structure of the material in question. This allows them to be used to eliminate possible structures from a list of possible candidates when they do not produce a similar spectrum.

In hydrogen, this IR absorption provides the clearest difference between the 2\textsuperscript{nd} and 3\textsuperscript{rd} phase [84]. In phase II there is no absorption spectrum suggesting that in this phase none of the hydrogen’s phonon modes involve dipole vibrations. The sudden onset of IR signal in phase III has been cited as evidence that the transition is due to the structure attempting to minimize induced dipole interactions instead of quadrupole interactions [85, 86].

Due to the lack of information from the IR spectrum, most information about these phases comes from the Raman spectrum. Due to the limited measurements that can be carried out in DAC and the lack of information available in IR and x-ray experiments, Raman experiments offer the most detailed constraints on theoretical models [79].

2.2 Hydrogen and Helium

2.2.1 Hydrogen Phase Diagram

Hydrogen is the simplest atom on the periodic table. Despite this, it displays a wide variety of phases under high pressure. Even after many years of
experimental and theoretical work, much is still unknown about these various phases. This is partly due to the quantum mechanical nature of the hydrogen atom, which has a particularly pronounced effect due to its low mass. However, a picture of the high-pressure phase diagram is beginning to emerge through a combination of simulations and experimental evidence.

The simplest phase, phase I, is understood to consist of freely rotating H$_2$ molecules in an hcp lattice [83]. At low temperatures and as low pressures increase, the hydrogen molecules undergo a symmetry breaking transition, locking the molecules into a fixed orientation [87]. This is thought to be driven by minimising the energy due to the quadrupole-quadrupole interaction (Eqq). A number of possible symmetries have been proposed for this, with none perfectly matching the experimental data [79, 88, 89].

The transition from phase II to III is accompanied in experimental data by a large IR peak [101, 102], which is not seen in the lower pressures phases. This suggests that the molecules of the new phase are polarised. Whilst the structure of this phase is still undetermined an Ab initio random structure searching (AIRSS) carried out by Pickard et.al. [103] identified 4 energetically favorable structures $P6_3/m$, $C2/c$, $Cmca$ – 12 and $Cmca$ – 4. $P6_3/m$ was found to be the most stable at pressures lower than 105 GPa and thus suggested as a phase II candidate. Of the other candidates $C2/c$ was put forward as the most likely candidate for phase III due to the predicted Raman and IR signatures most closely matching the experimental results. While the vibrational data matches well with the $C2/c$ structure, the x-ray data suggest that the hydrogen molecule centres sit closer the the ideal hcp sites than is seen in the $C2/c$ structure.

Since then AIRSS calculations which have accounted for thermal and quantum nuclear effects have found that a similar structure $P6_122$ is favoured [104]. Both qualitatively match the vibrational data, with a non-centrosymmetric structure allowing IR-active modes, however, the $P6_122$ molecules sit more closely on the hcp sits improving its fit to the x-ray data. It has been suggested that the region of the phase diagram designated as phase III may consist of both structures, with $P6_122$ transitioning to $C2/c$ – 24 at higher pressures. As well as this additional candidates for the phase II structure have been proposed. The structure $P2_1/c$ has been found to be more energetically favourable in quantum Monte Carlo calculations where both quantum nuclear effects and an-harmonics are accounted for [105]. Despite this none of these structures have been conclusively shown to be the phase II or III structure.
Figure 2.2: This figure taken from Ref. [79] shows an up-to-date understanding of the hydrogen phase diagram. The solid phase transitions represent experimental data from Howie et. al. 2012 [90], Eremets et. al. 2011 [91] and Goncharov et. al. [92]. Data shown representing the melting has been taken from both experimental and theoretical sources. The Experimental sources Datchi et. al. [93] (crosses), Gregoryanz et. al. [94] (left triangles), Deemyad et. al. [95] (crosses), Eremets et. al. [96] (up triangles) and Subramanian et. al. [97] (circles). The theoretical sources are Bonev et. al. [98] (triangles), Morales et. al. [99] (solid line) and Attaccalite et. al. [100] (square).

Upon heating, or further pressurization at room temperature, phase III transitions into phase IV. This structure known as $Pc - 48$, shown in Fig. 2.4 consists of graphene (G) like layers interspaced with nearly free rotors (B) [106, 107, 90]. Due to this Many similar structures have been proposed. Whereas phase IV consists of layers stacked BGBG, phase IV’ consists of slightly modified graphene layers stacked BG’BG”. These modified layers
Figure 2.3: A figure taken from ref. [104] showing the structure of the two-phase III candidates a) $P6_122$ and b) $C2/c - 24$.

are similar to the $C2/c$ molecular layers, with layers alternating in which direction the molecules are orientated. Due to the dynamic nature of this structure, the use of both static and molecular dynamics calculations has been required to explain the vibron signals seen in the experiments. Calculations show that a broadening of the IR and Raman modes explains the difference between the signals predicted from the structure and those seen in experiments.

The proposed phase V is a continuation of the distortion seen in phase IV’ [108, 109]. One proposal for this phase has the atoms of G layers of phase IV finally atomised and transition into a fully graphene-like structure, again inter-spaced with the free rotor B layers, however, such a partly-atomic phase would be metallic, while the experimental ”phase V” is not.

The various phases beyond III and IV can be interpreted as the beginning of complete atomisation and the long theorised metallic phase- first proposed
by Wigner and Huntington in 1935. Despite the initial pressure estimation of 25 GPa being an order of magnitude too small, the predictions of properties of solid metallic hydrogen have made it a holy grail of high-pressure physics [41]. Whether this metalization transition is molecular, due to a closing of band gaps, or due to atomisation has yet to be determined. Although claims of an observed transition have been made [43, 110] they remain controversial, and further experiments are required to conclusively prove that this state can be reliably reached and studied.

2.2.2 Helium Phase Diagram

Helium is, in some ways, even simpler than hydrogen. Due to the unreactive potential of helium, the quantum mechanical effects - whilst smaller than hydrogen - are more influential. These effects are so pronounced that even at zero Kelvin, ambient pressure helium remains a liquid. Even more unusual is the superfluidity of the liquid state that arises in Helium. This Bose-Einstein condensate is formed when the Helium atoms can no longer be treated as distinguishable particles. The wavefunctions of the nuclei are no longer localised: they overlap, and quantum nuclear exchange dominates. This gives the superfluid remarkable properties, such as having quantised angular momentum, flowing without resistance, and through solid objects. Much of the study for low-temperature helium has been driven by investigations of this phase.
While a solid cannot be produced at atmospheric pressures, upon compression, helium does solidify. More recently, there has been increased interest in the low-temperature solid phase of helium, sparked by a claimed observation of supersolidity in a series of torsional oscillator experiments [111, 112]. This supersolid phase is counter-intuitively similar to the superfluid phase, which can flow without resistance whilst breaking translational symmetry. The signal found in the torsional oscillator experiments that were interpreted initially as evidence for superfluidity was later found to be due to structural effects that are classical in nature [51, 113].

This, however, doesn’t conclusively disprove that some fraction of the helium particles are in a supersolid state. Recent experiments by several groups using trapped rubidium atoms have been found to display both broken translational symmetry along with the phase invariance of a superfluid [114]. Whilst this is not a naturally stable state of matter, it does suggest that there is no fundamental reason why this supersolid state cannot exist in helium. There are still a series of unresolved experimental results which could suggest superfluid-like behaviour in conditions where helium is well within its solid phase [51]. However, supersolidity in Helium is still a controversial issue. All possible claims of supersolid Helium are being rigorously studied, as many alternative explanations have yet to be ruled out, including the possibility of the traditional superfluid phases coexisting with solid samples and unique but classical effects that might emerge from such an extreme state of matter.

Recent experiments have demonstrated that, supersolid or not, there are still unexplained behaviours present in low-pressure helium. The syringe effect occurs when a sample of solid helium at pressures and temperatures far from the melting line is placed between two samples of superfluid helium [115]. If pressure differences are induced in the superfluid samples, transportation through the solid is observed. At extremely low temperatures 15 mk there have been observations of anisotropic and reversible giant plasticity [116]. This is brought about through dislocations that can freely move parallel to the crystals’ basal planes. Others have attempted to explain anomalous measurements through a metastable glassy phase [117]. In particular, pointing to the specific heat’s deviation from that of a perfect Debye crystal and sample preparation dependent relaxation times in torsion oscillator experiments. Multi-mode torsion oscillators attempt to separate the known classical structural effects from any supersolid behaviour. They have met with some tentative success, however, more study is required before any conclusions can be drawn [118].
At high pressure and temperature, both isotopes $^3$He and $^4$He take on a face-centred cubic (FCC) structure and experience a transition to hcp at lower pressures [119, 120]. As pressure is decreased, $^3$He will eventually become body-centred cubic (bcc), whereas $^4$He at low enough temperatures is hcp to the melting line. $^4$He does have two small pockets of bcc in its phase diagram, although these are both along its low-pressure melting line. The bcc phase is stabilized over hcp through entropic effects. As $^3$He is lighter thermal effects are larger, stabilizing bcc to lower temperatures. The fact that zero-point motion extends this effect down to 0 kelvin demonstrates how much the difference in isotope behaviour is driven by their masses and the importance of quantum nuclear effects in this system. This difference can also be seen in the low-pressure phase equation of state where the isotope’s pressures differ by almost a third for a fixed volume [32].

![Figure 2.5: This figure created using data from Ref. [121] displays the low pressure phase diagram of $^4$He](image)

Simulations of helium in this low-pressure phase emphasize the quantum nature of the atom, with PIMC and QMC being the most commonly used methods. In the PIMC simulations, a pairwise potential is fitted to exper-
Figure 2.6: This figure taken from Ref. [121] displays the low pressure phase diagram of $^3$He. In comparison with $^4$He (Fig. 2.5), note both the lower temperature that superfluidity sets in as well as, the larger bcc phase.

imental data [122]. These PIMC calculations allow much larger simulation cells than QMC (up to 1000 atoms), however, struggle to accurately simulate extremely low temperatures [120]. This has been shown to give reasonable equations of state and accurately predict transition pressure and temperatures. On the issue of fully commensurate perfect crystals, most simulations agree that there should be no supersolid behaviour. Consequently, much of the current interest is in whether or not this is the actual state that helium takes in experiments, as well as the behaviour of defects in the crystal.

The simplest defect to consider in a crystal is a vacancy. The behaviour of vacancies in helium, however, is not simple [123]. As it is easy for a neighbouring atom to jump to a vacancy site, the vacancy is free to move throughout the solid. Some have even theorised that zero-point effects might induce vacancies even in helium’s ground state [51, 124]. In simulations, the energy needed to form a vacancy is large enough that zero-point vacancies are unlikely to be found. However, some have argued that the QMC simulations needed to reach low enough temperatures are limited by simulation size and do not allow for a proper understanding of crystal deformation effects. The story is further complicated by the relatively strong interactions between...
vacancies [120]. To correctly understand their behaviour, multiple vacancies must be simulated, requiring increasingly large cell sizes. Simulations suggest that an attractive interaction occurs between vacancies. Introducing many vacancies to a simulation cell can result in the system relaxing into a dislocation. Whilst a number of path integral Monte Carlo studies have suggested superfluid behaviour occurs in the atoms along a dislocation [125]. A metastable glassy phase has been proposed as an alternative to the perfect crystal ground state. PIMC simulations indicate that some regions of a sample may remain in a superfluid glassy phase but that these regions would only comprise a small fraction of a sample [117, 126, 127].

Most of this behaviour only occurs at relatively low pressures ~50 atm as electron interactions begin to dominate over quantum mechanical behaviour at higher pressure. These higher pressure phases are still of interest, particularly for the planetary sciences. As helium atoms are compressed many-body electron interactions become increasingly important, and the pairwise potential used in the low-pressure PIMC simulations begins to fail [119]. Some have attempted to fit the PIMC potential to DFT calculations. Whilst this has little effect on the equation of state, they find that the quasiharmonic approximation fails to capture the correct zero-point effects, underestimating the displacement of helium atoms at zero temperature [128].

The high-pressure melting line has been well parameterized by laser heated DAC experiments up to 80 GPa [129, 130, 93]. DFT molecular dynamics two-phase simulations have been found to agree with the experimental data up to this point and have been carried out to up to 35 TPa [131]. At these pressures, we can see the change in the importance of simulation techniques when compared to lower pressures. Both PBE and vdw-DFT functionals agree, producing almost identical melting lines within the error bars of the simulation.

Another area of interest in the high-pressure phase diagram is the pressure and temperature ranges relevant to the Jovian planets and white dwarf atmospheres. One area of uncertainty is the exact pressures under which the helium band gap closes and therefore undergoes its metallization. Optical measurements of laser driven shock studies have provided the best experimental evidence of the conditions required for the metalization of helium. These experiments suggest a transition to a semiconducting metal that occurs in the liquid phase as temperatures rise above ~20 kK and as density increases above ~1.9 g/cm$^3$ [132].

Ab-initio simulations of the non-metal to metal transition in the < 1.9
g/cm$^3$ i.e. the temperature driven transition have shown broad agreement with the experimental results [130]. DFT molecular dynamics simulations were carried out and compared to a chemical model derived from a GW approximation. It was found that a standard GGA functional approach, while accurate for the EOS, miscalculated the band gap by 6-7 eV. This was driven by self-interaction errors and was found to be corrected for in hybrid GGA functionals such as PBE0. Further ab-initio studies have mapped the properties of warm dense helium up to 100 kK and 6 g/cm$^3$ finding good agreement with experimental results as well as a strong dependence of the bad gap closer on temperature effects [133, 134].

2.2.3 Hydrogen-Helium Mixtures

Being the two most abundant and simple elements in the universe, the interaction between hydrogen and helium is of interest to both the astronomical community and acts as a useful example of the theoretical limits in condensed matter physics. Much of the current literature is primarily concerned with the behaviour of each element at conditions found in the Jovian planets, Saturn and Jupiter [138, 139, 140]. These planets are primarily made up of hydrogen and helium. Jupiter has an upper atmosphere helium mass fraction of $Y = 0.234 \pm 0.005$, and Saturn’s is approximately $Y = 0.215 \pm 0.035$ [141]. As such, understanding the interaction of helium and hydrogen over a range of pressures and temperatures is vital in building models of the interior of the Jovian planets.

Most models of the interior are composed of 3 layers. An upper layer of mostly molecular hydrogen, helium and trace amounts of other molecules. At approximately 85% of the radius of Jupiter, this hydrogen is thought to undergo a transition to its metallic phase [142]. This marks the start of the second layer. At some point in this layer, helium also undergoes ionisation due to the extreme temperatures and pressures. The final layer, the core, is assumed to be made of heavier elements that have fallen through to the centre of the planet. Of particular importance to these models are the EOS of each element as well as at which pressures and temperatures they separate and how readily they mix when they do. The most up-to-date understanding of the EOS of both the individual elements and the mixed states comes from DFT simulations and high-pressure shock experiments.

Phase separation of hydrogen and helium at extreme pressures and temperatures has been a proposed explanation for an unexplained difference in
Figure 2.7: This phase diagram taken from Ref. [132] shows the liquid conductivity of warm dense helium as it transitions from a non-metal to a metal. Here the diamond symbols are data points from the [132] experiment and the coloured dashed lines indicate suggested contours of different conductivity and the colours indicated conductivity as shown in the inset. The black lines show estimated ionisation boundaries. The dotted black lines are taken from [135] and the dashed black lines from [136]. The solid line in the melt curve is a fit to experimental data from [93] while the dotted line in the melt curve is an extrapolation. The temperature density of the white dwarf star is taken from [137].

the luminosity of Saturn and Jupiter [138]. If, as the theory postulates, helium and hydrogen are insoluble at some specific pressure region that occurs in Saturn but not Jupiter, then helium might condense and fall through the less dense hydrogen atmosphere, releasing energy as it does. Models of hydrogen-helium miscibility are then incorporated into models of Jupiter and Saturn’s internal structure and compared against measurements taken from the surface of the planets taken by spacecraft such as the Galileo and Juno [143, 144]. This begins to give us an idea of what is happening under the surface of these planets.
A number of ab-initio molecular dynamics studies have been carried out on the miscibility gap of the hydrogen and helium phase diagram. While they qualitatively support that for a region in Saturn, demixing does occur, there is still some debate over the exact position of the miscibility gap. This change is significant enough to change the internal dynamics of Saturn. This would change the helium rain’s effect on the luminosity, as well as the dynamics of the build-up of helium around the core, which could act as a protective layer around the denser elements [145]. Some studies have also implied the existence of demixing in Jupiter, which could have consequences for its internal dynamics. This would include a similar effect as in Saturn increasing the luminosity. However, this would imply another cooling effect is present in Jupiter. This could also imply a process of helium depletion from the surface layer of Jupiter. At the layer where demixing occurs, helium would fall to the point where the elements mix again, thus separating it from the surface layer [146].

The main disagreements in the calculated miscibility gap come from the different functionals used as well as the method for calculating the entropy of mixing. The two functionals most commonly used are the PBE and vdw-DFT functionals [140, 147, 148, 149, 150]. Simulations suggest that demixing is brought on by the onset of metalization in hydrogen [150], which could explain the difference due to the functionals. PBE is known to underestimate the band gap in Hydrogen, leading to a lower metalization pressure [151]. This could explain the increase in the size of the miscibility gap in the PBE calculations and why these calculations suggest a demixing layer in Jupiter’s atmosphere, as shown in figure 2.8.

Calculating the Gibbs free energy of a DFT molecular dynamics simulation is not a trivial task. Gibbs free energy can be defined by the equation

$$\Delta G = \Delta U(x) + P \Delta V(x) - T \Delta S(x)$$  \hspace{1cm} (2.24)

where the internal energy $U(x)$ and the pressure-volume term $P \Delta V(x)$ are given by the DFT simulation. The temperature-entropy term, however, is not. This must be calculated by other means. The easiest is to assume an ideal entropy of mixing. This is simply given by the equation

$$T \Delta S(x) = -k_B T \left[ x \ln(x) - (1 - x) \ln(1 - x) \right]$$  \hspace{1cm} (2.25)

Alternatively, this can be calculated through thermodynamic integration [140, 150]. These non-ideal methods, such as coupled constant integration
(CCI), dramatically change the shape of a miscibility gap as seen in figure 2.8. This is particularly important to make sure the miscibility gap fits the low pressure (< 10 GPa) DAC experiments which find demixing in the liquid regime [147, 3]. It is also required to compare to other simulation methods, which properly include the statistical mechanics terms such as Gibbs free energy Monte Carlo calculations [152].

The demixing is thought to be brought about by metalization, this allows us to use reflectivity measurements to be an indicator for the phase transition from the mixed to demixed phase. DFPT calculations carried out on the optical properties of the mixed phase carried out by Soubiran et. al. [157] set a benchmark to compare to experimental measurements. As the hydrogen and helium enter the two-phase region, the reactivity will rise to that of the pure hydrogen and then decrease as it exits this phase.

Recently laser driven shock experiments have used this method to measure the demixing along the Hugoniot curve of the 11% He mixture [153]. Samples were first compressed in DAC to 4 GPa to ensure the Hugoniot reached relevant temperatures and pressures. The results of this experiment are compared to DFT calculations in figure 2.8. This experiment suggests that the pressure induced transition falls roughly within the bounds of the DFT results. However, it also suggests that the demixing phase survives to significantly higher pressures that are predicted by either PBE or vdw-DFT calculations. This would imply a much larger immiscibility region in Jupiter than was predicted by any DFT calculations.

A few experiments have explored the relatively low pressure and low-temperature regime accessible by DAC’s [2, 22, 158]. Of particular interest in these studies is the unique behaviour of the hydrogen vibron as measured by the Raman spectrum. The frequency of the hydrogen vibron increases with increased helium concentration with a number of explanations being proposed to explain this behaviour. Recently claims of detection of chemical bonding between hydrogen and helium were made on the basis of Raman signature of this vibron by Yoo et. al. [2]. Other experiments however suggest this is due to a contamination of the sample with atmospheric nitrogen [22]. Still, others have proposed localised pressure on the hydrogen molecules induced by the introduction of helium to explain the unique behaviour of the hydrogen molecule [158]. Despite these debates, only a few ab-inito calculations exist in the literature to explore this regime. In this work we attempt to rectify this and propose a new mechanism, a reduction of hydrogen-hydrogen coupling, to explain the large vibron shifts seen in
Figure 2.8: This figure taken from Ref. [153] compares the predicted transition line for the mixed to demixed phase according to the experiment in [153] and various DFT calculations taken from [147]. The experimental data measurements of 11% He are represented by the red triangles with a solid red line fitted through these points. A dotted red line represents these experimental results corrected to an 8% mixture, the protosolar concentration. The green and blue lines show the DFT predictions from both PBE and vdw-DFT functionals, respectively, with the solid and dashed lines representing the non-ideal and ideal entropy calculations, respectively. The solid black line is the non-isentropic temperature profile of the interior of Jupiter [143], and the thick grey curve is the envelope of three different isentropes based on the H$_2$-He EOS [154, 155, 156]

these hydrogen-helium mixtures. This is explored further in Chapter 4.
Chapter 3

Low Pressure Helium

3.1 Density Functional Perturbation Theory

3.1.1 Introduction

Helium, one of the simplest elements, is particularly interesting to the condensed matter community. It is the second most common element in the universe and makes up a large fraction of the internal composition of most gas giant planets. As such, an understanding of its behaviour under high pressures is required for an accurate model of the interiors of these planets [79]. Helium’s light nucleus, combined with a lack of strong electron interactions, gives rise to unique behaviours at low temperatures. It remains a liquid down to arbitrarily low temperatures at ambient pressure, eventually transitioning into a superfluid phase. Only upon compression does helium solidify; at temperatures lower than 1 K, this occurs at $\sim 2.5$ MPa in $^4$He and $\sim 3$ MPa in $^3$He [121]. This solid phase is of particular interest due to the potential existence of a supersolid fraction. Experimental and computational studies seem to have come to the broad consensus that supersolidity doesn’t exist in a perfect hcp crystal [51, 113, 120]. However, the role vacancies and dislocations play in any superfluid behaviour are still an open question [121].

Even in the absence of supersolidity, this helium phase has a number of unique properties that are not fully understood. These include giant plasticity, the syringe effect and a possible metastable glassy phase [115, 116, 117].

Much of the current literature on the solid phases of Helium is focused on extremely high pressures, such as those found in gas giants such as Jupiter and Saturn or near the fluid-solid phase transition at low pressures. In high-
pressure calculations, density functional theory (DFT) is often used to treat electron dynamics and the quasiharmonic approximation gives a reasonable estimate of the phonon behaviour. At low pressures, however, the quantum behaviour of helium nuclei is much more pronounced. Previous studies carried out in this area have treated the electrons using a simple pairwise interaction potential which allows for more expensive Path Integral or Quantum Monte Carlo techniques to account for the quantum motion of the nuclei.

Many pairwise potentials have been developed for the specific purpose of studying helium in the low-pressure regime. The most successful of these resemble a damped Hartree-Fock dispersion form, with much of the development being driven by Aziz and collaborators [122, 159]. The low-pressure equation of state (EOS) of helium is well captured by these potentials, and their simplicity allows for much larger simulations on the order of thousands of atoms. However, many-body interactions become increasingly important at higher pressures, and the simple pair-wise approximation breaks down. Recently progress has been made in extending this technique using three body potentials fitted to DFT calculations [31].

The zero-point motion of the helium nuclei and its contribution to the pressure of the structure are of particular importance to helium in the low-pressure range. Accounting for this effect is needed to reproduce an accurate EOS and phase diagram. Diffusion Monte Carlo (DMC) and Path Integral Monte Carlo (PIMC) are most commonly used with these simplified potentials to treat the helium atoms quantum mechanically. Whilst, in theory, PIMC can reach arbitrarily low temperatures, the computational cost realistically limits its use in understanding low-temperature dynamics. DMC techniques allow for an accurate calculation of the atom’s ground state. However, the size of DMC simulation cells is limited due to the relative complexity of this near-exact method.

At higher pressures, a simple quasi-harmonic approximation is used to calculate the phonon spectrum. The zero-point motion contributions can then be added by integrating over the density of states. Due to the strength of the electron interaction at very high pressure, the zero-point motion contribution is relatively small and makes little difference to the EOS. As of yet, no studies have extended DFT to the low-pressure regime. In this work, we have used DFT to reproduce the solid phase experimental EOS of both Helium isotopes at low pressures, considering both bcc and hcp phases, with the aim of quantifying the limits of DFT in this system.

A number of DFT methods exist for the calculation of zero-point energies.
The most commonly used are the quasi-harmonic methods, including the finite displacement method and the density functional perturbation theory method (DFPT). These are the simplest and most computationally efficient, with DFPT being the most efficient for the majority of systems. As such, our first attempt to account for zero-point energy (ZPE) effects relied on DFPT, and whilst this dramatically improved the accuracy of the predicted EOS for pressures < 1 GPa, there remain significant discrepancies which increase as the pressure lowers. It is known that helium has an-harmonic modes at lower pressures which could account for the discrepancy.

This chapter explores the limits of what is currently technologically feasible when considering quantum nuclear effects (QNE) in a first principles approach. We show the limits of density functional theory’s ability to account for QNE in helium using the quasiharmonic approach. As well as the significance of the systematic error in the choice of functional.

### 3.1.2 Method

Most work in the low temperature and pressure regime has been carried out using classical potentials. A clear indicator of the importance of QNE in this regime is demonstrated by its proximity to the superfluid regime, as shown by the phase Helium-4 and Helium-3 phase diagrams in chapter 2. Despite these isotopes both being present in the hcp phase and the nuclear spin of $^3$He not coming into effect until much lower temperatures [32, 33, 120], $^3$He has a pressure of up to $\frac{1}{3}$ larger than $^4$He at the same volume [32, 33]. As the He-He interaction is so weak, and so QNE dominate the EOS at this pressure. The equation 3.1 shows how the ZPE of a harmonic oscillator depends on mass. This explains the difference seen between the isotopes. As such, reproducing this pressure difference using ab-initio methods should give an accurate picture of DFT’s ability to model QNE.

$$E_0 = \frac{1}{2} \left( \sqrt{\frac{k}{m}} \hbar \right)$$  \hspace{1cm} (3.1)

Helium provides a particular challenge for standard DFT techniques. Van der Waals interactions are of particular importance in the low-pressure helium solid. As DFT doesn’t explicitly include the dispersion effects, these must be included in our parameterisation of the functional. As well as considering which pseudopotential and exchange-correlation functional to use,
<table>
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Table 3.1: Calculations were carried out in a simulation cell with 16 atoms in a hcp structure using a PBE functional with DFT-D2 dispersion corrections and a 4x4x3 k-point grid. Zero-point energies were taken from Gamma point DFPT calculations.

we must also consider and compare various methods of including Van der Waals interactions [160, 161]. DFT calculations were carried out using the CASTEP software [63] to reproduce a volume-pressure graph of hcp helium using a range of functionals and compared them to experimental data from [32, 33] to determine the accuracy of each functional and the significance of different assumptions made about helium in this regime.

We check to ensure that the electronic structure is sampled sufficiently, the k-point density for a simple 2-atom cell bcc helium was found to converge to less than 1 meV for a Monkhorst-Pack grid of 6x6x6, and the cut-off was found to converge to less than 1 meV at a cutoff energy of 900 eV. It is also important to converge the cell size for phonon calculations as long-range interactions significantly contribute to phonon behaviour. A cell size of 16 Helium atoms was found to be sufficient to converge the ZPE less than 1 meV for the simulation. As such the following bcc calculations were carried out with a 4x4x4 k-point sampling grid, in cells containing 16 atoms. As it is important to sample the long-range effects of phonon behaviour along each axis equally, a 36 atom cell was used for hcp calculations with a 3x3x3 k-point sampling grid. Results of convergence calculations for the hcp simulation cells are shown below.

The following calculation parameters hold true for all calculations in this chapter unless stated otherwise. A norm-conserving pseudopotential was generated in CASTEP using the string ”1|1.0|18|21|24|10N(qc = 8)”.

53
<table>
<thead>
<tr>
<th>k-point grid</th>
<th>Total Energy (eV)</th>
<th>ZPE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x2x2</td>
<td>-1246.12919</td>
<td>0.14515</td>
</tr>
<tr>
<td>3x3x3</td>
<td>-1246.12907</td>
<td>0.14460</td>
</tr>
<tr>
<td>4x4x4</td>
<td>-1246.12911</td>
<td>0.14482</td>
</tr>
<tr>
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<td>0.14439</td>
</tr>
<tr>
<td>6x6x6</td>
<td>-1246.12894</td>
<td>0.14436</td>
</tr>
<tr>
<td>7x7x7</td>
<td>-1246.12900</td>
<td>0.14442</td>
</tr>
<tr>
<td>8x8x8</td>
<td>-1246.12927</td>
<td>0.14526</td>
</tr>
</tbody>
</table>

Table 3.2: Calculations were carried out in a simulation cell with 16 atoms in a hcp structure using a PBE functional with DFT-D2 dispersion corrections and a cut-off of 900 eV. Zero-point energies were taken from Gamma point DFPT calculations. Note that the energies shown here are for the whole simulation cell.

<table>
<thead>
<tr>
<th>Number of Atoms (eV)</th>
<th>K-point Grid</th>
<th>Total Energy (eV/atom)</th>
<th>ZPE (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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<td>-77.63364</td>
<td>0.054287</td>
</tr>
<tr>
<td>8</td>
<td>6x6x8</td>
<td>-77.63364</td>
<td>0.08273</td>
</tr>
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<td>16</td>
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</tr>
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<td>36</td>
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<td>-77.63364</td>
<td>0.08211</td>
</tr>
<tr>
<td>64</td>
<td>3x3x4</td>
<td>-77.63364</td>
<td>0.08210</td>
</tr>
</tbody>
</table>

Table 3.3: Calculations were carried out in a simulation cell with 16 atoms in an hcp structure using a PBE functional with DFT-D2 dispersion corrections and a cut-off energy of 900 eV. Zero-point energies were taken from Gamma point DFPT calculations.

<table>
<thead>
<tr>
<th>Q-point Grid</th>
<th>ZPE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x1x1</td>
<td>2.956133</td>
</tr>
<tr>
<td>2x2x2</td>
<td>2.956133</td>
</tr>
<tr>
<td>3x3x3</td>
<td>2.956133</td>
</tr>
</tbody>
</table>

Table 3.4: Calculations were carried out in a simulation cell with 36 atoms in a hcp structure using a PBE functional with DFT-D2 dispersion corrections, a cut-off energy of 900 eV and a k-point grid of 4x4x4.
electron density was treated as spin neutral and a fixed occupancy was enforced through the calculation, treating the crystal as an insulator. The electronic minimisation cycle was carried out using a Broyden mixing scheme and converged to a tolerance of $10^{-11}$ eV/atom. DFPT calculations were solved using the Baroni Green density mixing method [162] and converged to a tolerance of $10^{-6}$ eV/Å$^2$. The helium isotope masses were set to 4.002600 AMU for $^4$He and 3.0160294 for $^3$He.

Figure 3.1: These figures show a comparison between GGA, hybrid and LDA functionals. The solid lines show the GGA functionals, the dashed and dotted lines show hybrid functionals and the dotted line shows the LDA functional. Experimental data depicted by the black circles are taken from [32, 33]. The figure on the left shows that on the scale of $> 1$ GPa there is good agreement between the GGA and hybrid functionals, however, the LDA functional differs dramatically even at lower volumes. The figure on the right shows that in the $< 1$ GPa regime that we are interested in, there is a significant spread over different GGA and Hybrid functionals.

The most common types of functionals are the local-density approximation (LDA) functional and generalized gradient approximations (GGA) functionals. As the LDA assumes a homogeneous electron gas and only depends on the electron density which often works well in describing metals. This is because the homogeneous electron gas-free is an accurate enough model of the free-moving electrons in the metal which are often the most relevant to understanding the bulk properties of the metals. GGA also uses the first-
order derivative of the electron and so is more accurate, particularly for insulating materials and molecules where the electron density can be quite inhomogeneous.

As such we should expect GGA functionals to work better for helium at lower pressures. This can be seen in figure 3.1 where the LDA functional gives the worst fit to the data whilst both the Hybrid and GGA functionals agree with each other at pressures in the < 10 GPa scale, however, there is quite a significant spread between them at the < 1 GPa scales which we are interested in. Hybrid functionals use combinations of the Hartree–Fock exchange functional and a local density functional [163]. The two used here, B3LYP and PBE0, are combinations with two commonly used GGA functionals BLYP and PBE. As we can see from figure 3.1 the difference due to the Hartree–Fock contribution is smaller than the uncertainty due to the difference between GGA functionals.

Figure 3.2 compares a range of GGA functionals. Here we see that the parameterisation of the GGA functional used gives an error of approximately 0.2 GPa, which is acceptable for pressures < 1 GPa but becomes a significant issue for the pressures we are interested in. Figure 3.3 shows a comparison
between the GGA functionals with and without compensating for Van der Waals effects. To do this we look at two corrections to GGA functionals developed by Grimme (DFT-D2) [59] and Tkatchenko-Scheffler [60]. The EOS of the VDW-DFT, shown by the dashed lines, are shifted to lower pressures in both the PBE and BLYP formulations. These shifts are relatively consistent between functionals, and of a similar scale to the uncertainty between GGA functionals. Thus the Van der Waals corrections are an important effect to include to properly characterise the behaviour of Helium. Whilst there is a difference between the Grimme and Tkatchenko-Scheffler Van der Waals corrections these are significantly smaller than the error due to the GGA functionals as such it should be safe to just use one. From here on, we will use the Grimme parameterization of the corrections.

Figure 3.3: These figures show a comparison between a variety of GGA functionals with and without Van der Waals corrections. Experimental data depicted by the black circles are taken from [32, 33]. While the difference due to the Van der Waals corrections is on the same scale as the uncertainty due to the GGA functionals this difference acts to decrease the pressure of the simulation systematically. This suggests that Van der Waals corrections are important, particularly in the < 1 GPa region.

Finally, helium is an element where the quantum nature of the nucleus has a dramatic effect on the bulk properties of the material. As such, it is also important to understand how functionals interact not just with the static nuclei in DFT but also with the phonon behaviour and, in particular zero-point effects. To do this, DFPT calculations were carried out with
VDW-DFT functionals and the EOS was calculated with and without the zero-point effects included, as shown in figure 3.4.

Here we see both functional’s volumes increase when ZPE is included. This is what we would expect, as zero-point motion means each atom takes up more space. This, however, is a dramatic increase compared to other elements. For example, in the PBE case near 0 GPa, the volume increases by approximately a quarter. It is important to note that this is not a physically relevant model as, at low enough pressures, helium exists as a liquid. This increase is also bigger in the PBE case when compared to the BLYP case, particularly in the low GPa regime. Again we find this shift is in a consistent direction and is of the same scale as the error due to GGA functional parameterization, so it is important to include it in our models of Helium. While the initial Van der Waals corrections appeared to worsen the fit to experimental data can see that by including both ZPE and Van der Waals effects we can accurately reproduce the EOS of helium. At least within the systematic error expected due to caused by our choice in GGA functional.

Figure 3.4: These figures show a comparison between a variety of GGA functionals with Van der Waals corrections, with and without zero-point contributions calculated with DFPT. Experimental data depicted by the black circles are taken from [32, 33]. While the difference due to the zero-point effects is on the same scale as the uncertainty due to the GGA functionals the effect increases the pressure of the simulation for both functionals. To accurately calculate the pressure, we must include pressure contributions from zero-point effects.
3.1.3 Results

Due to the relatively large ZPE in the low-pressure solid, it is stable at volumes that would otherwise correspond to negative pressures in ordinary DFT calculations. This can be seen in Figure 3.2 where a range of GGA functionals give negative pressures at volumes where the experimental. This means that commonly used geometry optimisation methods, which regard zero-point as a perturbation, fail to give realistic results. However, helium isotopes only take relatively simple and highly symmetric configurations. We can therefore find solutions in the NVE ensemble. The relative positions of helium atoms in a bcc or hcp unit cell are fixed by symmetry, so calculations can simply be done at fixed volumes. However, the $c/a$ ratio can vary from its ideal value in materials with an hcp structure, so it must be optimised for each volume. This is not straightforward because we must ensure that the ideal $c/a$ ratio remains the lowest energy arrangement from both electronic and ZPE contributions, and there is no analytic form for the zero-point stress. As the results will be fixed volume calculations, we will also need a way to calculate the associated pressure.

To do this, we use the Birch-Murnaghan equation of state [35]. The pressure is given by equation 3.2. Where $B_0$ is the bulk modulus, and $B'_0$ is the derivative of the bulk modulus with respect to pressure, and $V_0$ is the reference volume. These parameters can be found by fitting to the equation for energy given by equation 3.3 where $E_0$ is the reference energy. These equations are fit to our calculated Energy-Volume curves and then used to calculate pressure. This fitting is done in Matlab [164] using the Nelder-Mead simplex algorithm, with none of the fits having an error larger than 2 meV.

$$P(V) = \frac{3B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$  \hspace{1cm} (3.2)

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - 1 \right\}^3 B'_0 + \left[ \left( \frac{V_0}{V} \right)^{\frac{5}{3}} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{\frac{2}{3}} \right]$$  \hspace{1cm} (3.3)

Initial calculations were carried out to determine the theoretical hcp $c/a$ ratio using DFPT using PBE+G06. To do this, we fixed the $a$ and $b$ axis of the simulation cell whilst varying the $c$ axis to determine the optimal
$c/a$ ratio. This was carried out over a range of $a/b$ axis values as shown in the second graph in figure 3.5, where each line corresponds to a different $a/b$ axis value. The colour bar shows the energy level of each calculation. The first graph in figure 3.5 gives a clearer idea of the change in energy over the $c/a$ ratio. From this, we can see a phase shift as the $a/b$ ratio changes. For the $c/a$ ratio expected from experiment $c/a = 1.54$, we see this transition happens around the volume that the DFPT simulation gives a negative pressure. Thus the change in behaviour can be explained by the simulations’ preference for reducing the volume over matching the preferred $c/a$ ratio. Thus we can safely use the other $c/a$ ratio, which is in good agreement with the experimental $c/a$ ratio of 1.54.

Figure 3.5: Above are results from DFPT calculations carried out on 36 atom Helium lattice over a range of $c/a$ ratios and volumes. On the left is a plot of the $c/a$ ratio and energy, and on the right, the same data is plotted, showing the $c/a$ ratio against the volume per atom. The colours in both graphs indicate the energy of each configuration to make comparisons between each graph possible. The left figure shows two distinct behaviours leading to two different stable $c/a$ ratios. In the right figure, we can see that the $a/b$ axis of the simulation cell drives this phase change. For the expected $c/a$ ratio, $c/a = 1.54$, this phase change occurs slightly above the volume where the simulation begins to experience negative pressures. This suggests this transition is driven by the simulation finding it energetically favourable to reduce the volume even if it breaks to the preferred $c/a$ ratio of the crystal.

Now we have determined the ideal $c/a$ ratio. We can now find the DFT’s preferred structure as we know that the only stable structures in either iso-
tope of helium are bcc and hcp in this region of the phase diagram. Therefore we need to compare which of these structures is most energetically favourable according to DFT in the region we are interested in DFPT calculations. Figure 3.6 shows the energy cost of the bcc structure over the hcp structure for a range of volumes per atom for both $^4$He and $^3$He. It also shows that hcp is energetically favourable over the volumes we are investigating. This is in agreement with other simulations and experimental results.

![Figure 3.6](image.jpg)  
Figure 3.6: This figure shows the energy cost of the Helium bcc structure over the hcp for both $^4$He and $^3$He. It shows that the hcp structure is energetically favourable for every volume in our DFT calculations.

Dispersion plots of the phonons from PBE+G06 hcp DFPT calculations are shown in figure 3.7. We can see at larger volumes, some of the phonons are shown as having a negative frequency. This is not a physical result - but
rather comes from negative energy modes where the phonon displacement lowers the energy. If we were to (erroneously) assume the phonon energy to be the square of its frequency, that frequency would be imaginary. These are artefacts of the quasi-harmonic approximation used in DFPT and arise when the potential explored by the perturbation in the calculation is inverted. This can be due to two main reasons either due to a negative restoring force along the direction of that phonon mode or due to an an-harmonic but stable potential. These an-harmonic modes are known to be an issue in calculations involving helium [34, 165]. In the calculation of ZPE DFPT simply chose to ignore any contributions that might result from the imaginary modes. As such, the calculations at volumes larger than these will not give accurate ZPE contributions and should be ignored. Doing this improves the Birch-Murnaghan fit and matches more closely with the experimental data.

Figure 3.4 shows the EOS of both helium isotopes calculated with DFPT, we include results from both PBE+G06 and BLYP+G06 functionals. These functionals are the PBE and BLYP functionals with the DFT-D2 dispersion correction as described by Grimme in 2006 [59]. Results are also shown without ZPE contributions as green lines, these EOSs are the same for both isotopes. This suggests that the difference in pressure seen between the isotopes is purely due to the effect the mass difference has on the ZPE. We can see a first-order approximation of this effect as given by the ZPE of a quantum harmonic oscillator, shown by the equation 3.1. This leads to such a large difference in behaviour between the isotopes only because the zero-point contribution to the pressure is so significant at this volume.

Looking at the BLYP+G06 results, we can see that for each individual isotope, we get a similar accuracy as the PBE+G06 results. However, the BLYP+G06 fails to reproduce the pressure gap that is seen in experiments and so fails to qualitatively reproduce the expected behaviour. While the functional does a reasonable job at quantitatively reproducing the EOS. As the pressure gap is due to the zero-point contribution to the pressure, it suggests that it is the phonon behaviour that the BLYP functional fails to capture accurately. Whilst the PBE+G06 functional doesn’t give an exact match to the experimental data, particularly for the volumes above 23 Å³, it does qualitatively match experimental data. The PBE+G06 functional predicts a similar-sized gap in pressure between the isotopes and suggests that it is only the zero-point motion of the nuclei that stabilises solid hcp at these volumes.

This sets the limits of what is reasonably possible when using DFT at low
Figure 3.7: Shown above dispersion plots taken from fixed cell DFPT calculations of the hcp helium structure over a range of volumes. From this we can see the structure becomes unstable at 21 Å³/atom, at much higher volumes than would be expected from experimental measurements [32, 33]. This could be explained by the presence of anharmonic modes in the hcp structure [34, 165]. Dispersion plots were produced using the post-processing features of CASTEP [166].

pressures and temperatures. It appears that the accuracy of the functional is the limiting factor. GGA and hybrid functionals give a reasonable accuracy down to approximately 1 GPa. The LDA functional performed poorly for all volumes investigated. Both Van der Waals corrections and the zero-point contributions are particularly important to account for. Below 1 GPa the systematic error due to the parameterization of the GGA functional is large enough that the simulation is no longer able to quantitatively reproduce the EOS. However, with the right choice of functional it is still possible to qualitatively reproduce helium’s behaviour in the solid hcp phase.
3.1.4 Conclusion

Traditionally low-pressure (< 1 GPa) solid helium studies have used simple pair-wise potentials with complex path integral Monte Carlo and quantum Monte Carlo techniques to simulate the quantum mechanical behaviour of the helium atoms accurately. In this study, we attempt to reproduce the experimental EOS of low-pressure solid helium isotopes using density functional theory. Particular interest is paid to the uniquely large difference in pressure between isotopes for a given volume. We find that the limiting factor to DFT in the simulation of low-pressure hydrogen and helium is the systematic error due to the choice of functional. The LDA functional is the least accurate of the tested functionals. This is likely due to the helium’s electrons being strongly bonded to the nucleus and, therefore, poorly described by the free electron assumptions used in the LDA model. Hybrid and GGA functionals produce a similar spread of EOS fits. This spread of results fits better to experimental results than the LDA functional. However, the GGA functionals have a systematic error of approximately 0.2 GPa due to the choice of parametrization. Van der Waals corrections to GGA functionals produce a consistent and significant shift to lower pressures, suggesting that these corrections are important to account for.

It was also found that the inclusion of ZPE significantly increased the calculated pressure. The value of this zero-point pressure increase differed by volume and functional, with the contribution approaching zero as volumes increased. We concluded that the pressure difference between isotopes seen in experiments can be explained by zero-point pressure as it is reproduced by the calculations using the PBE+G06 functional. Without this contribution, there was no difference between the calculated isotope EOS.

Of the functionals with Van der Waals corrections, those that were based on BLYP failed to reproduce the pressure gap between isotopes. From this, we conclude that PBE based functionals most accurately reproduce the behaviour of helium isotopes at low pressures, particularly when it comes to modelling the phonon behaviour. It was found that Helium was not stable at the volumes found in experiments without the inclusion of ZPE. This means that the initial geometry optimisation of the calculation carried out by CASTEP using only DFT fails to give realistic results. For structures with variable parameters, an additional calculation must be carried out taking ZPE contributions into account. We also find that the quasiharmonic approximation used in DFPT eventually results in imaginary modes, which
gives unrealistic ZPE contributions.

3.2 Self-Consistent Phonon Method

3.2.1 Introduction

In the previous chapter, we saw that one source of error in producing an accurate EOS for solid helium in the low-pressure regime is in the calculation of the ZPE. This zero-point contribution to the pressure makes up a significant percentage of the pressure in the < 10 GPa regime. This zero-point contribution is what stabilises the solid helium phase at densities higher than ~ 1/23 atoms per Å$^3$. The predicted destabilisation occurs at densities much higher than solid hcp helium found is known to exist down to densities of ~ 1/37 atoms per Å$^3$ [167, 168]. At these densities, DFPT with its quasi-harmonic assumption returns phonon modes with imaginary frequencies. These imaginary modes either result from an unstable mode in the structure or are due to the breakdown of the harmonic approximation in a stable helium structure; However, helium has been known to be affected by an-harmonic potentials [34, 35] which leads to a bimodal potential well in the bcc phase [165].

The self-consistent ab initio lattice dynamical method (SCAILD) has been developed to calculate the lattice dynamics of an-harmonic systems using DFT [1]. In this chapter, we will use SCAILD to investigate what change, if any, the an-harmonic mode has on the helium solid hcp low-pressure EOS. First, we will develop a superscript to interface the CASTEP [63] code with the SCAILD code [1]. Our results show that the SCAILD method fails to account for the quantum nature of the solid. This quantum nature is an issue as at low enough pressures the helium solid only exists below the Debye limit. This establishes the need for an alternative method to account for the anharmonic behaviour of helium-helium interactions.

3.2.2 Method

The SCAILD method works by solving a mean-field Hamiltonian employing a self-consistent iterative cycle and ab-inito calculations. Initial mean-squared atomic displacements are approximated from standard quasi-harmonic calculations. These displacements are then used to calculate a new force matrix.
which can be used to calculate a new set of mean-squared atomic displacements. This process is iterated until a self-consistent solution is found.

The Hamiltonian of a lattice dynamical system can be expressed as a sum of the harmonic and an-harmonic components.

\[ \mathcal{H} = \mathcal{H}_h + \mathcal{V}_{anh} \]  

(3.4)

By letting \( N \) be the number of atoms and \( M \) the atomic mass. We can express the atomic displacement \( \mathbf{U}_R \) and momentum \( \mathbf{P}_R \) as the canonical phonon coordinates \( \mathbf{Q}_{qs} \) and \( \mathbf{P}_{qs} \) respectively as

\[ \mathbf{U}_R = \frac{1}{\sqrt{MN}} \sum_{qs} \mathbf{Q}_{qs} \epsilon_{qs} e^{i\mathbf{q} \mathbf{R}} \]  

(3.5)

\[ \mathbf{P}_R = \frac{1}{\sqrt{MN}} \sum_{qs} \mathbf{P}_{qs} \epsilon_{qs} e^{i\mathbf{q} \mathbf{R}} \]  

(3.6)

Where \( \mathbf{R} \) labels the Bravais lattice cells, \( \mathbf{k} \) the wave vector and \( s \) the branch of the phonon mode, for the eigenvalues \( \omega_{qs} \) and eigenvector \( \epsilon_{qs} \). With these, we can write the harmonic part of the Hamiltonian as

\[ \mathcal{H}_h = \sum_{qs} \frac{1}{2} \left( \mathbf{P}_{qs}^2 + \omega_{qs}^2 \mathbf{Q}_{qs}^2 \right) \]  

taking the thermodynamic average of the operators \( \mathbf{Q}_{qs} \mathbf{Q}_{qs}^\dagger \) gives the mean squared atomic displacement. This is given as

\[ \langle \mathbf{Q}_{qs} \mathbf{Q}_{qs}^\dagger \rangle = \frac{\hbar}{\omega_{qs}} \left[ \frac{1}{2} + \frac{1}{e^{(\hbar \omega_{qs})/(k_B T)} - 1} \right] \]  

(3.8)

For sufficiently high temperatures, in the classical limit, the operators \( \mathbf{Q}_{qs}/\sqrt{M} \) can be replaced with real numbers

\[ \mathbf{A}_{qs} = \pm \sqrt{\frac{\langle \mathbf{Q}_{qs} \mathbf{Q}_{qs}^\dagger \rangle}{M}} \]  

(3.9)

using ab-initio methods, we can calculate the restoring force

\[ \mathbf{F}_R = \sum_{R'} \Phi (\mathbf{R} - \mathbf{R}') \mathbf{U}_R \]  

(3.10)
where $\Phi$ is the inter-atomic force constant matrix. Taking this, we can then write the Fourier transform of this as

$$F_q = \sum_s M \omega_{qs} A_{qs} \epsilon_{qs}$$  \hspace{1cm} (3.11)$$

using the orthogonality of the phonon modes we can write the phonon frequencies as

$$\omega_{qs} = \left[ -\frac{1}{M} \frac{\epsilon_{qs} F_q}{A_{qs} \epsilon_{qs}} \right]$$  \hspace{1cm} (3.12)$$

For a system close to the harmonic approximation these equations can be solved exactly. Weakly an-harmonic systems can be described using harmonic calculations over a range of volumes in the quasi-harmonic method. In a dynamically stable system, any small atomic displacement will lead to an increase in the total energy of the system. For systems that are strongly anharmonic, this displacement can lead to the system finding a lower energy state, which leads to imaginary phonon frequencies. To correctly account for these an-harmonic modes the interactions between phonons must be taken into account.

To understand how the SCAILD method takes these interactions into account it is useful to rewrite the Hamiltonian using the canonical phonon coordinates as shown in equations 3.5 and 3.6

$$H = \sum_{qs} \frac{1}{2} \left[ \mathcal{P}^2_{qs} + \omega^2_{qs} \left( 1 + \frac{1}{3} \sum_{q_1, q_2, s_1, s_2} \bar{R}(q, q_1, q_2, s, s_1, s_2) \times \frac{Q_{q_1 s_1} Q_{q_2 s_2}}{Q_{qs} \epsilon_{qs}} + ... \right) \right]$$  \hspace{1cm} (3.13)$$

where

$$\bar{R}(q, q_1, q_2, s, s_1, s_2) = \frac{1}{(MN)^{3/2}} \sum_{R, R_1, R_2} \sum_{\alpha, \beta, \gamma} \Phi_{\alpha \beta \gamma}(R, R_1, R_2)$$
\times \epsilon_{qs} \epsilon_{q_1 s_1} \epsilon_{q_2 s_2} e^{i(R_1 q_1 + R_2 q_2)}$$

This Hamiltonian can no longer be separated into $3N$ independent Hamiltonians. However, if we replace the $Q_{qs}/\sqrt{M}$ with the $A_{qs}$ as defined in equation 3.9 we can write a mean field equation as

67
\[ H^{MF} = \sum_{qs} \frac{1}{2} \left( P_{qs}^2 + \omega_{qs}^2 Q_{qs} \right) \]  

(3.14)

where

\[ \tilde{\omega}_{qs}^2 = \omega_{qs}^2 \left( 1 + \frac{1}{3} \sum_{q_1, q_2, s_1, s_2} \tilde{R}(q, q_1, q_2, s, s_1, s_2) \frac{A_{qs_1 s_1} A_{qs_2 s_2}}{A_{qs s}^2} + ... \right) \]  

(3.15)

with the equations 3.8, 3.9, 3.14 and 3.15, an initial set of guess displacements and the interaction terms \( \tilde{R}(q, q_1, q_2, s, s_1, s_2) \) we can self-consistently solve the mean field Hamiltonian.

For our calculations, CASTEP [166] was used for all ab-initio calculations to make it easier to compare with calculations carried out in other chapters. The DFT calculations were carried out in a 36 atom hcp cell, with a k-point sampling of a 3x3x3 Monkhorst-Pack grid. As the SCAILD code was developed to be used with VASP [169, 170] it was necessary to write a simple superscript to reformat and pass data between the two existing codes.

In practice, we get our initial guess for starting frequencies from a quasi-harmonic calculation. SCAILD uses a finite displacement calculation based on the PHON framework [171]. The frequencies from these calculations are taken by the SCAILD code which uses the equations 3.5, 3.8 and 3.9 to work out a series of displacements for each atom. Any imaginary phonon frequencies due to the harmonic approximation will cause problems with this calculation and so the absolute value of the imaginary frequencies is used as an initial guess. The sign in front of \( A_{qs} \) is chosen at random with equal probability to be positive or negative. These initial displacements are then used to generate input files to the ab-initio calculations.

These ab-initio calculations are used to calculate the restoring force on each atom. It can be shown that the equation 3.12 holds for \( \omega_{qs} \) found in the mean-field Hamiltonian described by 3.14 [1]. This allows the SCAILD to use equation 3.12 to calculate a new set of frequencies from the Fourier transform of the force matrix. This is then checked for self-consistency with equations 3.5, 3.8 and 3.9. If self-consistency isn’t found, then a new set of displacements is generated from these frequencies and used to set up a new ab-initio calculation. This process is iterated until self-consistency is achieved.
3.2.3 Results

When applying the self-consistent phonon method to low pressure helium we, unfortunately, run into an issue. The issue comes from an assumption implicit to SCAILD that we are in the high-temperature regime. To create the mean-field Hamiltonian approximation SCAILD replaces the $Q_{qs}/\sqrt{M}$ operators in the an-harmonic Hamiltonian with the real number $A_{qs}$, as shown in equation 3.9. This equivalence only holds true above the Debye temperature, the temperature at which the highest energy phonon is excited. The Debye temperature is defined in the Debye model as

$$\Theta_D = \frac{h v_S}{k_B \lambda_{\text{min}}} \tag{3.16}$$

where $v_S$ is the speed of sound within the solid and $\lambda_{\text{min}}$ is the minimum wavelength of a phonon due to the unit cell. From this, we can see that the Debye temperature is proportional to the speed of sound within the solid. As such, the Debye temperature is a measure of the hardness of a solid and is dependent on a material’s density. The use of this assumption to formulate the mean-field Hamiltonian meant that the self-consistent cycle solution can only be found above this limit, and so we must be careful of what temperature we run our calculations at. The other temperature limit of the SCAILD simulation is that we are required to stay within the solid regime. At high enough temperatures all solids melt, this creates issues with the self-consistent phonon calculation as the simulated structure will not be stable.

These limits come into conflict for materials where the Debye temperature is above the melting line. This means that for a given solid there may be a minimum pressure below which it is not possible to use the SCAILD method, as shown in figure 3.8. Unfortunately for the pressures we are interested in the melting line has a range of 5-17 K and the Debye temperature has a range of 40-100 K [33]. It is not until pressures near 40 GPa that helium is stable as a solid above 100 K.

This means that while we can run SCAILD calculations, and even get out an estimate for the ZPE there is no guarantee that the results will be anything sensible. The pressure limit of SCAILD in helium was only found during the process of this investigation. Here we will look through the data collected in this investigation to demonstrate in what ways the SCAILD calculation fails in this regime.
Figure 3.8: This illustration shows how the overlapping temperature limitations can exclude certain pressures from being investigated by SCAILD. SCAILD can only be used below the melting line, shown by the solid black line, and above the Debye temperature. Thus the self-consistent model is only valid in the portions of the graph coloured green.

Below we show the convergence process of SCAILD by tracking a few different outputs. We will do this for calculations in the high-temperature liquid range, 100 K, and the low-temperature solid range, 2 K. First, we will look at the mean squared displacement as given by $<U(R)^2>$ in Angstroms squared. For a typical SCAILD calculation, we would expect this to converge to a particular value as the SCAILD calculation arrives at a self-consistent solution. Figure 3.9 and figure 3.11 show the change in mean squared displacement over the 100 iterations of the self-consistent cycle at a range of volumes, from the high-temperature and low-temperature calculations respectively.

Figure graphs in figure 3.9 show how the ZPE and mean squared displacement $<U(R)^2>$, respectively, converges in over the 100 iterations of the SCAILD calculations carried out at 100 K cycle at a range of volumes. Whilst this calculation did not find a self-consistent solution to the equa-
Figure 3.9: This graph shows the convergence of SCAILD calculations carried out at 100 K for a range of volumes. The figure on the left shows the mean squared displacement of the helium atoms for each iteration of the self-consistent cycle. The figure on the right shows the ZPE per atom calculated at each iteration of the self-consistent cycle.

Sections 3.5, 3.8 and 3.9 do appear to converge to a particular value. We can see from the spikes in $<U(R)^2>$ and the dramatic jumps in the ZPE that the simulation is jumping between meta-stable states as it tries to find a self-consistent solution. This demonstrates that the calculated solid helium crystal structure is not stable at this temperature.

If we look at the convergence of the mean squared displacement and the zero point energy for the low-temperature calculations, 2 K, in figure 3.11 we can see this instability in the ZPE over a range of volumes shown in the first graph in figure 3.10. These zero-point energies are an average of the final 10 iterations of the self-consistent cycle. We would expect the ZPE to decrease as volumes increase but in this graph, we see a noisy spread of values. While the values trend downward as the volumes increase this is not true for every volume. This is because the temperature of the SCAILD calculation is high enough that it explores meta-stable states. Finally, we can see the EOS that results from this estimated ZPE in figure 3.10. We see a lower pressure EOS resulting from these high-temperature calculations, this suggests softer phonon modes are being explored at higher temperatures.

Next, we will look at SCAILD calculations carried out at 2 K below the melting line and the Debye limit. In figure 3.11 the convergence of the mean squared displacement and ZPE for $^4$He calculations are carried
Figure 3.10: The graph on the left shows the average ZPE of the last 10 iterations of SCAILD calculations carried out at 100 K, with the error bars showing the root mean squared error of this average. The graph on the right shows the EOS of $^4$He found in experiments with a variety of computational methods. The experimental data are taken from [32, 33]. The blue dash-dotted line comes from DFT calculations without accounting for ZPE, the solid yellow line is estimated from DFPT calculations and the green dashed line is estimated from SCAILD calculations taken at 100 K.

out. We see a smaller spread in the mean squared displacement with no dramatic spikes as we can see in the high-temperature calculations. This suggests the convergence process is more stable. This is in keeping with what we would expect as the calculation is exploring a smaller range of possible displacements. Despite this, we can see in the ZPE convergence that there are still sudden step changes in the convergence process. This can be explained by phonon-phonon interactions which are present in the force matrix extracted from the ab-initio calculations, but not accounted for in the self-consistent cycle used by SCAILD.

At low temperatures, we saw an improvement in the predicted $^4$He EOS when compared to DFPT, due to this calculations were extended to include the $^3$He EOS. If we look at the final zero-point energies of each calculation taken as an average ZPE of the last 10 iterations, shown as the left image in figure 3.12, we can see a less noisy trend for the zero-point energies of both isotopes. We see that all calculations appear to have converged to some stable state although some of these stable states give unexpected zero-point energies. For example, those volumes which appear to have a higher ZPE
Figure 3.11: This graph shows the convergence of SCAILD calculations carried out at 2 K for a range of volumes. The figure on the left shows the mean squared displacement of the helium atoms for each iteration of the self-consistent cycle. The figure on the right shows the ZPE per atom calculated at each iteration of the self-consistent cycle.

than those at a lower density. There are two trends in the ZPE data which are suggestive of the issue being caused by the requirement to be above the Debye temperature. The noise we see in the converged zero-point energies appears to be worse at lower density, where the quantum nuclear motion plays a larger role. We also see this issue more prominently in the $^3\text{He}$ calculations which due to its lighter mass again experiences a greater nuclear motion.

The EOS that we would expect using these zero point energy values is shown in the right images of figure 3.12. This image compares the EOS from SCAILD calculations to those using DFT and DFPT as covered in the previous section of this chapter as well as experimental data taken from [32, 33]. When looking at the Helium-4 data, it does appear that the SCAILD calculation improves the prediction, particularly at lower densities. However, due to the noise in the converged ZPE values taken from SCAILD, this doesn’t hold true for the $^3\text{He}$ case. When you compare the two EOS lines taken from SCAILD the qualitative behaviour is not what we would expect, such as the Helium-3 isotope taking up less volume than the Helium-4 isotope at lower pressures. When fitting to a Birch-Murnaghan EOS we get a RMSE of approximately 2 meV in the SCAILD $^4\text{He}$ fit and approximately 3 meV in the $^3\text{He}$ case. This may not seem like much initially but is large when compared to the approximately 0.1 meV root mean squared error from the fits.
Figure 3.12: The graph on the left shows the average ZPE of the last 10 iterations of SCAILD calculations carried out at 2K, with the error bars showing the root mean squared error of this average. The red squares show the results from $^3$He calculations and the blue squares from $^4$He calculations. The graph on the right shows the EOS of $^4$He and $^3$He found in experiments with a variety of computational methods. Red lines show fits to data from $^3$He calculations, and blue lines show fits to $^4$He calculations. The experimental data are taken from [32, 33]. The green dash-dotted line comes from DFT calculations without accounting for ZPE, the solid lines are estimated from DFPT calculations and the dashed line is estimated from SCAILD calculations carried out at 2 K.

to DFPT calculations. The breakdown in the approximation of the SCAID calculation at low temperatures decreases the accuracy of the calculations and so limits the use of SCAILD in this pressure regime. Despite this, there appears to be some improvement to EOS which suggests that an-harmonic approximations are a part of the remaining error in the DFT helium EOS. However, it is hard to know if the SCAILD method is performing as intended as we are well below the limits set in the formulation of the method.

3.2.4 Conclusion

Helium-helium interactions are known to be poorly described by the quasi-harmonic approximations accessible to DFPT [34, 35] calculation. To account for this the an-harmonic contributions to the phonon spectrum must be included in our calculation. As there is still a significant error between the
results we get from DFPT and those from experiments. It is important to quantify what effect if any an-harmonic contributions have on the calculated ZPE. SCAILD has been developed to account for these an-harmonics in a self-consistent iterative process. However, the approximation used to reformulate the phonon Hamiltonian in a way that can be written as a mean field solution requires certain approximations. One of the approximations shown by equations 3.8 and 3.9 assume that calculations are carried out above the Debye limit.

Due to helium’s weak bonding and light nucleus, there are portions of the phase diagram where the melting line is below the Debye limit. It is not until significant pressures $> 10$ GPa that the solid phase exists above the Debye limit. As such we cannot be sure that SCAILD will work as intended to investigate the pressure regime we are interested in. In this section we took two approaches to this issue: one set of calculations was carried out above the Debye limit but at temperatures where we expect the structure to melt and below the Debye limit at temperatures we expect the solid to remain stable. We find problems with both sets of calculations.

The high-temperature calculations, 100 K, regularly jump between seemingly stable solutions as the iterative process attempts to converge to a reasonable solution. This is due to the simulation exploring a range of metastable states as the random displacements that the calculation use to explore the phase space are larger than those which would be seen in the solid helium crystal. This results in erratic jumps of the ZPE between calculations carried out at different volumes. This results in softer phonon modes than those calculated with quasi-harmonic approximations, which leads to a lower calculated pressure for a given volume as shown in figure 3.10.

Lower temperature calculations have some of the same issues, however, do suggest that the an-harmonic modes are significant enough to contribute to the difference we see between DFPT predictions and experimental results. These calculations did experience unexpected jumps in the zero-point energies that were seen in the higher temperature calculations but to a lesser extent. For the low-temperature calculations, this noise became more of an issue the more prevalent the quantum behaviour of the nuclei. Such as at lower densities and in calculations on the $^3$He isotope. This suggests the source of the noise in the low-temperature regime is the breakdown of the approximation shown by equations 3.8 and 3.9. Whilst this noise does mean the parameterization of the Birch-Murnaghan EOS is poor we still see what appears to be an improvement in the predicted EOS when compared to those
using DFPT. Suggesting that the an-harmonic modes do contribute to at least part of the error seen in previous sections of this chapter. However, as SCAILD is operating outside of the intended assumptions it is unclear how to interpret these results.

3.3 Path Integral Molecular Dynamics

3.3.1 Introduction

So far we have tried a few methods to calculate the ZPE contribution to the helium EOS in this chapter. The first method DPFT relies on the quasi-harmonic approximation and therefore ignores the an-harmonic modes contribution to the ZPE. The second SCAILD does account for an-harmonic modes, however, it relies on a semi-classical formulation which assumes that calculations are carried out above the Debye temperature. Both of these methods fail to completely describe the an-harmonic and highly quantum nuclear motion of solid helium. To do that we need a fully quantum method that doesn’t rely on the quasi-harmonic approximation. The difficulty with any exact solution to a many-body quantum system is the large computational time. Therefore we need a way to approximate the exact quantum solution for a reasonable computational time.

Path integral molecular dynamics (PIMD) uses parallel instances of classical molecular dynamics simulations to approximate a fully quantum solution. Each atom in the classical molecular dynamics simulations is connected to itself in two other parallel simulations by a simple harmonic oscillator so that a chain forms connecting all the simulations. As the number of simulations in this chain approaches infinity the PIMD simulation approaches a fully quantum description of the nuclear motion.

As PIMD is a molecular dynamics simulation and not a static calculation it will fully account for any an-harmonicity in the helium potentials. In this section, we will explore the use of ab-initio PIMD in low-pressure solid helium. We will try to recreate the EOS of both helium isotopes. We will compare the results to previous methods investigated in this chapter in an attempt to quantify the limits of ab-initio methods in materials with significant quantum nuclear monition.
3.3.2 Method

To understand path-integral molecular dynamics we must first write the canonical ensemble in the path-integral formalism. First we must reformulate the Greens function $\mathcal{G}(x, y, t)$. This is a propagation operator where

$$|\mathcal{G}(x, y, t)|^2$$

(3.17)

gives the probability of a system going from $x \rightarrow y$ over a time period $t$. This function can be written with the inclusion of a middle state as

$$\mathcal{G}(x, z, t) = \int dy \mathcal{G}(x, y, t_1) \mathcal{G}(x, z, t - t_1)$$

(3.18)

We can repeat this process multiple times so that we have $N$ time sections each of time $\Delta t$. If we keep taking time slices so that $\Delta t \rightarrow 0$ we can rewrite this as the integral [172]

$$\mathcal{G}(x, y, t) = \int dt \mathcal{D}[\tilde{q}(t)] \cdot e^{iS[\tilde{q}(t)]/\hbar}$$

(3.19)

where $S[\tilde{q}(t)]$ is the classical action potential defined as

$$S[\tilde{q}(t)] = \int_{t_1}^{t_2} dt \mathcal{L}[\tilde{q}(t)]$$

(3.20)

A classical system will follow the path for which the action potential is a minimum. The path integral denotes an integration over all potential paths. Due to the action term being a part of a complex exponent in this formulation, we can see that the changing action potential of different paths leads to a complex phase term, which creates interference between the terms from different paths [172]. We can see that for paths with large action potentials, the oscillation of this phase is very rapid. This leads to a decoherence effect between the paths with a large action. In turn, the interference caused by this phase change leads to the coherence of paths that are similar to the classical path. This makes the initially daunting task of having to integrate over all possible paths into a more manageable one where we only need to account for enough paths closest to the one with the least action to give us the accuracy desired.

To use the path integral formalism to construct our path integral molecular dynamics we start with the one-particle canonical ensemble
\[ Z(\beta) = Tr \left( e^{-\beta H} \right) \int dx \, \langle x | e^{-\beta H} | x \rangle \]  

(3.21)

As the Hamiltonian can be written as a sum of the kinetic and potential parts, we can use the Trotter expansion

\[ e^{\lambda (A+B)} = \lim_{P \to \infty} e^{\frac{\lambda}{2P} A} e^{\frac{\lambda}{2P} B} e^{\frac{\lambda}{2P} A} \]  

(3.22)

This allows us to do the same discretisation trick as before, and so we can write the canonical ensemble as

\[ Z_P(\beta) = \left( \frac{mP}{2\pi\beta\hbar^2} \right)^\frac{P}{2} \int dx_1...dx_P \exp \left[ \sum_{i=1}^{P} \frac{mP}{2\beta\hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \phi(x_i) \right] \]  

(3.23)

as the error in the Trotter expansion goes as \( (\frac{\beta}{P})^2 \) we should expect to be able to approximate the exact solution with a high enough value of \( P \). It is also useful to note that this form of the Hamiltonian looks exactly like a set of \( P \) oscillating beads connected by springs in a chain where the \( P + 1 \) bead is the same as the first bead. We can write the external potential as

\[ U_{eff}(x_i...x_P) = \sum_{i=1}^{P} \left[ \frac{mP}{2\hbar^2} (x_{i+1} - x_i)^2 + \frac{1}{P} \phi(x_i) \right] \]  

(3.24)

With this, we have shown that the imaginary time in a quantum mechanical system is mathematically equivalent to a statistical mechanics simulation at finite temperatures. Finally, to run this as a molecular dynamics simulation we need to add a momentum operator. With all of this, we get the canonical ensemble

\[ Z_P(\beta) = N \int dp_1...dp_P \int dx_1...dx_P \exp \left[ \sum_{i=1}^{P} \frac{p_i^2}{2m_i^2} + U_{eff}(x_i...x_P) \right] \]  

(3.25)

This description can be used to implement our path integral molecular dynamics simulation. To do this we will run a series of parallel classical simulations where each particle is connected to an identical particle in another simulation by a simple spring. This is continued until all particles or
beads in all the simulations are connected in a chain with the final simulation connecting to the initial first one so that all beads are connected to two others. Each of these chains represents a quantum particle. The chains have harmonic modes and frequencies just like normal springs. We can see from the above equation 3.25 that the frequencies $W_P$ will be given as $\sqrt{\frac{P}{\beta \hbar}}$ this means that the time step of the simulation may be limited by this frequency. This issue can be circumvented by using a change of variables known as a staging transformation which allows us to decouple the mass of the chain from the mass of the particles. We can therefore adjust this mass so that the frequency of the chain is independent of the number of beads.

The number of beads required to approximate the quantum particle accurately increases at lower temperatures. As we are in a low-temperature regime $< 2$ K where QNE dominate converging the number of beads could be difficult. Therefore to ensure that we can properly converge other important values such as the bead number and the length of the simulation we have to relax other parameters. The two most costly factors in our previous calculations are the cell size and the k-point sampling. As simulation size is particularly important to ensure a proper relaxation of any molecular dynamics calculation we will be reducing the k-point sampling from 3x3x3 to 1x1x1 for calculations in this chapter. To converge the number of beads we have run PIMD calculations of 36 Helium atoms sampled using 1x1x1 k-point grid using a PBE functional with a Grimme (DFT-D2) Van der Waals correction [59, 54]. The simulations were set to run for 4000 iterations with a time step of 1 fs at a target pressure of 1 GPa.

As this calculation inherently includes all quantum nuclear motion effects we use an NPT simulation cell. This means we will set a specific pressure and allow the molecular dynamics simulation to relax to an appropriate volume. An Anderson-Hoover barostat was used throughout all NPT calculations. If we were to use an NVT as we did in previous sections and ran calculations above the expected volume at 0 GPa then there is no guarantee that the simulation would remain solid throughout the simulation run. As the PIMD simulation is non-ergodic we must be careful to choose a thermostat which does not assume ergodicity. Currently, the only thermostat implemented in CASTEP which meets these requirements is the Langevin thermostat.
3.3.3 Results

Figure 3.13 shows the total energy of the simulation over the calculations run for simulations of different bead numbers. From this, we can see that the simulation takes approximately 3 ps to equilibrate. Looking at figure 3.14 we can see that this is mostly driven by the relaxation of the volume as the simulation attempts to find the correct pressure. We can also see that the volume never quite fully settles during the simulation run as it oscillates around the actual equilibrium. This is important as the equilibrium volume is the value that we need to construct the EOS diagram. Figure 3.15 shows us that again the desired pressure is achieved around the 3 ps mark. We can therefore average out the values after this point to get an idea of what the actual equilibrium values are.

The notable exception to this is the 256 bead calculation which was unable to complete the full 4000 iterations as the calculation grew more expensive. As calculations above this bead number where unable to be run for a sufficiently long time to equilibrate none of those results are included in this study. For calculations using 256 beads, the last 1000 iterations were averaged over to estimate the equilibrium values.

The equilibrium pressure, volume per atom and total energy per atom is plotted against bead number as shown in figure 3.16. These are the average values over the last 1000 iterations and error bars show the standard deviation from the average for each value. We can see that neither the volume nor the total energy has reached equilibrium for a bead number of 256. This means that ab-intio PIMD has limited usage for analysing helium in the pressure range that we are interested in, as to properly converge the number of beads is too computationally costly. Calculations at higher bead numbers were carried out but due to the computational expense, the simulations were not able to fully equilibrate. This means that results from these simulations are unreliable.

In Figure 3.17, we have plotted the results from PIMD calculations carried out with 128 beads against EOS predictions from other data covered previously in this chapter. We have carried this out for both $^4$He and $^3$He, as shown by the red and blue squares. From this, we can see that the volume estimated by PIMD is larger than those predicted by DFPT or seen in experiments. As we would expect increasing the bead number to increase the volume, we should expect that a PIMD calculation with a fully converged bead number would only increase this difference. This suggests that there is
Figure 3.13: This figure shows how the volume per atom changes over the run of an NPT PIMD calculation at 2 K with a target pressure of 1 GPa for different bead numbers.

another issue with the PIMD calculations other than just the bead number. This could be due to the limits of the simulation cell size. All these calculations are carried out on a simulation cell of 36 atoms. Whilst this is large enough for static calculations like DFPT and SCAILD, it may not be enough for the dynamic NPT molecular dynamics simulations used in PIMD. This quickly becomes an issue as increasing the cell size dramatically increases the computational cost quickly, making the calculations unfeasible. Finally, while the equation 3.25 fully describes the quantum behaviour of a single quantum particle, it ignores the possibility of quantum nuclear exchange [160], which may have a significant effect in Helium at this pressure. Methods such as Path Integral Monte Carlo simulations can account for this exchange term as such future studies could investigate the use of ab-initio
3.3.4 Conclusion

Path integral molecular dynamics calculations are a method of fully describing the quantum nuclear effect of a quantum nucleus. This is done by noting PIMC to see if this has a significant effect.

Despite these issues, we also see the correct qualitative behaviour with the quantum nuclear motion causing a significant difference in volume between both isotopes. Regardless of the issue being driven by the simulation cell size or the number of beads in the PIMD chain, this study puts a limit on the use of ab-initio PIMD in solid helium below 1 GPa.
Figure 3.15: This figure shows how the pressure of the simulation cell over the run of an NPT PIMD calculation at 2 K with a target pressure of 1 GPa for different bead numbers.

that the imaginary time component of the particles Hamiltonian is mathematically the same as a thermodynamic simulation of a 1-dimensional chain of beads connected by a simple spring. This, however, dramatically increases the cost of the simulation as each new bead requires an additional ab-initio molecular dynamics simulation. As the number of beads must be fully converged to accurately approximate the quantum behaviour, this can lead to excessively high computational costs. The number of beads required increases for systems where quantum nuclear behaviour dominates and at low temperatures, this means we might expect a particularly high requirement on the bead number for the conditions we are interested in.

In this study, we found that to fully converge the bead number for an ab-
Figure 3.16: This figure shows the converged pressure, volume and total energy of a PIMD simulation after 2 ps. From this, we can see that neither the total energy nor volume has converged by 258 beads. The NPT PIMD simulations have an external pressure of 1 GPa and a temperature of 2 K. The errorbars show the standard deviation of the last 1000 steps of the simulation which are averaged over to find the equilibrium values.

The 
initio simulation of the pressure regime understudy was prohibitively computationally expensive. As well as this, increasing the bead number past $\sim 128$ beads leads to the predicted EOS deviating further from experimental values. This indicates that either the simulation cell size was not converged at 36 helium atoms or that the lack of quantum nuclear exchange terms in the formulation of PIMD makes it unsuited to describe solid helium below 1 GPa.
3.4 Chapter Summary

In this chapter, we have looked at the potential and limitations of using ab-initio methods to investigate solid helium at pressures below 1 GPa. Due to helium’s weak interatomic potentials and low nuclear mass, it acts as a good test case for the use of ab-initio investigations of materials where quantum nuclear behaviour is significant. Any issues with the methods used...
to predict quantum nuclear motion will produce noticeable deviations from experimental results. In particular, the EOS of the helium isotopes differs dramatically from each other for pressures $< 1 \text{ GPa}$ [32, 33]. This difference is driven primarily by the difference in the quantum zero-point effects [119].

We, therefore, attempted to reproduce the EOS of both isotopes, as it depends on the ZPE. This helps to ensure that if we can reproduce the experimental results, it is not due to a convenient cancellation of systematic errors.

In the first section of this chapter, we used quasi-harmonic approximations such as density functional perturbation theory to calculate the ZPE contributions to the EOS. We found that due to the low pressures involved, the choice of functionals dramatically affects the predicted EOS. It was found that it is important to account for Van der Waals effects, although there was not much difference between the different Van der Waals corrections tested. It was also found to be important to have a GGA functional, with PBE appearing to provide the closest match to experiments.

While DFPT does qualitatively reproduce the expected pressure difference between the isotopes, the predicted EOS differs from the experimental results, particularly at higher volumes. Part of the reason for this deviation is the presence of imaginary phonon modes in the calculation. These cause a breakdown in the quasi-harmonic approach and are an indicator of anharmonic behaviour in a solid. To account for this effect we needed a method of calculating phonon behaviour which doesn't rely on the quasi-harmonic approximation.

SCAILD uses a self-consistent iterative method to approximate the anharmonic modes [1]. Unfortunately, in the development of the mean-field Hamiltonian used in the SCAILD method, an approximation is used that is only true above the Debye limit [1]. In helium, the Debye temperature is greater than the temperature that the solid melts for the majority of all pressures $< 10 \text{ GPa}$. This makes the calculation unreliable as there is no guarantee that the calculation will have a self-consistent solution. We found that whilst the SCAILD calculation does appear to fully converge to a stable state, many of the observables do converge to a particular value. The lack of proper convergence caused large errors in the Birch-Murnaghan parameterisation, and the difference between the isotopes is lost to noise.

Finally, we investigated if PIMD could be used to reproduce the EOS results we are interested in. PIMD can, in theory, reproduce the behaviour of a quantum particle to any accuracy given enough compute time and the
dynamical nature of the calculation means that it will accurately account for any an-harmonic behaviours. We found, however, that the computational cost of fully converging even a simulation cell of 36 atoms was prohibitively expensive. On top of this, it was found that increasing the bead number increased the equilibrium volume of the NPT calculations despite the unconverged PIMD simulations already overestimating the volume for a given pressure. This indicates that either the cell size is not sufficiently large enough, which would only exacerbate the computational requirements, or that due to PIMD failing to account for quantum nuclear exchange effects.

Alternative ab-initio methods do exist which can be used to account for an-harmonic quantum nuclear motion. Vibrational self-consistent field theory methods require an antiquate sampling of the 3N dimensional potential surface which is then used to solve the many-body quantum problem [173, 174]. These methods tend to be prohibitively expensive and as such were not explored in this study. As well as this, new methods have been developed since this study was carried out.

Of note is the stochastic self-consistent harmonic approximation (SS-CHA) [175] and the Quantum Self-Consistent Ab-Initio Lattice Dynamics (QSCAILD) [176]. SSCHA works by approximating the density distribution around each ion as a Gaussian. This simplifies the free energy calculation, which is then minimised by randomly sampling the Gaussian distributions using an ab-initio method. This allows for an an-harmonic approximation which doesn't make the assumption that we are in a classical limit, and so can properly account for quantum effects. As the name suggests, QSCAILD was based on the SCAILD method discussed in this chapter. However, in a similar manner to the SSCHA method samples the interatomic forces based on the quantum statistics of a harmonic model. We recommend that future works attempt to replicate this study using either the SSCHA or QSCAILD method to account for any an-harmonic behaviour. For the remainder of this thesis, we will concentrate on the higher pressure regime, > 1GPa where the DFPT calculations are well-behaved.
Chapter 4

Hydrogen-Helium Mixtures

4.1 Miscibility

4.1.1 Introduction

Hydrogen and helium are the two most abundant elements in the universe; as such, it is useful to understand their interactions under a wide range of conditions. Of particular interest to the astronomical community are the conditions found in the Jovian gas giants such as Jupiter and Saturn. As such, this is an area that a large number of papers have studied in detail. Despite this, there remains a large number of open questions regarding the behaviour of $\text{H}_2$-He mixtures in this regime. In particular, it has been an open question as to exactly when demixing occurs in the high pressure (Mbar) high temperature (Kk) phase of the pressure diagram. This is because a possible reason for the unexplained luminosity of Saturn is a region of immiscibility in which the heavier helium falls through the hydrogen realising energy as it does [138, 139, 140]. It is also an ongoing question as to how heavier elements interact with these $\text{H}_2$-He mixtures to form the different layers of these planets, with recent experiments finding evidence of these elements being found as far out as 63% of the radius of the planet [177]. Because of this, many ab-initio studies have been carried out in this high-pressure regime. However, to our knowledge, no ab-initio studies have investigated this behaviour at low pressures.

While helium is typically considered chemically inert, recent studies have claimed to show that helium can form stable structures with ionic compounds where the resulting structures are stabilised by long-range Coulomb
interactions rather than chemical bonds [178]. Experiments carried out in diamond anvil cells (DAC) have found that helium is immiscible in solid hydrogen and then hydrogen is immiscible in solid helium [158]. Mixing occurs only when both elements are in the fluid regime. At higher pressures, ab-initio calculations predict a region of insolubility in the fluid regime [140, 147, 149, 150, 179]. This transition appears to be brought on by the onset of metallization in the hydrogen fluid [150].

Recently a series of experiments was carried out by Yoo et al. [2] using DACs that claimed to detect evidence of mixing in the helium-rich solid, as well as chemical bonding between hydrogen and helium. The main evidence for this was a Raman signal of approximately 2400 cm$^{-1}$, which is presumed to be due to H-He bonding and another at 140 cm$^{-1}$ due to the lattice phonon of the interstitial hydrogen atom. This would be a dramatic shift from the understood behaviours of helium and hydrogen in this regime and be the first example of helium forming a stable compound through chemical bonding. As such, this claim necessitates further theoretical and experimental analysis. An alternative explanation has been put forward by Turnbull et al. [22]. This paper shows how the observed Raman signals can be reproduced in high-pressure hydrogen-nitrogen van der Waals solids, suggesting that nitrogen contamination could explain the initial results.

In this chapter, we will explore H$_2$-He mixtures using ab-initio techniques. Using the methods explored in the last chapter, we will account for quantum nuclear motion allowing us to compare our results directly with DAC measurements taken at pressures < 15 GPa. We will use this to explore the claims of mixing and chemical bonding seen by Yoo et al. [2]. We find no evidence of mixing in the solid regime and no sign of chemical bonding. This agrees with the established understanding of helium and hydrogen’s behaviour as well as with other ab-initio studies [23], which support the idea that the signals seen in the Yoo et al. [2] results are due to nitrogen contamination of the sample.

As well as this, we will attempt to explain the mechanism behind the blueshift of the hydrogen vibron seen in hydrogen-helium mixtures. To our knowledge, there have been no ab-initio studies into this phenomenon. We propose that a localisation effect brought about by the physical separation of hydrogen molecules by helium in the solution is responsible for the blueshift. This localisation is due to the reduction in the coupling between the vibration of hydrogen molecules. The coupling between hydrogen molecules reduces the frequency of vibration and has been linked to the turnover of the hydrogen
vibron at higher pressure [40]. We show that localisation does occur and leads to the increase in the frequency of the Raman active modes of the hydrogen vibron. We also demonstrate that other explanations, such as a “localised pressure” caused by the helium atoms or chemical bonding, are inconsistent with our models.

4.1.2 Method

In this chapter, we will investigate the miscibility of both helium and hydrogen in both the solid and fluid regimes. To do this, we will compare simulations of both helium and hydrogen with simulations of pure hydrogen and helium mixtures. The lightness of helium and hydrogen means that nuclear motion and zero-point effects play a large part in the dynamics of both elements. The limits of the ab-initio methods to account for this quantum nuclear motion were explored in the last chapter in a study of helium at < 1 GPa, where the zero-point effects are most prominent due to the helium’s weak bonding and the limited effects of external pressure. Because of this work, we can be confident that the ab-initio methods used in this chapter account for all the relevant contributions to phonon behaviour of H$_2$-He mixtures at these pressures. In particular, we can take from this chapter that quasi-harmonic approximation of density functional perturbation theory (DFPT) is adequate as an-harmonic effects are a secondary contribution to phonon behaviour for pressures > 1 GPa.

Previous works that have concentrated on astrophysically relevant conditions, < 100 GPa and < 1000 K, where van der Waals interactions and nuclear quantum effects can be safely ignored [180, 140, 181]. However, below 5 GPa, the largest contribution to the pressure comes from quantum nuclear effects: the pressure arising from changes in zero-point energy (ZPE) with density. This means there is no way to be exactly sure of the final pressure when choosing the initial conditions of the density functional theory (DFT) calculations. Moreover, as our calculations are at relatively low pressures and require us to account for Van der Waals interactions, we use a Grimme dispersion scheme and a Perdew–Burke–Ernzerhof functional [54, 182, 183]. As changing the concentration of a sample for a fixed volume changes the ZPE contribution to the pressure, we will have to use constant volume calculations. The calculated pressures will not be the same when comparing simulations which have significantly different concentrations, so interpolation is required.
The existence of miscibility in the solid regime proposed by Yoo et al. [2] was detected in a helium-rich region of the DAC. As well as this, the proposed explanation for the high frequency, 2400 cm$^{-1}$, Raman signal was a strong H-He chemical bond. To investigate these claims, we will carry out calculations of hydrogen defects at interstitial sites in a helium solid as well as calculations with substitutional defects. To get the energy cost of the interstitial defects, we will use the equation

$$E_{\text{cost}} = E_{\text{defect}} - \left( E_{\text{He}} + \frac{1}{N_X} E_X \right)$$

(4.1)

and the energy cost of the substitutional defects

$$E_{\text{cost}} = E_{\text{defect}} - \left( \frac{N_{\text{He}} - 1}{N_{\text{He}}} E_{\text{He}} + \frac{1}{N_X} E_X \right)$$

(4.2)

where $E_X$ is the total energy of the simulation of an object $X$ and $N_X$ is the number of objects in that simulation. If we assume a small number of defects, we can approximate the expected miscibility of a defect for a given temperature as

$$P = e^{\Delta E/k_B T}$$

(4.3)

This will give us an idea of how likely each of these defects is to occur at a particular temperature and how likely these defects are to be detected. In this chapter, we find that substitutional hydrogen molecule defects are helium’s most favourable form of hydrogen defect. To better understand the behaviour of these defects in the solid, we look at the bonding energy of these hydrogen molecules by comparing simulations of lone substitutional defects with simulations of up to four hydrogen molecules in the nearest neighbour hcp sites. If the hydrogen molecules exist as clusters of defects, this could affect the Raman signal due to the hydrogen-hydrogen bond if, as we propose coupling between vibrating molecules significantly affects the frequency of the Raman active mode.

We are also interested in the energy cost of mixing in the fluid regime. To this end, NVT molecular dynamics calculations are carried out for 1 ps over a range of concentrations substituting each helium atom with a hydrogen molecule. Five snapshots are taken from each simulation and relaxed using an NVT geometry optimisation calculation. A DFPT calculation is then carried out on the resulting structure to calculate the ZPE. We then averaged
Table 4.1: Calculations were carried out in a simulation cell with 36 lattice sites in an $X_{He} = 0.5$ helium-hydrogen mixture using a PBE functional with DFT-D2 dispersion corrections and a 2x2x2 k-point grid. Zero-point energies were taken from Gamma point DFPT calculations.

<table>
<thead>
<tr>
<th>Cut-off Energy (eV)</th>
<th>Total Energy (eV/atom)</th>
<th>ZPE (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>-53.7908</td>
<td>0.2903</td>
</tr>
<tr>
<td>600</td>
<td>-53.2633</td>
<td>0.2971</td>
</tr>
<tr>
<td>700</td>
<td>-54.1177</td>
<td>0.2937</td>
</tr>
<tr>
<td>800</td>
<td>-54.14899</td>
<td>0.2931</td>
</tr>
<tr>
<td>900</td>
<td>-54.1574</td>
<td>0.2933</td>
</tr>
<tr>
<td>1000</td>
<td>-54.1588</td>
<td>0.2925</td>
</tr>
<tr>
<td>1100</td>
<td>-54.1589</td>
<td>0.2925</td>
</tr>
</tbody>
</table>

To give the energy cost of an object, a helium atom or hydrogen molecule, in a mixture for a range of concentrations. Where $N_{total}$ is the total number of objects in a simulation, $N_{He}$ is the number of helium atoms in the simulated mixture and $E_X$ is the energy of a simulation of $X$. This will give us a way to compare the per-atom cost of mixing across a range of concentrations.

All calculations were carried out, starting with a pure helium simulation cell of 36 atoms. We converged the energy to 1 meV using a 2x2x2 k-point grid and a 900 eV cutoff for simulations of hydrogen defects in the helium solid initial NPT geometry optimisation calculations were carried out on pure helium. We then used lattice dynamics and the quasiharmonic approximation and varied the volume to calculate the true pressure. There is no analytic form for the variation of the ZPE with volume within DFT. This allows us to compare the enthalpy cost of the defects as the extra pressure due to the ZPE of a single defect is relatively small. NVT geometry optimisations were carried out before DFPT calculations to include zero-point effects for the other solid calculations.
Table 4.2: Calculations were carried out in a simulation cell with 36 lattice sites in an $X_{He} = 0.5$ helium-hydrogen mixture using a PBE functional with DFT-D2 dispersion corrections and a cut-off energy of 900 eV. Zero-point energies were taken from Gamma point DFPT calculations.

<table>
<thead>
<tr>
<th>k-point grid</th>
<th>Total Energy (eV/atom)</th>
<th>ZPE (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x2x2</td>
<td>-54.2559</td>
<td>0.2921</td>
</tr>
<tr>
<td>3x3x3</td>
<td>-54.2576</td>
<td>0.2933</td>
</tr>
<tr>
<td>4x4x4</td>
<td>-54.2576</td>
<td>0.2932</td>
</tr>
<tr>
<td>5x5x5</td>
<td>-54.2576</td>
<td>0.2933</td>
</tr>
</tbody>
</table>

Table 4.3: Calculations were carried out in a simulation cell with 36 lattice sites in an $X_{He} = 0.5$ helium-hydrogen mixture using a PBE functional with DFT-D2 dispersion corrections and a cut-off energy of 900 eV. Zero-point energies were taken from Gamma point DFPT calculations.

<table>
<thead>
<tr>
<th>Number of lattice sites</th>
<th>K-point Grid</th>
<th>Total Energy (eV/atom)</th>
<th>ZPE (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>6x6x4</td>
<td>-54.24567</td>
<td>0.27268</td>
</tr>
<tr>
<td>36</td>
<td>4x4x4</td>
<td>-54.24567</td>
<td>0.27346</td>
</tr>
<tr>
<td>64</td>
<td>3x3x4</td>
<td>-54.24567</td>
<td>0.27307</td>
</tr>
</tbody>
</table>

Table 4.4: Calculations were carried out in a simulation cell with 36 atoms in a hcp structure using a PBE functional with DFT-D2 dispersion corrections, a cut-off energy of 900 eV and a k-point grid of 4x4x4.

<table>
<thead>
<tr>
<th>Q-point Grid</th>
<th>ZPE (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x1x1</td>
<td>0.27346</td>
</tr>
<tr>
<td>2x2x2</td>
<td>0.27242</td>
</tr>
<tr>
<td>3x3x3</td>
<td>0.27234</td>
</tr>
</tbody>
</table>
Several thousand molecules are required to describe the liquid structure fully [184], but the phonon density of states is well sampled in much smaller cells. For each concentration, a random selection of helium atoms where replaced with hydrogen. We then carried out an NVT molecular dynamics calculation for 1 ps at 300 K on each mixture. Five snapshots were taken from each molecular dynamics run to ensure proper sampling of atomic configurations. The resulting snapshots were then relaxed to a local minimum with NVT geometry optimisation so that DFPT calculations could be carried out. This allows us to account for the ZPE effects without prohibitively costly PIMD calculations.

The following calculation parameters hold true for all calculations in this chapter unless stated otherwise. Norm-conserving pseudopotentials were used to facilitate DFPT calculations. The helium pseudopotential was generated in CASTEP using the string ”1|1.0|18|21|24|10N(qc = 8)” and the hydrogen pseudopotential was generated using the string ”70|0.7|2|6|8|10L(qc = 10)”. The electron density was treated as spin neutral and a fixed occupancy was enforced through the calculation, treating the simulation as an insulator. The electronic minimisation cycle was carried out using a Broyden mixing scheme and converged to a tolerance of $10^{-6}$ eV/atom. DFPT calculations were solved using the Baroni Green density mixing method [162] and converged to a tolerance of $10^{-6}$ eV/Å².

Molecular dynamics calculations are carried out using a Nose-Hoover thermostat at a temperature of 300 K with time steps of 1 fs. Geometry optimisations were carried out using the BFGS method [185] with the following convergence tolerances: a Total energy of $2 \times 10^{-2}$ eV/atom, a maximum ionic force $5 \times 10^{-5}$ eV/Å, and a maximum displacement of $10^{-4}$ Å.

### 4.1.3 Results

We first examined Hydrogen impurities in helium to determine miscibility within the solid regime. Both hydrogen and helium atoms form hcp solid phases in this pressure regime. As the most common position for interstitial defects in an hcp lattice are the octahedral and tetrahedral sites, we calculated the energy cost and enthalpy of hydrogen molecules in these sites with a substitutional hydrogen molecule defect. Initial DFT calculations found that while hydrogen atom defects were smaller and, therefore, more readily able to fit within the interstitial sites, the energy cost of losing the H-H bond made these defects significantly more costly, > 3 eV, than the hydrogen molecule.
<table>
<thead>
<tr>
<th></th>
<th>$\Delta H$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>Miscibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substitutional</td>
<td>0.164</td>
<td>0.048</td>
<td>0.2%</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>0.552</td>
<td>1.267</td>
<td>2x10^{-7}%</td>
</tr>
<tr>
<td>Octahedral</td>
<td>0.640</td>
<td>1.032</td>
<td>5x10^{-6}%</td>
</tr>
</tbody>
</table>

Table 4.5: The enthalpy and energy cost of including hydrogen molecules in hcp helium at 12 GPa for each site is given. The miscibility ($e^{-\Delta H/k_B T}$) at 300 K is calculated assuming a dilute regular solid solution.

equivalents and so where not explored further.

The calculated energy and enthalpy costs of hydrogen molecule defects in solid helium are given in table 4.5. From these results, we can see the enthalpy of solution only allows hydrogen to occupy substitutional sites. Even then, at room temperature, the same temperature as in experiments carried out by Yoo et al. [2], the calculated solubility limit is 0.2%. This is in keeping with the existing literature [23, 139, 140, 186]. Measuring such a small concentration experimentally is challenging: a weak vibron signal in the He-rich fluid has been noted by Yoo et al. [2]. Another recent DAC experiment [39] with a signal-to-noise ratio of 1:1000 saw no evidence of a hydrogen vibron Raman signal in solid helium.

A Mulliken population analysis, as described later in this chapter, showed no evidence of chemical bonding between hydrogen and helium and no Raman active phonon modes with a frequency near 2400 cm$^{-1}$ for any of the interstitial or substitutional defect calculations. These results are in keeping with our simulations and the conventional understanding of H-He interactions and, as such, support the analysis of Turnbull et. al. [22] that the signal seen at 2400 cm$^{-1}$ by Yoo et al. [2] was due to nitrogen contamination of the experiment not chemical bonding between hydrogen and helium.

Table 4.6 shows the binding energy for clusters of substitutional hydrogen molecules compared with isolated hydrogen molecules in solid helium. All the enthalpies of formation are negative, and become larger as more hydrogen is added, a strong suggestion that when within a helium lattice, hydrogen molecules tend to cluster rather than mix. Standard DFT calculations suggest a strong attraction between H$_2$ molecules relative to He, but unexpectedly this difference is significantly reduced when quantum nuclear motion is accounted for through DFPT. Nevertheless, the binding is close to the configurational entropy cost below room temperature, so significant
Figure 4.1: This graph shows the energy cost per object of mixing helium and hydrogen molecules in the fluid regime for different concentrations. Each data point represents an average over 5 snapshots taken from a molecular dynamics calculation carried out at 300 K and a volume of 9.6 Å³ per object (He or H₂).
numbers of H$_2$ microclusters can be expected. As we show later in this chapter, the blueshift seen in the Raman active hydrogen vibron is due to the reduction of coupling between hydrogen molecules. As such, this clustering could reduce the frequency of the hydrogen vibron in solid helium compared to an equivalent concentration of hydrogen in a fluid mixture.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$</th>
<th>$\Delta E+ZPE$(eV)</th>
<th>$k_BT\ln N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pair</td>
<td>-0.043</td>
<td>-0.006</td>
<td>0.017</td>
</tr>
<tr>
<td>Quadruplet</td>
<td>-0.185</td>
<td>-0.037</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Table 4.6: Formation energy for clusters of substitutional hydrogen molecules compared with a lone hydrogen molecule in an hcp helium lattice. Results with and without accounting for ZPE are shown, along with the configurational entropy cost to the free energy at room temperature. Calculations carried out at a constant volume of 7.16 Å$^3$ per lattice site.

In figure 4.1, we plot the enthalpy cost per object of a particular concentration of H$_2$-He mixtures. This graph suggests it is harder to include a helium atom in a fluid hydrogen mixture than the other way around. The highest enthalpy cost on this graph, $\sim 0.025$ eV, is equivalent to a temperature of 290 K. This is equivalent to temperatures seen in a number of DAC experiments and close to the temperature that the molecular dynamics calculations were carried out at. The effects of this high cost of mixing can be seen in experiments as the coexistence of two fluids [2, 39]. The diverging Raman signals from these two fluids indicate that each has a different $X_{He}$ concentration. This peak in energy cost pushes the mixture away from a perfect mixture to two separate fluids of different concentrations, each with a lower mixing cost. We can look at the partial radial distribution functions for each molecular dynamics run to ensure that no demixing occurs within the simulation.

In figure 4.2, we plot the results for each calculation used in figure 4.1. If the simulation had been remixed, we would expect to see a significant reduction in the hydrogen-helium distribution when compared with either the helium-helium or hydrogen-hydrogen distributions. As we can see in figure 4.2 our calculations remain fully mixed across all concentrations. This difference between the experiment and our calculations is due to the simulation cell size. This is beneficial for investigating the effects of concentration on the Raman vibron, as we can be sure that we are always in the fully mixed.
Figure 4.2: Each of the above graphs shows the weighted partial radial distribution function of the same molecular dynamics calculations carried out to produce figure 4.1. Each component of the radial distribution function has been weighted by the expected occupancy for a given concentration to allow for a direct comparison between components. This lets us ensure proper mixing is maintained throughout the simulation run. H-H contribution is given by the solid blue line, the He-He contribution is given by the dashed yellow line and the H-He contribution is given by the dot-dash red line.
regime.

Figure 4.3: Shown above are phonon density of state plots taken from DFPT calculation of hydrogen and helium mixtures over a range of concentrations in the solid regime. Due to the inherently disordered nature of the mixture’s reasonable dispersion plots, we were unable to accurately recover from the calculations in this study. Phonon modes are broadened with a 28 cm\(^{-1}\) Gaussian to obtain the resulting spectrum. The density of state plots were produced using the post-processing features of CASTEP [166].

### 4.1.4 Conclusion

We have investigated the miscibility of hydrogen and helium in both the solid and liquid regimes at pressures and temperatures below Jovian planet conditions. The investigation of the solid regime, in particular, was driven by recent claims of hydrogen-helium bonding in mixtures made by Yoo et al. [2]. DFPT was used to account for zero-point effects that affect the miscibility and contribute significantly to the calculated equation of state. Our ab-initio methods predicted no H-He bonding. As well as this, it was found that
hydrogen molecules were most stable as substitutional defects rather than in
the interstitial sites. This is at odds with the explanation provided in Yoo
et al. [2], which explains the splitting of the 2400 cm\(^{-1}\) Raman peak at 12.6
GPa as caused by the difference in environments between hydrogen molecules
in the octahedral and tetrahedral sites. We also do not see an explanation
for the signal seen at 2400 cm\(^{-1}\) in our H\(_2\)-He simulations. This suggests
supports the explanation provided by Turnbull et al. [22]. That anomalous
Raman signals seen in Yoo et al. [2] are caused by nitrogen contamination.

Despite this, we do predict some concentration of hydrogen in the solid
regime at low concentrations, \(< 0.2 \:\%\). This puts an upper bound on the
possible concentrations we could see hydrogen diluted in solid helium. This is
at the limit of what is possible to detect with current experimental methods.
Current experiments with a signal-to-noise ratio of 1:1000 find no evidence
of hydrogen vibron Raman signals in solid helium [39].

We also find that the hydrogen molecules are weakly attracted to each
other in the solid regime. This attraction is significantly weakened by the
inclusion of zero-point effects, again highlighting the importance of quan-
tum nuclear motion in understanding the behaviour of light elements in this
regime. Nevertheless, below room temperature, the binding is close to the
configurational entropy cost, so we can expect microclusters of hydrogen to
form in solid helium. As we show later in this chapter, we expect this clus-
tering to affect the hydrogen molecule vibron, meaning that the frequency of
the hydrogen vibron could be redshifted compared to what might be initially
expected for a given concentration.

Using DFPT calculations carried out on relaxed snapshots taken from
NVT molecular dynamics calculations carried out at 300 K we can compare
the energy cost of mixing per object, helium atom or hydrogen molecule over
a range of concentrations. We see a peak energy cost of 0.025 eV, which
is equivalent to a temperature of 290 K, we can see the effect of this high
energy cost of mixing in the existence of two fluid phases in the mixed regime
[2, 39]. To ensure that our molecular dynamics calculations did not experi-
ence demixing, we calculated the partial radial distribution function of our
molecular dynamics runs and found that the occupancy weighted hydrogen-
helium component did not significantly drop below the hydrogen-hydrogen or
helium-helium components, suggesting the simulation remained well-mixed
through the molecular dynamics run.
4.2 Raman Signal and Localisation

4.2.1 Introduction

The Raman signal of hydrogen vibron is a key signal in understanding the high-pressure phases of hydrogen [104, 103, 107, 90, 108] as well as many hydrogen compounds [187, 188, 189, 190]. Despite this, there are open questions surrounding the behaviour of hydrogen molecules under pressure. Understanding how hydrogen behaves under pressure is of interest both from a basic physics perspective, as hydrogen is the simplest element and for practical purposes in understanding high-pressure materials. In particular, the turnover of the hydrogen vibron in pure hydrogen, as shown in figure 4.4 and the blueshift caused seen in $\text{H}_2$-$\text{He}$ mixtures, are poorly understood. In this chapter, we show these effects are due to the coupling interaction between hydrogen molecules and explore the consequences of this behaviour.

Helium and molecular hydrogen are readily miscible in the fluid regime. In DAC experiments at pressures < 15 GPa, this fluid mixture has been observed with the characteristic signal being the Raman active mode of the hydrogen vibron [158]. The vibron frequency in the mixture is blueshifted with respect to the pure hydrogen vibron frequency, with the magnitude of this shift being dependent on the relative concentration of the mixture. This shift was either assumed to be caused indirectly through an increase in the pressure applied to the hydrogen molecule [3, 158] or in the case of the proposed solid miscibility directly through chemical bonding [2]. Despite this, the Raman signal seen in helium mixtures is higher than the frequencies in pure hydrogen at the same pressure. In this chapter, we will propose an alternative explanation primarily driven by the coupling between hydrogen molecules and the localisation of the phonon mode.

Both helium and hydrogen have been known to form stable alloys with other Noble gases [187, 188, 189, 190, 191]. A similar frequency shift is seen in the Raman spectrum of the hydrogen compounds. Others have proposed that this effect is caused by coupling between hydrogen molecules weakening as the chemically inert elements separate them [40, 192, 193]. A simple classical molecular potential with nearest neighbour interactions has shown that this effect is of the right order of magnitude to explain the behaviour in Argon-hydrogen mixtures. To our knowledge, no theoretical work has addressed this effect in H$_2$-He mixtures. Here we present a first-principles investigation into the cause of this effect and accurately reproduce the frequency shift seen...
4.2.2 Method

To model the behaviour of hydrogen molecules in a H$_2$-He mixture, we use DFT techniques to study both the fluid and solid regime. To be able to compare our results directly to experiments in the fluid regime we must properly account for the pressure of our simulations. To do this, we first built simulation cells of randomly distributed helium and hydrogen molecules on an hcp lattice. These simulation cells were then relaxed in the NPT ensemble to ensure isotropic stress. Each of these relaxed cells where then melted in a molecular dynamics run at 300 K which lasted 1 ps.

Five snapshots were taken from each molecular dynamics run to capture the disordered structure of the fluid regime and ensure proper sampling of atomic configurations. The resulting snapshots were then relaxed to a local minimum so that DFPT calculations could be carried out. These DFPT calculations allow us to properly account for the ZPE as well as calculate the Raman activity of the hydrogen vibrons. Several thousand molecules are required to fully describe the liquid structure [184], but the phonon density of states is well sampled in much smaller cells. This allowed us to simulate the hydrogen vibron, which occurs over relatively short time scales, including the effects of the disordered fluid without the computational cost of large molecular dynamics simulations. The true pressure is then calculated for each simulation, including contributions from the zero-point effects.

A similar process is used for the solid regime where initial NPT calculations were used to relax the simulation cells to an isotropic stress before DFPT calculations are carried out to determine zero-point effects as well as calculate the Raman active modes. As before, simulation cells were chosen so that the pure hydrogen simulations contained 72 atoms. For both fluid and solid regimes the enthalpy of each DFT calculation was converged to 1 meV using a 2x2x2 kpoint grid. Van der Waals functionals are essential for helium; however, it is also well known that these functionals overestimate the hydrogen vibron frequency [151]. To facilitate comparison with the experimental, calculated frequencies are shifted by 126 cm$^{-1}$ to match the experimental hydrogen vibron. The high-pressure calculations shown in the inset of figure 4.4 were carried out using simulation cells equivalent to 96 helium atoms and a 3x3x3 k-point grid again converged to an enthalpy of 1 meV. All calculations are carried out using the CASTEP code [63].
The Raman spectrum measured by experiments is caused by phonon modes interacting with light of the same frequency causing it to scatter. This Raman scattering can therefore give an insight into the vibrational behaviour of a material. By understanding the polarization caused by each specific phonon mode we can calculate the Raman susceptibility tensor as given by the equation

$$\tilde{A}_{\alpha\beta}^q = \sqrt{V} \sum_{i\gamma} \frac{\partial \chi^{(1)}_{\alpha\beta}}{\partial R_{i\gamma}} \frac{\epsilon_{i\gamma}^q}{\sqrt{M_i}}$$ (4.5)

where $\chi^{(1)}$ is the first order dielectric susceptibility and $i$ indexes each atom, at an equilibrium position $R_i$ in a unit cell of volume $V$. With $\epsilon$ representing the phonon eigenvector of each atom in the phonon mode $q$ and $\alpha, \beta$, and $\gamma$ are Cartesian directions. The derivative of $\chi^{(1)}$ is given by

$$\frac{\partial \chi^{(1)}_{\alpha\beta}}{\partial R_{i\gamma}} = -\frac{1}{\epsilon} \frac{\partial^3 E}{\partial \varepsilon_{\alpha} \partial \varepsilon_{\beta} \partial R_{i\gamma}}$$ (4.6)

where $E$ is the total energy of the system and $\epsilon$ is the electric field of a photon in a Raman experiment exciting the phonon. However, we can obtain this in simulation by displacing each atom along the direction of the eigenvector of each Raman active mode. The disadvantage of this finite displacement method is that we are required to carry out electric field perturbations for each Raman intensity.

CASTEP [63] implements a system using the "2n+1" linear response method, which states that it is possible to calculate the "2n+1"th order terms from the nth order wavefunction in a many-body perturbation theory. Miwa [76] has shown how to apply the "2n+1" linear response method to the case of the calculating Raman activity from the first order perturbations taken from simulations we can calculate the third order energy perturbation, $E^{(3)}$. We can then precalculate the 9 second-order derivatives with respect to the electric field and can then find the full set of Raman tensors for all phonon perturbations. Whilst this method does include costly upfront calculations, which limit its effectiveness for small simulation cells, the advantage over the finite displacement method increases with cell size. As we are interested in mixed systems this will be a useful method for reducing computation time.

We will use the Raman spectrum to compare our calculations directly with experiments, therefore, showing that our simulations accurately capture
the behaviour of the Raman blueshift in H$_2$-He mixtures. We will then use the simulation to investigate what drives the behaviour of the hydrogen vibron. To estimate the pressure difference caused by introducing a hydrogen molecule into a helium lattice we can compare the pressure of pure hydrogen and helium for a fixed volume per object including the effects of quantum nuclear motion.

CASTEP [63] is also capable of providing an estimate of the electron population of the bonds between atoms in a given simulation using Mulliken population analysis [36, 37, 38]. As the plane wave basis set doesn’t describe the location of each electron we must first project the basis set onto a localized basis set. To do this we use the Mulliken formalism [36] to create a description of our system as a linear combination of atomic orbitals which allows for an analysis of atomic charge, bond population and charge transfer. To ensure that the localised basis set provides a useful description of the plane wave basis we can calculate the splitting parameter as described by the equation 4.7

$$\sigma = \frac{1}{N_a} \sum_k w_k \sum_a \langle \psi_a(k) | (1 - \hat{p}(k)) | \psi_a(k) \rangle$$  (4.7)

where $N_a$ is the number of plane wave states, $w_k$ are the weights of the associated k-points and $\hat{p}(k)$ is the projection operator of Bloch functions with wavevector $k$ for a set of eigenstates $|\psi_a(k)\rangle$ in the plane wave basis set taken from the ab-initio calculation. The splitting parameter describes the orthogonality of the two basis sets, with one representing a fully orthogonal pair of basis sets, and zero a pair which perfectly describe one another. A splitting parameter of a few percent or less means that there is an accurate enough projection into the localised basis set to apply population analysis. As we are interested in ruling out the possibility of chemical bonding influencing the Raman signal in H$_2$-He mixtures it is the overlap population between atoms that is important to us. This can be found using the equation 4.8

$$n(AB) = \sum_k w_k \sum_{\mu}^{onA} \sum_{\nu}^{onB} 2P_{\mu\nu}(k)S_{\mu\nu}(k)$$  (4.8)

where $P_{\mu\nu}(k)$ is the density matrix, $|\phi_{\mu}(k)\rangle$ are the basis sets made of a linear combination of atomic orbitals and $S_{\mu\nu}(k)$ is the overlap matrix defined as

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\[ S_{\mu\nu}(k) = \langle \phi_{\mu}(k) | \phi_{\nu}(k) \rangle \] (4.9)

As this population analysis depends upon the selection of localised basis sets, it does not correspond to any physically real value. However, given a constant basis set and a low splitting parameter, relative comparisons can be relied on to extract useful information. For example, the overlap population can give an idea of simple bonds forming between two atoms, with a high value indicating the sharing of electrons due to a covalent bond and a low value indicating the transfer of electrons due to an ionic bond.

Finally, we need a way to measure the presence of coupling between hydrogen molecules. Thankfully the phonon mode of the hydrogen vibron is well isolated from the motion of the helium atoms and hydrogen molecular centres due to its frequency being approximately 10 times greater than those of the lattice phonon modes. The effect of coupling between the hydrogen vibrons can be thought of as a delocalization of the associated phonon mode across the hydrogen molecules. We can therefore use the degree of localisation of this phonon mode as an indicator of the strength of coupling between the hydrogen molecules.

We will be using the inverse participation ratio (IPR) to quantify the degree to which this phonon mode is localized. The IPR is a measure of the number of "sites" or hydrogen atoms participating in the particular mode, with one representing a system where only one site is participating and zero representing a fully delocalized system. As each site in our system represents a hydrogen atom, we would expect fully localized phonon mode to have an IPR of approximately 0.5. If we define \( \epsilon_i \) as the mode displacement vector of each atom \( i \), we can calculate the IPR using equation 4.10

\[ IPR = \frac{\sum_i \epsilon_i^4}{(\sum_i \epsilon_i^2)^2} \] (4.10)

If our hypothesis is correct, we should expect to see a significant degree of reduction of localization as the number of hydrogen molecules increases. This will indicate a strong coupling effect between the molecules, which in turn, we would expect to lead to a lowering of the frequency of the Raman active vibron. Complicating this analysis is the fact that other phenomena can lead to the localization of a phonon mode. A disordered system such as that of a fluid would lead to a difference in the local conditions of each hydrogen molecule. As such, we would expect such a system to be more
localized than, for example, a solid where each lattice site provides a relatively uniform environment for each molecule. To account for this, we will look at the localization in both regimes even though we do not expect mixing to occur in the solid and so cannot compare it directly to experiments.

### 4.2.3 Results

In multiple DAC experiments of H$_2$-He mixtures [2, 3, 22], it has been observed that the hydrogen vibron increases in frequency as the helium concentration $X_{\text{He}}$ increases. This effect has been observed across all pressures and temperatures in which helium and hydrogen readily mix. This has been observed within the fluid regime up to pressures of approximately 10 GPa. This means that the observables from the experiment that we are interested in are the pressure, concentration and hydrogen Raman spectrum. In figure 4.4, the calculated frequencies at different He concentrations at different pressures are presented together with experimental results taken from the Raman spectrum of hydrogen and helium mixtures in DAC [2, 3, 22].

To compare the vibrational frequencies across a range of pressures, we have plotted experimental data points and fitted how the frequency changes with pressure for each concentration. Each of these was fitted with a logarithmic function as a guide to the eye. A colour spectrum represents the concentration of each data point. When we plot this with the data points from DFPT calculations. We see that the DFPT calculations fall within the spread of experimental results. Demonstrating that the DFPT calculations can quantitatively reproduce the blueshift effect seen in H$_2$-He mixtures.

Our calculations show no evidence of vibrational modes in the frequency range around 2400 cm$^{-1}$, nor any high frequency modes involving He atoms. We also see no evidence of the splitting of the hydrogen vibron, which is suggested to be caused by the chemical bonding between hydrogen and helium, in any of our calculations. If, as we propose, the concentration dependence is due simply to the number of hydrogen atoms participating in the modes, then the effect will be largely independent of whether the hydrogen is diluted by He or N$_2$: by contrast, whereas H-He chemical bonding or local stresses [3] will depend on the composition of the solvent. Experiments show consistent vibron shifts with H$_2$ concentration, regardless of nitrogen content [2, 22].

As well as comparing directly with experiments, we have simulated an isolated hydrogen molecule in a helium fluid. These results are plotted on the figure as solid squares. In the inset of figure 4.4 we show that the frequency of
Figure 4.4: Comparison of experimental and calculated pressure-frequency relation with colour-coding used to show the atomic fraction of Helium ($X_{He}$). The colour scale represents the concentration of helium: only data of the same colour should be compared. The lowest helium concentrations shown are pure hydrogen, and the highest have a single hydrogen molecule in the simulation cell. Experimental data are taken from Turnbull et. al. [22], Lim et. al. [2], and Loubeyre et. al. [158] is plotted against DFT results from the fluid regime for a range of concentrations and pressures. All experimental data are fitted with a logarithmic function. A more direct comparison of concentration and frequency is given in figure 4.8. The Raman and phonon density of states shown in figure 4.8 is taken at 3.5 GPa as denoted by the grey vertical line. The inset shows the frequency of the isolated hydrogen molecule vibron up to 500 GPa. All frequencies have been shifted by 126 cm$^{-1}$ to account for the functionals over-binding of hydrogen molecules [151]. Pressures and horizontal error bars by combing errors from zero-point contributions to pressure as well as the spread of pressures taken from CASTEP [63]. Vertical error bars are simply the standard deviation of the 5 samples taken from each molecular dynamics calculation.
the isolated hydrogen vibron continues to increase as the pressure increases. This is in stark contrast with the known behaviour of the pure hydrogen vibron, which increases in frequency to a maximum of $\sim 4270 \text{ cm}^{-1}$ at a pressure of $\sim 30 \text{ GPa}$ [2, 22] after which it decreases as the pressure increases.

This behaviour can be fully explained if we propose the hydrogen vibron blueshift is brought about through a localisation of the phonon mode [40]. In this understanding, the behaviour of a hydrogen molecule under pressure is best described by the isolated hydrogen molecule in these DFT calculations. In a pure hydrogen sample, the hydrogen vibron is influenced by the coupling to the surrounding hydrogen molecules. While this is of interest from a purely theoretical perspective, it also has implications for the study of high-pressure hydrate compounds [194, 195]. These have recently become the subject of quite some interest as a number of stable superconducting compounds of this type have been found, including the current record for the highest critical temperature of a superconductor, Lanthanum decahydride [45, 46, 47, 48, 49].

This means we can now use the simulation to explain the mechanism driving the blueshift. To further rule out any chemical bonding effects, we carried out a Mulliken population analysis which shows no bonding between the hydrogen and helium atoms. The hydrogen vibron eigenmodes also show negligible participation of the He atoms in the motion. Again this demonstrates the absence of chemical interactions between helium and hydrogen and suggests that a similar mechanism would occur in any chemically inert mixture with hydrogen molecules.

Another proposed explanation is that helium acts as a pressure transmitting medium, applying an artificial pressure to the hydrogen molecules. To explore this proposal, we can look at how much the pressure changes with concentration for a given volume. This will give us an idea of how much "localised pressure" a particular hydrogen molecule might be under when in a hydrogen-helium mixture. We can then compare the frequency shift seen in mixture with that of a pure hydrogen sample of equivalent pressure. These results are shown in figure 4.5.

We can see that in a mixture of hydrogen and helium with a concentration of $X_{He} = 0.9722$ at a pressure of approximately $\sim 3.5 \text{ GPa}$, a hydrogen molecule occupies a similar volume to a hydrogen molecule in pure hydrogen at a pressure of $\sim 11.5 \text{ GPa}$, at $10 \text{ Å}^3$. If we look at the change in frequency over the same pressure range in pure hydrogen, we see an increase in the frequency of $40 \text{ cm}^{-1}$. However, the actual frequency shift seen in mixture
Figure 4.5: In this figure we have plotted the pressures of different concentrations of mixtures of helium and hydrogen as a function of volume. All pressures have been calculated to include contributions from ZPE, with error bars representing RMSE of the 5 snapshots taken from molecular dynamics calculations carried out at 300 K for 1 ps. Colours indicate the concentration of each mixture, with low $X_{He}$ concentrations shown in blue and high $X_{He}$ concentrations shown in red as shown in the colourbar.
$X_{He}$ is 140 cm$^{-1}$. This demonstrates that the "localised pressure" hypothesis cannot explain the blueshift seen in H$_2$-He mixtures. As well as this, in results from both experiments and simulations H$_2$-He mixtures achieve frequencies well above the maximum frequency reached by pure hydrogen under pressure. We, therefore, need to provide another explanation for the blue shift seen in mixtures.

**Figure 4.6:** (a) DFPT calculation plotted against experimental results [2, 22, 158], showing the change in Raman active vibron due to change in mixture composition at 3.5 GPa. DFPT frequencies at 3.5 GPa are interpolated from data shown in figure 4.4. Error bars on DFPT data are taken from the RMSE of the fits to data in figure 4.4. (b) Calculations of the inverse participation ratio of the calculated strongest Raman-active phonon modes. The error bars are taken from the standard deviation of three independent configurations in the solid regime at each concentration.

As mentioned previously, we propose that the coupling between hydrogen molecules causes a decrease in the frequency of the hydrogen vibron in mixtures of low helium concentration. If this were true, we would expect to see a localisation of the hydrogen vibron as we increase $X_{He}$. To measure this, we will calculate the inverse participation ratio of the hydrogen vibron for different concentrations, which will act as an indicator of coupling between molecules. As the disordered nature of the fluid state would also contribute to a localisation effect, we will use simulations carried out in the solid phase. This means that any localisation effect we see will be purely due to the introduction of helium to the mixture.

In figure 4.8 the graph on the left shows vibron frequencies of different
concentrations from DFT calculations carried out at 3.5 GPa as well as frequencies interpolated from fits to experimental data taken from figure 4.5. This allows for a clearer comparison between experiments and simulations. The graph on the right of figure 4.8 shows the IPR of different concentrations of hydrogen-helium mixtures. From this, we can see a strong correlation between concentration, $X_{He}$ and coupling between hydrogen molecules.

We can also see how this affects the Raman signal, the larger the number of hydrogen atoms participating in a vibron mode the lower its frequency. As each molecule has two atoms involved in the Raman active phonon mode the maximally localised phonon will have an IPR of 0.5. We can see this is almost achieved in the isolated hydrogen molecule, with an IRP value of $0.44 \pm 0.04$, as expected with a small contribution to the mode coming from the surrounding helium atoms. As we increase the $X_{He}$ concentration, we see an approximately linear decrease in the IPR down to a value of $0.04 \pm 0.01$ in pure hydrogen, indicating that each hydrogen atom in the simulation contributes equally to the Raman active mode. This shows that the change in coupling across concentrations is significant and as such, should lower the frequency of the hydrogen oscillation.

In our DFPT calculations, we have assumed that two elements are randomly distributed throughout the mixtures. However, if the hydrogen molecules are more clustered, this would enhance the coupling and drive down the vibron frequency of the high $X_{He}$ mixtures even more. To understand the potential magnitude of this effect, DFPT calculations were carried out on a simulation cell with $X_{He} = 0.8333$ with a single cluster of hydrogen molecules: This resulted in a drop in frequency of 22 cm$^{-1}$ and reduced inverse participation ratio. Thus we show that localization of the hydrogen vibron increases its frequency independent of concentration.

The story of the blueshift seen in experiments, however, is slightly more complex, because these are fluids. This requires us to look at the Raman activity of the phonon modes involved in the hydrogen vibron. The phonon localization effects we characterised in solids are seen in both the solid and the fluid. However, the solid vibron shift is larger because the pure H$_2$ fluid vibron is already partially localised due to the disordered nature of the fluid. At high H$_2$ concentrations the differences between solid and fluid are largest: all hydrogen molecules have many coupled neighbours, but the fluid vibron is still localised due to the disorder.

In figure 4.7 we have directly compared the Raman spectrum from the DAC experiment [22] with a simulated Raman spectrum taken from DFT
Figure 4.7: Comparison of experimental Raman peak with DFT data at 2.7 GPa and 50% He concentration. The DFPT Raman intensities shown in black are convolved with a 28 cm$^{-1}$ Gaussian broadening to obtain the resulting spectrum. Blue experimental data were collected during a previous campaign [22]. Both the experimental and DFT spectra are asymmetric with a high-frequency tail. This effect is due to the weaker, but still active, Raman modes at a higher frequency. Raman modes from all 5 snapshots taken at this pressure are shown in the figure.
calculations. The black lines show the exact phonon modes weighted by the Raman activity of each mode. The shift and multiplicity of the peaks due to species and fluid disorder are similar to the isotope disorder effect in hydrogen [196, 197]. A Gaussian broadening is then applied to provide a good fit to experiments. As expected we can see the lowest frequency mode, which involves all hydrogen molecules oscillating in phase, is the most Raman active. Figure 4.7 reveals that the Raman peak arises from a combination of several modes. The in-phase vibration of all molecules in a cluster is the strongest, but in the absence of perfect symmetry, many other modes acquire some Raman activity. These modes have a slightly higher frequency than the in-phase vibron, so cause a skew in the peak shape figure 4.7.

We see some evidence of this skew in the experimental data as it doesn’t perfectly follow a Gaussian curve. However, the effect is not as significant as that predicted by DFPT. There are two reasonable explanations for this difference. To produce the Raman signal the background noise sampled by the experiment [78]. As such an error in this process could overly favour one side of the Gaussian over correcting for the skew, we see in the calculations. Alternatively, the Raman activity of the higher frequency modes of the hydrogen vibron may have been overestimated by the DFPT calculation. Either way, this discrepancy should be explored in future studies.

In Figure 4.8 we compare the calculated Raman spectrum as shown in Figure 4.7 with the total phonon spectrum where all modes are equally weighted. This shows an additional effect on the frequency shift of the hydrogen vibron. We can see that as $X_{He}$ concentration decreases the phonon density of states band is not only shifted but also broadened. This means that the apparent Raman frequency shift due to concentration is enhanced by the broadening (figure 4.6) because Raman activity tends to be stronger for the lower frequency vibron modes as in figure 4.7. This means that the effects of coupling on the hydrogen vibron both act to increase the blueshift of the Raman signal seen in experiments.

4.2.4 Conclusion

In conclusion, we have carried out the first ab-initio study of the hydrogen molecular vibron in H$_2$-He mixtures. We have previously shown that including Van de Waals corrections and ZPE effects is essential to reproducing the equation of state below 10 GPa. The vibron blueshift with increasing He concentration is shown to be due to the reduction of hydrogen-hydrogen cou-
Figure 4.8: Phonon density of states and associated Raman intensities for a range of concentrations is taken from DFPT calculations carried out in the fluid model showing how the hydrogen vibron mode changes with concentration (colourbar shows $X_{He}$ concentration). The phonon density of states broadens and the average frequency undergoes a blueshift as the He concentration is increased. As the strongest Raman active mode is the lowest frequency of the phonon band this results in the Raman intensities diverging from the phonon density of states at lower He concentrations. Weaker Raman modes give a pronounced high-frequency "tail" to the Raman peak. All peaks fitted with a 25 cm$^{-1}$ FWHM Gaussian broadening. These spectra have been taken at 3.5 GPa as indicated by the grey dotted line in Fig 4.4.
change needed to cause the same change of frequency in pure hydrogen. Again we find no evidence of chemical bonding between the hydrogen and helium atoms excluding that as a possible mechanism. After showing that our DFPT calculations accurately reproduce the effect seen in experiments, we show how the localisation of the hydrogen vibron corresponds to an increase in frequency. The change in localisation is seen between different concentrations and in simulations where the concentration is maintained but the hydrogen molecules are assumed to form a single cluster. Thus we show that coupling between the hydrogen molecules is the mechanism behind the change of frequency of the hydrogen vibrons Raman signal. Exploring this mechanism we find that both the broadening of the vibron mode as well as a shifting of the vibron frequency combine to produce the observed Raman blueshift. observed broadening of the vibron in mixtures is because there are Raman active vibrations involving various numbers of H\textsubscript{2} atoms.

Our results may serve as a reference for future works on mixtures and alloys in general, and on hydrides in particular. Experimental mixtures are sometimes prepared in situ and the real concentration of the components may not be known. However, here we show a relationship between Raman shift, pressure and hydrogen concentration which could be used as a reference for concentration calibrations. On the other hand, this work highlights that attention should be paid not only to the shifting of the vibrons but also to the width as it can provide important information about concentrations and inter-molecular interactions. Here we characterise a system in which a hydrogen molecule can be confined without chemical interaction. These isolated hydrogen molecules act as an analogy for a confined hydrogen molecule which may in future be compared directly to experiments. As shown in the inset of figure 4.4 the frequency of the isolated hydrogen molecule in the helium pressure medium continues to increase as the pure hydrogen’s frequency decreases. This demonstrates the importance of coupling effects even at higher pressures.

The comparison with the experimental fluid measurements shows that the main effects involved in the frequency shift are qualitatively reproduced in this model. The primary experimental evidence of solid phase miscibility is the observation of a H\textsubscript{2} vibron mode in the helium [2]. Consistent with our calculations for substitutional and clustered H\textsubscript{2}, these observed modes are blueshifted with the less-blueshifted cluster mode being broader. It was
not possible to determine a precise $H_2$ concentration in the experiment\(^1\), but our calculated solubility is sufficient to produce an observable signal and therefore the calculations support the experimental data [2].

4.3 Chapter Summary

While there have been a number of ab-initio studies focused on hydrogen and helium mixtures, most have focused on conditions relevant to the Jovian planets [140, 147, 149, 150, 179]. This has meant that the low-pressure regime has received relatively little interest. This is despite a number of open questions existing about the behaviour of hydrogen and helium under these conditions. It was an open question as to the mechanism behind the blueshift of the hydrogen vibron in the helium mixture seen in DAC experiments.

There has also been a discussion surrounding the possibility of chemical bonding between helium and hydrogen, and mixing in the solid phase, based on Raman Spectrum measurements carried out in DAC experiments [2, 22]. We have applied ab-initio techniques to bring clarity to both of these questions.

We first show the importance of accounting for zero-point effects in reproducing the equation of state in these highly quantum systems. We find that the most energetically favoured hydrogen defect in a helium solid is a substitutionally exchanged hydrogen molecule. However, the enthalpy cost, 0.164 eV, of this defect is high enough to ensure that we would only expect to find trace amounts of hydrogen in a helium solid, < 0.2 %. The calculations support the possibility of small amounts of $H_2$ existing as substitutional impurities in solid He, but unequivocally rule out interstitial Hydrogen or any H-He chemical bonds. This along with an absence of evidence for a Raman active phonon mode near 2400 cm\(^{-1}\) in the simulation, leads us to conclude that the Raman signals seen in the Yoo et. al. [2] experiment were due to nitrogen contamination as suggested by Turnbull et. al. [22].

We also find clustering of hydrogen molecules in the helium solid. However, the attraction is significantly weakened when accounting for zero-point effects, again highlighting the quantum nature of these solids. Our calculations also predict mixing in the fluid regime at pressure for 3.5 GPa with a peak enthalpy of mixing that could affect the miscibility at approximately

\(^1\)C.S. Yoo, private communication
290 K. This is qualitatively in keeping with experiments where the two elements readily mix at low pressures but as the pressures increase separate into the two fluids [2, 3, 22]. One with a high helium concentration and one with a high hydrogen concentration.

Our simulations also predict a blueshift of the hydrogen vibron as the helium concentration increases. We see this effect in both the fluid and solid regimes. As well as this we can quantitatively reproduce the effect seen in DAC experiments [2, 3, 22]. This means we can reliably use these calculations to explain the mechanism behind this behaviour. As before we see no evidence of chemical bonding so we can rule that out as a possible mechanism. Others have suggested a "local pressure" effect which acts to increase the hydrogen vibron as the hcp lattice sites in the helium solid occupy less volume. We ruled this out as an explanation by showing that an equivalent volume change in pure hydrogen doesn’t lead to a frequency shift of the magnitude seen in hydrogen-helium mixtures.

This leads us to propose that helium acts only to decouple the hydrogen molecules’ vibrations from each other by physically separating them. This localises the hydrogen vibron and leads to the blueshift of the Raman signal seen in both experiment and our ab-initio calculations. This means that the turnover of the hydrogen molecule’s vibration in pure hydrogen is not due to the increase in pressure but the increase of this coupling effect as hydrogen molecules are packed tighter together [40]. Through calculating the IPR we show that the hydrogen vibron does localise as the concentration of hydrogen molecules decreases. As well as this we find that the Raman frequency is correlated to the degree of localisation even when maintaining the concentration within a simulation cell. We also show that this effect should hold true for higher pressures and that a confined hydrogen molecule does not undergo a turnover of the vibron frequency as seen in solid hydrogen.

In future, it may even be possible to compare calculations of an isolated hydrogen molecule directly with experiments opening up a new way to test our models against this classically simple case. As we can reproduce this blueshift in our calculations future experiments could use the Raman signal as a way of determining the concentration of H$_2$-He mixtures seen in samples. As this mechanism is due to the separation of hydrogen molecules and not a direct interaction with helium, we would expect the effect to be present in any compound or mixture where H$_2$. As such these results are relevant for a wide range of future studies on high-pressure mixtures and alloys, including the ongoing search for high-pressure hydrides.
Chapter 5

Beryllium

5.1 Defects in Bulk

5.1.1 Introduction

Beryllium is a material with a wide variety of industrial applications. Many of these applications involve highly irradiated environments. This includes current use as a neutron reflector in fission reactors [198, 199] and it also has been highlighted for its potential use in a tritium breeding blanket in future fusion reactors [4, 5, 6, 7, 8]. Most proposed fusion reactors propose using deuterium and tritium as fuel sources to power the reactor. This is due to the nuclear reaction shown in 5.1 with 17.6 MeV of energy released per reaction.

\[ D + T \rightarrow He + n \]  

(5.1)

This includes the ongoing International Thermonuclear Experimental Reactor (ITER) project. This prototype fusion reactor is being used to explore a variety of engineering hurdles ahead of the future prototype reactor DEMO [200, 201]. While deuterium is easily accessible in the form of heavy water extracted from ocean water, tritium is a much rarer element due to its short half-life of approximately 12.5 years. Most of this is produced as a by-product of the current function of fission reactors. While this is sufficient to provide fuel to the small number of prototype reactors being tested worldwide, the lack of a reliable tritium source is one of the major obstacles that must be overcome before fusion reactors can fulfil their potential as a future energy source. Tritium breeding blankets hope to solve this issue by using the fusion
reaction as a source of neutrons to irradiate lithium-6. This transforms the lithium-6 through the nuclear reaction

\[ Li + n \rightarrow T + He \] \hspace{0.5cm} (5.2)

As this reaction is neutron neutral we should expect some loss of neutrons to the environment. To ensure this reaction is sustainable, a source of neutron multiplication must be included in the blanket. While there are a number of proposed designs for potential tritium breeding blankets, many of them include beryllium as the neutron multiplication source. Beryllium works well as a neutron multiplier due to the low energy, 2.7 MeV, reaction

\[ Be + n \rightarrow 2He + 2n \] \hspace{0.5cm} (5.3)

In these extreme environments, one of the limiting factors in the longevity of these materials is the formation of helium bubbles in the beryllium bulk [5, 9, 10, 11, 12]. Both α-decay and neutron capture, such as that expected to occur within the tritium breeding blanket, are a source of helium defects in the beryllium lattice. To properly model the formation of these helium bubbles, an accurate understanding of the formation energy and behaviour of helium defects in α-Beryllium is required.

As the formation of helium is often caused by radiation events that do not have the energy to remove a beryllium atom from its position in the crystal lattice, the interstitial sites play an important role in the formation rate of helium defects in the metal. A number of ab-initio studies have been carried out on the formation and diffusion of helium defects in the beryllium bulk [11, 15, 13, 14, 202, 203]. Zero-point effects are important in obtaining the correct lattice constants for ambient pressure beryllium and, as we have shown, in bulk helium. In this study, we will investigate the role of zero-point energy (ZPE) in the formation of helium defects in beryllium bulk. While previous studies have included ZPE contributions to beryllium at ambient pressures, none have investigated how ZPE affects the strain of these defects. By calculating the zero-point effects over a range of volumes, we will be able to study how these defects behave over a range of pressures.

5.1.2 Method

Fixed cell calculations were used to relax simulation cells containing hcp beryllium lattices with a variety of defects. These ZPE contributions were
the energy-volume curves were used to parameterise a Birch-Murnaghan equation of state as defined in equations 3.3 and 3.2. This model was then used to estimate the enthalpy of each simulation cell over a range of pressures with and without ZPE.

We can then use these results to calculate the energy and enthalpy cost of each of these defects and analyse these results to investigate how the behaviour of these defects changes as pressures increase. We can calculate the energy cost of defects using the equation 5.4

\[ E_{\text{cost}} = E(X_{\text{defect}}) - \left[ N_{B\text{e}}E(B\text{e}_{\text{bulk}}) + N_{H\text{e}}E(H\text{e}_{\text{gas}}) \right] \] (5.4)

where \( E(X_{\text{defect}}) \) is the energy of the simulation cell containing the defect, \( E(B\text{e}_{\text{bulk}}) \) is the energy of a single beryllium atom in bulk, \( E(H\text{e}_{\text{gas}}) \) is the energy of a lone helium atom, \( N_{B\text{e}} \) is the number of beryllium atoms in the simulation cell, and \( N_{H\text{e}} \) is the number of helium atoms in the simulation cell.

Density functional theory (DFT) calculations were carried out using CASTEP [166] software, with ZPE contributions being taken from Density functional perturbation theory (DFPT) calculations. These calculations were limited by the computational time of the DFPT calculations due to the low symmetry of some of the defects simulation cells. Due to this calculations were carried out in a simulation cell with an equivalent of 64 beryllium atoms to account. As shown in Table 5.3 this gives an error due to the cell size on the order of 10's of meV. While higher electronic convergence has been achieved in the literature this is still in keeping with the difference between results calculated by different studies, as shown in Table 5.4. The difference in energy over the pressure ranges we are interested in is on the order of eV's and so is acceptable for our purposes. The cut-off energy was found to converge at a value of 1350 eV a defect in the 36 lattice site cell was found to be converged with a k-point grid of 9x9x9. Calculations of the 64 lattice site cells were sampled with a k-point grid of 6x6x6. \( \Gamma \)-point DFPT theory calculations were carried out to reduce computational time. As the true pressure of the simulation cell was not able to be calculated until after zero-point effects were taken into account, geometry optimisations were carried out with fixed lattice constants. A PBE [54] functional was used as it has been shown to accurately reproduce the lattice values of bulk beryllium [204].

The following calculation parameters hold true for all calculations in
### Table 5.1

<table>
<thead>
<tr>
<th>Cut-off Energy (eV)</th>
<th>BO defect cost (eV)</th>
<th>ZPE contribution (eV)</th>
</tr>
</thead>
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<tr>
<td>900</td>
<td>5.3926</td>
<td>0.0618</td>
</tr>
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<tr>
<td>1400</td>
<td>5.3837</td>
<td>0.06958</td>
</tr>
</tbody>
</table>

Calculations were carried out in a simulation cell with 36 beryllium atoms and a helium defect in the basal plane octahedral site using a PBE functional with DFT-D2 dispersion corrections and a 9x9x9 k-point grid. Zero-point energies were taken from Gamma point DFPT calculations.

### Table 5.2

<table>
<thead>
<tr>
<th>k-point grid</th>
<th>BO defect cost (eV)</th>
<th>ZPE contribution (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x3x3</td>
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<td>0.0537</td>
</tr>
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<td>6x6x6</td>
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<td>0.0651</td>
</tr>
<tr>
<td>9x9x9</td>
<td>5.3854</td>
<td>0.0698</td>
</tr>
<tr>
<td>12x12x12</td>
<td>5.3889</td>
<td>0.0710</td>
</tr>
<tr>
<td>15x15x15</td>
<td>5.3863</td>
<td>0.0714</td>
</tr>
</tbody>
</table>

Calculations were carried out in a simulation cell with 36 beryllium atoms and a helium defect in the basal plane octahedral site using a PBE functional with DFT-D2 dispersion corrections and a cut-off energy of 1350. Zero-point energies were taken from Gamma point DFPT calculations.

### Table 5.3

<table>
<thead>
<tr>
<th>Number of lattice sites (eV)</th>
<th>K-point Grid</th>
<th>Sub defect cost (eV)</th>
<th>ZPE contribution (eV)</th>
</tr>
</thead>
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<tr>
<td>16</td>
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<tr>
<td>36</td>
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<td>0.0521</td>
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<td>6x6x4</td>
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</tr>
<tr>
<td>128</td>
<td>6x6x3</td>
<td>3.1299</td>
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Calculations were carried out in a simulation cell with 36 beryllium atoms and a substitution helium defect using a PBE functional with DFT-D2 dispersion corrections and a cut-off energy of 1350. Zero-point energies were taken from Gamma point DFPT calculations.
this chapter unless stated otherwise. Norm-conserving pseudopotentials were used to facilitate DFPT calculations. The helium pseudopotential was generated in CASTEP using the string ”1|1.0|18|21|24|10N(qc = 8)” and the beryllium pseudopotential was generated using the string ”1|1.1|23|26|31|10N : 20N : 21L(qc = 9)”. The electron density was treated as spin-neutral and metallic. To approximate the effect of an electronic temperature a Gaussian smearing of 0.2 eV is applied to the electronic energy levels. The electronic minimisation cycle was carried out using a Broyden mixing scheme and converged to a tolerance of $10^{-6}$ eV/atom. DFPT calculations were solved using the Baroni Green density mixing method [162] and converged to a tolerance of $10^{-6}$ eV/Å$^2$.

Molecular dynamics calculations are carried out using a Nose-Hoover thermostat at a temperature of 300 K with time steps of 1 fs. Geometry optimisations were carried out using the BFGS method [185] with the following convergence tolerances: a Total energy of $2\times10^{-2}$ eV/atom, a maximum ionic force $5\times10^{-5}$ eV/Å, and a maximum displacement of $10^{-4}$ Å.

In this chapter, we investigate a number of different configurations of helium defects. We will model some of the more energetically favourable helium interstitial sites. These are the basal plane tetrahedral site (BT), the basal plane octahedral site (BO), the out-of-plane separated dumbbell site (S), and the in-plane separated dumbbell site (BS). The BT and BO sites have the same x and y coordinates as the hcp tetrahedral and octahedral sites respectively but are located in the basal plane. The separated dumbbell sites involve a beryllium atom and hydrogen atom forming a dumbbell at a lattice site. A visualisation of these defects in the beryllium lattice is given in figure 5.1. These interstitial defects are known to defuse through the lattice and bond with vacancies in the crystal [11, 13, 203]. To understand how helium defects interact with vacancy sites, we will also model a number of different configurations of helium atoms bonded to vacancy sites.

5.1.3 Results

The results of the Birch-Murnaghan equation of state fit with and without ZPE are shown in figure 5.2. These results give lattice parameters of $a = 2.267$ Å and $c = 3.559$ Å without ZPE, and $a = 2.281$ Å and $c = 3.581$ Å with ZPE. These results are in keeping with results from other ab-initio results [11, 15, 13, 15], as well as experiments [204]. We can see that accounting for zero-point effects increases the pressure for a given volume by 2.0 GPa.
Figure 5.1: This figure shows the positions of interstitial sites investigated in this study. Two layers of the hcp beryllium atom are shown along the c-axis in the left image and line with the basal plane in the right image. hcp beryllium atoms are colored grey and beryllium atoms in dumbbell defects are colored black. The position of the hydrogen atom defects is given by the colored atoms. The in-plane split defect (BS) is colored red, the out-of-plane split defect (S) is colored blue, the basal plane tetrahedral defect (BT) is colored pink, and the basal plane octahedral defect (BO) is colored yellow.

at the largest volumes modelled. This effect increased to 2.9 GPa at the lowest volumes modelled. Using the fits to interpolate between DFT, we can calculate the formation energy of defects over a range of 0-20 GPa.

The formation costs of vacancy defects with differing helium occupancy are shown in figure 5.3. From this, we can see that cost increases with increasing occupancy and by comparing with the energy costs of the interstitial defects in figure 5.4 that the substitutional defect is the most energetically favourable, in keeping with other ab-initio results [11, 13, 14, 15]. As expected, most defects, except the vacancy defect, including the ZPE contributions, increase the energy cost at fixed volume. However, when accounting for the change in pressures due to ZPE, the ZPE effect causes most interstitial defects to decrease in enthalpy at fixed pressure. While the change
Figure 5.2: This figure shows the pressure of α-beryllium over a range of volumes. These pressures were obtained by fitting a Birch-Murnaghan equation of state to energies taken from fixed volume DFT calculations. The solid and dashed lines show results with and without ZPE respectively.

due to ZPE is minor relative to the total formation energy cost, the absolute values are thermodynamically significant.

In table 5.4, we compare the energy and enthalpy of formation for each interstitial defect at zero pressure with results from other DFT studies. From this, we can see a wide variety of results for the BT interstitial. This has led to some confusion over the preference of the BT site over the BO site. In this study, we find the BO site to be slightly more favoured when compared to the BT site, in contrast to the majority of other studies. We suspect this is likely to be due to the reduced simulation cell size used in this study to allow for the increased number of DFPT calculations, as it has been shown
Figure 5.3: This figure shows the energy and enthalpy of vacancy defects with different helium occupancy. Results are given for a substitutional helium atom in blue, two substitutional helium atoms in red, and a vacancy defect in black. The squares and circles show results from DFT calculations with and without ZPE calculations respectively. The solid and dashed lines show interpolated results from fits to a Birch-Murnaghan equation of state, with and without ZPE calculations respectively.

that the energy of the BT site is highly dependent on the relaxation of the surrounding beryllium atoms [202].

We see no change in the order of preference for helium occupancy as pressure increases. The substitutional defect is favoured over the interstitial, and the BS site remains the lowest energy interstitial. We see a reduction in the energetic favourability of the BS site over the BO and BT sites at lower volumes. However, this effect appears less extreme when we look at the change in enthalpy over pressure. It might be possible that these lines cross at higher pressures. However, that is beyond the scope of this study. The difference between results, when presented as energy or enthalpy shown here and in other graphs, will be because simulation cells with different defects at the same volume have not relaxed to the same pressure. This effect can be reduced in future studies by increasing the simulation cell size.

In figures 5.5 and 5.6, we compare different configurations of defects to get an idea of how helium defects might interact with vacancies in the lattice. The results presented are the zero kelvin results and do not include the entropy terms of the Gibbs free energy given by the equation 5.5
Figure 5.4: This figure shows the energy cost of different interstitial helium defects. Results are given for a basal plane octahedral helium defect in blue, for a basal plane tetrahedral helium defect atoms in red, for an in-plane split defect in black, and for an out-of-plane split defect in green. The squares and circles show results from DFT calculations with and without ZPE calculations respectively. The solid and dashed lines show interpolated results from fits to a Birch-Murnaghan equation of state, with and without ZPE calculations respectively.

\[ G = U + PV - TS \]  (5.5)

A simple model for the number of configurations of a defect gives an entropy shown by equation 5.6

\[ S = k_B \log \Omega = k_B \log \frac{N_S!}{(N_S! - N_D!)} \]  (5.6)

where \( N_S \) is the number of available sites and \( N_D \) is the number of defects which can occupy these sites. This means that properly accounting for the entropy term would require estimating the number of defects in the beryllium lattice. That calculation is beyond the scope of this study. As such, all calculations presented are just the enthalpy \( (U + PV) \) results.

Figure 5.5 shows the strength of binding between helium atoms in their preferred interstitial site and a vacancy in the beryllium lattice. From this, we can see that the interstitial defect is attracted to the vacancy even when a
<table>
<thead>
<tr>
<th></th>
<th>BO (eV)</th>
<th>BT (eV)</th>
<th>BS (eV)</th>
<th>S (eV)</th>
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<tbody>
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<tr>
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<td>-</td>
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<tr>
<td>Xi et. al. [13]</td>
<td>-</td>
<td>5.833</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.4: In this table, we compare our calculated formation cost of interstitial sites at ambient pressure with results from other ab-initio studies. Results for interstitial sites which were not modelled are left blank.

Figure 5.5: This figure shows the binding strength between helium interstitial defects and vacancies in the beryllium lattice. Results are given for binding between a basal plain dumbbell defect and a vacancy in blue and between a basal plain dumbbell and a substitutional defect in red. The squares and circles show results from DFT calculations with and without ZPE calculations respectively. The solid and dashed lines show interpolated results from fits to a Birch-Murnaghan equation of state, with and without ZPE calculations respectively.

helium atom already occupies it. This figure also shows that the interstitial helium defect’s attraction to vacancy sites increases as pressure rises over the range studied in this work. However, no qualitative changes happen to
interactions between helium defects and vacancies up to 20 GPa.

Figure 5.6: This figure shows the binding strength of two substitutional helium defects to each other. The squares and circles show results from DFT calculations with and without ZPE calculations respectively. The solid and dashed lines show interpolated results taken from fits to a Birch-Murnaghan equation of state, with and without ZPE calculations respectively.

We find that, up to 20 GPa, it is always favourable for a single helium atom to occupy a vacancy when possible. Therefore, to model the bond state, we simulate two occupied helium vacancies in adjacent lattice sites in the same basal plane. The results from this calculation are shown in figure 5.6. At ambient pressures, there is an attractive force between substitutional defects. This is in keeping with other ab-initio results and the observation of helium bubble formation in experiments. This binding energy slightly increases as pressure is increased up to $\sim 4.0$ GPa. As the pressure is increased above this point, we see a decrease in the binding energy until at $\sim 18.6$ GPa, the substitutional helium defects become repulsive. To our knowledge, this is the first time this crossover from attractive to repulsive behaviour has been described in the literature. This discovery opens the possibility of the application of pressure as a method for combating the formation of helium bubbles in components made of beryllium and its alloys. This phenomenon could help inform the design of future materials and warrants further investigation.

A simple model of the substitutional defects can be used to explain the change in behaviour. In this model, we will assume that the enthalpy of formation for each arrangement of defects is dominated by two effects, the
distortion of beryllium lattice and the breaking of Be-Be bonds. The distortion of the beryllium lattice will be taken as a local strain due to the difference in the volume occupied by the helium atom compared to a beryllium atom. We then assume that the helium atoms remain chemically inert and only act to break the Be-Be bonds, and adjacent helium defects break one fewer bond. To first-order approximation we can approximate the bulk modulus as a constant and take the pressure as \( P = B \Delta V \), we can then write the enthalpy of binding in the form of equation 5.7.

\[
H_{\text{Binding}} = H_{2\text{He}} - 2H_{\text{He}} = 2E_{\text{Bond}} + \frac{B}{2V_{\text{Be}}} (\Delta V_{2\text{He}}^2 - \Delta V_{\text{He}}^2) \tag{5.7}
\]

where \( H_{2\text{He}} \) is the formation enthalpy of 2 adjacent substitutional defects, \( H_{\text{He}} \) is the formation enthalpy of a lone substitutional defect, \( E_{\text{Bond}} \) is the energy of a Be-Be bond in the pure crystal, \( V_{\text{Be}} \) is the original volume of the pure beryllium crystal, and \( \Delta V_{2\text{He}} \) and \( \Delta V_{\text{He}} \) are the change in volume of due to two adjacent and a lone substitutional defects respectively. In this model, we can see that at low pressures, the extra Be-Be bonds that can be formed by placing helium defects adjacent to each other dominate the difference in enthalpy between the two arrangements. This causes them to bind together. As the pressure increases, the strain caused by the lattice distortion begins to dominate. We see that the sign of this term is determined by the difference between the square of the change in volume caused by the helium-occupied defects. If the volume occupied by the two-vacancy structures is greater than that of two separated substitutional defects, then this term is positive. If this pressure term exceeds the energy gained by the extra bonds formed between beryllium atoms, then the helium defects no longer bind to each other.

With this model, we can explain the change in behaviour of the helium defects atoms as the competition between the beryllium lattice attempts to reduce the total volume and maximise the number of Be-Be bonds. This simple model qualitatively matches the results from our DFT calculations. The lone substitutional defect and the double vacancy structure both occupied a greater volume than the beryllium atoms they replaced. However, the change in volume due to the substitutional defects decreased as pressure increased, this was the opposite for the double vacancy structure. This is why when accounting for zero-point effects, the enthalpy of binding initially increases as pressure increases. While we do not explicitly calculate it in this work, the separated defects would have a higher entropy and therefore be
favoured by high temperatures as well as pressures.

5.1.4 Conclusion

We have conducted an ab-initio study into the behaviour of helium defects in the beryllium lattice up to a pressure of 20 GPa. Fixed volume DFT calculations of simulation cells containing a number of relevant defects were used to parameterise a Birch-Murnaghan equation of state. This allows us to include zero-point effects using DFPT, which shifts the beryllium EOS by some 3 GPa and the equilibrium volume by more than 1%. The energy and enthalpy of formation are presented for interstitial and substitutional defects with and without ZPE contributions. From these, we can see that while the absolute change due to the inclusion of ZPE is significant, there are no qualitative changes to the relationships between helium defect sites. We find no change in preference of the defect sites up to 20 GPa. This means that the substitutional defect remains the preferred site overall, and the BS defect remains the preferred site out of the interstitial sites.

We also examine how interstitial defects interact with the vacancies, finding that the attraction between vacancies and interstitial defects increases as pressures increase. The only significant change in behaviour over the range of pressures investigated is in the attraction between substitutional helium defects. At a pressure of ∼18.6 GPa, the substitutional defects begin to repulse each other. The pressure at which this transition occurs depends strongly on the inclusion of zero-point effects. This change in behaviour is due to the competition between the reduction of volume, which favours lone substitutional defects, and increasing the number of Be-Be bonds which favours the bonded configuration. This discovery opens the possibility of the application of pressure as a method for combating the formation of helium bubbles in components made of beryllium and its alloys. This phenomenon could help inform the design of future materials and warrants further investigation. Future ab-initio studies should investigate the effects of pressure on helium trapping in larger vacancy clusters to better understand how pressure affects the formation of helium bubbles.
5.2 Surface Interactions

5.2.1 Introduction

Another active area of interest is the interaction of hydrogen with the beryllium surface. Under irradiation damage large voids can form in materials;
helium or hydrogen in such voids can best be modelled as free surface interactions. The beryllium neutron reaction includes a number of pathways not shown above, these include some which produce hydrogen isotopes as a byproduct. This can lead to the build-up of hydrogen isotopes within the voids found in the beryllium lattice.
As well as this, the beryllium of the breeding blanket is expected to be
the plasma-facing layer, so understanding how hydrogen ions react with the
surface of a beryllium lattice is important to understanding the viability of
beryllium materials in these environments. To this end, experiments have
been carried out on beryllium crystals in a high hydrogen isotope ion flux
environment [16, 17]. Experiments, involving the bombardment of beryllium
crystals with deuterium ions, have found evidence of crystalline BeD$_2$
deposits in samples where the averaged deuterium areal densities were above
$2.0 \times 10^{17} \text{cm}^{-2}$ [16].

Motivated by this, we will investigate the interaction of hydrogen with a
beryllium surface using ab-initio techniques. Hydrogen and its isotopes are
known to be absorbed on the surface of beryllium layers. Many ab-initio
studies have simulated this interaction, and so the interaction of hydrogen
molecules with the beryllium surface is fairly well understood [12, 24, 25, 26,
27, 28, 29]. However, hydrogen and beryllium are known to bind to form a
variety of nanoparticles. These have been well characterised using ab-initio
techniques [18, 19, 20, 205].

Despite this, there is a lack of ab-initio studies on how beryllium hydride
chains interact with the beryllium surface. This chapter will pay particular
interest to the interaction of $(\text{BeH}_2)_n$ chains with the surface. In a gaseous
mixture, hydrogen and beryllium are known to form molecular chains, al-
ternating between beryllium atoms and two hydrogen atoms [18, 19, 20, 21].
These chains can exist in a variety of lengths in either linear or cyclical forms,
with the linear chains ending in a single hydrogen molecule at either end. Ex-
amples of linear chains up to a length of $n = 3$ are given in figure 5.9. As
such, the role that $(\text{BeH}_2)_n$ chains might play in hydrogen’s interaction with
the beryllium surface has yet to be properly characterised. In this chapter,
we will use ab-initio methods to model this interaction.

5.2.2 Method
First, we must converge our calculation for a simulation cell of beryllium
in bulk. Again all calculations are carried out in CASTEP [166]. In this
chapter, we used a 4x4x4 Monkhorst-Pack grid with a simulation cell of 96
atoms with a cut-off of 1350 eV. This was found to converge the simula-
tion cell to within 1 meV. We used norm-conserving pseudopotential with
a Perdew, Burke, and Ernzerhof (PBE) parameterization [54] generated by
CASTEP. As we will be using a plane wave basis set, we must use periodic
Figure 5.9: In this figure we show \((\text{BeH}_2)_n\) molecule up to a length of \(n = 3\). These were obtained by performing geometry optimisation calculations in CASTEP [166]. Beryllium atoms are shown in grey and hydrogen atoms in white.

reflections of our simulation cell. To model a surface interaction like the ones we are interested in for this chapter, we must build a simulation cell with a large enough beryllium crystal to represent a full crystal structure and a
large enough gap to ensure no interaction with the cell’s periodic boundary conditions. This means that as well as the parameters which must be converged normally in a DFT calculation, we must converge the number of layers of beryllium crystal as well as the size of empty space in the simulation cell. The hydrogen pseudopotential was generated in CASTEP using the string "1|0.8|14|16|19|10N(qc = 8)" and the beryllium pseudopotential was generated using the string "1|1.1|23|26|31|10N : 20N : 21L(qc = 9)".

This section will investigate \((\text{BeH}_2)_n\) chain interactions with the Basal plane \((0001)\). The \((0001)\) surface is the simplest and most well-studied. This provides a good basis to compare with our calculations. As we extend the simulation cell along the direction of the \(c\)-axis to create the vacuum, we can reduce the \(k\)-point sampling in this direction by giving us a final simulation \(k\)-point grid of \(4\times4\times2\). The beryllium atoms are then relaxed through an NVT geometry optimisation to give our beryllium surface. With a \(4\times4\times3\) repetition of the primitive unit cell, we have a surface consisting of 16 beryllium atoms and a depth of 6 layers. The simulation was initially started with experimental lattice constants of \(a = 2.286\,\text{Å}\), and \(c = 3.583\,\text{Å}\) [206]. When relaxed, the beryllium layer extended along the \(c\)-axis to a final lattice constant of \(c = 3.597\). This gave us a gap of 23.395 Å, between beryllium atoms allowing a significant enough space for the \((\text{BeH}_2)_n\) molecular chain to only interact with one instance of the beryllium layer. This gap acts as a limit on the size of the molecule that can be investigated.

It has been found that the stability of \((\text{BeH}_2)_n\) chains increases asymptotically as the \(n \rightarrow \infty\) [18, 19, 20]. As such, we might expect that an increase in the size of the chain would stabilise the molecular state. For example, recent calculations have found that the polymerisation energy of the \((\text{BeH}_2)_n\) tends to 1.455 eV [19]. As a compromise between these two constraints, we focus our study on the \(\text{Be}_3\text{H}_6\) molecule. For reference, the polymerisation energy of the \(\text{Be}_3\text{H}_6\) found in the same study was \(\sim 0.890\,\text{eV}\).

A \(\text{Be}_3\text{H}_6\) molecule was relaxed in a simulation cell. This gave a molecule with bond lengths of 1.97 Å between beryllium atoms, 1.34 Å between beryllium atoms and the hydrogen atoms at the end of the chain, and 1.49 Å between beryllium and the other hydrogen atoms. This is in keeping with other ab-initio calculations of the \(\text{Be}_3\text{H}_6\) molecule [21]. Molecular dynamics simulations were then run with the molecule started in contact with the beryllium surface. These calculations were run for 1000 time steps of 1 fs.

Fixed ion energy calculations are also carried out. To determine the molecule’s stability we carried out calculations on hydrogen absorption on
the beryllium surface. There are four high symmetry sites on the basal plane beryllium surface. Two of the sites have a threefold fold symmetry and are known as the fcc and hcp absorption sites. One exists between two beryllium atoms and is known as the bridge site. The final one is directly above a beryllium atom in the surface layer and will be referred to as the top site. The absorption profile for hydrogen at each of these sites was calculated. It has also been shown that in the case of hydrogen saturation, the beryllium surface has one hydrogen atom per beryllium atom. The low energy state is for an even spread of hydrogen atoms on the bridge sites [29]. This configuration is also simulated, which provides insight into how the \( \text{Be}_3\text{H}_6 \) molecule might behave in an environment with a high hydrogen concentration.

It should also be noted that the ZPE contributes significantly to the bulk beryllium and \( (\text{BeH}_2)_n \) molecules. However, due to the size of the calculations required to simulate the surface interacting with a complex molecule, DFPT calculations are not practical.

### 5.2.3 Results

In figure 5.10, we show the energy curve of a hydrogen atom being absorbed onto a beryllium surface. DFT calculations were carried out on a hydrogen atom near a beryllium surface at increasing distances. This gives us a profile of hydrogen absorption to the beryllium surface. This was carried out at four high symmetry sites on the surface. From this figure, we can see that the two most favourable sites are the fcc and hcp sites, with the hcp site being slightly more favoured. The next closest is the bridge site, with the weakest bonding occurring on the top site, in keeping with what other studies have found [24, 25, 28, 26]. We can see from this that the coordination number of the hydrogen impacts the bonding of a site the most, with both the fcc and hcp sites having the most adjacent beryllium atoms at three. The weak interaction with the second layer differentiates the hcp site from the fcc site, located directly above a beryllium atom on the second layer. We then performed a geometry optimisation with the hydrogen atom at the hcp site. This will act as a reference energy for the absorbed hydrogen molecule.

Two molecular dynamics calculations were carried out with a free beryllium surface and a \( \text{Be}_3\text{H}_6 \). One was initiated with the molecule far from the beryllium surface, and one with the molecule initiated close to the beryllium surface. In both cases, the molecule was initiated perpendicular to the basal
Figure 5.10: This figure shows a hydrogen atom’s absorption energy at various high-symmetry sites on a beryllium surface. DFT calculations were carried out with hydrogen atoms held at a fixed z-coordinate above the top layer of beryllium atoms. The energy calculations were then zeroed with reference to a hydrogen molecule far from the beryllium surface.

The calculation in which the molecule was started far from the surface, 5.5 Å, the Be$_3$H$_6$ molecule explored the gap within the simulation cell during the one ps simulation run. However, it was not observed to form any bonds with the beryllium surface. In the other molecular dynamics simulation, the molecule was oriented so that the hydrogen molecule at the end of the Be$_3$H$_6$ chain was within 1 Å of the beryllium surface. In this simulation, the hydrogen atom closest to the beryllium surface separated from the rest of the beryllium molecule, which from now on will be referred to as the Be$_3$H$_5$ molecule. Both the hydrogen atom and the Be$_3$H$_5$ molecule remained...
bonded to the beryllium surface and began freely moving between hcp and fcc absorption sites.

To understand the behaviour observed in these molecular dynamics simulations, calculations were carried out to map the interaction of both the Be$_3$H$_6$ and Be$_3$H$_5$ with the beryllium surface. Both molecules were oriented perpendicular to the basal plane, and energy calculations were carried out as the distance from the plane was increased. The results from both molecules are plotted in Figure 5.11, where the energy is zeroed with respect to the molecule far from the beryllium surface. Looking at the energy curve of the Be$_3$H$_6$ molecule, we see a barrier of 0.160 eV that must be overcome before the molecule can form a bond with the beryllium surface. This explains the lack of interaction within the simulations where the molecule started far from the beryllium surface. The barrier reduces the chance of bonding occurring within the limited simulation run time. We can also see part of the reason for the disassociation of the near beryllium surface hydrogen atom. While the Be$_3$H$_6$ molecule is weakly bonded to the surface, with a bond of 0.433 eV, the Be$_3$H$_5$ molecule has a significantly stronger bond, 2.572 eV. As well as this, the now free hydrogen atom also acts to lower the system’s energy.

To quantify this, we can compare relaxed calculations of these molecules in contact with the surface to a number of reference states. In general, the calculation of the energy cost of a molecule interacting with the beryllium surface will take the form of equation 5.8

$$E_{\text{cost}} = [E(X) - E(Be_{\text{Surface}})] - [N_{Be}E(Be_{\text{Bulk}}) + N_{H}E(H_{\text{ref}})]$$  (5.8)

where $E(X)$ is the energy of the cell containing the molecule interacting with the surface, $E(Be_{\text{Surface}})$ is the energy of the beryllium surface itself, $N_{Be}$ and $N_{H}$ are the number of beryllium and hydrogen atoms in the molecule respectively, $E(Be_{\text{Bulk}})$ is the energy of a beryllium atom in bulk, and $E(H_{\text{ref}})$ is the energy of a hydrogen atom single hydrogen atom.

To understand the behaviour of the Be$_3$H$_6$ molecule we will calculate its stability in different conditions with respect to three relevant reference hydrogen states. These will be when the hydrogen atom is in a free-floating hydrogen molecule when a lone hydrogen atom has been absorbed onto the hcp beryllium site, and when the beryllium surface has been saturated and is its lowest energy configuration as determined by [29]. This allows us to understand the behaviour of the Be$_3$H$_6$ molecule in a number of different environments. The results are given in table 5.5.
Figure 5.11: This figure shows the energy curve of a Be$_3$H$_6$ molecule being absorbed on the hcp site of a beryllium surface, this is shown by the blue circles. We also plot the energy curve of a Be$_3$H$_5$ molecule where the hydrogen atom at the end of the chain was removed, shown by the red squares. DFT calculations were carried out on the molecules held at fixed z-coordinate above the top layer of beryllium atoms. The energy calculations were then zeroed with reference with respect to a Be$_3$H$_6$ molecule far from the beryllium surface.

For all of the results, we can see that the absorbed molecule in the form Be$_3$H$_5$ + H is the most stable and that the desorbed Be$_3$H$_6$ molecule is the least stable. This table allows us to compare the stability of different Be$_3$H$_6$ molecule configurations when there are different hydrogen sites available. From these results, we can see that the only state that the beryllium hydride molecules are stable with respect to is the free-floating hydrogen molecule. They are least stable in the case where there are many unoccupied hydrogen absorption sites. This suggests that as long as there are available hydrogen
Table 5.5: In this table, we give the energy cost of different configurations of Be$_3$H$_6$ molecules interacting with the basal plane surface using different hydrogen reference states. The energy cost of each molecule is calculated using equation 5.8.

<table>
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<td>-3.729</td>
<td>3.299</td>
<td>0.028</td>
</tr>
<tr>
<td>Absorbed Be$_3$H$_6$</td>
<td>-2.370</td>
<td>4.668</td>
<td>1.387</td>
</tr>
<tr>
<td>Desorbed Be$_3$H$_6$</td>
<td>-1.809</td>
<td>5.219</td>
<td>1.948</td>
</tr>
</tbody>
</table>

absorption sites the Be$_3$H$_6$ molecule will be absorbed into the bulk. However, once the surface is saturated with hydrogen the desorbed Be$_3$H$_6$ is preferred to the formation of H$_2$ molecules.

When looking at the results of the highly saturated case, we must keep in mind that our calculations assumed that the molecules were able to bond to an unoccupied beryllium surface which is unrealistic in the highly saturated case. As such, these results don’t account for any complex reactions between the absorbed hydrogen atoms and the molecular chains. Any such behaviour is beyond the scope of this study. However, if it is the case that the absorbed molecules behave analogously to the absorbed hydrogen, we would expect that the occupation of other absorption sites would weaken the bond between the molecule and the beryllium surface. As such, the energy cost of the absorbed beryllium molecule would increase, meaning the qualitative behaviour suggested by these results would remain the same, assuming no significant interaction between the surface hydrogen atoms and the molecular chains.

Another metric we can use to compare the absorption of the Be$_3$H$_6$ molecule with the absorption of a hydrogen molecule is to look at how each affects the surface energy of the beryllium layer. We can calculate the surface energy of a beryllium layer with an absorbed molecule with the equation 5.9

$$E_{surface} = \frac{1}{2S} \left[ E(X) - N_{Be}^{surface} E(Be_{Bulk}) - E(X_{ref}) \right] \tag{5.9}$$

Here $S$ is the surface area of the beryllium layer, $E(X)$ is the energy of the molecule absorbed onto the beryllium layer, $N_{Be}^{surface}$ is the number of beryllium atoms in the simulated beryllium surfaces, and $E(X_{ref})$ is the energy of the molecule without the surface. Both the absorbed hydrogen molecule and an absorbed Be$_3$H$_6$ molecule occupy two absorption sites. Therefore, we
can compare the change in surface energy to see which is favoured by the beryllium surface. As well as this, because one of the occupied sites of the absorbed Be$_3$H$_6$ molecule is just a hydrogen atom on an hcp site, the difference between these two results will reflect the difference between an hcp site occupied by a hydrogen atom versus an hcp site occupied by a Be$_3$H$_5$ molecule. We find that the surface energy of the beryllium surface after absorbing the Be$_3$H$_6$ molecule is 1.462x10$^{-1}$ eV/Å$^2$ (J/m$^2$) higher than after absorbing a H$_2$ molecule. Thus we would expect that the Be$_3$H$_6$ molecule would not be able to displace an absorbed hydrogen atom on the beryllium surface.

From these results, we can conclude that (BeH$_2$)$_n$ chains will bond with the beryllium surface in an environment with a low hydrogen concentration. After overcoming an energy barrier of 0.160 eV, one of the end hydrogen atoms separated from the chain and both the hydrogen atom and the beryllium hydride chain bind to the beryllium surface. However, this new molecule would be unstable. The beryllium would be absorbed into the bulk, and the hydrogen atoms absorbed onto the beryllium surface. However, this was not observed in our molecular dynamics simulations of 1 ps. As such, it is the details of the dynamics of this process are unknown. Figure 5.12 gives a visual guide to this process.

In the case of high hydrogen concentration, absorbed hydrogen atoms would saturate the beryllium surface. Under these conditions, our calculations suggest we should not expect binding between (BeH$_2$)$_n$ chains and the beryllium surface, as the hydrogen atoms would block any possible absorption sites. However, As the (BeH$_2$)$_n$ chains are more energetically favourable than the H$_2$ molecule, (BeH$_2$)$_n$ chains will spontaneously form once all absorption sites are occupied. Figure 5.13 gives a visual guide to this process.

The process of the formation of the (BeH$_2$)$_n$ chains is not explicitly explored in this study. However, the calculations presented do suggest one process by which beryllium might be extracted from the bulk. If we imagine a beryllium basal plane surface saturated with hydrogen except for a beryllium atom defect occupying an absorption site. The next site for a hydrogen atom to bind to would be directly to the beryllium atom defect. Now this BeH pair is the same as the bond state of a chain of length one, as such, if there was more hydrogen available it would be energetically favourable to replace the BeH pair on the absorption site and create a BeH$_2$ chain. The exact process responsible for the deposits of BeH$_2$ crystals seen on the beryllium surface in experiments is beyond the scope of this study and could be
investigated in future work.

Figure 5.12: These figures show a representative image of the interaction between a beryllium hydride molecule and an unoccupied beryllium surface. The images shown are equivalent to the snapshots simulated and when ordered (a) $\rightarrow$ (c) describe the process of absorption of the simplest beryllium hydride molecule. The top two layers of the beryllium surface are shown in grey, the beryllium that starts in the BeH$_2$ molecule is shown in blue and hydrogen atoms are shown in white. (a) Initially, the BeH$_2$ molecule floats free from the beryllium surface. (b) With enough time the BeH$_2$ overcomes the initial repulsion to the beryllium surface, losing a hydrogen atom in the process which now freely moves between absorption sites. (c) The final hydrogen atom in the Beryllium hydride molecule is unstable with respect to the absorption site on the beryllium surface resulting in the low energy state, with two absorbed hydrogen atoms and a beryllium surface defect.
5.2.4 Conclusion

We have carried out the first ab-initio study, to our knowledge, of the interaction of \((\text{BeH}_2)_n\) chains with the beryllium surface. We carried out molecular dynamics simulations of the \(\text{Be}_3\text{H}_6\) chain near a beryllium surface. It was observed that if the \(\text{Be}_3\text{H}_6\) chain was started in contact with the slab, a hydrogen atom dissociated from the molecule. The hydrogen atom and the rest of the molecule remained bonded to the surface, moving freely between hcp and fcc sites. However, no spontaneous bonding was observed in simulations where the molecule was not initiated in contact with the surface.

The behaviour seen in the molecular dynamics calculations was further explored with DFT calculations. These showed that a barrier of 0.160 eV had to be overcome before binding could occur. Calculations were carried out on the stability of both the bound \(\text{Be}_3\text{H}_6\) and \(\text{Be}_3\text{H}_5\) molecule. These bound molecular states were then compared with calculations of different configurations of absorbed and desorbed hydrogen. It was found that the bound \(\text{Be}_3\text{H}_5\) molecule was the more energetically favourable of the two. In an environment where unoccupied hydrogen absorption sites are available both molecules would be absorbed into the beryllium bulk.

However, it was also found that the beryllium hydride molecules were more energetically favourable when compared to loose hydrogen molecules. This, along with calculations which show that the surface energy of the beryllium crystal is reduced more by an absorption site occupied by a hydrogen atom than the \(\text{Be}_3\text{H}_5\) molecule, suggest that the spontaneous desorption of beryllium hydride chains is possible when hydrogen ions fully saturate the absorption sites of the beryllium surface. These ab-initio calculations provide a theoretical explanation for the formation of beryllium hydride deposits in high ion flux environments [16, 17, 30].

Due to computational limits, we were unable to account for things such as the ZPE or longer \((\text{BeH}_2)_n\) chains. However, due to the magnitude of the energy involved, the qualitative behaviour suggested by these results should remain the same. Future studies could also address other simplifying assumptions made in this investigation. These could include investigations into complex interactions between bound chains and absorbed hydrogen atoms, looking into interactions with surfaces other than the basal plane, exploring how a \((\text{BeH}_2)_n\) might bind when parallel to the beryllium surface, or exploring the role that defects play in the formation of beryllium hydride chains. These calculations only describe a part of the process involved in the for-
mation of the beryllium hydride deposits seen in experiment. Future works should look into the dynamics involved in the absorption and desorption of beryllium hydride chains from the beryllium bulk. As well as the subsequent formation of the beryllium hydride crystal on the beryllium surface.
Figure 5.13: These figures show a representative image of the formation of a beryllium hydride molecule from a beryllium surface fully saturated with absorbed hydrogen atoms. The images shown are equivalent to the snapshots simulated and when ordered (a) → (c) describe the formation of the simplest Beryllium hydride molecule from a fully saturated beryllium surface. The top two layers of the beryllium surface are shown in grey, the beryllium that starts as a surface defect is shown in blue and hydrogen atoms are shown in white. (a) Initially, a beryllium surface defect is formed, as might happen in a high-radiation environment. (b) To create more space for additional hydrogen absorption sites a hydrogen atom binds to the beryllium defect creating a bound BeH molecule. (c) A free-floating hydrogen molecule donates one hydrogen to the beryllium hydride molecule and one to the beryllium surface resulting in a free-floating BeH$_2$ molecule and a fully saturated beryllium surface.
Chapter 6

Conclusion

The thesis has focused on studying highly quantum materials using ab-initio techniques, particularly the effects of quantum nuclear motion on the equation of state (EOS).

In this thesis, we have explored the limits of what is possible with current density functional techniques (DFT) by recreating the equation of the state of the helium isotopes at extremes of low temperature and low pressure, where the quantum effects are most pronounced. Having established under which conditions current DFT techniques break down, we demonstrate how the pressure due to zero-point energy (ZPE) contributions, or zero-point pressure, affects these quantum materials over various conditions. By ensuring that we include all the effects of quantum nuclear motion, we are able to answer open questions about these systems that exist in the literature.

In Chapter 3, we attempted to recreate the EOS of the hcp phase of both helium isotopes below 1 GPa using ab-initio techniques. This is a part of the phase space which, up until now, had only been described using simple pairwise potentials because DFT, without zero-point contributions, massively overestimates the equilibrium density. First, we did a systematic study of different possible functionals. We found that functionals which included GGA and Van der Waals effects most accurately reproduced the experimental results, with PBE+G06 producing the best fit. However, the helium lattice’s an-harmonic modes limit the accuracy of the quasi-harmonic DFPT method.

To address this, calculations were carried out using SCAILD. However, it was found that self-consistent cycles failed to converge. This is because the solid helium phase only exists below the Debye limit at these pressures.
It was also found that PIMD was too computationally expensive due to the high bead number required to reproduce the quantum effects at the relevant conditions. Having tested DFT methods in the highly quantum limit, we can reliably use these techniques to analyse the effects of zero-point pressure in other systems.

Since this work was carried out, a number of new methods for calculating the an-harmonic lattice dynamics have been developed. Of note are two that account for the quantum nature of the nuclei, the stochastic self-consistent harmonic approximation (SSCHA) [175] and the Quantum Self-Consistent Ab-Initio Lattice Dynamics (QSCAILD) [176]. These methods overcome the classical assumptions made in SCAILD by sampling the inter-atomic forces assuming a distribution based on quantum mechanics.

Having established the limits of DFPT, we use it in Chapter 4 to study hydrogen-helium mixtures up to a pressure of 15 GPa. This was motivated by recent claims of chemical bonding between hydrogen and helium atoms in the solid phase [2] as well as the poorly understood blueshift of the hydrogen vibron Raman signal in the mixed fluid phase [2, 3, 22]. The substitutional hydrogen molecule is shown to be the most energetically favourable form of hydrogen defect in solid He. We calculate the enthalpy of mixing in both the solid and fluid regimes finding a maximum concentration of hydrogen molecule defects at approximately 0.2%. These results, along with a Mulliken population analysis [36, 37, 38] showing a lack of chemical bonding, are at odds with the claims made by Yoo et. al. [2]. This suggestion supports the conclusions drawn by Turnbull et. al. that Raman signals cited as evidence for chemical bonding were in fact due to nitrogen contamination [22, 23].

By accounting for zero-point effects, we are able to recreate the pressure-concentration dependency of the hydrogen vibron in He-H mixtures. We then showed that a localised pressure on the hydrogen molecule could not explain the observed effects. Coupling between harmonic oscillators broadens and decreases the frequencies involved in the harmonic modes. We propose that the inclusion of helium in the mixture acts to weaken the coupling between hydrogen molecules, thus leading to an increase in the frequency of the Raman signal. As the Raman active mode is the lowest frequency mode, its frequency is lowered by both the decrease in average frequency as well as the broadening of the mode. To support our hypothesis, we show that in our model, the vibron mode’s localisation correlates with the vibron frequency change, both due to the change in concentration and when concentration is maintained. We show that this effect continues to higher pressures demon-
strating that the turnover in the pure hydrogen vibron is due to increased coupling between molecules.

This study sets the ground for future experiments to use the hydrogen vibron as a reliable indicator of hydrogen concentration. This would work in both the high and low pressure regimes. The behaviour of a hydrogen molecule in a potential well is an idealised simple model of chemical interaction. This study highlights that hydrogen molecules trapped in a helium mixture may act as an analogue to this theoretical model at low enough concentrations. With improved experimental sensitivity, this could one day act as a bridge between ab-initio calculations and experiments. Since this mechanism stems from the separation of hydrogen molecules rather than direct interaction with helium, we expect this effect to be present in any compound or mixture containing H$_2$. Therefore, the coupling effects between hydrogen molecules could hold relevance to future investigations involving high-pressure mixtures and alloys, including the ongoing exploration of high-pressure hydrides.

We then expand our study into the effects of zero-point pressure on the defects in highly quantum materials. Due to its potential use in high neutron flux environments, the study of helium defects in beryllium is an active area of interest. While previous studies have included ZPE calculations, none have expanded these above ambient pressures [15, 202]. Both beryllium and helium are light enough elements that quantum nuclear motion significantly impacts their EOS. By taking the zero-point effects into account, we are able to calculate the enthalpy of formation for a number of relevant defects up to a pressure of 20 GPa.

We find that in most cases, there are no qualitative changes to the formation of the defects due to the increase in pressure or the inclusion of zero-point pressure. The exception to this is the interaction between two substitu-tional defects. While the attraction between substituional defects initially increases as the pressure increases above 4.0 GPa, the attraction weakens until at approximately 18.6 GPa, the substituional defects no longer bind to each other. This behaviour change is driven by competition between the minimisation of the volume of the defect and the maximisation of the number of Be-Be bonds. Due to this dependence on volume, the change in lattice parameters caused by zero-point effects significantly impacts this behaviour. This behaviour change suggests that applying pressure to the beryllium lattice could be a possible method to combat the formation of helium bubbles. Future studies should focus on similar calculations involving larger vacancy
structures, as this could provide further insight into the formation of helium bubbles under pressure.

Due to interest in beryllium as a part of breeding blankets in fusion reactors, the retention of hydrogen and its isotopes on the beryllium surface is an area of active study [12, 24, 25, 26, 27, 28, 29]. Motivated by experimental measurements of beryllium hydride deposits on beryllium surfaces [16, 17], we investigated the interaction of beryllium hydride chains with the beryllium surface. To do this, we compare the absorption profiles of beryllium hydride chains with those of hydrogen molecules. We found that while absorption sites are available for the hydrogen atoms to occupy, the beryllium hydride chain is unstable and will be broken down and absorbed into the bulk of the beryllium. However, our calculations suggest that in the case of a saturated beryllium surface, beryllium hydride chains will spontaneously desorb from the beryllium surface. These results provide an explanation for experimental results, which find that beryllium hydride deposits form spontaneously on beryllium surfaces when under bombardment from hydrogen ions, but only above a particular areal density [16].

As this work is the first ab-initio study to describe this phenomenon, it opens up a number of questions which could be explored in future studies. This could include more complex interactions with the beryllium surface, including how the beryllium hydride molecule interacts with hydrogen atoms absorbed onto the beryllium surface, surfaces other than the basal plane, or other defects on the beryllium lattice surface. This work also failed to address the dynamics involved in the absorption or desorption of the beryllium hydride chains or the formation of the crystalline deposits on the beryllium surface.

In conclusion, this thesis has been a study of the often-overlooked effects of quantum nuclear motion. We have highlighted the ways in which current ab-initio methods break down when modelling highly quantum materials. We then show the importance of accounting for zero-point contributions to pressure in calculating important observables in a number of highly quantum materials, including the enthalpy of mixing, defect formation costs and Raman spectrum. By fully accounting for the effects of quantum nuclear motion, we are able to answer open questions that have existed in active areas of research, which up until now had gone unaddressed.
Bibliography


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[181] N. Nettelmann, B. Holst, A. Kietzmann, M. French, R. Redmer, and
D. Blaschke, “Ab initio equation of state data for hydrogen, helium,
and water and the internal structure of jupiter,” The Astrophysical

with a long-range dispersion correction,” Journal of Computational

in treating van der waals dispersion forces in density functional theory,”

anomalies and three distinct liquid-liquid transitions in warm dense

of crystals with the quasi-newton method,” Journal of Computational

helium demixing from first principles: From diamond anvil cells to
planetary interiors,” Physical Review B, vol. 87, no. 17, p. 174105,
2013.

Ar(H₂)₂: Structural stability and anomalous melting,” Physical Re-

[188] C. Ji, A. F. Goncharov, V. Shukla, N. K. Jena, D. Popov, B. Li,
J. Wang, Y. Meng, V. B. Prakapanka, J. S. Smith, R. Ahuja, W. Yang,
and H.-k. Mao, “Stability of ar(h2)2 to 358 gpa,” Proceedings of the

van der waals compound Kr(H₂)₄ discovered in the krypton-hydrogen

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